Dispersion and Confinement of Multiwall Carbon Nanotubes in Immiscible Polymer Blends

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by

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Abstract

Dispersibility of multiwall carbon nanotubes (MWNTs) has been investigated in aqueous and organic media in the presence of various modifiers, viz., sodium dodecyl sulphate (SDS) (a classical surfactant), sodium salt of 6-amino hexanoic acid (Na-AHA) and 1-pyrenecarboxaldhyde (PyCHO) (a pyrene-based modifier). Modified MWNTs have exhibited higher UV-vis absorbance value and lower average 'agglomerate' size as compared to unmodified MWNTs. SDS and PyCHO modified MWNTs have exhibited larger MWNTs 'agglomerate' size through 'segregation' of modifier molecules leading to 're-agglomeration' of MWNTs at higher concentration of the modifier. On contrary, Na-AHA molecules have shown an enhanced dispersion of MWNTs with increasing concentration of Na-AHA content. The effect of solvent parameters [electron pair donicity (β), hydrogen bonding parameter (α) and solvochromic parameter (π *)] on MWNTs 'dispersibility' has been investigated.

MWNTs have been melt-mixed in immiscible 'co-continuous' blends of polyamide 6 (PA6) and acrylonitrile butadiene styrene copolymer (ABS) using a 'simultaneous' mixing protocol in order to investigate the state of dispersion of MWNTs in PA6/ABS blends. The processing protocol was optimized, where it was found that 50/50 (wt/wt) PA6/ABS blend composition of varied amount of MWNTs (3–5 wt%) prepared at intermediate screw speed and with longer mixing time (R100 t15) (the corresponding DC electrical conductivity of ~1.01x 10⁻⁹ S/cm) exhibited the highest electrical conductivity values amongst the remaining composite samples prepared by following varying processing parameters, viz., screw speed of 100 rpm and mixing time of 15 minutes at 260 °C. Blend composition has been varied from 40/60 (wt/wt) to 60/40 (wt/wt) in PA6/ABS blends, which exhibited 'co-continuous' type morphology in the presence of MWNTs. State of dispersion of MWNTs in these blends has been assessed

through bulk electrical conductivity measurements, morphological analysis, solution experiments and UV-vis spectroscopic analysis. A strong dependence of electrical conductivity on the blend composition has been revealed in case of PA6/ABS blends with 5 wt% unmodified MWNTs ($\sim 10^{-11}$ to $\sim 10^{-5}$ S/cm). A significant improvement in the bulk electrical conductivity of PA6/ABS blends over the entire 'co-continuous' range was observed in the presence of 5 wt% Na-AHA modified MWNTs ($\sim 10^{-7}$ to $\sim 10^{-5}$ S/cm) and PyCHO modified MWNTs ($\sim 10^{-5}$ -10^{-4} S/cm). Transmission electron microscopic analysis confirmed the presence of MWNTs in both the phases (PA6 and ABS) in case of PA6/ABS blends with MWNTs. The rheological studies showed increased complex viscosity and storage moduli in lower frequency region in case of blends with Na-AHA modified MWNTs confirming a refined 'network-like' structure of MWNTs. Dynamic mechanical thermal analysis (DMTA) showed higher storage moduli values in PA6/ABS blends with Na-AHA modified MWNTs.

Raman spectroscopic analysis indicated 'G-band' shift from ~1581.9 cm⁻¹ for unmodified MWNTs to ~1590.2 cm⁻¹ for Na-AHA modified MWNTs and ~1588.8 cm⁻¹ for PyCHO modified MWNTs, indicating an interaction between MWNTs and modifier molecules. FTIR analysis showed a shift of the peaks at ~1413 cm^{-1} and ~1571 cm^{-1} for Na-AHA modified MWNTs confirming an interaction between Na-AHA molecules and MWNTs. Further, PyCHO modified MWNTs showed a shift in peak position corresponding to aromatic ring at ~1590 cm⁻¹ and >C=O at ~1680 cm⁻¹ to ~1589 cm⁻¹ and ~1650 cm⁻¹ respectively confirming ' π - π ' interaction between PyCHO molecules and MWNTs. SEM observations indicated that on incorporation of unmodified MWNTs in PA6/ABS blends, transformation to 'co-continuous' phase morphology has been observed irrespective of the blend composition. Further, overall PA6/ABS blends exhibited coarser 'co-continuous' phase morphology in the presence of modified MWNTs. However, 40/60 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs, which depicted a 'matrixdispersed droplet' type morphology. TEM observations showed that a majority fraction of unmodified MWNTs was 'nano-agglomerated' both in PA6 and ABS phases in case of 40/60 (wt/wt) blend unlike 60/40 (wt/wt) blend, which depict mostly 'individualized' MWNTs in the PA6 phase. Further, the corresponding PA6/ABS blend with Na-AHA and PyCHO modified MWNTs showed 'nano-agglomerated' and 'individualized' MWNTs in both the phases as well as at the interface. Ratio of the crystallization peak (H_1/H_2) height at lower temperature (H_1) to the peak height at higher temperature (H_2) obtained from non-isothermal crystallization studies showed lower values in case of blends with

unmodified MWNTs as compared to Na-AHA and PyCHO modified MWNTs manifesting in the higher extent of interfacial crystallization of PA6 phase on unmodified MWNTs surface. TGA studies indicated the formation of thicker 'interphase' on MWNTs surface in the blends.

Moreover, MWNTs were modified with Na-AHA and PyCHO to achieve improved dispersion, which further were encapsulated with styrene-maleic-anhydride copolymer (SMA). PA6/ABS blends with SMA encapsulated MWNTs were melt-mixed 'simultaneously' in a conical twin screw microcompounder. Blends with SMA encapsulated unmodified MWNTs showed electrically insulating behaviour, however, blends with SMA encapsulated Na-AHA modified MWNTs exhibited DC electrical conductivity of $\sim 10^{-9}$ to $\sim 10^{-8}$ S/cm and blends with SMA encapsulated PyCHO modified MWNTs of $\sim 10^{-12}$ S/cm to $\sim 10^{-4}$ S/cm at 5 wt% MWNTs content (except for 40/60 blend composition). FTIR analysis showed imide peaks at ~ 1736 cm⁻¹ and ~ 1776 cm⁻¹ confirming 'melt-interfacial' reaction between -NH₂ end groups of PA6 and anhydride functionality of SMA. Blends with SMA encapsulated Na-AHA modified MWNTs showed low H₁/H₂ values indicating pronounced 'interfacial crystallization' of the PA6 phase. Rheological studies indicated that the variation in complex viscosity might be due to 'melt-interfacial' reaction, various interactions between modifier molecules/ SMA copolymer/ polymer phase and MWNTs. Dynamic mechanical thermal analysis have shown that the presence of SMA copolymer and state of dispersion of MWNTs significantly influence the dynamic mechanical properties and polymer chain dynamics.

An attempt has been made to explain the variation in electrical conductivity of PA6/ABS blends in the presence of MWNTs through morphological observations, solution experiments. Rheological analysis, Dynamic mechanical thermal analysis, non-isothermal crystallization behaviour, TGA analysis and various spectroscopic analyses were carried out to establish various interactions between polymer chains and MWNTs.

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Abbreviations

ABS	Acrylonitrile-butadiene-styrene copolymer
AHA	6-aminohexanoic acid
BET	Brunauer-Emmet and Teller analysis
BTPC	Benzoyl triphenyl phosphonium chloride
CCVD	Catalytic carbon vapor deposition process
CF	Crystalline fraction
СМС	Critical micelle concentration
CNTs	Carbon nanotubes
CVD	Chemical vapour deposition
DMF	Dimethylformamide
DMTA	Dynamic mechanical thermal analysis
DTPB	Dodecyl triphenyl phosphonium bromide
FTIR	Fourier transform infra-red spectroscopy
MAF	Mobile amorphous fraction
MDSC	Modulated differential scanning calorimetry
MWNTs	Multiwall carbon nanotubes
Na-AHA	Sodium salt of 6-aminohexanoic acid
OsO ₄	Osmium tetraoxide
OTPB	Octadecyl triphenyl phosphonium bromide
PA6	Polyamide 6
PP-g-MA	Polypropylene-grafted-maleic anhydride
РуСНО	1-pyrenecarboxaldehyde
RAF	Rigid amorphous fraction

SAN	Styrene-acrylonitrile
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SMA	Styrene-maleic-anhydride copolymer
SWNTs	Single wall carbon nanotubes
TEM	Transmission electron microscopy
TGA	Thermo-gravimetric analysis
THF	Tetrahydrofuran
XPS	X-ray photoelectron spectroscopic analysis

List of Symbols

[ŋ]	Intrinsic viscosity
Ca	Capillary number
D _{avg}	Average diameter of MWNTs 'agglomerates'
I _D	Intensity of 'D-band' peak from Raman spectroscopic analysis
I_D/I_G	Ratio of intensities of 'D-band' and 'G-band' peaks
I _G	Intensity of 'G-band' peak from Raman spectroscopic analysis
$M_{\rm v}$	Molecular weight (Viscosity average)
Tg	Glass transition temperature
α	Hydrogen bond donor parameter
β	Lewis basicity
η_d	Melt-viscosity of dispersed phase
η_{m}	Melt-viscosity of matrix phase
η_r	Melt-viscosity ratio
π	Pi

 π^* Solvochromic parameter

Chapter 1: Introduction

An incredible ability of carbon to hybridize in various ways leads to structures like diamond (sp³) and graphene (sp²), which exhibit extra-ordinary properties. A strongly bonded planar structure with covalent bonds and π -bonds normal to the plane allowing the 'delocalization' of electrons makes the graphene structure an extremely attractive material for developing multifunctional engineering materials. Carbon nanotubes (CNTs) are described as extremely large molecular wires by Schönenberger and Forró [1], in which the electrons can move in a similar way as they propagate in metals. Dresselhaus et al. [2] reported that the outstanding properties of CNTs are due to 1-D quantum behaviour and symmetry properties of CNTs. A graphene sheet is electronically 'semi-metal' or a 'zero band-gap' semiconductor, however, CNTs are either true metals or true semi-conductors [1, 3]. The wide spectrum of applications of CNTs in specific engineering applications includes high performance materials in space applications, automotive applications, electronic devices, electromagnetic shielding (EMI) and electrostatic dissipative (ESD) materials [4].

CNTs are synthesized in many forms: single wall carbon nanotubes (SWNTs), double wall carbon nanotubes (DWNTs), and multiwall carbon nanotubes (MWNTs). MWNTs sustain the structure made up of rolled concentric cylinders through van der Waals attractive forces between the layers [5]. Thus, the structure of MWNTs becomes complicated in terms of physical understanding as well as characterization of MWNTs. The properties of MWNTs are influenced by factors such as diameter, chirality and method of synthesis [6]. High L/D

ratio and high flexibility along with attractive forces between MWNTs surfaces manifest in highly 'agglomerated' structure of 'as-received' MWNTs [7]. MWNTs dispersed in aqueous or organic media exhibit poor dispersibility leading to 'sedimentation' phenomenon due to intertube attractive forces and 'hydrophobic' nature of MWNTs surface. However, the dispersibility of MWNTs may vary based on the 'functionality' associated with MWNTs.

Incorporation of MWNTs in various polymer matrices has been exploited as a strategy to obtain electrically conducting composites with superior mechanical and thermal properties [8, 9, 10]. CNTs pose some issues during processing with polymer matrices, arising from 'agglomeration' and 'entanglement' of MWNTs [4, 7, 11, 12], 'slippage' of nanotubes during deformation [6] and, poor polymer/ MWNTs interfacial interaction [13, 14]. It is a challenging task to achieve a uniform dispersion of MWNTs in a polymer matrix through melt-mixing technique due to the formation of 'agglomerated' structure [15, 16].

Polymer blends are of immense commercial interest as high performance alloys, due to their excellent properties for potential applications, where materials with high thermal stability, good chemical resistance, enhanced toughness and excellent dimensional stability are required [17]. Blends of polyamide 6 (PA6) and acrylonitrile-butadiene-styrene copolymer (ABS) with MWNTs exhibit both enhanced electrical and thermal properties. An improvement in the properties of PA6/ABS blends with MWNTs has attracted attention of researchers [18, 19, 20] as well as of many polymer processing industries. However, it is essential to find ways to reduce MWNTs concentration through lowering the electrical percolation threshold in order to reduce the cost of CNTs in general [21]. Melt-blending of polymers with MWNTs is an effective strategy to prepare electrically conducting composites of lower electrical percolation threshold. This technique exploits shear applied during processing to improve dispersion of MWNTs in polymer matrices.

A lower electrical percolation can be achieved by selectively localizing MWNTs in one of the polymer phases or at the interface of a 'co-continuous' blend. Percolation of polymer phases may arise due to 3-D interconnecting structure in 'co-continuous' blends. Further, this structure is accompanied by the percolation of conducting particles predominantly in one of the phases or at the interface via implementation of 'double percolation' phenomenon, which significantly reduces the percolation threshold [22, 23, 24, 25]. The lowest percolation threshold will be achieved when one can restrict MWNTs at the interface of the co-continuous phases [26]. Dispersion and localization of MWNTs in PA6/ABS blends has been investigated for various issues such as the state of dispersion of MWNTs, polymer/MWNTs interaction and formation of the 'network-like' structure of MWNTs in the polymer blends [19, 27, 28].

PA6/ABS blends with MWNTs can be prepared by melt-mixing via the use of continuous extruder (twin-screw extruder) or a batch mixer (microcompounder). The 'agglomerate' formation of MWNTs even after ultra-sonication and an inadequate interfacial interaction between the polymer matrix and MWNTs lead to less wetting or less infiltration of polymer chains into MWNTs 'agglomerates' during melt-mixing process [27, 29]. The number and size of primary 'agglomerates' of MWNTs can be minimized by applying appropriate shear during melt-mixing [29, 30]. A 'sequential' mixing and/or 'masterbatch' approach manifests in a lower electrical percolation threshold in case of PA6/ABS blends with MWNTs [28]. The blend composition, varying processing parameters during melt-mixing and thermodynamic factor (surface free energy difference) affect the phase morphology, dispersion and localization of MWNTs in polymer blend components [19, 20, 24, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40].

Non-covalent functionalization of CNTs is often preferred over covalent functionalization of CNTs, which improves 'dispersibility' of nanotubes without deteriorating the intrinsic properties associated with MWNTs [41, 42, 43, 44]. In this context, various studies have reported the modification of MWNTs using organic molecules such as sodium salt of 6-aminohexanoic acid (Na-AHA) [15, 28] and polyaromatic molecules [45, 46, 47, 48]. Na-AHA has been reported as an effective modifier for MWNTs, which manifests in an improved MWNTs dispersion in PA6 matrix [15], PA6/acrylonitrile-butadiene-styrene copolymer (ABS) blend system [27], PA6/Surlyn blend system [49] and PP/ABS blend system in the of PP-g-MA [50, 51]. Na-AHA molecules facilitate the 'debundling' of MWNTs via 'electrostatic charge repulsion' and 'steric stabilization' in aqueous dispersion [50]. Further, the amine functionality of Na-AHA engages in 'melt-interfacial' reaction with acid end group of PA6 or maleic anhydride functionality of compatibilizer during melt-mixing, thereby retaining the finer 'network-like' structure of MWNTs even in the melt.

The anchoring ability of aromatic moiety on nanotube surface was exploited to achieve a significant enhancement in the state of dispersion of SWNTs in chloroform [52]. Amino-pyrene derivative has been used in order to improve the dispersion of MWNTs in an

apolar matrix viz., PP [53]. Pyrene–capped–polystyrene (PyPS) acted effectively as a dispersant for SWNTs via establishment of ' π - π ' interaction with SWNTs surface. PS/PyPS/SWNTs composites showed significant enhancement in the DC electrical conductivity [52]. Moreover, various organic modifiers viz. benzoyl triphenyl phosphonium chloride (BTPC), dodecyl triphenyl phosphonium bromide (DTPB), octadecyl triphenyl phosphonium bromide (OTPB) have successfully been utilized for modification of MWNTs in PA6/ABS blends. PA6/ABS blends with modified MWNTs exhibited enhanced DC electrical conductivity values in the presence of organic modifiers [54].

Encapsulation of MWNTs by various polymers has also been utilized as a strategy to improve the dispersion of nanotubes by exploiting the interaction between MWNTs and encapsulating polymer [55, 56, 57, 58]. Dispersion of SWNTs has been facilitated by the conjugated polymer wrapping [55]. Block copolymer of poly(styrene-b-pyrene) (PS-b-PAH) assists to disperse MWNTs in epoxy matrix through 'non-covalent' interaction [56]. 'Polymerization-filling technique' [59] has also been reported as an effective way to overcome the filler 'agglomeration' and as a consequence surface-coated carbon nanotubes could be utilized as a 'masterbatch' in commercial polymer matrices. Styrene maleic anhydride copolymer (SMA) encapsulated SWNTs have exhibited uniform dispersion when melt-mixed with polyamide12 (PA12) through 'reactive coupling' between PA12 and SMA-encapsulated SWNTs [57].

1.1 Objectives

In order to achieve a uniform dispersion of MWNTs in immiscible polymer blends it is necessary to overcome challenges including enhancement of extent of 'debundling' of MWNTs and selective localization of MWNTs in one of the phases or at the interface. It is difficult to determine the state of dispersion of MWNTs using a specific characterization technique. Hence, it is important to carry out investigations at various length scales in order to study the dispersion of MWNTs in the polymer blend. This study has been planned to investigate MWNTs dispersion and their localization in binary immiscible polymer blend (PA6/ABS) by using a novel organic modifier, in combination with a suitable compatibilizer. The objectives of this work are as follows:

<u>I) State of dispersion of multiwall carbon nanotubes: Investigating influence of organic</u> <u>modifiers and dispersion media</u>

To study the dispersibility of MWNTs in aqueous as well as organic media in presence and absence of non-covalent organic modifiers including conventional surfactant – sodium dodecyl sulphate (SDS), sodium salt of 6-aminohexanoic acid (Na-AHA) and 1pyrenecarboxaldehyde (PyCHO). The effect of six various organic solvents, which belong to three classes viz., 1. polar aprotic – tetrahydrofuran (THF), acetone, dimethylformamide (DMF); 2. polar protic – ethanol, methanol and 3. apolar aprotic – xylene, on the state of dispersion of MWNTs has been studied in this section. The dispersion of MWNTs has been studied through optical microscopic analysis (through the determination of average 'agglomerate' size of MWNTs), Raman spectroscopic analysis and UV-vis spectroscopic analysis (through increased concentration of individual nanotubes), and transmission electron microscopic analysis (TEM) (observation of separation between the nanotubes). Theoretical factors, which determine the state of dispersion of MWNTs, have also been compared with I_D/I_G ratio obtained from Raman spectroscopic analysis and UV-vis absorbance values in order to establish a conceptual understanding of MWNTs dispersibility in organic media.

II) Dispersion, migration and 'network-like' structure formation of MWNTs in 'cocontinuous' PA6/ABS blends

This study has been planned to investigate the influence of non-covalent modification of MWNTs by Na-AHA and PyCHO molecules to assess the state of dispersion of MWNTs on the basis of the morphology and the electrical conductivity of melt-mixed, 'co-continuous' PA6/ABS blends. The effect of 'simultaneous' mixing protocol on the state of dispersion of MWNTs viz., selective localization in one of the phases, re-distribution of MWNTs to other phase, and interface localization has been assessed via morphological observations. The dispersion and confinement of MWNTs in the immiscible blends affect the final properties of the blend such as electrical conductivity (through percolative network of CNTs), thermal conductivity (through efficient phonon transfer by reducing interfacial resistance), crystallization behaviour (enhancing heterogeneous nucleating action), thermal degradation (delaying through immobile phase on MWNTs surface), dynamic mechanical properties (through efficient stress transfer via improved polymer/MWNTs interaction) and rheological behaviour (through changed rheological network of MWNTs in the polymer matrix). Thus, the study of the state of dispersion of MWNTs becomes essential in order to study the structure and properties of MWNTs incorporated polymer blends. Various mixing parameters during 'simultaneous' mixing and surface modifications of MWNTs have been investigated. in order to restrict MWNTs at the interface of PA6/ABS blends. The choice of suitable modifier depends on its ability to disperse MWNTs effectively, and to interact with the compatibilizer.

III) Influence of non-covalent modification on the state of dispersion of multiwall carbon nanotubes in co-continuous binary polymer blends

The state of dispersion of MWNTs has been assessed through investigation of phase morphology and electrical conductivity of melt-mixed, 'co-continuous' PA6/ABS blends to study the effect of non-covalent modification of MWNTs with Na-AHA and PyCHO comparatively. The presence of organic modifier molecules on MWNTs surface has been determined through X-ray photoelectron spectroscopic (XPS) analysis and Fourier transform infra-red spectroscopic (FTIR) analysis. The distribution and state of dispersion of MWNTs has been studied through investigating 'selective localization', 'interfacial crystallization' and morphological observations. Further, phase morphological alteration in the presence of unmodified versus modified MWNTs has also been analyzed to assess the variation in electrical conductivity in PA6/ABS blends in the presence of unmodified/modified MWNTs. The role of organic modifiers in establishing various interactions with MWNTs and also with the respective polymer phases has been addressed to critically analyze MWNTs dispersion in blends. The 'interfacial crystallization' of PA6 in the presence of MWNTs has been discussed in context to electrical conductivity of PA6/ABS blends. The 'interphase' formation in the blends in the presence of MWNTs has also been studied in connection with the corresponding electrical conductivity of the blends.

IV) Evolution of phase morphology and 'network-like' structure of multiwall carbon nanotubes in binary polymer blends during melt-mixing

In order to investigate the effect of unmodified and modified MWNTs on the phase morphology development as a function of melt-mixing time and the formation of 'networklike' structure of MWNTs two selective compositions viz., 40/60 (wt/wt) and 60/40 (wt/wt) PA6/ABS blends were prepared by melt-mixing technique via 'simultaneous' mixing
protocol for varying melt-mixing time. Phase morphology development of the blends with MWNTs was studied to understand the effect of state of dispersion of various MWNTs along with their 'network-like' structure on the formation of 'co-continuous' type of morphology. The state of dispersion and the 'network-like' structure of the MWNTs as a function of meltmixing time were assessed through electrical conductivity measurements, morphological observation and through non-isothermal crystallization behaviour of PA6 phase in the respective blends.

V) Dispersion of non-covalently modified multiwalled carbon nanotubes in binary immiscible polymer blends: Effect of encapsulation of nanotubes with a conventional reactive compatibilizer

This section has been aimed at utilizing SMA copolymer encapsulated MWNTs in 'co-continuous' PA6/ABS blends. Further, MWNTs were modified using Na-AHA/PyCHO and subsequently encapsulated by SMA copolymer. The influence of SMA encapsulated modified MWNTs on the phase morphology and the localization of MWNTs in PA6/ABS blends has been investigated considering the fact that 'reactive coupling' between amine end group of PA6 chains and MA moiety of SMA copolymer would take place, while MWNTs dispersion and localization would also take place during 'simultaneous' melt-mixing. Understanding the complexity of the issue, it is also planned to utilize various characterization techniques, viz., DC electrical conductivity measurement, TGA analysis, non-isothermal crystallization behaviour through DSC, melt-rheological analysis and DMTA analysis to capture events, which would possibly influence various interactions among MWNTs, organic modifier, SMA copolymer and polymer phases. Moreover, this study also aims at addressing 'interphase' formation, 'interfacial' interactions with crystalline phase of PA6 and the 'network-like' structure of MWNTs in PA6/ABS blends.

1.2 Organization of the thesis

The organization of the thesis is as follows:

Chapter 1: Introduction

Chapter 2: Literature survey

Chapter 3: Experimental details and characterization techniques

- Chapter 4: Results and discussion
- **Chapter 5: Summary and conclusions**

Chapter 2: Literature survey

The present literature survey has been carried out with the aim of establishing an understanding of the concept of 'dispersion' of MWNTs in various media such as aqueous/organic medium and in polymeric phases, factors influencing the state of dispersion of MWNTs in polymer matrices such as concentration of blend and interactions of MWNTs with polymer phases, modifier molecules and reactive compatibilizer.

2.1 Multiwall carbon nanotubes

Carbon nanotubes are rolled up sheet of graphene with sp² hybridized structure of the diameters in the range of nanometres (*Figure 2-1*) [3, 60]. Carbon nanotubes have been exploited as potential conducting filler owing to exceptional electrical properties offered by nanotubes when incorporated in an immiscible polymer blend [61, 62, 63, 64, 65, 66]. Electrical conductivity achieved on incorporation of MWNTs is known to be a consequence of the formation of 'network-like' structure of MWNTs of high aspect ratio [length to diameter ratio (L/D) ratio \approx 10,000]. However, highly 'agglomerated' structure of 'asreceived' MWNTs has been recognized as a stumbling block in developing polymer-CNTs composites. The advantages of carbon nanotubes as filler have not been fully realized so far due to the difficulty in obtaining well-dispersed CNTs in nanocomposites.

2.1.1 Synthesis, structure and properties:

CNTs (1-D filler) are characterized by an exceptionally large surface area (about 1000 m^2/g for SWNTs). Appropriate surface modification of fillers results in high interfacial strength via improvement of the compatibility of fillers with polymer matrix. Melt-mixing, solution mediated processes, and *in-situ* polymerization are the commonly practiced techniques employed for incorporation of CNTs into a polymer matrix [67, 68].

Figure 2-2 depicts that the volume of interfacial region exceeds the volume of the particle when the fillers are reduced to nanoscale and δ (particle size) is in the range of ~1–10 nm. The weak forces between particles, such as van der Waals, are more pronounced for nano-sized particles due to lower surface roughness, smaller average particle separations resulting in higher dispersive forces. Nano-scale fillers possessing high-aspect-ratio exhibit a percolation thresholds at of 1–5 vol% and thereby exhibit large increment in bulk mechanical and transport properties of corresponding composites at low loadings of filler [67].

2.1.1.1 Techniques of synthesis

CNTs exhibit a different topology, which differentiates CNTs from other carbon structures. There are two types of processes to synthesize carbon nanotubes: single step process (thermal pyrolysis and flame synthesis) and double step processes (physical vapour deposition, solution based catalyst precursor, chemical vapour deposition) [69]. The nanotubes can be produced in bulk using arc discharge method, laser ablation and chemical vapour deposition (CVD) [70, 71, 72, 73]. The arc discharge method is reported to produce nanotubes along with the main product, which is 'fullerene' [74]. This is one of the simplest methods to synthesize nanotubes on a large scale. However, multiple purification steps are required in order to separate the various products [71].



Figure 2-1 Various types of sp² hybridized structures of carbon: a) graphene sheet, b) C-60 fullerene, c) SWCNTs, d) DWCNTs, e) MWCNTs [Courtesy Ref. 60].



Figure 2-2 The aspect ratio and δ (particle size) are defined in the schematic where (r is radius, l is length, h is height) [Courtesy Ref. 67].

The basis of an arc discharge and a laser ablation technique is the condensation of hot gaseous carbon atoms produced via evaporation of the solid carbon [70]. An electric arc of high-current is passed through the graphite electrodes and with the help of metal catalyst; the nanotubes are formed as one of the product [74] at a high temperature [71]. These techniques produce nanotubes on a few grams scale. In spite of being the most commonly used techniques, these methods are demanding in terms of equipment required for several purification steps [71] and energy consumption. In addition to this, the nanotubes on a substrate is difficult with these methods. These limitations make the arc discharge method and laser ablation less suitable for high scale nanotube production [70].

Chemical vapour deposition (CVD) [*Figure 2-3*] is a technique, in which volatile compounds of carbon are decomposed and the process is catalyzed by metallic nanoparticles [70, 71, 72]. The simple apparatus consisting of an oven, tubular reactor, and a set of mass flow controller to feed the gas mixture makes the CVD method a popular technique in CNTs production [66, 75]. In addition, specific morphologies, such as CNTs forest, can be produced if a flat substrate is used for nanotube growth. In the catalyzed chemical vapour deposition (CCVD) process the most important factor is the thermodynamics of the formation of solid carbon are the temperature and pressure at which the reaction takes place. Further, these methods have been modified as per the requirements of the specific application [76], as well as the processes were improvised to synthesize CNTs from various starting material like carbon dioxide [77] or from the plastic waste [78].

2.1.1.2 Physics of MWNTs

High aspect ratio is an important factor that makes MWNTs an attractive material for composites with polymers [79]. There is a strong chemical linkage between the carbon atoms with three neighbouring atoms in the graphene sheet when rolled into a tube [1]. The highest known basal-plane modulus of graphite and the strong association between the atoms, make the CNTs ultimate high-strength fibres (exceptionally high elastic modulus E ~1 TPa).



Figure 2-3 Schematic of chemical vapour deposition system utilized to work in high vacuum conditions (one of the various types)[Courtesy Ref. 71].



Figure 2-4 Representation of the hydrolyzed poly(styrene-co-maleic anhydride) (HSMA) wrapping on the MWNTs [Courtesy Ref. 103].

Nanotubes are reported to bend over a large angle when a force above the bending strength is applied, then they start to ripple and further develop kinks. However, these deformations are found to be elastic and vanish when the load is removed [1]. Thus, the nanotubes are stiff for smaller loads and flexible for larger loads, which make the nanotubes an extremely attractive material for high performance applications. CNTs allow a flow of electrons similar to the metals [1]. Whereas, the graphene sheet is electronically a semi-metal or a 'zero band-gap' semiconductor, the nanotubes, however are either true metals or true semi-conductors [1].

2.1.2 Surface characteristics and dispersibility of MWNTs in fluids

2.1.2.1 Dispersibility of MWNTs: Factors affecting the dispersibility in fluids

The physico-chemical nature of CNTs can be comprehended as fully conjugated polyaromatic macromolecules with a hollow, inert interior and reactive exterior ends. Fundamental research of nanotubes focuses on the intrinsic properties of isolated carbon nanotubes, whereas the applications rely strongly on interactions of nanotubes with their environment. These interactions are influenced by the chemical structure of dispersion medium, type of dispersion media and the presence of other molecules. These interactions are due to various non-covalent forces acting between the nanotube and molecular, ionic or macromolecular species constituting the nanotube environment [80]. MWNTs are incorporated in polymer matrix with the goal of achieving individual and separated nanotubes which can be utilized to attain enhanced properties at lower concentration of nanotubes [7]. An investigation of 'sedimentation' behaviour of nanotubes in various media and in the presence of various modifiers is an important step in estimation of dispersibility of MWNTs in polymer blends [81, 82]. The dispersibility of CNTs is strongly influenced by entangled structure of tubes within the 'as-produced' primary MWNTs 'agglomerates'. Two factors have been identified to influence the MWNTs dispersion viz., attractive forces between the MWNTs and high aspect ratio in addition to high flexibility, which significantly increase the possibility of 'agglomeration' of MWNTs in suspensions as well as polymer matrices [7].

Further, the purity and presence of functional groups on surface of the nanotubes contribute to dispersibility of nanotubes in different media due to different impregnation or wetting characteristics. For samples with equivalent surface chemistries, nanotubes having a more 'agglomerated' and 'entangled' structure in 'as-received' state results in poor dispersion, which manifests in marginal enhancement in mechanical properties as compared to a less 'agglomerated' material. CNTs dispersion has been found to improve by a lesser degree of entanglement, smaller average 'agglomerates' size and enhanced 'debundling', when various surface modification approaches were utilized [80, 83].

2.1.2.2 Criteria for improved dispersibility

Various strategies have been exploited including the covalent/non-covalent modification of nanotubes and use of suitable organic medium. Dispersion is often studied at a nanoscale, whereas it has been recognized that dispersion over larger length scales (micrometer) can be equally crucial in developing a thorough understanding of the state of dispersion of MWNTs in polymer matrix.

2.1.2.3 Effect of media of dispersion

For an organic liquid to be a good solvent for nanotubes there are a few important factors, which should be considered:

- 1. Dielectric constant/ relative permittivity
- 2. Surface tension
- 3. Solvochromic parameter (π^* 'Taft and Kamlet parameter')
- 4. Lewis basicity (β = electron-pair donicity)
- 5. Hydrogen bond donor parameter (α)

Non-hydrogen-bonding Lewis bases with high electron-pair donicity are known to be good solvents for carbon nanotubes [84, 85]. CNTs sedimented in a solvent with high polar (δ_p^2) and hydrogen-bonding (δ_h^2) Hansen solubility parameter components, as no specific dependency was found on the total solubility parameter [86]. Vaisman et al. [86] have also concluded that role of surfactants in dispersion of CNTs follows classical colloidal chemistry.

2.1.2.4 Ways to enhance dispersibility of MWNTs: Covalent and non-covalent surface modification

Functionalization of CNTs is one of the strategies utilized to enhance their dispersion in organic or aqueous media. In addition to prevent 'agglomeration', functionalization also leads to better dispersion, alignment and strong interaction between the polymer and the nanotubes [87]. Covalent functionalization alters the chemical structure of the nanotubes in such a way that the sp^2 hybridized state of carbon atoms changes to the sp^3 hybridized state. Functional groups such as -COOH and -OH are formed on MWNTs surface either during the oxidation while with acids process or treating concentrated during purification/functionalization. Various strategies have been discussed in a review paper by Spitalsky et al. [88], which include ester linkages, amide linkages between oxidized CNTs and polymers, grafting by radical mechanism and other coupling reactions. CNTs have also been reported to be covalently functionalized at the end caps or at the sidewall to enhance the dispersion in organic media or in polymer matrices [87].

Farzi et al. [89] functionalized MWNTs successfully through a simple radical grafting approach based on the use of dicumyl peroxide as an alkane hydrogen abstractor. Whereas, in blends with untreated MWNTs, nanotubes were found to be 'agglomerated' in clusters of a few tens of micrometers. Treated MWNTs showed clusters of reduced sizes as compared to the untreated MWNTs. This study concluded that the grafting of PP onto MWNTs provided a low steric barrier against the strong intermolecular van der Waals interactions among nanotubes within the PP matrix. In case of covalent functionalization, an enhanced interaction between the nanotube surface and polymer molecule influenced the C–C bond in nanotubes, which resulted in the deterioration of mechanical properties. Though the dispersion of CNTs improved in the presence of the covalent functionalization, the length of the nanotubes decreased, which resulted in lower electrical conductivity [87].

2.1.3 Non-covalent surface modification

Non-covalent functionalization or modification of the nanotubes is often preferred since it improves the dispersibility of the nanotubes without deteriorating the intrinsic properties of CNTs [87, 90]. Such non-covalent surface modifications work mainly on the basis of ' π - π ' stacking interaction or van der Waals type of interaction. These interactions involved in non-covalent modifications are thermodynamically controlled.

2.1.3.1 Non-covalent modification through polymer wrapping

The modification of the nanotubes with polymer wrapping has been reported to be an effective way to improve the dispersion of the nanotubes in aqueous solutions [91, 92, 93, 94] and in organic solvents [87, 93]. Further, such polymer wrapped nanotubes when incorporated in the polymer matrix, are found to show better interaction with the polymer matrix [95, 96, 97, 98]. An interaction between a polymer and nanotubes is governed by the thermodynamic factor, i.e. the difference in the corresponding value of surface free energy of that polymer and the surface free energy of nanotubes. When the difference is lower, a better interaction exists between the polymer and the nanotubes, which results in effective wetting of the nanotubes with the polymers. However, such interaction is difficult, either due to low polarity of the polymers or due to the lack of functional groups on the MWNTs to interact with the polymer. Therefore, the wrapping of MWNTs with polymers provides functional groups on the MWNTs, which facilitates the interaction between the polymer matrix and MWNTs. In such cases it is essential that the wrapping polymer must establish non-covalent interaction with nanotube surface. In most of the studies, such polymers were chosen that can interact through π -stacking interactions. Also, it has been reported that the weak interaction between polymer wrapping and nanotubes may be the reason for poor stress transfer [87].

Polymers with aromatic groups in the main chain are more likely to interact well with the nanotube surface through ' π – π ' stacking interaction [99]. Therefore, polymers such as polystyrene [95], poly(styrene maleic anhydride) [96, 100, 101], and pyrene-based polymer [102] have been utilized for non-covalent functionalization of MWNTs. As shown in *Figure* 2-4, HSMA molecules interact with MWNTs and are reported to lead to effective exfoliation of nanotubes [103]. Such polymer wrapped nanotubes may be utilized in immiscible blend systems to compatibilize the blend through reactive compatibilization. Bose et al. [100] reported that the storage modulus of PA6/ABS blends with MWNTs in the presence of SMA copolymer enhanced (~10³ Pa) by 2 orders of magnitude as compared to the corresponding neat blend (~10¹ Pa) due to increased interfacial area, higher entanglements and MWNTs being located at the interface. However, presence of SMA copolymer is reported to deteriorate the electrical properties due to formation of an insulating layer on the surface of MWNTs [100, 101].

2.1.3.2 Surfactants

Nanotubes have an exceptionally strong tendency to 'agglomerate' in aqueous solutions due to their hydrophobic surfaces, which makes it difficult to disperse them in water [104,105]. Surfactants are necessary to achieve colloidal stability, which are able to encapsulate and reduce the intertube van der Waals forces and thus debundle the nanotubes. This necessitates the presence of strong interactions between the CNTs and a dispersing agent. Traditional surfactants, such as sodium dodecyl sulphate (SDS) (*Figure 2-5*), satisfy these requirements and provide stable MWNTs dispersions [106]. However, the short-comings of these surfactants are that stable dispersions are formed only when these surfactants are present in very high concentrations, which is often undesirable for subsequent nanotube processing [107].

As shown in *Figure 2-6*, surfactant molecules get adsorbed on the surface of the nanotubes through the hydrophobic tail interacting with the nanotube surface, and hydrophilic head establishes the interaction with the water phase. The long organic tail involving 8 to 18 carbon atoms do not exhibit surfactant properties, whereas longer chains are not water soluble [60]. Molecules with aromatic groups effectively interact with nanotubes surface through ' π - π ' interaction.

2.1.3.3 Chemical modifiers

The adsorption of various molecules on the surface of the nanotubes is one of the strategies to improve the dispersion of MWNTs [43]. Non-covalent modification using organic modifiers helps to keep the electronic structure of MWNTs in-tact and yet improves the debundling of MWNTs. In this context, various studies have reported the modification of MWNTs using variety of molecules such as SDS and Na-AHA, polyaromatic molecules and polymers.

Choi et al. [108] studied the dispersion of MWNTs, which were non-covalently functionalized using poly(styrene-co-maleic anhydride)-block-polystyrene (PMAS-CNTs). PMAS modified MWNTs showed improved and more stable dispersion in toluene as well as improved electrical conductivity. Tuncel [55] reported that conjugated polymers are widely utilized for surface modification of MWNTs because of the following reasons: (1) solubility and as a result processability is improved due to effective interaction between the extensive

conjugated backbone of the polymer and side walls of the nanotubes through ' π - π ' interactions; (2) composites with synergistic effect from high electrical conductivity and mechanical strength of nanotubes and good optoelectronic properties of conjugated polymer; (3) conjugated polymers can be used for purification of the nanotubes; and (4) luminescent properties of conjugated polymers can be useful. It has been reported that conjugated polymers with flexible as well as with rigid backbone can be used to disperse the nanotubes.

Use of sodium salt of suberic acid when half neutralized and full neutralized (HNSA and FNSA) is reported by Ratna et al. [109] as one of the ways to improve the state of dispersion of MWNTs in aqueous solution and which is maintained in the polymer composites with poly(ethylene oxide) matrix as well [*Figure 2-7*]. A study by Khare et al. [50] reported the debundling of purified MWNTs via neutralized acid functionalized MWNTs (with the help of NaOH solution). A novel modifier – sodium salt of 6-aminohexanoic acid is reported to be an effective organic modifier for MWNTs in case of PA6 [15] and PA6/ABS blend system [54]. It can be seen from *Figure 2-8* (a) that the AC electrical conductivity increased in the presence of Na-AHA modified MWNTs, in PA6 matrix. In contrast, various modifiers benzoyl triphenyl phosphonium chloride (BTPC), dodecyl triphenyl phosphonium bromide (DTPB), octadecyl triphenyl phosphonium bromide (OTPB) and Na-AHA were utilized for modification of MWNTs. AC electrical conductivity values showed a dependence on the length of organic tail of the modifier in case of PA6/ABS blends, which manifests in higher electrical conductivity of the blends in the presence of OTPB and DTPB modified MWNTs as compared to other modifiers.

Polyaromatic molecules are reported as effective modifiers for MWNTs owing to the availability of aromatic rings to establish a ' π - π ' interaction between the organic modifier and MWNTs surface. Molecules containing the pyrene moiety are used as linkers to nanotube surfaces [45, 46]. A study by Yang and Pan [47] using a non-covalent method of modifying MWNTs with the help of six-armed star poly(lactic acid) with a triphenylene core showed that MWNTs debundling as well as the non-covalent functionalization of the MWNTs was achieved in one step. Similarly, Luan et al. [56] found enhanced electrical and mechanical properties when MWNTs were modified using a block copolymer of poly(styrene-b-pyrene) (PS-b-PAH).

2.2 Interactions between MWNTs and polymer chains

2.2.1 Structural features – contour length and persistence length

There are some structural similarities between polymer chains and nanotubes related to the contour length and the persistence length. The contour length is the end to end distance of the polymer chain when stretched out, whereas the persistence length is the measure of chain flexibility. Therefore, a higher persistence length indicates that the chain is less flexible. The values of the contour length of SWNTs and polyethylene molecule are comparable, ~1 μ m and ~0.9 μ m respectively. Whereas, the persistence length of nanotubes (~50 μ m) and the persistence length of polymer chain (~0.6 nm) differs significantly [60]. There is also a similarity in the method of synthesis as mentioned by Grady [60] that the process involves a solid catalytic particle and the gas that contains the reactive agent. However, polymer melt exhibits viscoelastic nature; on contrary, CNTs cannot be hence could not form a viscoelastic fluid. CNTs can be dispersed in polymers via melt-blending and through liquid medium.



Figure 2-5 Different possible organizations of the SDS molecules on the surface of a CNT (A) The SDS molecules could be adsorbed perpendicular to the surface of the nanotube, forming a monolayer; (B) The SDS molecules could be organized into half cylinders oriented parallel to the tube axis; (C) The SDS molecules could form half-cylinders oriented perpendicular to the tube axis [Courtesy Ref. 106].



Figure 2-6 (a) Structure of some common surfactants; (b) schematic representation of the mechanism of debundling of the nanotubes in the presence of the surfactants; steps involved:
1) tubes are bundled, 2) a tube is removed from the bundle, 3) finally a surfactant dispersant adsorbs to the bundle [Courtesy Ref. 60].



Figure 2-7 SEM micrographs of (a) unmodified and (b) HNSA modified MWNTs (dispersed in ethyl alcohol) [Courtesy Ref. 109].

2.2.2 Polymer blends with MWNTs

2.2.2.1 Origin and properties of polymer blends

Reinforced thermoplastics which possess superior properties constitute a major sector of the thermoplastics industry that is growing in importance both commercially and technically. Similarly, the industry, which deals with composites materials mainly involving thermoplastics filled with inorganic fillers, is also growing larger each year. The reinforced plastics industry essentially began with incorporation of glass fibres in thermosetting materials. Currently, thermoplastics filled with various materials have also gained popularity owing to the ease of processability that they have offered. Improved performance must be accompanied by lower cost which can be obtained by three ways which are: automated fabrication techniques, lower cost fibres and cheaper thermoplastic resins [110]. Mixtures of polymers exhibit enhanced properties and influence melt processing conditions and also need appropriate characterization methods owing to the complex nature of the blends [111].



Figure 2-8 Variation of AC electrical conductivity of (a) PA6/MWNTs composites where MWNTs and Na-AHA modified MWNTs are used [Courtesy Ref. 15] and (b) PA6/ABS blends with MWNTs modified with BTPC, DTPB, OTPB and Na-AHA [from left to right in (c)] [Courtesy Ref. 54].

Such blends of polymers show physical properties based on the interaction between the constituent polymers. Polymer blends can be characterized by their phase behavior as being either miscible or immiscible [112]. Miscible blends show comparable surface energies and hence, are able to form a single phase, whereas a large difference in the surface energies lead to immiscible blend that exhibits more than one phase. Interfacial and surface tensions of polymers are important in the technology of plastics, coatings, textiles, films and adhesives through their roles in the processes of wetting, adsorption, and adhesion [113]. Immiscible blends show separate amorphous and/or semi-crystalline phases due to their inability to form one phase. Each phase of a completely immiscible blend contains an essentially pure blend component whereas; the phases of partially immiscible blends may contain some of each material in the blend. Mechanical, thermal, rheological, and other properties of a polymer blend depend strongly on its state of miscibility. This state has been determined by the thermodynamics of interaction between the blend components, which is a function of their physical and chemical structures [112, 113].

The final morphology has a control on the properties of the blend, for example, the 'matrix-dispersed droplet' morphology enhances impact strength of the blend. Most of the high polymers are very viscous at high temperatures and exhibit non-Newtonian rheology [113]. When blending incompatible polymers in the melt, the resulting morphology is strongly dependent on the interfacial tension, other parameters influencing the morphology of the blend are: mixing temperature, viscosity of the polymers and the type of mixing utilized [114, 115, 116, 117, 118, 119]. The critical temperature for mixing of polymers, at which point viscous flow begins, is the melting temperature for semi-crystalline polymers and above the glass transition temperature for amorphous polymers.

However, during melting or softening there will be a broad distribution of temperature, stress and strain within the sample depending upon the processing technique. Although from thermodynamic point of view an amorphous polymer can be considered as 'liquid' above the T_g , from a rheological point of view it cannot be regarded as 'liquid' until the temperature is increased far above its T_g . Therefore, in case of amorphous polymers a new concept of 'critical flow temperature' that is $T_{cf} \sim T_g + 55$ ⁰C was used by Han [117]. The final morphology is dependent on the type of flow, the composition of the blend, interfacial tension of the blend and visco-elasticity of the components [119].

2.2.2.2 Phase morphology of the polymer blends

Numerous polymer blend systems have been studied in order to establish an understanding of the development of morphology as well as the stability of the morphology. The properties of multiphase materials are determined by the properties of the component polymers, by the adhesion between phases, and by the blend morphology that is created during the melt mixing process. As mentioned in a review by Pötschke and Paul, the morphology development depends on the rheological properties of the blend components that are viscosity ratio, interfacial tension, blend composition and processing conditions [24]. The proposed mechanism is summarized in the *Figure 2-9*, which is obtained on the basis of micrographs obtained from electron microscope [120]. *Figure 2-9* indicates that reduction of domain size begins primarily from the formation of a sheet or ribbon of the dispersed phase. Owing to interfacial forces and shear flow, holes form in the ribbon and grow until a lace structure is formed. This lace is then broken down into irregularly shaped particles, and finally into nearly spherical particles.

2.2.2.3 Phase morphology development in immiscible polymer blends: uncompatibilized blends

The incompatible nature of the blend components is characterized by large domain size, wider domain size distribution and a sharp interface [121, 122]. Inferior properties of an immiscible blend are due to the sharp interface caused by high interfacial tension which lacks phase adhesion. This obstacle can be overcome, and the properties tuned, by introduction of a graft or block copolymer. To achieve better interactions at the interface in case of a polymer blend, there are two ways: first involves an incorporation of copolymer (physical method) and second method involves formation of copolymer *in-situ* via chemical reaction between two reactive sites.

In both the cases if the interfacial tension is reduced, the morphology will be stabilized. Final droplet size is reduced due to suppression of rate of coalescence. The mechanical properties of these compatibilized blends are better than those of the corresponding uncompatibilized blends. The understanding of the evolution of the morphology demands a thorough knowledge of flow of the melt, viscosity ratio, elastic properties of the polymers [24] and effect of external factors such as shear rate, temperature of mixing, equipment used for mixing [117, 118,], complex strain field of the extruder [123],

presence of compatibilizer [115]. It has been observed that during blending of two polymers one of the phases is mechanically dispersed inside the other. Invariant morphology is seen in the batch mixers and in extruders (*Figure 2-10*) owing to rapid establishment of equilibrium between drop breakup and coalescence [115]. The behavior of a single drop is controlled by the type of flow, viscosity ratio (ratio of the viscosity of dispersed phase and the continuous phase respectively) ($\eta_r = \eta_d/\eta_m$) and the capillary number (C_a), which is associated with the relative influence of the shear stress and the stress corresponding to interfacial tension [115, 116].

2.2.2.4 Various types of morphology

The structure obtained after mixing of immiscible polymer pairs can be categorized into four basic morphology types (*Figure 2-11*) [24]:

- Matrix-dispersed droplet structure
- Matrix–fiber structures
- Lamellar structures
- Co-continuous structures

Often, commercial polymer blends exhibit 'matrix-dispersed droplet' type morphology, especially in rubber toughened systems, where the size of the droplets depend upon rubber particle size, rubber concentration, rubber content and interfacial properties [17, 24, 124, 125]. The thermo-physical, rheological and interfacial properties of the polymer blend systems differ from blend to blend. Co-continuous structures are found to be attractive since blends having this type of morphology can offer better combinations of component properties as compared to the dispersed-type structures. A co-continuous structure provides the maximum contribution to the mechanical modulus from each component, whilst synergistic effects on impact properties could also be observed. For a binary co-continuous blend, the surface of each phase is understood to be an exact topological replica of the other; they are complementarily reversed (antitropic), as shown in *Figure 2-12*. It is known that the co-continuous structures, a complete network structure of both polymers, can be formed over a certain interval of volume fractions.



Figure 2-9 Proposed mechanism for initial morphology development in polymers [Courtesy Ref. 120].



Figure 2-10 Schematic description of the blend morphology development along the axis of a twin-screw extruder for a polymer pair AB, where the melting point of polymer A, $T_{m,A}$, is lower than that of polymer B, $T_{m,B}$ [Courtesy Ref. 24, 118].

Co-continuous morphology is also important in case of blends with conductive fillers, since this reduces the electrical percolation threshold. The co-continuous morphology was found as an intermediate state in the initial part of the extruder for all blends, in which phase inversion occurred because the minor component melts first but is predicted to be the dispersed phase based on volumetric and rheological properties. It has been concluded by various studies that there is a critical value of mechanical energy required to transform the co-continuous morphology into a dispersed one.

Multi-component systems based on their phase morphology, polymer-polymer interaction at the interface, thermodynamic interaction depict certain properties, in absence of any chemical interaction at the interface. An unfavorable interaction causes a large interfacial tension in the melt, poor interfacial adhesion in the solid state makes uniform dispersion difficult and consequently it shows inferior properties relative to the individual components [110]. Reactive compatibilization using *in-situ* compatibilizer, block or graft copolymers is the way to achieve better adhesion at the interface of the two polymers and hence, yield improved properties. Morphology development in case of compatibilized blends shows refinement in dispersed droplet morphologies, as well in some cases elongated droplets and finer domains with co-continuous structures are observed.

2.2.2.5 Blends with MWNTs

When the filler has one dimension approaching nanometre range and if the polymer chain dimensions are within 20-30 Å of the filler surface then synergistic modulus and strength results are observed in the polymer blends with nanofillers. Inorganic fibres and fillers are known to contribute to the compatibilization of phase separated polymer blends. This has been attributed to the change in polymer T_g as the polymer chains in the vicinity of the rigid phase become bound, and is significant if the specific interactions tether the chains to the filler surface. An increase in T_g and resultant synergy in properties as a result of improved 'polymer/filler' interactions at nanometer scale.

Many researchers have reported that organically modified clay nanoparticles play an important role in improving the dispersion of phase separated blends as well as the mechanical properties [110, 126, 127]. Reduction in particle size is attributed to prevention of coalescence due to clay acting as a physical barrier, hence leading to refined morphology.



Figure 2-11 Types of morphology in immiscible polymer blends illustrated by SEM photomicrographs of cryofractures: (a) Dispersed structure (TPU/PP = 80/20 blend); (b) matrix–fiber-structure (PA6/SAN = 30/70 blend); (c) lamellar structure (PP/EPDM = 80/20 blend); (d) co-continuous structure (PE/PS compatibilized 25/75 blend, PS etched) [Courtesy Ref. 24].



Figure 2-12 Model of the antitropic structure of both components (a and b) of a cocontinuous blend [Courtesy Ref. 24].

The layered silicates (clays if they are of natural origin) may be exfoliated and/or intercalated in the respective nanocomposites, whilst they are present in 'agglomerates' in micro-composites. Carbon black, owing to its cost advantage, has been considered in a wide range of commercial applications. Furnace black and thermal black are the two forms of carbon black grades typically used as a conductive filler. High electrical percolation threshold is the main obstacle in case of carbon black due to low L/D ratio. However, this obstacle is overcome in case of clay and CNTs by the virtue the corresponding high L/D ratio.

2.2.2.6 Double percolation phenomenon

When one of the polymer phases forms a percolated phase in the presence of the other polymer phase and the filler forms a continuous phase via selective localization in one of the polymer phases, the phenomenon is termed as 'double percolation' [21, 22, 128]. 'Double percolation' phenomenon leads to the lowest electrical percolation threshold. Meincke et al. [20] carried out a study for PA6/ABS/MWNTs system to study dispersion and morphology with respect to electrical and mechanical properties. Selective localization of MWNTs in the PA6 phase is seen from the TEM micrograph (*Figure 2-13*). MWNTs could localize selectively in PA6 phase due to lower melt viscosity of PA6 and a lower difference in the surface free energies of MWNTs and the PA6 phase.

These blends showed (*Figure 2-13* plot on right) electrical conductivity at significantly lower filler loadings, as compared to the filled homopolymer, which has been explained on the basis of 'double percolation' phenomenon. The nanotubes are known to percolate in the PA6 phase (first percolation), which itself percolates in the blend (second percolation) [24]. The presence of MWNTs in the polymer blend either distributed in both the phases or preferentially confined in one of the phases results in the alteration of phase morphology as well as crystallization behaviour accompanied by varied rheological behaviour [24, 129, 130, 131].

2.2.3 Interaction between MWNTs surface and polymer chains

2.2.3.1 Properties of polymer/MWNTs composites

The measurement of the properties of individual nanotubes is difficult and they vary depending on the type of CNTs. Numerous studies and investigations by researchers have shown that CNTs offer the potential for fabricating electrically conducting polymer composites without deteriorating the inherent polymer properties. Insulating materials are known to show surface resistivity of $>10^{12} \Omega$ /square. Protection against electrostatic discharge can be achieved by static dissipation if the surface resistivity of the polymer is in the range 10^5 - $10^{12} \Omega$ /square, preferably at the low end of this range. For electromagnetic interference shielding, a higher electrically conducting polymer composites is required (< $10^5 \Omega$ /square).

The addition of a small concentration of MWNTs to a polymer matrix may have a remarkable impact upon its electrical properties. At concentration as low as 0.05 vol %, the surface resistivity of film fabricated using PP as the matrix decreases from its virgin polymer value of $>10^{12} \Omega$ /square to a value of $\sim 10^5 \Omega$ /square, which indicates that the MWNTs/PP composites film has a percolation threshold as low as 0.05 vol % [66]. Various approaches to study the effect of MWNTs content and processing conditions on the end-properties of the composites have been exploited by many groups.

Dispersion of MWNTs in various types of PC with MWNTs composites melt-mixed with LDPE was studied by Kasaliwal et al. [132]. This study showed that the polymer melt has infiltrated into MWNTs 'agglomerates' and MWNTs could be separated individually from the 'agglomerated' structure via the mechanism of 'erosion'. Further, the effect of melt viscosity and processing protocols on MWNTs dispersion was investigated. These studies indicated that improved dispersion was achieved at low mixing speed for high melt viscosity matrix and at high mixing speed for low viscosity matrix suggesting that high shear rates are necessary in order to obtain enhanced dispersion. Infiltration of polymer melt into MWNTs 'agglomerates' was identified to be a crucial step in reducing the strength of MWNTs 'agglomerates'.



Figure 2-13 TEM-micrographs of PA-ABS-NT-5 composite (a: 500 nm scale bar, b: 200 nm scale bar) and (right side) resistivity of PA-NT-x and PA-ABS-NT-x composites plotted versus the absolute filler content. The PA-ABS-NT-x composites show a decrease in the resistivity at lower filler loadings as compared to the PA-NT-x composites [Courtesy Ref.20].



Figure 2-14 TEM micrograph showing matrix infiltration and subsequent separation of nanotubes due to erosion from the agglomerates [Courtesy Ref. 132].

'Co-continuous' phase morphology in blends with fillers has been reported to result in lower electrical resistivity. PC/PP blends showed significantly enhanced electrical conductivity (*Figure 2-15*) in the composition range where PC formed a continuous phase, due to selective localization of MWNTs in the PC phase [133]. PC-MNWTs (~2 wt%) /PP-MMT (~3 wt%) blends with 50–80 wt% of PC-MWNT masterbatch showed electrical conductivity in the range of ~10⁻⁶ – ~10⁻⁴ S/cm. In case of PE/PS/carbon black composites the electrical percolation threshold was found to be varying according to the location of CNTs. An electrical percolation threshold was observed at 5 wt% when CNTs were preferentially localized in PE matrix and at 3 wt%, when CNTs were preferentially localized in PE matrix of 45/55 PE/PS blend. Further, the lowest electrical percolation threshold was observed at 0.4 wt %, when nanotubes were confined at the interface of PE/PS blend [21]. Thus, co-continuous blend of PE/PS with CNTs exhibited 'double percolation' phenomenon [21,133].

The presence of CNTs in polymer blends has been reported to influence the droplet size as well as the ligament thickness [54, 129]. The droplet size reduced on incorporation of nanotubes; therefore it has been concluded that CNTs caused 'physical compatibilization' (*Figure 2-16*). 50/50 (wt/wt) PA6/ABS blends with unmodified MWNTs exhibited refined 'co-continuous' morphology as compared to the corresponding neat blend. Further, 50/50 (wt/wt) PA6/ABS blend showed refined phase morphology in the presence of 2 wt% Na-AHA modified MWNTs [54]. However, the coarse phase morphology was observed in case of 50/50 (wt/wt) PA6/ABS blend with phosphonium based modifiers along with a change in the shape of ligaments from 'concave' to 'convex' type suggesting compositions near phase inversion region.

2.2.3.2 Thermal conductivity of MWNTs/polymer composites

Polymer/CNTs composites with high thermal conductivity are potential replacement for metal tools and equipment parts in electronic, heat-exchangers and automotive applications [134]. Thermal conductivity of composites has shown only modest improvement in contrast to a significant enhancement achieved in the electrical conductivity with very low loading of CNTs. Thermal conductivity of isolated nanotubes has been an active area of research, which reported values as low as 30 W/mK, to the highest reported nanotube thermal conductivities are of the order of 10^3 W/mK [60]. This variation is a manifestation of experimental difficulties in measurement of thermal conductivity of 'individual' MWNTs.



Figure 2-15 Electrical volume conductivity versus PC-2MWNT content in blends with PP-3MMT [Courtesy Ref. 133].



Figure 2-16 Schematic representation for the breakup process of the dispersed article under the influence of the CNTs [Courtesy Ref. 129].

The reason for lower magnitude of increase in thermal conductivity is a high interfacial thermal resistance between MWNTs surface and polymer phase. In this connection, Moisala et al. [135] have reported that the experimental thermal conductivity values were much lower than the predicted values due to the fundamental difficulty in transferring heat from polymer matrix to CNTs. A large interface resistance to the heat flow associated with poor phonon coupling between the 'stiff' SWNTs and the relatively softer polymer matrix has also contributed in lower thermal conductivity values.

Relationship between thermal conductivity and electrical conductivity [as shown in *Figure 2-17* (a)] has been studied in order to investigate the 'network-like' structure formation of MWNTs [136]. *Figure 2-17* (b) showed a marginal enhancement in the thermal conductivity with increasing filler content. Thermal resistance posed at nanotube-nanotube junction (contact resistance) due to the limited surface area contact and thermal resistance at the nanotube-polymer junction (interfacial resistance) due to the mismatch between the phonon spectra caused lower thermal conductivity in case of polymer-MWNTs composites. The unwrapped interface with non-covalent interactions is reported to be micrometer long Kapitza resistance and hence, is found to be inefficient by Xu et al. [137].

The Kapitza resistance may be reduced by modifying the molecular structure at the interface such that the phonon spectra matching can be enhanced and phonon coupling can be achieved [137]. Polymer wrapping is one of the methods utilized for decreasing interfacial resistance. However, a specific arrangement of the polymer molecules provided an enhanced thermal transfer. On the other hand, Cai and Song [138] reported that wrapping around CNTs enhance interfacial phonon scattering, as well as the amorphous interface may destroy the lattice vibration and thus, consequently result in decreased thermal conductivity. In case of 'non-covalent' wrapping of MWNTs, the structure of the nanotubes is unaffected; however, weak forces between the wrapping molecules and MWNTs may lead to high interfacial thermal resistance [134].

2.2.4 Preferential localization of MWNTs at the interface

Yan and Yang [139] have reported the interfacial localization of CNTs in case of PA6/PS blend (*Figure 2-18*). Localization of MWNTs was explained on the basis of

exclusion of MWNTs from both the polymeric phases due to poor wettability of the nanotubes by the polymers. The enhancement of phase dispersion and stabilization of the dispersed phase for long mixing time and at lower filler content was reported by Baudouin et al. [140] in case of polyamide (PA) and ethylene methyl acrylate random copolymer (EA) blends with un-functionalized CNTs.

According to the authors, the main reason for stabilization of the dispersed droplet phase is the barrier provided by the nanotubes localized at the interface as shown in *Figure* 2-19 (a-e). Göldel et al. [141] described the shape dependency on the diffusion of MWNTs from one phase to other via the 'slim-fast' mechanism. According to the authors, the rate of transfer of the nanotube is higher when nanotube is perpendicular to the interface, whereas, the transfer speed depends on the nanotube orientation during the melt-mixing process, when the nanotubes comes in contact with the blend interface for the first time. Hence, it is expected that for the fillers with higher aspect ratios, the state of dispersion plays an important role in the localization of the nanotubes at the interface.

2.2.4.1 Rheological behaviour of blends with MWNTs

Rheological properties of a polymer such as, rigidity modulus and viscosity can change even at low applied stress. This change may occur either in a short period of time or may take a long time [142]. Rheological studies have played a significant role in understanding the influence of MWNTs on the properties of polymer blends [18, 140, 143, 144]. Rheological studies not only provide an insight into the flow behaviour of the polymeric component influenced by blending with another polymer, but also provides the influence of state of dispersion of nanotubes [*Figure 2-20*], interaction with the polymer matrices and the 'network-like' structure formation of CNTs on the flow behaviour [143, 145, 146]. Studies on variation in the complex viscosity and the storage modulus help in understanding the dispersion and confinement of MWNTs in polymer blends [18, 147].

In case of 75/25 (wt/wt) PA/PE blend prepared by simultaneous mixing, MWNTs were located at the interface, which showed increase in 'solid-like' flow behaviour at lower frequencies [147]. This observation has been explained on the basis of an increased elasticity caused by decelerated shape variation of PE domains and/or coalesced PE domains. PE coated nanotubes act like points of connection that are dispersed throughout the volume of PA phase in case of PE pre-mixed samples of PA/PE blends [147]. Bose et al. [18] have

assessed the state of dispersion of MWNTs and the effect of a novel organic modifier –Na-AHA. Rheological studies revealed significantly enhanced debundling of Na-AHA modified MWNTs. The rheological percolation was observed at 0.25 wt% of MWNTs in PA6/ABS blends, which matched the electrical percolation threshold. Thus, Na-AHA played a crucial role in controlling the state of dispersion of MWNTs in case of PA6/ABS blends with MWNTs.

2.2.4.2 Formation of immobile phase on the MWNTs surface

A semi-crystalline polymer molecule may exhibit a contour length of 1 µm to 1 mm, therefore a single molecule may take part in more than one nanophases [148]. Polymer chains may form ordered phase during crystallization process (semi-crystalline phase) and there is a fraction, which cannot crystallize (amorphous phase) due to thermodynamic factor (extremely high viscosity) and kinetic factor (strain induced in polymer chain contributing to multiple crystallites). Crystallization behaviour of polymer varies in the presence of solid filler depending upon the interaction between polymer and filler. On incorporation of MWNTs in polymer matrix, a large fraction of polymer interacts with MWNTs owing to a large surface area of MWNTs. This concept of polymer fraction interacting with MWNTs is applicable to both semi-crystalline and amorphous polymers.

The 'heterogeneous' nucleation in the presence of MWNTs resulted in 'transcrystalline' polymer phase; whereas the amorphous polymers changed the polymer chain conformation [60, 149]. Two exothermic peaks corresponding to polyamide phase have been observed in the presence of MWNTs. Crystallization peak observed at higher temperature is due to the 'trans-crystalline lamellar' structure formation of PA6 phase, which is directly in contact with MWNTs surface [149]. The amorphous mobile fraction contributing to the glass transition is decreased in the presence of MWNTs, indicating a strong interfacial binding of the polymer in presence of MWNTs [60].



Figure 2-17 (a) Electrical conductivity as a function of thermal conductivity and (b) thermal conductivity as a function of filler content in wt% [Courtesy Ref. 136].



Figure 2-18 TEM micrographs of 1 wt% MWNTs-filled (a) 80/20 PA6/PS blends and (b) 70/30 PA6/PS blends [Courtesy Ref. 139].



Figure 2-19 Ethylene-methyl acrylate random copolymer/polyamide blend (a) – (d) [Courtesy Ref. 140]; (e) shape of typical commercial MWCNT and shape-dependent efficiency of slim fast mechanism, section 1: accelerated transfer, section 2 and 3: slow down sections [Courtesy ref. 141].



Figure 2-20 Schematic of (a) a single tube, (b) nanotube bundle, (c) 'aggregate' of single tubes, (d) 'aggregate' of nanotube bundles and (e) 'aggregate' of single tube and nanotubes bundles [Courtesy Ref. 144].



Figure 2-21 Storage modulus versus frequency plots for (a) neat materials and blends, (b-d) blends with varied blend composition and processing parameters [Courtesy Ref. 147].



Figure 2-22 Complex viscosity versus frequency for PA6/ABS blends with (a) MWNTs, (b) Na-AHA modified MWNTs; storage modulus and versus frequency for PA6/ABS blends with varied concentration of (c) MWNTs and (d) Na-AHA modified MWNTs [Courtesy Ref. 18].

A three phase model consisting of crystalline fraction (CRF), mobile amorphous (MAF) and rigid amorphous fraction (RAF) is represented as shown in *Figure 2-23* [150]. The RAF phase can be observed between the crystalline phase and mobile amorphous fraction. The thickness of MAF was ~10–200 nm, whereas the thickness of RAF was ~2–4 nm. In spite of a small thickness, RAF has significant contribution to the overall properties of blends with MWNTs [151, 152, 153]. The formation of RAF phase has been described as the consequence of vitrification of material in the vicinity of smaller secondary crystals in cooling cycle. Restricted polymer chain mobility in amorphous structure is the reason for 'vitrification' of amorphous fraction. The confinement effect (confinement due to MWNTs) has also been reported as a reason for the 'vitrification' [150].

It is important to investigate the effect of RAF on the crystallization and mechanical properties of the samples. The presence of a stiff layer of polymer on MWNTs has been reported to result in improved mechanical properties such as stiffness due to an enhanced 'stress transfer' between MWNTs and polymer phase [154]. An increase in the crystalline fraction through 'trans-crystalline' phase formation resulted in improved storage modulus [155]. Thus, it can be seen that the immobile layer formed on the nanotubes, either trans-crystalline or rigid amorphous fraction, plays an important role in the resultant properties of CNTs based polymer composites.

2.3 Variation in phase morphology, electrical properties and crystallization in the presence of a compatibilizer

2.3.1 Effect of compatibilization in immiscible polymer blends

Compatibilization techniques are mainly based on reducing the interfacial tension between polymer blends components. Reactive compatibilization has resulted in decreased domain size and increased phase adhesion between CNTs surface and polymer phase yielding improved mechanical properties. A compatibilizer can be considered as a polymeric 'surfactant' that concentrates at the interface and stabilizes the phase morphology. A typical reactive compatibilizer is a copolymer localized at the interface between two immiscible polymers having a miscible part with one blend component and forming covalent bond with the other blend component [110].



Figure 2-23 Sketch of the arrangement of crystalline, rigid amorphous and mobile amorphous fraction (indicating a three phase model) in a lamellae stack [Courtesy Ref. 150].



Figure 2-24 DSC cooling scans of PA6/EVA and PA6/EVA-g-MA blends and scanning electron micrographs of uncompatibilized and compatibilized (on right) [Courtesy Ref. 122].

The penetration of blocks into phases makes the interface region much broader when compared with that of the uncompatibilized binary mixtures [110]. A decrease in the crystallization temperature as compared to uncompatibilized blends (as can be seen in *Figure 2-24*) is attributed to the formation of graft copolymer between amine end group of polyamide and anhydride functionality at the interface [122]. This graft copolymer, in turn, influenced the mobility of EVA chain, thus lowering the crystallization temperature. Thus, the reactively compatibilized PA6/EVA-g-MA blends were separately crystallizing at the bulk temperature of crystallization corresponding to the individual components accompanied by lower heat of crystallization. SEM micrographs indicate that compatibilized blends were characterized by smaller average domain size with narrow size distribution, broader and immobile interface, whereas the uncompatibilized blends were characterized by sharp and mobile interface.

Maleic anhydride has been more reactive with PA6 than the oxazoline units. The decreased 'dispersed-droplet' size in the presence of a compatibilizer was primarily due to the suppression of rate of coalescence due to steric stabilization effect of compatibilizer [165]. Morphology of dispersed phase obtained during melt-blending depends on complex shear and elongational deformation. Thus, the addition of an emulsifying agent (the copolymer) has been found to modify the interfacial tension and hence, the domain size can be varied over a wide range. Another factor controlling size of the 'dispersed-droplets' is molecular weight of the copolymer. It has also been suggested that symmetric copolymers should be used in case of strongly incompatible system [156].

In the case of ABS/PA blends, two strategies are mainly used for compatibilization. The first strategy involves the addition of a polymer that is compatible with the styrene– acrylonitrile copolymer (SAN) matrix of ABS, and able to react with the amine or carboxylic acid end groups of the PA phase. In the other strategy, functional groups capable of reacting with PA were attached to SAN prior to blending with PA. Functional groups, such as acid or anhydride, epoxide, and oxazoline, which can react with the amine or carboxylic acid end groups of PA have been utilized. Oxazoline based compatibilizers are well established for various polymer blends [157, 158, 159]. The oxazoline functionality is particularly interesting because this group can easily react with both the carboxylic acid group and the amine group. Interaction parameters for mixtures of polymers can be determined on the basis of depression in melting point. Comparative studies of the phase morphology and mechanical properties of
PE/PS mixtures have shown that the introduction of a styrene–butadiene block copolymer with separated blocks induced a greater compatibilization effect as compared to a simple diblock copolymer.

Bose et al. [160] have reported the phenomenon of fractionated crystallization in 20/80 (wt/wt) PA6/ABS blend in the presence of a reactive compatibilizer (SMA) and MWNTs. When the semi-crystalline polymer formed a continuous phase and the amorphous phase was dispersed as well as could wet the semi-crystalline polymer, then the interface could act as a heterogeneous nucleation site. However, if the crystallizable polymer existed as a minor phase and was dispersed as droplets in an immiscible matrix, then instead of crystallizing at their bulk crystallization temperature, a series of crystallization exotherms appeared at much lower temperatures. This phenomenon is often referred as a fractionated crystallization. Incorporation of SMA led to further delay in occurrence of first crystallization exotherm and the suppression of a second exotherm peak (*Figure 2-25*). This led to an inference that either the concentration of SMA could not generate heterogeneous nucleating sites. Presence of MWNTs and SMA modified MWNTs influenced the crystallization behavior of the PA6 phase of PA6/ABS blend.

Individually dispersed clay platelets have been shown (*Figure 2-26*) in the meltblended nanocomposites of nylon 6 with organoclay [161]. In this comparative study it has been revealed that dispersion is better in case of blends formed *in situ* in comparison to the melt blended systems. It has been mentioned that the melt-blending technique relies on the shear induced delamination of the organoclays for dispersion, which become swollen and intercalated in the presence of the polymer melt. The 'agglomeration' takes place when the cohesive forces of the 'agglomerates' exceeded the hydrodynamic separating forces applied by the matrix fluid. Melt-blending was found to be less effective for dispersion of clay platelets due to organoclay 'agglomerates' formation. Crystallization studies showed that there was an enhancement in γ - form crystal structure on incorporation of the nanoclay. The crystallites were formed near the polyamide/clay interface. Polymer chains penetrated into the galleries of layered silicates, and led to delamination and dispersion of the individual silicate layers in the polymer matrix, either during the polymerization process or through melt-blending process.

In the course of exploring the possibility of functionalization of SAN or ABS through acrylonitrile content in making the blend compatible, Liu et al. [157] found that

functionalized SAN exhibited a compatibilization effect with regard to the mechanical properties of PA6/ABS blends (*Figure 2-27*). Morphological studies in this case indicated that such modified SAN copolymers could be used as compatibilizers for PA/SAN blends and PA/ABS blends. Higher nitrile group content in the SAN copolymers increased the yield of oxazoline groups in modified SAN-m and further enhanced the efficiency of SAN-m for reducing the SAN-domain size in a PA/SAN/SAN-m blend. SAN-m produced from a SAN grade with higher nitrile content was found to be more efficient as a compatibilizer.



Figure 2-25 DSC: (a) cooling and (b) second heating scans of blends of PA6/ABS with and without SMA modified MWNT and (below) SEM micrographs of PA6/ABS and PA6/ABS/SMA blends [Courtesy Ref. 160].



Figure 2-26 TEM micrograph of melt-blended nanocomposites [Courtesy Ref. 161].



Figure 2-27 SEM micrographs of cryo-fractured surfaces of PA 6/SAN-blends, specimens shown in (c) to (f) were etched by acetone to reveal the morphology. (a) PA6/SAN-1 80/20, (b) PA6/SAN-1/SAN-1-m 76/19/5, (c) PA6/SAN-1/SAN-2-m 76/19/5, (d) PA6/SAN-2/SAN-2-m 76/19/5, (e) PA6/SAN-1/SAN-3-m 76/19/5, and (f) PA6/SAN-2/SAN-3-m 76/19/5 [Courtesy Ref. 157].

Scaffaro et al. [159] carried out work addressing issues relating to the possibility of modification of nitrile groups of an ABS copolymer into oxazoline by way of a condensation reaction of ethanolamine in the presence of catalyst in a melt. The relatively high conversion obtained in the first few minutes of reaction suggested that the reaction was relatively easily carried out in a continuous apparatus such as a twin screw extruder. The preliminary analysis of the kinetics of the reactions indicated that the modification of nitrile groups occurred on time-scale compatible with the residence times, which were in the order of a few minutes. When a reinforcing component is added into the blends like nanoclay or nanotubes, end properties are improved and thus, attract a great interest in both academia as well as industry.

2.3.2 Immobile and broad interphase (Reactive compatibilization: Chemical bond formation)

The most important requirement for reactive blending is a polymer possessing sufficient reactive sites. The presence of reactive functionality is necessary for covalent or ionic bond formation between components. These reactive groups are generally end groups for one component or statistically distributed-groups along the chain of one polymer. If a polymer does not have such reactivity, it is functionalized by introducing functional groups like carboxyl, epoxy, oxazoline, isocyanate. The second condition is an intensive and controlled mixing to achieve the desired dispersed morphology of one polymer in another. The chemical bonds formed should remain stable in subsequent processing steps, and there should not be any thermal degradation during the processing [110].

When a compatibilizer is used in the blend system consisting of two polymers having sufficient reactivity, there is a change in morphological and rheological behaviour. A study carried out on a commercially important blend system viz., compatibilized PA6/ABS, by Jafari et al. [17] shows that in the presence of compatibilizer, a refined co-continuous morphology was observed and a coarse co-continuous morphology in PA6/ABS blend. Melt rheology of a blend also showed an increase in the viscosity at low frequencies, which indicated the formation of co-continuous structures and also chemical bonds formed at the interface in the presence of a compatibilizer. In case of systems having polymers with no sufficient reactivity, functionalization becomes essential in order to initiate reactive blending.

Functionalization of polymers is the introduction of reactive sites by incorporation of functional groups which are distributed on the polymer backbone. Functionalization can be performed before the blending process by the following ways:

- Solution grafting [162]
- Melt grafting [163, 164]
- Copolymerization [165]
- Polymer Polymer reaction [165]
- End-capping [166]
- Surface functionalization [167]

Chandrasiri and Wilkie [162] found that grafting and functionalization of a polymer phase via introduction of functional groups was possible. However, this led to a thermally unstable polymer phase. Non-polar nature of poly-olefin led to immiscible nature of blends characterized by sharp interface and lack of phase adhesion. Therefore, PP was functionalized in case of blends of PP/PBT and PP/PA6. A study of these systems carried out by Hietaoja et al. [163] revealed the role of a novel oxazoline compatibilizer which caused droplet size reduction. A study of particle size and shape by Takeda and Paul [164] revealed that the size of styrene acrylonitrile (SAN) particles in PA6 rich blends decreased dramatically as acrylonitrile content of the copolymer increased in absence of any reaction. This was quantitatively related to the decrease in SAN/PA6 interfacial tension because the styrenic phase becomes more polar similar to the PA6 phase.

Chapter 3: Experimental details and characterization techniques

3.1 Materials

Polyamide 6 (PA6) with a zero-shear viscosity of 180 Pa.s at 260 °C was acquired from GSFC, Gujarat, India. (Gujlon M28RC, relative viscosity 2.8, M_v is 38642 in 85% formic acid). Copolymer of acrylonitrile-butadiene-styrene (ABS) of acrylonitrile of 24 wt%, rubber content of 16.5 wt% and styrene content of 59.5 wt% was procured from Bayer India Ltd. Catalytic carbon vapor deposition process (CCVD) synthesized thin purified multiwall carbon nanotubes (MWNTs) were obtained from Nanocyl SA, Belgium (NC 3100; thin multi-wall carbon nanotubes, D = 9.5 nm, $L = 1.5 \mu m$, purity> 95% as per manufacturer; I_D $/I_G = 1.18$, from Raman spectroscopic analysis; elemental analysis showed the presence of oxygen along with carbon on the MWNTs surface; average diameter ~9.9 nm from TEM analysis). Sodium dodecyl sulfate (SDS) was purchased from Sigma Aldrich (as per manufacturer specifications: purity ~99 %, melting point ~204-207 °C, formula weight ~288.38). 6-amino hexanoic acid (M_w =132.18; purity = 98%) was procured from Sigma Aldrich and was neutralized with stoichiometric amount of sodium hydroxide (Sisco Research Laboratory, purity=98%) to obtain sodium salt of 6-amino hexanoic acid (Na-AHA). MWNTs were modified with Na-AHA in the ratio of 1:1 (wt/wt). Stoichiometric amount of SDS/dried Na-AHA and MWNTs were added to de-ionized water to achieve the desired weight ratio of MWNTs: SDS/Na-AHA of 1:1 (wt/wt). MWNTs were initially dispersed in de-ionized water by ultrasonication (Ultrasonicator, Vibronics, India, frequency

20 KHz; sonication time: 20 min). SDS/Na-AHA solution was then slowly added to aqueous dispersion of MWNTs followed by continuous stirring. The resultant dispersion was continuously stirred and heated over a hot plate at 100 °C to obtain dry SDS/Na-AHA modified MWNTs. It was then dried in vacuum oven at 80 °C for 24 h to remove the traces of water. MWNTs were initially ultrasonicated in THF (Ultrasonicator specifications: Vibronics, India, frequency 20 KHz; sonication time: 10 min). Solution of PyCHO in THF was then slowly added to the dispersion of MWNTs (keeping the ratio of MWNTs: PyCHO of 1:1, wt/wt) followed by continuous stirring with glass rod. The resultant dispersion was heated with continuous stirring over a hot plate at 100 °C to obtain dry PyCHO modified MWNTs. PyCHO modified MWNTs were further dried in a vacuum oven at 80 °C for 24 h to remove the traces of solvent.

SMA encapsulation of unmodified and modified MWNTs was carried out by ultrasonicating unmodified/modified MWNTs with SMA solution in THF. Subsequently the solvent was removed by constant heating accompanied with stirring. Resultant mixture of 'MWNTs+SMA' or 'modified MWNTs+SMA' (Na-AHA or PyCHO) is dried in a vacuum oven to ensure the removal of solvent traces.

3.2 Processing

Blends of PA6/ABS with MWNTs were prepared by melt-mixing using a conical twin-screw micro-compounder (MICRO 5, DSM Research, Netherlands) in a nitrogen atmosphere to avoid any degradation due to thermal oxidation. PA6 and ABS was vacuum dried for 24 h at 80 °C before melt-mixing. Weighed polymers and MWNTs were fed simultaneously at 260 °C. The micro-compounder is a vertical, co-rotating conical twin-screw extruder with a re-circulating channel to recycle melt for more intensive mixing [168]. In order to study the effect of blend composition in PA6/ABS blends over the co-continuous range, PA6 content has been varied from 40-60 wt% with the incorporation of 5 wt% MWNTs (see Table 1 for detail blend composition). The processing protocol was optimized, where it was found that 50/50 (wt/wt) PA6/ABS blend composition of varied amount of MWNTs (3–5 wt%) prepared either at intermediate screw speed and with longer mixing time (R100 t15) [the corresponding DC electrical conductivity of ~1.01x 10⁻⁹ S/cm] or at higher screw speed with intermediate mixing time (R150 t10) [the corresponding DC electrical

conductivity of ~ 1.56×10^{-8} S/cm] have shown comparable DC electrical conductivity values, which are the highest electrical conductivity values amongst the remaining composite samples prepared by following varying processing protocols. In a similar manner, PA6/ABS blends with Na-AHA modified MWNTs (1:1, wt/wt) were prepared at the optimized set of processing parameters, viz. screw speed of 100 rpm and mixing time of 15 minutes at 260 °C.

Injection moulded samples (as per ASTM D 638, Type V) were prepared using miniinjection moulding machine from DSM Research, Netherlands. The injection moulding parameters utilized for all the blend compositions were - injection pressure of 4 bar, melt temperature of 260 °C, mould temperature of 60 °C, holding time of 60 seconds and cooling time of 2–3 minutes.

3.3 Characterization techniques

3.3.1 Optical microscopic analysis

Samples were prepared by dispersing 3 mg in 20 ml solvent and ultrasonicating the MWNTs for a constant duration in respective solvents (SDS and Na-AHA in distilled water; for PyCHO in DMF, THF, ethanol, methanol, Xylene and acetone). A drop of this suspension is placed on a glass slide and immediately covered with a covering slide in order to retain the distribution of nanotubes. 0.1 g of the composite sample was dissolved in 20 ml of formic acid to dissolve the PA6 phase. These samples were further ultrasonicated for a short duration of 2 minutes in order to ensure that state of dispersion of MWNTs is not altered significantly. A drop of this suspension was then placed on a glass slide and immediately covered with a covering slide in order to retain the distribution of MWNTs. Optical micrographs were obtained using Olympus optical microscope (Gx51, USA). Average diameter of the MWNTs 'agglomerate' was determined using software – Olysia m3 using the corresponding optical micrographs. The percent error in determination of average 'agglomerate' size is in the range of 8 to 10%.

3.3.2 Raman spectroscopic analysis

Raman spectroscopic analysis was performed using a HR 800 micro-Raman (HORIBA Jobin Yovon, France) on unmodified and modified MWNTs samples. The scanning range was from 200 to 2000 cm⁻¹ with incident laser excitation wavelength of 514 nm.

3.3.3 UV-Visible spectroscopic analysis

UV-vis spectroscopic measurements were carried out on aqueous solutions of unmodified and Na-AHA modified MWNTs using Cintra 202 (GBC Scientific Equipment Ltd., Australia). Solutions were ultra-sonicating (Ultrasonicator, Vibronics, India, frequency 20 KHz; sonication time: 10 min). Similarly, PyCHO modified MWNTs were dispersed in THF solution by ultra-sonicating for 10 minutes and UV-vis measurements were carried out using UV Jasco V650 dual beam spectrophotometer (Jasco Analytical Instruments, Japan). The concentration of both aqueous and THF solutions was 0.03 g/l.

PA6/ABS blend samples with MWNTs and Na-AHA modified MWNTs were taken in equal amounts (approximately 0.1 g), and the ABS phase was dissolved using THF (20 ml). Samples were kept for a minimum of 12 h to ensure complete dissolution of ABS phase. Further, samples were ultra-sonicated for 10 minutes. UV-vis spectroscopic analysis was carried out on these samples using UV Jasco V650 dual beam spectrophotometer (Jasco Analytical Instruments, Japan). Equivalent amounts of neat blends were dissolved in equal amounts of THF and this solution was used as a reference solution during measurement.

3.3.4 Transmission electron microscopy

Unmodified MWNTs and Na-AHA modified MWNTs were dispersed in de-ionized water and PyCHO modified MWNTs were dispersed in THF solvent. Further, a drop of this dispersion was placed on the grid and dried to remove the solvent. TEM investigations were carried out on a JEOL JEM-2100 F (Japan) field emission electron microscope.

Composites samples were microtomed to obtain ultrathin sections at room temperature using Leica Ultramicrotome Microsystems, Germany. Samples were collected on a TEM grid and the butadiene phase of ABS was selectively stained with OsO₄. TEM investigations were carried out on a JEOL JEM-2100 F (Japan) field emission electron microscope.

3.3.5 AC electrical conductivity measurement

AC electrical conductivity measurements were performed on the injection-molded samples in the frequency range between 10^{-1} to 10^{6} Hz, using Novocontrol Technologies (Alpha A analyzer (3 µHz - 20 MHz) and Agilent E4991A RF analyzer (1 MHz - 3 GHz), Germany). The DC electrical conductivity was determined from the AC electrical conductivity plot in low frequency region plateau by fitting Jonscher's 'Universal Power law' equation ($\sigma_{AC} = \sigma_{DC} + A\omega^n$, 0<n<1) ('A' is the constant dependent on temperature and 'n' is an exponent dependent on the frequency as well as on the temperature) [169].

3.3.6 Solution experiments

In order to completely dissolve one phase, small pieces of extruded strands (maintaining a constant concentration of MWNTs of 3 mg) were put in the respective solvent viz. formic acid for PA6 phase and THF for ABS phase. The vials were kept for 24 h and then photographed to evaluate the presence of MWNTs in each phase for various blend composition.

3.3.7 Scanning electron microscopy (SEM)

Unmodified MWNTs and Na-AHA modified MWNTs were dispersed in de-ionized water and PyCHO modified MWNTs were dispersed in THF solvent. A drop of this dispersion was placed on a carbon paste coated stub. State of dispersion of MWNTs was investigated using an FEG-SEM (accelerating voltage = 10 kV, JSM-7600F, Japan).

Extruded samples were cryofractured in liquid nitrogen and etched in THF or formic acid to selectively remove ABS or PA6 phase respectively. The etched surface was gold sputtered to avoid charging of the sample. Samples, thus prepared were observed under SEM using a Hitachi (S3400N, Japan) instrument. Morphological features such as type of phase morphology and ligament thickness in case of 'co-continuous' blends along with the state of dispersion and localization of MWNTs in the PA6/ABS blends were determined through SEM observations.

3.3.8 Thermal conductivity measurements

Thermal conductivity measurements were carried out using the TCi (C-Therm Technologies, Canada) on the injection moulded samples at ambient temperatures. A thermally-conductive silicone paste, supplied by Ctherm was used as a thermal contact agent to ensure good thermal contact between the sample and sensor. The samples were dried at 80 °C under vacuum for 24 hours before measurements.

3.3.9 Thermo-gravimetric analysis

Heating scan was carried out from room temperature to 800 °C for PA6/ABS blends with unmodified, corresponding blends with Na-AHA modified MWNTs and PyCHO modified MWNTs in nitrogen environment at the heating rate of 10 °C/min using TA Instruments (SDT Q600 V8.3 Build 101, USA). The residual weight fraction of MWNTs was determined at 500 °C when both the polymer phases have been completely degraded.

3.3.10 Rheological measurements

Rheological measurements were carried out using an oscillatory rheometer (ARES rheometer, TA Instruments, USA) on the cryogenically ground composite samples. For the purpose of cryo-milling the SPEX freezer/mill was utilized. The powdered samples were dried in a vacuum oven at 80 °C for 24 h in order to remove the residual moisture. The

rheometer has parallel plate geometry with the diameter of 25 mm and the thickness of ~ 1 – 2 mm was maintained. The measurements were carried out at 260 °C and under nitrogen atmosphere in order to avoid thermal degradation. The strain rate in the linear viscoelastic region was identified through a strain sweep from 0.01 to 100 % strain at a constant frequency (10 rad/s). Further, the frequency sweep from 10^{-1} to 10^{2} rad/s was carried out for all the samples.

3.3.11 Intrinsic viscosity measurement

Samples of PA6/ABS blends with MWNTs were first dissolved in formic acid. ABS+MWNTs were removed from the formic acid solution using glass microfiber membrane filters, and a colorless filtrate (formic acid+PA6) was obtained. Clear filtrate was reprecipitated in distilled water which is a non-solvent. Several washings were given in order to remove traces of solvent. Extracted PA6 was then dried in the oven at 80 °C to remove traces of water. The viscosity was determined using Ubbelohde viscometer.

To calculate the M_v of PA6 from the intrinsic viscosity value:

 $[n] = K.M_v^a$ Equation 3-1

For PA6, $K = 0.32 \times 10^{-2}$ at 25 °C in formic acid and a = 0.62. The M_v values were calculated and are tabulated in subsequent chapters.

3.3.12 Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical thermal analysis was carried out using a Perkin Elmer DMA 8000 to analyze the dynamic mechanical behaviour of the samples. The samples used for the DMTA analysis were injection moulded using DSM mini-injection moulding and were cut in the dimensions of 45 mm X 10 mm X 3 mm. The samples were dried at 80 $^{\circ}$ C in a vacuum oven for 24 h in order to remove any traces of moisture. The measurements were carried out in the dual cantilever mode with the temperature scan from 0 $^{\circ}$ C to 150 $^{\circ}$ C at 1 Hz frequency and with the heating rate of 2 $^{\circ}$ C/min.

3.3.13Brunauer-Emmet and Teller analysis (BET)

Surface area measurements were carried out by nitrogen adsorption method using surface area analyzer (Smart Instruments, Thane, India) for unmodified MWNTs, Na-AHA modified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt).

3.3.14 Fourier transform infra-red spectroscopy (FTIR)

Fourier transform infra-red spectroscopic (FTIR) analysis of powdered composite samples was carried out using Nicolet (MAGNA 550, USA) for powdered samples of PA6/ABS blend samples with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs (1:1, wt/wt). The powdered composite samples were analysed over the scanning range of 400–4000 cm⁻¹ at room temperature. KBr pellet was used for calibration purpose.

3.3.15 X-ray photoelectron spectroscopic analysis (XPS)

The XPS analysis was carried out using the MULTILAB from Thermo VG Scientific, equipped with Concentric Hemispherical Analyzer. The X-ray used was Al K α . O 1s and C 1s runs were carried out in order to determine the functional groups present in the vicinity of MWNTs surface. The take off angle was 90°, the resolution for the HR scan was 0.5 eV and the survey scan pass energy was 100 eV with the resolution of 2 eV.

3.3.16 Modulated differential scanning calorimetry (MDSC)

Q200 differential scanning calorimeter (DSC from TA Instruments, USA) was used to analyze the non-isothermal crystallization behaviour of PA6 phase of PA6/ABS blends with unmodified and modified MWNTs. The skin layer of the extruded sample was removed in order to prevent any contamination and further the samples were pre-dried under vacuum at 80 °C for 12 hr to remove residual moisture. DSC measurements of PA6 and the blends of

PA6/ABS with MWNTs were carried out under N₂ atmosphere. The sample was first heated up to 260 °C and held isothermal for 3 minutes to erase the thermal history of the sample. Further, the sample was cooled at 10 °C/min to – 40 °C. The sample was then equilibrated at – 40 °C, held at this temperature isothermally for 3 minutes and again heated up to 260 °C at 20 °C. Percent crystallinity of the samples (% X_t) was calculated from the heat of fusion (Δ h), the heat of fusion of 100% crystalline PA6 (Δ h₀) was taken from the literature was 204.8 J/g [100].

The rigid amorphous fraction was calculated as follows:

MAF = mobile amorphous fraction, CF = crystalline fraction, RAF = rigid amorphous fraction, ΔC_p corresponds to the difference in the specific heat experimentally obtained from the crystallization studies, ΔC_p (am) is the difference in the specific heat capacity of 100 % amorphous polymer (taken from the ATHAS database).

$MAF = \Delta C_p / \Delta C_{p (am)}$	Equation 3-2
$CF = \% X_t = \Delta h / \Delta h_o$. Equation 3-3
RAF = 1 - MAF - CF	Equation 3-4

For PA6 the values of the specific heat capacity are: $\Delta C_{p(am)}$ at T_g = 53.7 J/K. mol = 0.475 J/°C. g (molar mass of PA6 = 114 , molecular weight of the repeating unit) from ATHAS data bank given in ref. [170].

Chapter 4: Results and discussion

4.1 State of dispersion of multiwall carbon nanotubes investigating influence of organic modifiers and dispersion media

'Dispersibility' of MWNTs depends on various interactions between MWNTs and the dispersion medium. Further, the interaction between MWNTs and modifier molecule is important in case of dispersion of modified MWNTs. Investigation of the dispersion of MWNTs is carried out at two scales: 'microscale', where the average diameter of MWNTs 'agglomerates' is determined and at 'nanoscale', where the 'individualization' of MWNTs is examined.

4.1.1 Investigation of the extent of MWNTs dispersion in the presence of SDS, Na-AHA and PyCHO

Figure 4-1 (I) shows the primary 'agglomerates' of unmodified MWNTs when dispersed in de-ionized water (a) and in THF (b). It can be seen that higher number of unmodified MWNTs 'agglomerates' with smaller average 'agglomerate' size are present in THF as compared to the dispersion in de-ionized water. Often the wettability of organic

solvent in case of MWNTs is higher than the wettability of deionized water. Thus, MWNTs 'agglomerate' size is found to be lower in case of THF (\sim 81.5 µm) as compared to aqueous dispersion (\sim 107.9 µm).

Figure 4-1 (II) shows optical micrographs of MWNTs 'agglomerates' in de-ionized water for MWNTs modified with SDS [*Figure 4-1* (II) (a)–(c)] and Na-AHA [*Figure 4-1* (II) (d)–(f)]. The PyCHO modified MWNTs were dispersed in THF solvent [*Figure 4-1* (II) (g)–(i)]. The weight ratio was varied from 1:1, 1:2 and 1:4 (wt/wt) of MWNTs: modifier. Average diameter (D_{avg}) of primary MWNTs 'agglomerates' is reduced with increasing weight ratio of SDS; however for 1:4 (wt/wt), larger size of MWNTs 'agglomerates' is observed. Overall, smaller average of MWNTs 'agglomerates' size is observed irrespective of weight ratios in case of Na-AHA modified MWNTs. Whereas, PyCHO modified MWNTs has shown an increased D_{avg} with increasing modifier weight ratio.

Image analysis was carried out in order to quantitatively investigate the effect of the presence of organic modifier on the average diameter of MWNTs 'agglomerate' on the basis of the optical micrographs. D_{avg} value for MWNTs is observed to be ~107.9 µm; whereas with increasing weight ratio of Na-AHA, it is progressively decreasing (~21.8 µm). It can be observed from D_{avg} values provided in *Table 4-1* that there is a reduction in MWNTs 'agglomerate' size on incorporation of SDS in case of all the three weight ratios (for 1:1 (wt/wt) D_{avg} ~43.4; 1:2 (wt/wt) D_{avg} ~36.5 and for 1:4 (wt/wt) D_{avg} ~47.7 µm as compared to that of unmodified MWNTs agglomerate (~107 µm). There is a marginal deviation in the trend of decreasing diameter values of nanotube 'agglomerates' that is found at higher SDS content (1:4, wt/wt, MWNTs: SDS). Na-AHA modified MWNTs showed a significant decrease in the average diameter of MWNTs 'agglomerates' with increasing Na-AHA concentration.

Figure 4-2 shows the percent reduction in an average 'agglomerate' size of modified MWNTs with respect to the 'agglomerate' size of unmodified MWNTs (in de-ionized water and THF) with increasing weight ratio of the modifiers – SDS, Na-AHA and PyCHO. The most effective reduction in 'agglomerate' size of MWNTs is exhibited by Na-AHA modified MWNTs as compared to the corresponding MWNTs modified with SDS and PyCHO. PyCHO modified MWNTs exhibit a lower %reduction in the average 'agglomerate' size of MWNTs. Also, there was a decrease in %reduction of average diameter of MWNTs with

increasing weight ratio of PyCHO modifier, presumably indicating a 're-aggregation' phenomenon.

It has been reported by Jiang et al. [171] that any amount lesser or greater than the critical micelle concentration of SDS leads to a large 'agglomerate' size of MWNTs. Insufficient surfactant concentration is unable to produce an efficient coating that will induce 'electrostatic' repulsion and counterbalance the intertube van der Waals attractions. At higher SDS concentration, the 'clusters'/'agglomerates' are observed to be larger and denser. Such behaviour has been associated to inadequate 'electrostatic' repulsive forces between the nanotubes due to the large ionic strength and the increasing concentration of surfactant micelles, known as micelles, in the aqueous solution. The critical micelle concentration for SDS is reported to be ~2.49 wt%, [171], exceeding which in the cases of 1:2 and 1:4 (wt/wt) SDS modified MWNTs dispersed in aqueous medium may result in 're-agglomeration' of MWNTs. This observation is supported by the finding reported by Moore et al. [172] for single wall carbon nanotubes (SWNTs) in aqueous dispersions with anionic, cationic and non-ionic surfactant, which indicated uniform coverage of SWNTs by surfactant molecules.

The finding in the current study is in accordance with the known fact that if the amount of surfactant is too low, insufficient surfactant molecules are adsorbed onto the nanotube surface and many nanotube bundles remain 'agglomerated'. As a result, only a fraction of MWNTs is able to get effectively exfoliated. On the other hand, if the amount of surfactant is too large with respect to the number of MWNTs, then attractive 'depletion-type' interaction between the MWNTs are induced by the presence of surfactant micelles, leading to the 'agglomeration' of MWNTs [173]. A half-cylinder arrangement of the double-chain lipids on the surface of nanotubes was reported in this study, but another investigation by Yurekli et al. [174] led to an inference based on the difficulty of forming stable 'hemimicelles' on the high-curvature nanotube surfaces that the dispersion of nanotubes by SDS might be due to the formation of a structure-less, adsorbed layer of surfactant on the individual nanotubes. Therefore, it is important to achieve and maintain an optimum concentration of the surfactant in MWNTs dispersions.

A pyrene based modifier has been reported to interact strongly with the nanotube surface, with high surface area coverage. It is also likely that PyCHO molecules may form a 'layer-like structure', while covering the nanotube surface, owing to better packing offered by similar aromatic chemical structure. Further, an increase in the concentration of modifier may lead to 're-aggregation' of the modifier molecules, leaving 'agglomerated' nanotubes in the dispersion, which may be on the same lines to a 'critical micelle concentration' (CMC) situation in case of conventional surfactants. An interaction induced by electrostatic type, which minimizes the opposing ' π - π ' repulsive interactions and may sustain up to temperature of ~400 °C [175]. The stacking of the pyrene molecules on nanotube surface has been reported by Lerner et al. [176] through an increased thickness of nanotube diameter as observed in AFM studies.



Figure 4-1 MWNTs 'agglomerates' observed through optical microscope for (1) unmodified MWNTs dispersed in (a) de-ionized water, (b) in THF; (II) (a)-(c): SDS modified MWNTs, (d)-(f): Na-AHA modified MWNTs and (g)-(i): PyCHO modified MWNTs for varying weight ratio of MWNTs: modifier (1:1, 1:2, and 1:4, wt/wt).

Raman spectra of MWNTs modified with SDS [Figure 4-3 (a)], Na-AHA [Figure 4-3 (b)] and PyCHO [Figure 4-3 (c)] with various weight ratios have been shown in Figure 4-3. Unmodified MWNTs as well as modified MWNTs display two characteristic peaks: the first at ~1340 cm⁻¹, assigned to the D-band (derived from disordered graphitic structures) and the second peak cantered at ~1574 cm⁻¹, assigned to the G-band (associated with tangential C–C bond stretching for ordered graphitic structure). Variations in the ratio of intensity of D-band to G-band (I_D/I_G) of unmodified MWNTs and MWNTs modified with SDS, Na-AHA and PyCHO with different ratios are depicted in Figure 4-3 (d). The extent of dispersion shown in case of SDS depicts that there is an overall decrease in the tendency to 'agglomerate' with increasing SDS content, which is manifested in the decreased intensity ratio (I_D/I_G) value (~1.15 for 1:1, wt/wt; ~1.26 for 1:2, wt/wt and ~1.01 for 1:4, wt/wt). Na-AHA modified MWNTs have shown a consistent decrease in I_D/I_G ratio with increasing concentration of Na-AHA from ~ 0.96 for 1:1, wt/wt to ~0.8 for 1:4, wt/wt. Further, Raman peak intensity ratio is increased with increasing concentration of PyCHO, where 1:1 (wt/wt) MWNTs: PyCHO, (wt/wt) shows I_D/I_G value of ~0.75, 1:2 (wt/wt) has I_D/I_G value of ~0.8, which further increased to ~0.94 in case of 1:4 (wt/wt).

Modifier	Weight ratio	D _{avg (} µm)
	1:1	44
SDS	1:2	33
	1:4	47
Na-AHA	1:1	49
	1:2	27.3
	1:4	21.8
РуСНО	1:1	69.2
	1:2	62.5
	1:4	103.3

Table 4-1 Average diameter size of the MWNTs 'agglomerate' in the presence of variedmodifiers: SDS, Na-AHA and PyCHO

Raman scattering in principle involves inelastic scattering of light, where the intensity of scattered light is depicted as a function of frequency downshift in a Raman spectrum [177]. Individual nanotubes show sharper and more intense absorption feature as reported in ref. [178] and eventually leads to an increase in the intensity of tangential mode G-band. Strano et al. reported an increase in the intensity of tangential mode at 1591 cm⁻¹ (G-band) during the ultrasonication process of SWNTs [178]. This observation has been further utilized to investigate the exfoliation of SWNTs during the ultrasonication process in the presence of a surfactant. A decrease in I_D/I_G ratio of MWNTs indicates an enhanced resonance process after MWNTs exfoliation in Raman spectroscopic analysis [179].



Figure 4-2 Percent reduction in average diameter size (D_{avg}) of MWNTs 'agglomerates' determined from image analysis of optical micrographs of SDS, Na-AHA and PyCHO modified MWNTs at varying weight fraction of modifier (MWNTs: Modifier, 1:1, 1:2 and 1:4, wt/wt).

Wise et al. also reported a similar observation in case of polyimide/SWNTs composites [180]. In this context, a study [50] has shown that the 'cluster' size of MWNTs may decrease in the presence of neutralized-MWNTs during ultrasonication in the aqueous medium, which was still persistent in the solid mixture.



Figure 4-3 Raman spectra for (a) SDS modified MWNTs, (b) Na-AHA modified MWNTs, (c) PyCHO modified MWNTs, and (d) characteristic peak intensity ratio (I_D/I_G) values for varying weight fraction of modifier: 1:1, 1:2 and 1:4 (wt/wt).

A persistent decrease in intensity ratio (I_D / I_G) was found in case of Na-AHA modified MWNTs, which may be due to the enhanced dispersion of MWNTs in the presence of Na-AHA. Effective dispersion of MWNTs in Na-AHA solution, thus leads to a better exfoliation as the concentration was increased. On the contrary, SDS deteriorated the dispersion of MWNTs at higher concentration of the surfactant (From 1:1–1:4, wt/wt of MWNT: modifier). Na-AHA has exhibited improved 'debundling' through electrostatic charge repulsion and steric stabilization [50]. It is noteworthy that Na-AHA could not exhibit a typical 'micelle' formation tendency as that of a conventional surfactant. Instead, Na-AHA modified MWNTs showed a consistent enhancement in the 'dispersibility' in aqueous dispersion with increasing fraction of Na-AHA. Larger 'agglomerates' observed in case of

PyCHO at higher concentration (1:4, wt/wt) may be due to 're-aggregation' caused by layered structure developed by 'stacking' phenomenon of PyCHO molecules [176].

Figure 4-4 (a) shows the plot of UV-vis absorbance versus wavelength for SDS and Na-AHA modified MWNTs dispersions. *Figure 4-4* (b) shows UV-vis absorbance values as a function of ultrasonication time for varying concentration of SDS in SDS modified MWNTs. Unmodified MWNTs also exhibit marginal UV-vis absorbance owing to the polarity in MWNTs due to the presence of oxygen functionality on the MWNTs surface (which was confirmed through XPS analysis [181]). UV-vis absorbance value of 1:1 (wt/wt) SDS modified MWNTs is increased with increasing ultrasonication time. 1:2 (wt/wt) SDS modified MWNTs show further increase in UV-vis absorbance as compared to 1:1 (wt/wt) SDS modified MWNTs. After 20 minutes of ultrasonication the UV-vis absorbance value remains almost unchanged up to 45 minutes for 1:1 and 1:2 (wt/wt) SDS modified MWNTs as compared to both 1:1 and 1:2 (wt/wt) SDS modified MWNTs.

Figure 4-4 (c) shows the variation in UV-vis absorbance value as a function of wavelength for Na-AHA modified MWNTs. *Figure 4-4* (d) reveals the dependence of UV-vis absorbance values on the ultrasonication time for varied concentrations of Na-AHA in Na-AHA modified MWNTs. Na-AHA modified MWNTs exhibit higher UV-vis absorbance values as compared to the corresponding SDS modified MWNTs irrespective of the modifier weight ratio. *Figure 4-4* (d) shows that UV-vis absorbance values have increased significantly in the presence of Na-AHA modified MWNTs as compared to the values in case of unmodified MWNTs. UV-vis absorbance values are increased with increasing Na-AHA concentration up to 25 minutes of ultrasonication.

Individual MWNTs absorb in the region ~273 nm of wavelength and the magnitude indicates the concentration of 'individualized' MWNTs. A maximum in UV-vis absorbance at ~273 nm corresponds to UV-vis absorbance due to bulk ' π -plasmon' [182]. An increase in UV-vis absorbance value indicates an increased concentration of 'individualized' nanotubes, which confirms an enhanced 'debundling' of MWNTs [183, 184]. In the presence of SDS modified MWNTs, there was an increase in UV-vis absorbance values noted at ~273 nm with increasing ultrasonication time for 1:1 and 1:2 (wt/wt); however in case of 1:4 (wt/wt) there has been a decrease in the absorbance values, confirming 're-aggregation' of MWNTs due to

SDS concentration being higher than CMC (~2.49 wt%, [171]). Further, it is interesting to observe that Na-AHA modified MWNTs show an enhanced 'debundling' of MWNTs with increasing concentration of Na-AHA. This observation confirms that Na-AHA is an effective organic modifier for MWNTs.

Figure 4-5 (a) shows the UV-vis spectra for unmodified MWNTs in THF (1 min, 45 mins); PyCHO in THF and PyCHO modified MWNTs in THF solution. The magnitude of UV-vis absorbance corresponding to MWNTs is significantly lower as compared to UV-vis absorbance values in case of PyCHO and further PyCHO modified MWNTs. In the presence of PyCHO and MWNTs the maxima is shifted to a higher wavelength as compared to the peak observed in case of PyCHO solution in THF, indicating a 'red shift'. *Figure 4-5* (b) shows the UV-vis spectra for the PyCHO modified MWNTs in the THF solution for varying ultrasonication time. The dispersions show sharp UV-vis absorbance peaks between 200 to 400 nm wavelength with the peak maxima at ~251 nm, ~271 nm, ~290 nm and ~370 nm. Increasing ultrasonication time has resulted in a slight 'blue shift' in the absorbance peak ~273 nm.

The maxima of the UV-vis absorbance may vary depending on the various interactions between MWNTs and the modifier molecules as well as the interaction of modified MWNTs with the dispersion media and environment. The 'blue shift' indicates that the ' π - π ' interaction between the PyCHO molecules and MWNTs may lead to an effective MWNTs surface coverage. Higher energy may be required for the electronic transition as the interaction between the modifier molecules and the side walls of the MWNTs is improved. This phenomenon may lead to a 'blue shift' in case of PyCHO modified MWNTs. Presence of 'conjugation' affects the absorption maxima in such a way that the maxima shifts to a higher wavelength [185]. Closely spaced electronic energy levels are responsible for the 'blue shift' and thus, lower required energy to produce the transition from occupied to unoccupied levels.

PyCHO molecules possess four aromatic rings and an electron withdrawing substituent –CHO. However, in case of aromatic compounds, the 'bathochromic shift' is essentially dependent on the extent of 'conjugation'. Hence, PyCHO molecules may introduce an added 'conjugation', which further has resulted in a 'red shift' in UV-vis absorbance peak in case of MWNTs (which by definition are fully conjugated polyaromatic

macromolecules with a hollow, inert interior and reactive exterior ends [80]). An increased extent of 'conjugation' may be the reason of lower energy required for the excitation of electrons. It has been reported by Nakashima et al. [186] that a 'red shift' was observed as compared to the original dispersion, which indicated ' π - π ' interaction between the pyrene moiety of modifier molecules and SWNTs. An absorption spectrum for pyrene exhibits sharp and intense bands in 200–350 nm [187]. An absorption spectrum of pyrene and the absorption spectrum of PyCHO might exhibit a small difference in the transition probability due to the –CHO functional group attached to the pyrene moiety [188].



Figure 4-4 UV- vis spectroscopic analysis indicating effect of varied weight ratio of (a) UVvis absorbance as a function of wavelength for SDS modified MWNTs, (b) variation in UVvis absorbance values at 273 nm with varying ultrasonication time for varied weight fraction of SDS, (c) UV-vis absorbance as a function of wavelength for Na-AHA modified MWNTs, (d) variation in UV absorbance values at 273 nm with varying ultrasonication time for varied weight fraction of Na-AHA.

Figure 4-5 (c) shows UV-vis absorbance values exhibited by unmodified MWNTs in de-ionized water and THF medium. UV-vis absorbance values of unmodified MWNTs dispersed in THF are higher than the values exhibited by corresponding MWNTs dispersed in de-ionized water. *Figure 4-5* (d) shows the comparison of normalized UV-vis absorbance values in case of SDS, Na-AHA and PyCHO modified MWNTs (1:1, wt/wt after 20 minutes of ultrasonication). UV-vis absorbance values exhibited by modified MWNTs were normalized on the basis of UV-vis absorbance value exhibited by unmodified MWNTs dispersed in de-ionized water. Normalized UV-vis absorbance values for SDS modified MWNTs were lower as compared to the corresponding Na-AHA modified and PyCHO modified MWNTs.

Figure 4-6 (I) shows the TEM micrograph of unmodified MWNTs in THF, and exhibit a highly 'agglomerated' structure. *Figure 4-6* (II) [(a)-(c)] shows the TEM micrographs of MWNTs modified with SDS, *Figure 4-6* (II) [(d)-(f)] shows the TEM micrographs of Na-AHA modified MWNTs and *Figure 4-6* (II) [(g)-(i)] are TEM micrographs of MWNTs modified with PyCHO with varying weight ratio of the modifier. TEM micrographs show that Na-AHA modified MWNTs exhibit well 'debundled' structure as compared to other modified MWNTs irrespective of the weight ratio of modifier.





Figure 4-5 (a) UV-vis spectra for PyCHO solution in THF and for PyCHO modified MWNTs in [MWNTs: PyCHO (1:1) wt/wt] in THF solution, (b) UV-vis spectra for PyCHO modified MWNTs 1:1 (wt/wt) for varying ultrasonication time, (c) effect of varied sonication time on state of dispersion of unmodified MWNTs in de-ionized water and THF (d) effect of the presence of Na-AHA, SDS and PyCHO (1:1, wt/wt) through variation in normalized UV-vis absorbance as a function of ultrasonication time.

Figure 4-7 represents a schematic representing the 'debundling' of MWNTs by various modifiers in respective dispersions. SDS molecules interact with MWNTs surface through the 'hydrophobic' part and with aqueous medium through 'hydrophilic' end. MWNTs are debundled via counterbalancing attractive forces between MWNTs with 'electrostatic' repulsion induced by surfactant layer on MWNTs surface [171]. Na-AHA molecules are adsorbed on MWNTs surface and lead to 'debundling' of MWNTs through electrostatic charge repulsion and steric stabilization [50].

Na-AHA molecule is different than a conventional surfactant molecule because it has $-COO^-$ and $-NH_2$ ends, which are hydrophilic in nature. It has also been observed that higher concentration of Na-AHA does not lead to micelle formation, presumably due to the unique chemical structure with both hydrophilic ends. Further, PyCHO molecules interact with MWNTs surface through ' π - π ' interaction and layer of PyCHO molecules reduce the intertube attractive forces resulting in effective debundling of MWNTs.



Figure 4-6 TEM micrographs of (I) unmodified MWNTs, (II) MWNTs modified with SDS [(a) to (c)], Na-AHA [(d) to (f)] and PyCHO [(g) to (i)] for varying weight ratios 1:1, 1:2 and 1:4 (wt/wt) respectively.



Figure 4-7 Schematic representation of mechanisms for (I) SDS modified MWNTs, (II) Na-AHA modified MWNTs, and (III) PyCHO modified MWNTs.

4.1.2 Influence of dispersion media and PyCHO modifier on dispersion of MWNTs

Dispersion medium is an important factor affecting the state of dispersion of MWNTs. Physical parameters and properties of organic solvent may influence the interaction between MWNTs and the corresponding organic medium. It is also important to study the effect of modification of MWNTs with PyCHO molecules on the state of dispersion of MWNTs in various organic media.

Figure 4-8 shows optical micrographs of unmodified MWNTs dispersed in various organic solvents. A significant variation in average 'agglomerate' size of MWNTs in various solvents is observed from the optical micrographs. The ability of the solvent to break the bigger 'agglomerates' into smaller 'agglomerates' is assessed through the average 'agglomerate' size. Polar aprotic solvents with higher surface tension values show lower 'agglomerate' sizes: DMF (~83.7 µm) [*Figure 4-8* (d), *Table 4-2*], THF (~81.5 µm) [*Figure*

4-8 (e)] and apolar aprotic solvent with higher surface tension: Xylene [*Figure 4-8* (f)] shows the lowest 'agglomerate' size of ~56.9 μ m. Polar protic solvents viz., methanol and ethanol show higher average bigger 'agglomerate' size of MWNTs [*Figure 4-8* (a) and (c)] of ~139.5 and ~89.3 μ m respectively. On the other hand, MWNTs dispersed in acetone show a high average 'agglomerates' size ~122 μ m [*Figure 4-8* (b)].

Figure 4-9 [(a)–(f)] shows the variation in 'agglomerate' size and *Table 4-2* provides the average 'agglomerate' size of MWNTs in the presence of PyCHO modified MWNTs (1:1, wt/wt). Average 'agglomerate' size is decreased in the presence of PyCHO as compared to the corresponding dispersion of unmodified MWNTs. It is to be noted that there is an exception observed in case of ethanol, where the D_{avg} is found to be higher as compared to D_{avg} of corresponding dispersion of unmodified MWNTs. Percent reduction in D_{avg} was calculated (based on the corresponding D_{avg} values of unmodified MWNTs) in order to determine the effect of modification of MWNTs with PyCHO. *Figure 4-10* indicates the values of % reduction of the average 'agglomerate' size when unmodified MWNTs were dispersed in the solvents in the presence of the modifier. DMF, THF and xylene showed higher values of % reduction as compared to the methanol, ethanol and acetone.

Figure 4-11 show TEM micrographs of MWNTs and PyCHO modified MWNTs (1:1, wt/wt) dispersed in the organic solvents. Debundling of MWNTs has been observed in all the cases; however, PyCHO modified MWNTs dispersed in DMF and THF exhibit a significant separation between the nanotubes. On the other hand, remaining solvents exhibit a lesser extent of 'debundling' of nanotubes resulting in 'agglomerated' structure of MWNTs.

Figure 4-12 shows UV-vis absorbance values associated with 'individualized' MWNTs dispersed in organic solvents. UV-vis absorbance values are increased in the presence of PyCHO as compared to unmodified MWNTs indicating a higher concentration of 'individualized' nanotubes in dispersion due to an enhanced debundling of MWNTs. However, it is to be noted that the magnitude of increase in UV-vis absorbance is varied with varying dispersion medium. Thus, it is confirmed that solvent parameters and solvent-MWNTs interactions influence the dispersibility significantly. Therefore, it will be interesting to study the variation in state of dispersion as function of various solvent parameters.



Figure 4-8 Optical micrographs of the MWNTs with varying dispersing medium, (a) methanol, (b) acetone, (c) ethanol, (d) DMF, (e) THF and (f) xylene.

Table 4-2 Average	'agglomerate'	' diameter o	of MWNTs f	or unmodifie	d MWNTs	and PyCHO
m	odified MWNT	's dispersio	ons in varyin	g organic m	edium	

Solvent	MWNTs D _{avg} (µm)	PyCHO mod D _{avg} (µm)
Methanol	139.5	117.1
Acetone	122.6	120.4
Ethanol	89.3	110.9
DMF	83.7	72.3
THF	81.5	64.2
Xylene	56.9	39.8



Figure 4-9 Optical micrographs of the PyCHO modified MWNTs 1:1(wt/wt) with varying dispersing medium, (a) methanol, (b) acetone, (c) ethanol, (d) DMF, (e) THF and (f) xylene.



Figure 4-10 Percent reduction in the average diameter of the MWNTs 'agglomerates' in the presence of varied organic media – varied dispersants methanol, acetone, ethanol, DMF, THF and xylene.

Solvent	p-MWNT	PyCHO modified MWNT (1:1)	Solvent	p-MWNT	PyCHO modified MWNT (1:1)
DMF	50 nm	50 nm	Ethanol	50 nm	50 nm
THF	50 nm	50 nm	Methanol	50 nm	50 nm
Xylene		50 nm	Acetone	50 nm	50 nm

Figure 4-11 TEM micrographs for MWNTs and MWNTs modified with a pyrene based noncovalent modifier PyCHO (1:1) utilizing various solvents: DMF, THF, Xylene, Ethanol, Methanol, Acetone.



Figure 4-12 UV-vis spectroscopic analysis of the MWNTs with varied organic dispersant showing the dependence of the fraction of individual MWNTs on the medium of dispersion.

Figure 4-13 Figure 4-13 [(a) – (f)] shows I_D/I_G ratio as a function of various solvent parameters. A high relative permittivity value [Figure 4-13 (a)] and high dipole-moment [Figure 4-13 (b)] is favourable for good stability of solution. An organic medium requires comparable surface tension values in order to establish a strong interaction with MWNTs surface [Figure 4-13 (c)]. Interaction between the solvent and nanotube through charge transfer plays a vital role in the dispersion of MWNTs in various organic solvents. In addition, charge transfer between the modifier molecule and the nanotube is also a crucial affecting the interaction between the nanotubes and the modifier molecules, thus subsequently the dispersion of the nanotubes in the solvents. It has been reported in literature that class of solvents having high values for β (electron-pair donicity), negligible value for α (H-bond donation parameter) and high value of π^* (solvochromic parameter) are the best solvents for nanotubes. Along with these factors two more factors, which are considered important, are: relative permittivity and electron affinity [84]. Non-hydrogen-bonding Lewis bases with high electron-pair donicity and low hydrogen-bonding parameters are known to be good solvents for carbon nanotubes [85, 189].

Figure 4-13 (d), (e) and (f) exhibit the dependence of state of dispersion (via I_D/I_G ratio) on electron pair donicity, hydrogen bonding parameter and solvochromic parameter respectively. The study of MWNTs dispersions in order to examine the dispersibility with various organic solvent is a crucial step to achieving well-dispersed nanotube dispersion in an organic media and subsequently to the various polymer matrices. For an organic liquid to be a good solvent for nanotubes there are few important factors which essentially could be considered:

- 1 Dielectric constant/ relative permittivity
- 2 Surface tension
- 3 Solvochromic parameter (π^* "Taft and Kamlet parameter")
- 4 Lewis basicity (β = electron-pair donicity)
- 5 Hydrogen bond donor parameter (α)



Figure 4-13 State of dispersion of MWNTs influenced by various parameter such as (a) relative permittivity, (b) dipole moment, (c) surface tension, (d) β (electron pain donicity), (e) α (hydrogen bonding parameter) and (f) π^* (solvochromic parameter) based on an assessed through Raman spectroscopic analysis.



Figure 4-14 State of dispersion of MWNTs influenced by various parameter such as (a) relative permittivity, (b) dipole moment, (c) surface tension, (d) β (electron pain donicity), (e) α (hydrogen bonding parameter) and (f) π^* (solvochromic parameter) based on an assessed through UV-vis spectroscopic analysis.

Figure 4-14 [(a) – (f)] shows dependence of extent of MWNTs dispersion on various physical parameters of organic solvent as a function of UV-vis absorbance. It can be observed that better exfoliation is seen in case of few solvents fulfilling all the three conditions. It can be observed that the DMF and THF are the most effective solvents for dispersing MWNTs, owing to negligible hydrogen bonding, high electron-pair donicity and high solvochromic parameter. Overall, the variation in UV-vis absorbance as a function of various solvent parameters confirms the observation from *Figure 4-14* [(a) – (f)] that the MWNTs dispersion is a multiparametric function, because multiple physical parameters influence the dispersibility of MWNTs in the corresponding dispersions.

4.2 Dispersion, migration and 'network-like' structure formation of MWNTs in 'co-continuous' PA6/ABS blends

4.2.1 State of dispersion and migration of MWNTs: Effect of blend composition and organic modifier

Variation of electrical conductivity in immiscible polymer blends in the presence of conducting fillers has been reported in the literature [11, 62, 190, 191, 192, 193, 194]. These studies have reported various ways in which the blend morphology influences the electrical conductivity in the presence of conducting filler. Thus, it would be interesting to study the effect of varying blend composition on the electrical conductivity in the 'co-continuous' region of PA6/ABS blends, wherein the percent co-continuity of the two phases does not vary significantly over the entire range of blend composition. The details of the blend compositions along with the sample codes are provided in *Table 4-3*.

Figure 4-15 (a) shows the variation in the AC electrical conductivity as a function of frequency for varied blend composition (40/60 to 60/40, wt/wt) of PA6/ABS blends containing 5 wt% of MWNTs. As observed from *Figure 4-15* (a), 40/60 (wt/wt) PA6/ABS blend with MWNTs (5 wt%) shows insulating behavior whereas, 60/40 (wt/wt) PA6/ABS blend shows a DC electrical conductivity of ~10⁻⁵ S/cm. In the aforementioned regime, PA6/ABS blends with 5 wt% of MWNTs exhibit the DC electrical conductivity values in the
range of $\sim 10^{-11} - \sim 10^{-5}$ S/cm. The insulating nature of 40/60 (wt/wt) PA6/ABS blend indicates the lack of a percolating 'network-like' structure of MWNTs due to the possibility that MWNTs may be distributed in both the phases, and may exhibit highly 'agglomerated' state. *Figure 4-15* (b) shows a significant improvement in the bulk electrical conductivity of the blends over the entire blend composition range in the presence of Na-AHA modified MWNTs as compared to the corresponding blends with unmodified MWNTs.

It was earlier reported that 50/50 (wt/wt) PA6/ABS blends with 4 wt% unmodified MWNTs and 3 wt% Na-AHA modified MWNTs (1:4, wt/wt) prepared by 'sequential' meltmixing showed DC electrical conductivity of ~2.6x10 ⁻⁸ S/cm and ~1x10⁻⁶ S/cm respectively [18]. However, in the present context, 50/50 (wt/wt) PA6/ABS blend with 5 wt% unmodified and Na-AHA modified MWNTs (1:1, wt/wt) showed DC electrical conductivity of ~10⁻⁸ S/cm and ~10⁻⁵ S/cm respectively. Thus, it is clearly observed that 'sequential' mixing is more effective over 'simultaneous' mixing in developing 'network-like' structure of MWNTs. During 'sequential' mixing, MWNTs were melt-mixed with the PA6 phase for 10 minutes followed by the addition of ABS phase for 5 minutes. The processing protocol followed during 'sequential' melt-mixing has led to the localization of majority fraction of MWNTs in the PA6 phase. On contrary, the 'simultaneous' melt-mixing may lead to the distribution of MWNTs in both the phases.

Based on the thermodynamic and kinetic factors, MWNTs are expected to localize in the PA6 phase of PA6/ABS blends. Thermodynamically, MWNTs would localize preferentially in the phase, wherein the surface free energy difference between that phase and MWNTs would be minimum. Considering the surface free energy values of PA6 (~36.4 mN/m), MWNTs (~40–45 mN/m) and ABS (~29.4 mN/m), it is expected that the MWNTs should localize predominantly in the PA6 phase. The lower melt-viscosity of PA6 also enhances the possibility of MWNTs being in the PA6 phase. Higher concentration of PA6 phase in the blends thus, might be facilitating the localization of a majority fraction of MWNTs in the PA6 phase resulting in the formation of 'network-like' structure of MWNTs in PA6/ABS blends.

Sample	Codes	
Polyamide 6	Ν	
Acrylonitrile-butadiene-styrene	А	
Screw speed	R	
Thin purified MWNTs	Т	
MWNTs modified with Na-AHA (MWNTs: Na-AHA 1:1)	М	
PA6/ABS blends with MWNTs [PA6+ABS+(z wt%) MWNTs] Simultaneous melt-blending	$N_x A_y T_z$ (T or M) S_n	
Processing conditions	Screw speed (rpm) R,	
Temperature = 260 °C	Mixing time (min) t	
S1	R50 t15	
S2	R100t15	
\$3	R150 t15	
S4 R150 t5		
S5	R150t10	

Table 4-3 Sample codes with their composition for PA6/ABS blends with MWNTs



Figure 4-15 Variation of AC Electrical conductivity as a function of frequency for various blend compositions (40-60 wt% of PA6) of PA6/ABS blends (a) with MWNTs and (b) with Na-AHA modified MWNTs 1:1(wt/wt) at R100t15.

Modification of MWNTs with Na-AHA may result in a lower 'agglomerate' size of MWNTs and may exhibit enhanced debundling in the aqueous dispersion due to: (i) electrostatic charge repulsion between negatively charged MWNTs surface and carboxylate ions and (ii) steric stabilization through the presence of five '-CH₂' groups containing organic modifier [50]. Moreover, the dispersion of MWNTs in blends may be facilitated after modification with Na-AHA due to the faster rupture of MWNTs 'agglomerates'. Further, the Na-AHA molecules are likely to be desorbed from MWNTs surface during the melt-interfacial reaction between -NH₂ functionality of Na-AHA and -COOH end groups of PA6 chains. Na-AHA modified MWNTs may lead to refined 'network-like' structure formation of MWNTs, which has manifested in higher electrical conductivity values of the PA6/ABS blends with Na-AHA modified MWNTs irrespective of the blend composition.

The power law exponent (*n*) obtained from AC electrical conductivity data varies in the range 0–1, which characterizes the charge transport mechanism [169, 195]. The '*n*' values vary in the range of 0.7–1.0 for PA6/ABS blends with unmodified MWNTs, which is reported to be the characteristic of 'tunneling' or 'hopping' mechanism of the electron flow in a disordered material [18]. However, PA6/ABS blends with Na-AHA modified MWNTs exhibit that the value of 'n' is in the range of 0.5–0.6, which is indicative of the polarization effect in the presence of Na-AHA [195].

The localization of MWNTs in blends has been studied through solution experiment by dissolving blend samples in formic acid (to dissolve the PA6 phase) and in THF (to dissolve the ABS phase). *Figure 4-16* (a) and (c) show the photograph of the vials after dissolution of the ABS phase of blends and *Figure 4-16* (b) and (d) show the photograph of vials after dissolution of the PA6 phase of varying compositions (40/60, 45/55, 50/50, 55/45 and 60/40 PA6/ABS, vial 1 to 5 respectively) with unmodified and Na-AHA modified MWNTs, respectively. It is observed from *Figure 4-16* (a) that MWNTs are visibly present in the ABS phase in case of 40/60 and 45/55 (wt/wt) PA6/ABS blends and *Figure 4-16* (b) shows the presence of MWNTs in the PA6 phase irrespective of the blend composition. Interestingly, in case of PA6/ABS blends with Na-AHA modified MWNTs, MWNTs can as well be seen in the ABS phase [*Figure 4-16* (c)] for at least four compositions viz. 40/60, 45/55, 50/50 and 55/45 (wt/wt) of PA6/ABS blends. *Figure 4-16* (d) indicates the presence of Na-AHA modified MWNTs in the PA6 phase in all the blend compositions.

In order to confirm the above observation, these dispersions (where the ABS phase has been dissolved into THF) have been examined further through UV-vis spectroscopic analysis. It is widely known from the literature that higher absorbance values are observed for solutions containing higher fraction of individualized MWNTs in the dispersion [183, 184]. It can be seen from the plot of UV-vis absorbance versus PA6 concentration [*Figure 4-16* (e)] that for 40/60 and 45/55 PA6/ABS blends, UV-vis absorbance values are significantly higher than other blend compositions indicating a higher fraction of unmodified MWNTs localized in the ABS phase of these blends. For all the blend compositions in case of PA6/ABS blends with Na-AHA modified MWNTs, the absorbance values are higher as compared to those shown by the PA6/ABS blends with unmodified MWNTs. Higher UV-vis absorbance values in case of blends with Na-AHA modified MWNTs would also imply a greater fraction of individual MWNTs migrating towards the ABS phase of the blends.

However, it must also be noted that the UV-vis absorbance value of Na-AHA modified MWNTs is generally higher as compared to the corresponding blends with unmodified MWNTs in both aqueous solution and in THF, as observed from the plot. The modification step of MWNTs with Na-AHA leads to a lower 'agglomerate' size with higher fraction of individual MWNTs and thus, exhibits higher UV-vis absorbance values in the aqueous as well as THF solution.





Figure 4-16 UV-visible absorbance value of MWNTs corresponding to ABS phase for PA6/ABS blends with MWNTs for varying blend composition and solution experiments using THF and formic acid to show qualitatively the fraction of MWNTs migrated to ABS phase (1 to 5 indicates 40/60 to 60/40 (wt/wt) PA6/ABS blends with MWNTs).

4.2.2 MWNTs 'agglomerate' size, dispersion and blend morphology

Figure 4-17 (a) exhibits the optical microscopic images of the blend samples after dissolving into formic acid. The PA6 solution was taken on a glass slide to evaluate the 'agglomerate' size of MWNTs present in the PA6 phase. The average MWNTs 'agglomerate' size is decreased with increasing PA6 weight fraction in case of PA6/ABS blends with unmodified MWNTs. Further, in the presence of Na-AHA modified MWNTs, the MWNTs 'agglomerate' size is significantly reduced as compared to the 'agglomerate' size corresponding to unmodified MWNTs.

Figure 4-17 (b) shows the variation of average 'agglomerate' size as a function of PA6 concentration in PA6/ABS blends. MWNTs were extracted from the PA6 phase of PA6/ABS blends with unmodified and Na-AHA modified MWNTs. Since, MWNTs were ultrasonicated in either THF or deionized water before melt-mixing, the corresponding 'agglomerate' size in the respective dispersants was also indicated. Unmodified MWNTs show an average diameter of MWNTs 'agglomerates' of ~108 µm when dispersed in deionized water. The corresponding D_{avg} value is ~81.5 µm in THF. On modification with Na-AHA, the average 'agglomerate' size is decreased to ~49 µm in de-ionized water and the corresponding D_{avg} value in THF is ~27 µm.

Further, D_{avg} for unmodified MWNTs extracted from the PA6 phase varies from ~74 µm to ~28.5 µm for 40/60 to 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs. PA6/ABS blends with Na-AHA modified MWNTs, lower 'agglomerate' size of MWNTs has been observed over the entire blend composition range. 40/60 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs shows D_{avg} value of ~60 µm, which is decreased with increasing concentration of PA6 to ~31 µm for 60/40 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs. Thus, it can be observed that the primary 'agglomerate' size of MWNTs is decreased with increasing PA6 concentration for blends with unmodified MWNTs. Moreover, modification of MWNTs with Na-AHA has resulted in further decrease in primary 'agglomerate' size in all the blend compositions, which confirms that Na-AHA molecules facilitate the break-down of larger MWNTs 'agglomerates'.

Composition	p-MWNT	Na-AHA modified MWNT (1:1)	Composition	MWNT in de-ionized water and THF	(a)
N40A60S2	<u>500 шт</u>	<u>500 µm</u>	MWNT in de-ionized water	<u>500 um</u>	
N45A55S2	<u>500 ш</u> п	- <u>500 µ</u> m	Na-AHA modified MWNT (1:1 weight ratio) in de-ionized water	<u>500 ш</u> т	
N50A50S2	<u>500 ш</u> п	<u>500 µm</u>	MWNT in THF	<u>500 ш</u> п	
N55A4582	<u>500 µm</u>	5 <u>00 ш</u> т -	Na-AHA modified MWNT (1:1 weight ratio) in THF	<u>500 µm</u>	
N60A40S2	<u>500 µm</u>	<u>500 µm</u>			



Figure 4-17 (a) Optical microscopic images and (b) average diameter of MWNTs 'agglomerates' indicating the variation in the 'agglomerate' size of the MWNTs in the PA6/ABS blends with unmodified MWNTs and with Na-AHA modified MWNTs (5 wt%) at varied blend composition to 60/40 (wt/wt) PA6/ABS blends with MWNTs).

SEM micrographs have shown in *Figure 4-18* [(a) – (e)] that PA6/ABS blends of varying PA6 concentration exhibit various phase morphological type from droplet dispersed (40/60) to co-continuous (45/55, 50/50) and again droplet dispersed type (55/45 and 60/40). Further, in the presence of 5 wt% unmodified MWNTs, it can be observed from *Figure 4-18* [(f) to (j)] that all the blend compositions show a well-developed co-continuous morphology. It has also been observed that the ligament size decreases in the presence of unmodified MWNTs, as compared to Na-AHA-modified MWNTs. PA6 ligaments coarsened and the thickness is noted to be much higher (~7–9 µm) than the corresponding blends with unmodified MWNTs (~3–4 µm) in the presence of Na-AHA modified MWNTs as shown in *Figure 4-18* [(k) – (o)].

Figure 4-19 (a) depicts the 'agglomerated' and 'network-like' structure of MWNTs present in the PA6 phase in case of 40/60 PA6/ABS blends with unmodified MWNTs, whereas, finely dispersed MWNTs could be observed in the PA6 phase for 40/60 (wt/wt) PA6/ABS in the presence of Na-AHA modified MWNTs (*Figure 4-19* (c)). Similarly, *Figure 4-19* (b) and (d) show the morphology of 60/40 (wt/wt) PA6/ABS blend with 5 wt% unmodified MWNTs and Na-AHA modified MWNTs (1:1, wt/wt) respectively. The SEM micrographs could serve as a direct evidence of finer dispersion of modified MWNTs in 40/60 (wt/wt) PA6/ABS blends contributing towards the electrical conductivity of blends with modified MWNTs. SEM micrographs [*Figure 4-19* (e) and (f)] also show that MWNTs are present in the ABS phase in case of 40/60 PA6/ABS blends with unmodified as well as with Na-AHA modified MWNTs, which is also supported by the solution experiment and the UV-vis spectroscopic analysis mentioned earlier.

Figure 4-20 (a) shows the TEM micrograph of 50/50 PA6/ABS blend and 50/50 (wt/wt) PA6/ABS blend with MWNTs wherein the ABS phase has been stained with OsO_4 , which appears darker. Two distinct phases of PA6/ABS blend could be observed; brighter phase being the PA6 phase. *Figure 4-20* (c) and (d) indicate that MWNTs are present in the PA6 phase of 40/60 and 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs [*Figure 4-20* (e)]. In case of 40/60 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs, the MWNTs are observed in the PA6 phase and located near the interface and may be penetrating to the ABS phase. On the other hand, it can be seen from *Figure 4-20* (f) that for 60/40 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs are predominantly observed in the PA6 phase.



Figure 4-18 SEM micrographs of PA6/ABS blends with varied blend composition 40/60 (wt/wt) to 60/40 (wt/wt), [(a) - (e)] neat blends; [(f) - (j)] with 5 wt% MWNTs and [(k) - (o)] with 5 wt% Na-AHA modified MWNTs 1:1(wt/wt) (All images are taken at 1k magnification, scale bar of 50 μ m).



Figure 4-19 SEM micrographs of (a) 40/60 (wt/wt), (b) 60/40 (wt/wt) PA6/ABS blend with 5 wt% unmodified MWNTs and (c) 40/60 (wt/wt), (d) 60/40 (wt/wt) PA6/ABS blends with 5 wt% Na-AHA modified MWNTs (1:1, wt/wt) wherein ABS phase was removed using THF, (e) 40/60 (wt/wt) and (f) 60/40 (wt/wt) PA6/ABS blend with 5 wt% MWNTs wherein PA6 phase was removed using formic acid.



Figure 4-20 TEM micrographs of (a) 50/50 (wt/wt) PA6/ABS neat blend, (b) 50/50 (wt/wt) PA6/ABS blend with 5 wt% MWNTs, (c) 40/60 (wt/wt), and (d) 60/40 (wt/wt) PA6/ABS blend with 5 wt% MWNTs; (e) 40/60 (wt/wt), and (f) 60/40 (wt/wt) PA6/ABS blend with 5wt% Na-AHA modified MWNTs (1:1, wt/wt); (g) 50/50 (wt/wt) PA6/ABS blend with MWNTs and (h) 50/50 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs (1:1, wt/wt), ABS phase has been stained using OsO₄.



Figure 4-21 HR-TEM micrographs of 50/50 (wt/wt) PA6/ABS blends with (a) unmodified MWNTs (5 wt%) and (b) Na-AHA modified MWNTs (5 wt%, 1:1, wt/wt), ABS phase has been stained using OsO₄.

Figure 4-20 (g) and (h) show the state of dispersion of MWNTs in 50/50 (wt/wt) PA6/ABS blend with unmodified MWNTs and Na-AHA modified MWNTs. It can clearly be seen that MWNTs form 'network-like' structure in the PA6 phase in both cases however; the network being refined in the presence of Na-AHA. This observation is supported by *Figure 4-21* (a) and (b), which show the high resolution TEM micrographs of 50/50 (wt/wt) PA6/ABS blends with unmodified and Na-AHA modified MWNTs (1:1, wt/wt) respectively. The MWNTs are preferentially localized in the PA6 phase.

4.2.3 Chain scission and variation in extent of localization of MWNTs in PA6 phase

Figure 4-22 (a) depicts the variation of normalized torque values obtained during melt-mixing of PA6/ABS with unmodified MWNTs and Na-AHA modified MWNTs as a function of concentration of the PA6 phase. The torque values for the blends with unmodified MWNTs have been normalized with the corresponding torque value of neat PA6/ABS blends. The torque values for the PA6/ABS blends with Na-AHA modified MWNTs have been normalized with the corresponding PA6/ABS blends with Na-AHA modified MWNTs have been normalized with the torque values of the corresponding PA6/ABS blends with Na-AHA, in order to investigate the influence of MWNTs on the melt-viscosity of the blends. The

torque values are increased with increasing PA6 concentration; however, in the case of Na-AHA modified MWNTs, the normalized torque values are significantly higher than the torque values of the corresponding blends with unmodified MWNTs, suggesting the existence of refined 'network-like' structure of MWNTs.

Figure 4-22 (b) shows the variation of the normalized torque value as a function of PA6 concentration in the blends. In order to investigate the effect of Na-AHA on the melt-viscosity of the PA6 phase, the torque value for the blends with Na-AHA modified MWNTs has been normalized with the corresponding torque value of PA6/ABS blends with unmodified MWNTs. Further, the torque value of the PA6ABS blends with unmodified MWNTs has been normalized with the torque value of the corresponding neat blend. The normalized torque values are increased in case of PA6/ABS blends with unmodified MWNTs, whereas the normalized torque values for the blends with Na-AHA modified MWNTs are decreased with increasing concentration of PA6 phase, which confirms the chain scission of PA6 phase in case of the blends with Na-AHA modified MWNTs [18].



Figure 4-22 Normalized torque values to study: (a) the effect of MWNTs: torque values of PA6/ABS blends with unmodified MWNTs are normalized based on the torque values of the corresponding neat blends and for blends with Na-AHA modified MWNTs the torque values are normalized with the torque values of the blends with Na-AHA; and (b) the effect of Na-AHA: torque values of PA6/ABS blends with unmodified MWNTs are normalized based on the torque values of the corresponding neat blends and for blends with unmodified MWNTs are normalized based on the torque values of the corresponding neat blends and for blends with Na-AHA modified MWNTs the torque values are normalized with the torque values of the blends with unmodified MWNTs.

4.2.4 Thermal conductivity measurements

Carbon nanotubes are known to exhibit very high thermal conductivity values between 350 to 10,000W/mK and believed to be highly anisotropic [4, 74] In spite of an impressive thermal conductivity value of the nanotubes; the incorporation of the nanotubes does not lead to significant enhancement in the thermal conductivity of the composite, due to interfacial thermal resistance [73]. It is well-understood that the reason for modest enhancement of the thermal conductivity in case of polymer-MWNTs composites is caused by the resistance to transfer of heat at the nanotube-polymer boundary (called as Kapitza resistance) [196]. Hence, an important strategy to reduce the interfacial resistance might be to modify the nanotube-polymer interface.

In case of electrical conductivity, in order to improve the electrical conductivity the surface of the nanotubes is modified to enhance the debundling or separation of the MWNTs [15]. Similarly, it will be important that the surface of the nanotubes is tuned in such a way that the Kapitza resistance may be reduced, in order to improve the thermal conductivity. It has been reported by Bafekrpour et al. [197] that by tuning the microstructure and composition, transient temperature gradient field within the composite could be reduced, which may improve the thermal properties of the composites to endure the thermal shocks.

Figure 4-23 shows the effect of the blend composition on the thermal conductivity values for PA6/ABS blends with MWNTs and Na-AHA modified MWNTs 1:1 (wt/wt). Overall the thermal conductivity increased in the presence of the MWNTs as compared to the blends. And, the thermal conductivity increased with PA6 wt% in case of MWNTs (from 0.285 W/mK – 0.410 W/mK) as well as for Na-AHA modified MWNTs (0.371 W/mK – 0.403 W/mK). The thermal conductivity values increase with increasing PA6 wt% in case of MWNTs, on the other hand in case of Na-AHA modified MWNTs 1:1 (wt/wt) showed higher values irrespective of the blend composition. Also, the thermal conductivity value of 60/40 (wt/wt) blends with MWNTs (~ 0.410 W/mK) and with Na-AHA modified MWNTs (~ 0.403 W/mK) showed comparable values, which are in accordance with the observations of electrical conductivity measurements. Thus, it can be inferred that the state of dispersion of MWNTs plays a crucial role in electrical as well as thermal conductivity of the PA6/ABS blends with MWNTs and Na-AHA modified MWNTs.

The thermal conductivity of isolated nanotubes is an active area of research with some reports giving values as low as 30 W/mK, at the same time the highest reported nanotube thermal conductivities are of the order of 10^3 W/mK [73]. The reason for lower magnitude of increase in the thermal conductivity is the high interfacial thermal resistance between nanotubes. It has also been observed by Moisala et al. [135] that the experimental thermal conductivity values were much lower than the predicted values which they reasoned on the fundamental difficulty in transferring heat from the matrix to the nanotubes. Also, they concluded that there must be a large interface resistance to the heat flow associated with poor phonon coupling between the stiff single walled nanotubes and the relatively softer polymer matrix. There was a decrease noted in the thermal conductivity values in the presence of the SWNTs which was explained on the basis of the dampening of the phonon vibrations in the inner walls without hindrance.

Figure 4-24 (a) shows the variation in the weight percent as a function of temperature of 40/60 (wt/wt) PA6/ABS blend with unmodified MWNTs (N40A60T5), the corresponding blend wherein the ABS phase was removed using THF (N40T5) and the corresponding blend with Na-AHA modified MWNTs, wherein the ABS phase was removed using THF (N40M5). *Figure 4-24* (b) depicts the residual weight fraction of nanotubes (which are localized in the PA6 phase) obtained for varying PA6 concentration. The residual weight is higher in case of MWNTs modified with Na-AHA. It can also be observed that the weight fraction of unmodified MWNTs in case of 40/60 (wt/wt) PA6/ABS blends is lower as compared to 60/40 (wt/wt) PA6/ABS in the presence of 5wt% of unmodified MWNTs, which supports the findings from UV-vis spectroscopic analysis as well. The extent of MWNTs migration to the ABS phase is dependent on the PA6/ABS blend composition, which is decreased with increasing PA6 concentration.



Figure 4-23 Variation in the thermal conductivity (a) as a function of the wt% of PA6 in the PA6/ABS blends with 5 wt% MWNTs, Na-AHA modified MWNTs 1:1(wt/wt).



Figure 4-24 (a) TGA analysis 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs and the corresponding blend with unmodified MWNTs and Na-AHA modified MWNTs wherein ABS phase was removed by THF; (b) residue wt% obtained during the heating scan at temperature ~ 600 °C indicating the wt% of the MWNTs present in the sample; for 40/60, 50/50 and 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs (N_xA_yT5) and Na-AHA modified MWNTs (N_xA_yM5); and blends with unmodified (N_xT5) and Na-AHA modified MWNTs (N_xM5) wherein the ABS phase was removed by THF.

A lower extent of MWNTs migration in case of blends with higher concentration of PA6 phase is due to adequate PA6 content that aids in wetting MWNTs. However, in case of Na-AHA modified MWNTs, the additional driving force for MWNTs to get confined in the PA6 phase is the melt-interfacial reaction between the $-NH_2$ functionality of Na-AHA and acid end group of PA6. The intrinsic viscosity values were determined using Ubbelohde viscometer to ensure that the chain scission phenomenon of PA6 may be responsible for the decreased normalized torque values. Further, M_v values were calculated from the MKH equation and are mentioned in *Table 4-4*. M_v value of neat PA6 is ~29326.4 and in case of the blends with unmodified MWNTs the M_v value of the PA6 phase is lower as compared to that of pure PA6. This might be due to shear induced chain scission of PA6 during melt-mixing. In case of blends with Na-AHA modified MWNTs, the intrinsic viscosity values are significantly lower as compared to the corresponding blends with unmodified MWNTs, which confirm the chain scission of PA6 phase in the presence of Na-AHA.

4.2.5 Variation in the melt-viscosity and dynamic mechanical properties

Figure 4-25 (a) shows the variation in the complex viscosity (η^*) as a function of frequency for 40/60 (wt/wt) PA6/ABS blends with Na-AHA, unmodified MWNTs and Na-AHA modified MWNTs. It can be seen from the plot that PA6 shows frequency independent complex viscosity, whereas ABS shows higher complex viscosity as compared to PA6 and exhibits – shear thinning behaviour with a prominent yield stress. 40/60 (wt/wt) PA6/ABS neat blend, the corresponding blend with Na-AHA, blends with unmodified MWNTs and Na-AHA modified MWNTs showed a similar linear decrease in the complex viscosity with increasing frequency. However, the complex viscosity values in case of 40/60 (wt/wt) blend with Na-AHA are found to be lower than the neat blend and blends with unmodified MWNTs. Although in the presence of MWNTs; there is no significant increase in the complex viscosity as compared to the blends with unmodified MWNTs.

An increase in complex viscosity in case of the blends as compared to PA6 is due to the high melt-viscosity and the presence of yield stress of ABS. The presence of solid filler like MWNTs enhances melt viscosity of the blends, which is reflected in an increase in the complex viscosity. Similarly, the storage modulus values are higher in the presence of both unmodified and Na-AHA modified MWNTs for 40/60 wt/wt PA6/ABS blends [*Figure 4-25* (b)]. *Figure 4-25* (c) and (d) show the variation of the complex viscosity and the storage modulus as a function of frequency for 60/40 wt/wt PA6/ABS blends. It was found that the complex viscosity decreases in case of neat blend and blend with Na-AHA. Unmodified MWNTs leads to an enhancement in the complex viscosity as well as in the storage modulus. In case of blend with Na-AHA modified MWNTs, lower complex viscosity and storage moduli are observed. The reduction of the complex viscosity in case of the neat blend might be an indication of the immiscible nature of PA6/ABS blend. Further, addition of Na-AHA has resulted in lower complex viscosity as compared to the neat blends. This might be the consequence of chain scission of PA6 phase caused by Na-AHA molecules. The storage moduli values also reflect the chain scission phenomenon of PA6 chains, wherein the lower values of storage modulus has been observed in case of blend with Na-AHA.



Figure 4-25 Complex viscosity versus frequency curves for PA6, ABS, neat blend PA6/ABS (N_xA_y) , PA6/ABS blend with Na-AHA (N_xA_yNa5) , PA6/ABS blends with MWNTs (N_xA_yT5) and Na-AHA modified MWNTs (1:1, wt/wt) (N_xA_yM5) storage modulus versus frequency: (a) and (c) for 40/60 (wt/wt); (b) and (d) 60/40 (wt/wt) PA6/ABS blends respectively (obtained at 260 °C).

The variation in complex viscosity and the storage moduli values in the lower frequency range during the frequency sweep indicate the transition from 'liquid' to 'solid-like' behaviour prominently, which is a consequence of a rheological percolative 'network-like' structure formation between the polymer and the filler. In case of 40/60 PA6/ABS blends with unmodified MWNTs and Na-AHA modified MWNTs, terminal behaviour in the lower frequency region disappears, although the increase in the magnitude is higher for the 60/40 blends. In this case the concentration of the MWNTs in the blends is higher than the electrical percolation threshold for the PA6/ABS system.

Table 4-4 Intrinsic viscosity values of PA6 extracted from the PA6/ABS blends using formic acid and re-precipitated in deionized water, viscosity measurements carried out using Ubbelohde viscometer. PA6 phase was extracted in order to determine the variation in the molecular weight of PA6 in the absence of the MWNTs and ABS phase

Composition	[n](d]/a)	М	Standard
Composition	[it] (ui/g)	IVI _V	Deviation
Pure PA6	1.883	29326.4	0.06
N40A60T5	1.36	17351.5	0.08
N45A55T5	1.3275	16687.6	0.03
N50A50T5	1.343	17003.0	0.06
N55A45T5	1.268	15497.9	0.02
N60A40T5	1.237	14891.4	0.07
N40A60M5	0.672	5565.6	0.02
N45A55M5	0.7262	6307.4	0.05
N50A50M5	0.688	5780.9	0.05
N55A45M5	0.754	6701.4	0.03
N60A40M5	0.728	6332.6	0.01

The intrinsic viscosity values indicated higher extent of chain scission of PA6 chains in case of 40/60 (wt/wt) blend in the presence of Na-AHA as compared to 60/40 wt/wt PA6/ABS blend. On the contrary, the rheological studies showed higher magnitude of the decrease in the complex viscosity in case of 60/40 (wt/wt) PA6/ABS blend in the presence of Na-AHA. In this context, it is important to note that the rheological studies might show the effect of ABS more prominently owing to high melt viscosity. Hence, in case of PA6/ABS blend composition, which has ABS as a minor phase (60/40, PA6/ABS), might exhibit the effect of ABS more significantly as compared to the blend composition which has ABS as the major phase. Thus, the presence of a blend component with high viscosity and yield stress may mask the variation of smaller magnitudes in the rheological studies.

Sample	Storage modulus (GPa)		T_g (°C) (from tan delta peak)		
	Glassy region (25 °C)	Rubbery region (140 °C)	PA6	ABS	
PA6	4.4	0.715	54.2	_	
ABS	3.27	0.086	_	128.1	
N60A40	4.42	0.356	54.9	115.1	
N60A40T5	4.22	0.386	63.4	121.5	
N60A40M5	4.8	0.388	58.8	120.3	
N40A60	4.64	0.515	63.2	129.4	
N40A60T5	5.76	0.425	66.6	128.3	
N40A60M5	5.29	0.928	75.1	126.5	

Table 4-5 Variation in the storage modulus and glass transition temperature for the PA6/ABSblends with unmodified and Na-AHA modified MWNTs

Table 4-5 enlists the storage moduli values, glass transition values obtained from tan delta peak. The glass transition temperature determined through the tan delta peak corresponds more closely to the transition midpoint or inflection point of decreasing log E' from glassy state to rubbery state transition [198]. The storage modulus is increased in the presence of unmodified MWNTs. The corresponding blends with Na-AHA modified MWNTs showed higher modulus in case of 60/40 (wt/wt) PA6/ABS blend (~4.8 GPa, at 25 °C) as compared to the corresponding blend with unmodified MWNTs (~4.22 GPa) in the glassy region.

On the other hand, 40/60 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs shows storage modulus value of ~5.29 GPa, which is lower than the value exhibited by the corresponding blend with unmodified MWNTs, ~5.76 GPa. There is a significant enhancement in the glass transition temperature of the PA6 phase in the presence of unmodified MWNTs as well as Na-AHA modified MWNTs. However, T_g of the PA6 phase in the presence of Na-AHA is lower in both 40/60 (wt/wt) and 60/40 (wt/wt) blend composition. The decrease in T_g as well as in the storage modulus (in case of 40/60, wt/wt blend) may be the consequence of the chain scission of PA6 phase due to Na-AHA molecules. Therefore, it can be observed from the storage moduli values in the rubbery region that though the melt viscosity decreased in the presence of Na-AHA modified MWNTs might be resulting in the enhanced storage moduli of the PA6/ABS blends in the rubbery region.

4.3 Influence of non-covalent modification on the state of dispersion of multiwall carbon nanotubes in co-continuous binary polymer blends

4.3.1 Interaction between organic modifier molecules and MWNTs

Physico-chemical nature of carbon nanotubes, which essentially can be viewed as fully conjugated polyaromatic macromolecules with a hollow, inert interior and reactive exterior and ends, drives applications in all these fields. While fundamental research of nanotubes focuses on the intrinsic properties of isolated carbon nanotubes, applications rely heavily on interactions of nanotubes with their environment which is influenced by the basic structure, solvent and the presence of other molecules. These interactions are due to various non-covalent forces acting between the nanotube and molecular, ionic or macromolecular species constituting the nanotube environment [80]. The investigation of sedimentation behaviour of nanotubes in various media and in the presence of various modifiers is an important step in estimation of dispersibility of MWNTs in polymer blends [81, 82].

Surface modification of MWNTs utilizing an organic modifier is a well-established strategy to enhance the 'debundling' of MWNTs. In this context, various types of interactions between the organic modifiers and the MWNTs have been exploited to 'debundle' MWNTs 'agglomerates'. A detailed comparative assessment of the state of dispersion of MWNTs and the interactions existing in the presence of the organic modifier would bring interesting insight in understanding the state of dispersion of MWNTs in the binary polymer blends investigated here. In the current study, sodium salt of 6-aminohexanoic acid (Na-AHA) and 1-pyrenecarboxaldehyde (PyCHO) have been utilized for modifying MWNTs. Further, the influence of modified MWNTs has been investigated in the 'co-continuous' range of PA6/ABS blends with MWNTs (*Table 4-6*).

Morphology of unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs as observed from TEM and SEM observations is shown in *Figure 4-26* [(a)–(c)] and *Figure 4-26* [(d)–(f)] respectively. Unmodified MWNTs exhibit a highly 'agglomerated' MWNTs structure, whereas MWNTs modified with either Na-AHA or PyCHO depict presence of dispersed MWNTs. The presence of organic modifier on MWNTs surface is evident from the increase in the average diameter of MWNTs as determined from TEM analysis [for unmodified MWNTs, $D_{avg} \sim 9.2$; for Na-AHA modified MWNTs, $D_{avg} \sim 13.2$ nm; for PyCHO modified MWNTs, $D_{avg} \sim 13.5$ nm]. Morphological analysis shows that the modifier molecules are adsorbed on MWNTs surface and subsequently result in effective 'debundling' of MWNTs.

Raman spectroscopic analysis exhibits D-band at ~1332 cm⁻¹ corresponding to 'double resonance' phenomenon of MWNTs, which involves resonant Raman coupling to the excited photon [199]. Further, G-band at ~1582 cm⁻¹ is observed due to the C=C stretching vibrations of all pairs of sp² atoms in the graphene plane [199]. Raman spectra of unmodified MWNTs,

Na-AHA modified MWNTs and PyCHO modified MWNTs [*Figure 4-26* (g)] show that the G-band corresponding to the ordered graphitic structure of MWNTs shifts to higher wavenumber in the presence of Na-AHA (~1590.2 cm⁻¹) and PyCHO (~1588.8 cm⁻¹) as compared to the unmodified, pristine MWNTs (~1581.9 cm⁻¹).

Table 4-6 Sample codes with their compositions for PA6/ABS blends with MWNTs

Sample	Codes	
Polyamide 6 (PA6)	Ν	
Acrylonitrile-butadiene-styrene copolymer (ABS)	А	
PA6/ABS blends	$N_{x}A_{y}$ $(y = 100 - x)$	
PA6/ABS blends with 5 wt% of unmodified MWNTs 'simultaneous' melt-blending	N _x A _y T5 'x' varies from 40, 45, 50, 55, 60 (wt%)	
PA6/ABS blends with 5 wt% of Na-AHA modified MWNTs 'simultaneous' melt-blending	N _x A _y M5 'x' varies from 40, 45, 50, 55, 60 (wt%)	
PA6/ABS blends with 5 wt% of PyCHO modified MWNTs 'simultaneous' melt-blending	N _x A _y Py5 'x' varies from 40, 45, 50, 55, 60 (wt%)	

The shift in Raman characteristic peak may be due to an interaction between organic modifier molecules and MWNTs. A similar shift in G-band for MWNTs has also been earlier noticed in case of Na-AHA modified MWNTs of 1:1 and 1:4 (wt/wt) mixture of MWNTs: Na-AHA [15]. Moreover, unmodified MWNTs exhibit I_D/I_G value of ~1.18; whereas Na-AHA modified MWNTs show ~0.96 and PyCHO modified MWNTs depict the characteristic intensity ratio of ~0.75.

Increase in the I_D/I_G ratio is reported to indicate a higher fraction of defects in graphitic structure [200]. Further, the reduction in the I_D/I_G ratio indicates that MWNTs are well 'debundled' in the presence of the modifier [50, 172]. It has been reported earlier for SWNTs that the corresponding I_D/I_G ratio is decreased after ultra-sonication indicating 'debundling' of SWNTs, due to increased intensity of the tangential mode [178]. This observation can be extended to MWNTs as well, where it is postulated that due to 'debundling' of MWNTs, the photon absorption may increase when higher ordered graphitic fraction of MWNTs is exposed to the laser. Thus, it may lead to a decrease in I_D/I_G ratio. However, the intensity of characteristic D-band may not enhance significantly, as 'non-covalent' modification of MWNTs will not introduce any further defects on the MWNTs surface. In brief, Raman spectroscopic analysis depicts the presence of enhanced interaction between MWNTs.

Presence of Na-AHA molecules on the MWNTs surface is also confirmed through the characteristic peaks at ~1413 cm⁻¹ (weak peak) and ~1571 cm⁻¹ (strong stretch) corresponding to the strong carboxylate ions [*Figure 4-27* (a) and (b)]. Adsorption of Na-AHA molecules on MWNTs surface is evident as carboxylate band shifts to higher wavenumber in case of Na-AHA modified MWNTs. FTIR spectra of PyCHO and PyCHO modified MWNTs (1:1, wt/wt) [*Figure 4-27* (c)-(f)] showed a shift in vibrational peak of aromatic ring corresponding to PyCHO molecules from ~1590 cm⁻¹ to ~1589 cm⁻¹. The C=O stretch peak at ~1680 cm⁻¹ has also shifted to a lower wavenumber of ~1650 cm⁻¹, in case of PyCHO modified MWNTs. Further, the 'wagging' vibration has shifted from ~841 cm⁻¹ and ~706 cm⁻¹ to lower wavenumbers ~836 and ~704 cm⁻¹ respectively. A shift of vibrational peaks to lower wavenumber is an indication of the formation of strong ' π - π ' interaction and 'hydrophobic' interactions between aromatic rings of PyCHO and MWNTs surface [48].





Figure 4-26 The effect of modification on the state of dispersion of MWNTs after the modification step; Raman spectra and the corresponding I_D/I_G values of various MWNTs, surface area of unmodified and modified MWNTs obtained by BET analysis, SEM and TEM analysis (MWNTs average diameter obtained by image analysis) for unmodified MWNTs, Na-AHA modified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt).



Figure 4-27 FTIR spectra for (a) Na-AHA, (b) MWNTs and Na-AHA mod. MWNTs 1:1 (wt/wt), (c) PyCHO, (d) PyCHO mod. MWNTs and (e) PyCHO mod. MWNTs and (f) MWNTs and PyCHO modified MWNTs (different wavenumber range).

Brunauer-Emmet and Teller analysis (BET) was carried out in order to determine the variation in the surface area of MWNTs on non-covalent modification with Na-AHA and PyCHO. BET theory relates to the rate of adsorption and desorption of one monolayer of adsorbate on the surface [201]. Unmodified MWNTs showed the surface area of ~269.9 m²/g.

Na-AHA modified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt) exhibited the surface area of ~40.7 m²/g and ~40.4 m²/g respectively. BET analysis also supports the fact that modifier molecules are adsorbed on MWNTs surface, which in turn result in lower free surface area associated with modified MWNTs.

Figure 4-28 (a) shows the XPS spectra obtained from the O 1s scan and *Figure 4-28* (b) shows the XPS spectra obtained from the C 1s scan for unmodified, pristine MWNTs and PyCHO modified MWNTs. The peaks for carbonyl C and O are observed in the presence of PyCHO molecules in the range of ~531.65 eV – ~531.94 eV and ~286.45 – ~287.92 eV respectively [202]. This observation further substantiates the existence of PyCHO molecules on MWNTs surface.

FTIR spectra of PA6/ABS blends with 5 wt% of unmodified MWNTs, the corresponding blends with Na-AHA modified MWNTs and the corresponding blends with PyCHO modified MWNTs are shown in *Figure 4-29* (a), (b) and (c) respectively. *Figure 4-29* (a) exhibits that in case of PA6/ABS blends with unmodified MWNTs [for the varying blend compositions–40/60, 45/55, 50/50, 55/45 and 60/40 (wt/wt)], the FTIR spectra show characteristic peaks at ~1630 cm⁻¹, ~1543 cm⁻¹, and ~1258 cm⁻¹, which correspond to amide I, amide II and amide III respectively, which is characteristics for PA6 phase. PA6/ABS blends with PyCHO modified MWNTs and PA6/ABS blends with Na-AHA modified MWNTs show amide I peak at ~1641 cm⁻¹, amide II peak at ~1538 cm⁻¹ and amide III peak at ~1245 cm⁻¹.

In addition to this observation, FTIR spectra of PA6/ABS blends with PyCHO modified MWNTs show additional peaks at ~693 cm⁻¹ and ~849 cm⁻¹. These peaks are corresponding to the C–H wagging owing to the presence of aromatic rings associated with the PyCHO molecules. Further, a peak at ~1726 cm⁻¹ is observed, which indicates the existence of hydrogen bonding, which may be associated with the interaction between PyCHO molecules and PA6 chains through 'hydrogen bonding' between –NH₂ functionality of PA6 phase and –CHO functionality of PyCHO molecules [203].



Figure 4-28 XPS spectra for (a) O 1s scan and (b) C 1s scan for MWNTs and PyCHO modified MWNTs



Figure 4-29 FTIR spectra for PA6/ABS blends of varying blend composition – 40/60, 45/55, 50/50, 55/45 and 60/40 (wt/wt) with 5wt% (a) unmodified MWNTs, (b) Na-AHA modified MWNTs (1:1, wt/wt) and (c) PyCHO modified MWNTs (1:1, wt/wt).

The variation in normalized amide peak intensity with increase in PA6 concentration in PA6/ABS blends with Na-AHA modified MWNTs is shown in *Figure 4-29* (d). Normalized intensity of amide I peak with respect to intensity of peak corresponding to C-C stretching (which is not affected because of the 'melt-interfacial' reaction) is increased with increasing PA6 concentration. This observation indicates that the extent of 'melt-interfacial' reaction increases with increasing PA6 concentration. Increasing PA6 concentration may provide higher number of –COOH functional groups to react with the –NH₂ groups of Na-AHA, which results in higher extent of 'melt-interfacial' reaction. Variation in meltinterfacial' reaction may influence the extent of 'preferential' localization of Na-AHA modified MWNTs in the PA6 phase of PA6/ABS blends.

4.3.2 Average size of MWNTs 'agglomerates': Influence of blend composition and modification with organic modifiers

Average 'agglomerate' size of the remaining MWNTs 'agglomerates' extracted from the PA6 phase was determined using optical microscopic analysis of PA6/ABS blends with unmodified MWNTs, corresponding blends with Na-AHA modified MWNTs and PyCHO modified MWNTs for varied blend composition [*Figure 4-30*]. Average 'agglomerate' size of MWNTs for various blend compositions is shown in *Table 4-7*. D_{avg} is decreasing monotonically with increasing PA6 concentration in case of unmodified MWNTs (~73.7 µm for 40/60 to ~28.6 µm for 60/40, (wt/wt) PA6/ABS blend) and Na-AHA modified MWNTs (~59.9 µm for 40/60 to ~31.4 µm for 60/40, (wt/wt) PA6/ABS blend). However, PyCHO modified MWNTs show a progressively increasing D_{avg} with increasing concentration of PA6 content in the blend (~24.3 µm for 40/60 to ~47.9 µm for 60/40, wt/wt blend). Blends with Na-AHA modified MWNTs showed an overall lower D_{avg} values than the blends with unmodified MWNTs.

A consistent decrease in D_{avg} in PA6/ABS blends with unmodified MWNTs for increasing PA6 concentration may be due to the 'break-up' of large primary MWNTs 'agglomerates' during 'melt-mixing', facilitated through higher concentration of PA6 chains, which may wet and infiltrate in to the MWNTs 'agglomerates'. Primary 'agglomerate' size is lower in case of Na-AHA modified MWNTs (~49 µm in de-ionized water and ~27 µm in THF) and PyCHO modified MWNTs (~61.2 μ m in THF) irrespective of the medium of dispersion (aqueous or organic, THF) as compared to unmodified MWNTs (D_{avg} ~108 μ m in de-ionized water, ~81.5 μ m in THF) [*Figure 4-30*]. 'Melt-interfacial' reaction between PA6 chains and Na-AHA molecules may result in further 'break-up' of MWNTs 'agglomerates' through enhanced infiltration of PA6 chain into MWNTs 'agglomerates'. An interaction between PyCHO modified MWNTs and ABS phase is expected to be much higher than the interaction between PA6 and PyCHO modified MWNTs. Therefore, 40/60 (wt/wt) blend with PyCHO modified MWNTs exhibit a higher fraction of MWNTs localized in the ABS phase.

However, it would be difficult to accommodate PyCHO modified MWNTs in the ABS phase as the concentration of ABS phase decreases in the respective blend. Thus, the fraction of PyCHO modified MWNTs remaining in the PA6 phase increases with decrease in ABS concentration. This might lead to the increased average 'agglomerate' size of MWNTs in the PA6 phase, which results in increased D_{avg} values with increasing PA6 concentration. Although the average 'agglomerate' size in case of PyCHO modified MWNTs is lower than the corresponding blend composition with unmodified MWNTs based compositions. It is higher than the average 'agglomerate' size of the corresponding blends with Na-AHA modified MWNTs. Hydrogen bonding between PA6 chains and PyCHO molecules was noticed through FTIR analysis. However, this interaction may not be sufficiently strong enough as compared to 'melt-interfacial' reaction in presence of Na-AHA modified MWNTs.

SEM micrographs of PA6/ABS neat blends [*Figure 4-31* (a)–(e)]; the corresponding blends with 5wt% unmodified MWNTs [*Figure 4-31* (f)–(j)]; the respective blends with Na-AHA modified MWNTs 1:1 (wt/wt) [*Figure 4-31*(k)–(o)] and PyCHO modified MWNTs 1:1 (wt/wt) [*Figure 4-31* (p)–(t)] are shown in *Figure 4-31* [(a)–(t)]. In case of neat blends, 40/60 (wt/wt) PA6/ABS blend shows that PA6 forms the dispersed droplets in the ABS matrix, further 45/55 and 50/50 (wt/wt) blend compositions show a 'co-continuous' phase morphology; whereas phase inversion is observed in case of 55/45 and 60/40 (wt/wt) blend compositions. On incorporation of unmodified MWNTs in PA6/ABS blends, transformation to 'co-continuous' phase morphology is observed [*Figure 4-31* (f)–(j)] irrespective of the blend composition. 40/60, 45/55 and 50/50 (wt/wt) PA6/ABS blends show coarser 'co-continuous' phase morphology in the presence of Na-AHA modified MWNTs (1:1, wt/wt). In

case of 55/45 and 60/40 (wt/wt) blends with Na-AHA modified MWNTs, the phase morphology changes to 'co-continuous' type morphology with sub-inclusions of elongated ABS droplets. *Figure 4-31* (p) shows the SEM image of 40/60 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs, which depicts a 'matrix-dispersed droplet' type morphology. Further, the phase morphology changes to a well-developed 'co-continuous' type morphology from 45/55 to 60/40 (wt/wt) blends with PyCHO modified MWNTs.

Composition	MWNTs	Na-AHA modified MWNTs (1:1, wt/wt)	PyCHO modified MWNTs (1:1, wt/wt)	Composition	MWNTs in de-ionized water/ THF
N40A60	<mark>500 µm</mark>	<u>500 μm</u>	<mark>500 µm</mark>	Unmodified MWNTs in de-ionized water	500 µm
N45A55	500 µm	<u>500 µ</u> m	<u>500 µm</u>	Na-AHA modified MWNTs (1:1, wt/wt) in de-ionized water	500 µm
N50A50	500 µm	<mark>500 µ</mark> m	<u>500 µm</u>	Unmodified MWNTs in THF	500 μm
N55A45	<u>500 µm</u>	<u>500 µm</u>	<u>500 µm</u>	Na-AHA modified MWNT (1:1 weight ratio) in THF	500 μm
N60A40	500 µm	<u>500 µm</u>	<u>500 µm</u>	PyCHO modified MWNTs (1:1, wt/wt) in THF	т. •

Figure 4-30 (a) Optical micrographs to determine the remaining MWNTs 'agglomerate' size for PA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs 1:1 (wt/wt) for varying blend compositions: (a) 40/60, (b) 45/55, (c) 50/50, (d) 55/45 and (e) 60/40 (wt/wt) PA6/ABS; optical microscopic images of unmodified MWNTs in de-ionized water and in THF as well as of Na-AHA modified MWNTs in de-ionized water and PyCHO modified MWNTs in THF are provided for reference.



Figure 4-31 SEM micrographs of neat PA6/ABS blends of varying blend composition: 40/60, 45/55, 50/50, 55/45and 60/40 (wt/wt) [(a) – (e)], corresponding PA6/ABS blends with 5 wt% unmodified MWNTs [(f) – (j)]; blends of respective blend compositions with Na-AHA modified MWNTs (1:1 wt/wt) [(k) - (o)] and the respective blend compositions with PyCHO modified MWNTs (1:1 wt/wt) [(p) - (t)] where PA6 phase was removed using formic acid for (a) and (p) and for remaining samples the ABS phase was removed using THF.

Co-continuous structure formation during melt-mixing of polymer blend depends on the probability of establishment of connectivity between the polymer phases. Therefore, equally viscous polymers melt-mixed in equal volume fraction may result in 'co-continuous' structure, which corresponds to 'melt-viscosity' ratio close to 1 and volume fraction of polymer component of ~0.5. However, often polymers show significantly different 'meltviscosity' values. In this context, sufficiently low fraction of low melt-viscosity polymer and high fraction of high melt-viscosity polymer may result in 'co-continuous' structure as per the qualitative relation reported by Pötschke and Paul [24]. PA6 and ABS exhibit significantly different 'melt-viscosity'. MWNTs (surface free energy ~40–45 mN/m [18]) may prefer to localize in the PA6 phase (surface free energy ~36.4 mN/m [18]) as compared to the ABS phase (surface free energy ~29.4 mN/m [18]) due to lower difference in the surface free energy values. Further, lower melt-viscosity of PA6 also favours the localization of MWNTs in the PA6 phase rather than the ABS phase of the corresponding PA6/ABS blend. The transformation from the 'dispersed-droplet' morphology to a well-developed 'cocontinuous' morphology may be due to the alteration of melt-viscosity of PA6 due to 'preferential localization' of MWNTs. It is important to note that though MWNTs prefer to localize in PA6 phase, unmodified MWNTs are observed to be distributed in the ABS phase as well when 'simultaneous' melt-mixing protocol is utilized [204].

A decrease in melt-viscosity of PA6 phase due to 'chain scission' of PA6 in the presence of Na-AHA molecules may lead to a variation in the phase morphology of PA6/ABS blends in the presence of Na-AHA modified MWNTs [204]. Transformation from a 'co-continuous' structure (50/50, wt/wt PA6/ABS blend with Na-AHA modified MWNTs) to a partial 'co-continuous' structure with 'sub-inclusions' of ABS droplets (55/45 and 60/40, wt/wt PA6/ABS blends with Na-AHA modified MWNTs) indicates that blend composition is near to the 'phase inversion' composition. Transformation from the 'dispersed-droplet' morphology to a well-developed 'co-continuous' morphology may be due to the alteration of melt-viscosity of the 'PA6+MWNTs' phase and 'ABS+MWNTs' phase in the presence of PyCHO modified MWNTs. Localization of MWNTs in the PA6 phase may result in an increase in 'melt-viscosity' of 'PA6+MWNTs' phase, therefore it may lead to the 'cocontinuous' type morphology at the end of 15th minute of melt-mixing. On increasing PA6 concentration, the relative amount of ABS phase decreases in case of 45/55, 50/50, 55/45 and 60/40 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs. As mentioned earlier, PyCHO molecules may also engage with PA6 chains through hydrogen bonding, therefore it may result in enhanced melt-viscosity of 'PA6+PyCHO modified MWNTs' phase. Thus, the presence of well-debundled MWNTs and hydrogen bonding between PA6 phase and PyCHO molecules may lead to the alteration in 'melt-viscosity' ratio and consequently may result in 'co-continuous' phase morphology.

The % co-continuity did not alter significantly in PA6/ABS blends which exhibit 'cocontinuous' morphology investigated. However, it may be interesting to find out the variation in ligament thickness of one of the phases in these blends in the presence of unmodified and modified MWNTs. *Figure 4-32* shows the variation of ligament size of PA6 phase with varying PA6 concentration. PA6/ABS blends with unmodified MWNTs show the lowest ligament size, whereas PA6/ABS blends with Na-AHA modified MWNTs and PyCHO modified MWNTs show a gradual increase in ligament size with increasing PA6 concentration. Increased ligament thickness of PA6 may accommodate higher fraction of MWNTs, which may facilitate the 'network-like' structure formation of MWNTs.



Figure 4-32 Ligament thickness variation in PA6/ABS blends with unmodified MWNTs (N_xA_yT5) , Na-AHA modified MWNTs (1:1, wt/wt) (N_xA_yM5) and PyCHO modified MWNTs (1:1, wt/wt) (N_xA_yPy5) for varying blend compositions (40/60, 45/55, 50/50, 55/45 and 60/40, wt/wt).

4.3.3 Localization and state of dispersion of MWNTs in PA6/ABS blends

PA6/ABS blends with MWNTs exhibit 'co-continuous' composition range from 40/60 to 60/40 (wt/wt) PA6/ABS. Therefore, in order to investigate the variation in the phase morphology of PA6/ABS blends with MWNTs over the 'co-continuous' range 40/60 and

60/40 (wt/wt) PA6/ABS blend compositions are selected as representative blend compositions for the detailed morphological analysis.

Higher magnification SEM micrographs [Figure 4-33 (a)-(f)] exhibit the state of dispersion of unmodified MWNTs and modified MWNTs (Na-AHA and PyCHO) in 40/60 [Figure 4-33 (a)–(c)] and 60/40 [Figure 4-33 (d)–(f)] (wt/wt) blends of PA6/ABS blends. SEM micrographs of 40/60 PA6/ABS blend with unmodified MWNTs [Figure 4-33 (a)], the corresponding blend with Na-AHA modified MWNTs [Figure 4-33 (b)] and the corresponding blend with PyCHO modified MWNTs [Figure 4-33 (c)] indicate that it is difficult to differentiate the state of dispersion of MWNTs with the corresponding 60/40 (wt/wt) PA6/ABS blends except PyCHO modified MWNTs based compositions. [Figure 4-33 (d)-(f)]. Figure 6 (c) shows that the 40/60 (wt/wt) PA6/ABS blend with PyCHO modified MWNTs exhibits a majority of MWNTs 'agglomerated' in the PA6 phase along with 'agglomerated' or 'individualized' MWNTs in the ABS phase. Moreover, 60/40 composition shows well-developed 'network-like' structure of MWNTs spanned in both the phases. Therefore, it may be inferred that PyCHO modified MWNTs are localized in both the blend components. Overall, it is hard to compare the state of dispersion of unmodified and modified MWNTs in 40/60 and 60/40 (wt/wt) PA6/ABS blends, as observed from SEM images.

TEM micrographs of 40/60 (wt/wt) PA6/ABS blend with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs are depicted in *Figure 4-34* (a)–(f). *Figure 4-34* (a) and (b) show the presence of 'nano-agglomerates' (indicated by outline) of unmodified MWNTs in the PA6 and in the SAN phase of 40/60 (wt/wt) PA6/ABS blend (where bright region indicates PA6 phase, grey region indicates SAN phase and dark region indicates polybutadiene phase of ABS). *Figure 4-34* (c) and (d) exhibit TEM micrographs of the corresponding blend with Na-AHA modified MWNTs, where 'nano-agglomerates' and 'individually' dispersed MWNTs are observed (indicated by arrows). MWNTs are also distributed in the ABS phase. Further, MWNTs appear perpendicular to the 'interface', where they act like a 'bridge' spanning between the phases [204]. Further, in case of PyCHO modified MWNTs [*Figure 4-34* (e) and (f)], MWNTs are present in both the phases as well as at the 'interface' of PA6/ABS blend.



Figure 4-33 High magnification SEM micrographs of PA6/ABS blends of varying blend composition 40/60 (wt/wt) and 60/40(wt/wt) with: [(a)-(b)] 5 wt% MWNTs, [(c)-(d)] 5wt% Na-AHA modified MWNTs 1:1 (wt/wt) and [(e)-(f)] 5 wt% PyCHO modified MWNTs 1:1(wt/wt).


Figure 4-34 TEM micrographs of 40/60 (wt/w)t PA6/ABS blends with (a) Na-AHA modified MWNTs 1:1(wt/wt) and (b) PyCHO modified MWNTs 1:1 (wt/wt) (scale bar = 100 nm).



Figure 4-35 TEM micrographs of 60/40 (wt/w)t PA6/ABS blends with (a) Na-AHA modified MWNTs 1:1(wt/wt) and (b) PyCHO modified MWNTs 1:1 (wt/wt) (scale bar = 100 nm).

Figure 4-35 [(a)–(f)] shows TEM micrographs of 60/40 (wt/wt) PA6/ABS blend with unmodified MWNTs, the corresponding blends with Na-AHA modified MWNTs and PyCHO modified MWNTs (1:1, wt/wt). 60/40 (wt/wt) [Figure 4-35 (a)-(b)] blend with unmodified MWNTs shows a lower fraction of MWNTs 'nano-agglomerates' as compared to 40/60 (wt/wt) blend with unmodified MWNTs. Unmodified MWNTs are mostly 'individualized' forming a 'network-like' structure in case of 60/40 blend. A fraction of unmodified MWNTs is even observed in the ABS phase as well as at the 'interface' (perpendicular to the 'interface' acting like a 'bridge' between the phases). 60/40 (wt/wt) blend with Na-AHA modified MWNTs [Figure 4-35 (c)-(d)] exhibits significantly lower fraction of MWNTs 'nano-agglomerates' along with a higher fraction of 'individualized' MWNTs. MWNTs are distributed in ABS phase as well as at the interface. The corresponding blend with PyCHO modified MWNTs [Figure 4-35 (e)-(f)] exhibits the presence of MWNTs in both PA6 and ABS as well as at the 'interface'. Further, lower fraction of MWNTs 'nano-agglomerates' is also observed in case of 60/40 (wt/wt) PA6/ABS blend with PyCHO modified MWNTs. Overall, unmodified MWNTs are observed in PA6 as well as ABS phase, where MWNTs exhibit 'nano-agglomerates' of various sizes. In the presence of organic modifiers, the size of 'nano-agglomerates' decreases and higher fraction of 'individualized' MWNTs is seen. Further, a higher fraction of MWNTs is also observed at the 'interface' of the blend in case of modified MWNTs.

Figure 4-36 depicts the photographic images of MWNTs dispersions in THF solvent in order to investigate the localization of MWNTs in the ABS phase. Unmodified MWNTs show black coloration associated with MWNTs fraction distributed in the ABS phase. The extent of black coloration is decreased with increasing concentration of PA6 phase in the blend. Na-AHA modified MWNTs are also observed in the ABS phase for the entire blend composition range from 40/60 to 60/40 (wt/wt) PA6/ABS blends, where the extent of black coloration is decreased as a function of PA6 concentration in the blend. PyCHO modified MWNTs are localized in the ABS phase for 40/60 to 50/50 (wt/wt) PA6/ABS blends, further the intensity of black coloration is decreased for 55/45 and 60/40 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs. Transfer of 'debundled' MWNTs to the ABS phase may be facilitated as compared to unmodified MWNTs for PyCHO modified MWNTs. Localization of unmodified MWNTs and Na-AHA modified MWNTs in the ABS phase has earlier been reported as well in PA6/ABS blends [204].



Figure 4-36 Solution experiment using THF as a solvent for the ABS phase to determine the presence of MWNTs in the ABS phase in case of blends with unmodified MWNTs, respective blends with Na-AHA modified MWNTs and PyCHO modified MWNTs 1:1 (wt/wt) with varying blend composition (Numbering indicates increasing PA6 concentration 40, 45, 50, 55 and 60 wt% respectively from 1 to 5).

4.3.4 Formation of MWNTs 'network': Influence of blend composition and organic modifier molecules

Variation in DC electrical conductivity with increasing PA6 concentration for PA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs is depicted in Figure 4-37. The DC electrical conductivity increases with increase in PA6 concentration in case of unmodified MWNTs (10⁻¹¹-10⁻⁶ S/cm). In the presence of Na-AHA modified MWNTs (the corresponding DC electrical conductivity in the range of $\sim 10^{-7} - 10^{-6}$ S/cm) and PyCHO modified MWNTs (the corresponding DC electrical conductivity in the range of $\sim 10^{-5} - 10^{-4}$ S/cm), the electrical conductivity is also increased irrespective of the blend composition. The electrical conductivity values for the 60/40 (wt/wt) PA6/ABS blends with unmodified and Na-AHA modified MWNTs are in the order of $\sim 10^{-5}$ S/cm. Our earlier study has shown that PA6 phase could wet MWNTs effectively at the early stages of melt-mixing in case of 60/40 (wt/wt) PA6/ABS blend with unmodified MWNTs. This phenomenon facilitates the infiltration of the PA6 chains in the MWNTs 'agglomerates', which subsequently led to formation of unmodified MWNTs 'network' at higher PA6 concentration of PA6/ABS blend [205]. Higher electrical conductivity in blends with Na-AHA modified MWNTs as compared to unmodified MWNTs may be associated with a refined 'network-like' structure of MWNTs. The electrical conductivity values in case of PyCHO modified MWNTs are found to be higher (~2 orders of magnitude) than the values observed in case of respective blends with Na-AHA modified MWNTs.

A fraction of MWNTs may also localize in the ABS phase as a consequence of the 'simultaneous' melt-mixing protocol, as mentioned in earlier section [204]. Re-distribution of MWNTs, which are confined in the ABS phase to the PA6 phase, is suppressed due to high melt-viscosity of the ABS phase. The transfer of MWNTs occurred in two steps; first is the contact between the nanotube and the interface, followed by the diffusion of MWNTs to the preferred polymer phase [206]. The 'masterbatch' approach leads to the selective localization of the nanotubes in the PA6 phase [207] as compared to the 'simultaneous' melt-blending protocol, wherein a minor fraction of MWNTs could as well be observed in the ABS phase [204]. In the presence of Na-AHA (1:1, wt/wt Na-AHA modified MWNTs, 2 wt% in 50/50, wt/wt PA6/ABS exhibits DC electrical conductivity of ~8x10⁻¹⁰ S/cm) and other phosphonium based organic modifier, viz., BTPC (showed lower DC electrical conductivity

of ~ 10^{-10} S/cm), DTPB (1:1, wt/wt Na-AHA modified MWNTs, 2 wt% in 50/50, wt/wt PA6/ABS exhibits DC electrical conductivity of ~ $7.1x10^{-7}$ S/cm), OTPB (1:1, wt/wt Na-AHA modified MWNTs, 2 wt% in 50/50, wt/wt PA6/ABS exhibits DC electrical conductivity of ~ $7x10^{-7}$ S/cm), the nanotubes have resulted in a refined 'network-like' structure of MWNTs [54].



Figure 4-37 AC electrical conductivity as a function of varying concentration of PA6 in PA6/ABS blends with 5 wt%, 1:1(wt/wt) PyCHO modified MWNTs.

Table 4-7 Remaining 'agglomerate' size of MWNTs in the PA6 phase in PA6/ABS blendsdetermined by the image analysis of the optical micrographs

Wt% of PA6	MWNTs (D _{avg} in µm)	Na-AHA modified MWNTs (D _{avg} in μm)	PyCHO modified MWNTs (D _{avg} in μm)
40	73.7	59.9	24.3
45	70.5	53.9	27.7
50	64.6	47.4	30.7
55	55.5	44.0	45.1
60	28.6	31.4	48.0

Non-covalent modification of MWNTs by PS-b-PAH has resulted in homogeneous dispersion of MWNTs in epoxy matrix, which was confirmed through lower electrical percolation threshold (~0.18 wt%) as compared to unmodified MWNTs (~0.7 wt%) and enhanced electrical conductivity values (DC electrical conductivity of $\sim 10^{-4}$ S/cm at 1 wt% loading) as compared to the corresponding electrical conductivity values for composite with unmodified MWNTs (DC electrical conductivity of $\sim 10^{-6}$ S/cm at 1 wt% loading) [56]. This has been explained on the basis of pyrene rings interacting with MWNTs to improve dispersion as well as to facilitate the electron transport. Therefore, it is highly probable that the increase in the electrical conductivity caused by PyCHO modified MWNTs is due to formation of refined 'network-like' structure of MWNTs and facilitated electron transport due to 'conjugation' [55, 208, 209].

State of dispersion of MWNTs significantly influences the nature of the 'network-like' structure of MWNTs formed in PA6/ABS blends. PA6/ABS blends with unmodified MWNTs exhibit 'network-like' structure formation of MWNTs through preferential localization of MWNTs in the PA6 phase. Remaining MWNTs 'agglomerates' observed through optical microscopic analysis may consist of 'nano-agglomerates' of varying sizes based on the blend composition, which is observed through TEM micrographs. Further, the fraction of 'individualized' MWNTs can be observed through TEM micrographs. PA6/ABS blends with Na-AHA modified MWNTs show significantly refined 'network' of MWNTs via higher fraction of 'debundled' MWNTs as well as 'preferential' localization of MWNTs in the PA6 phase. This observation is supported by significantly lower value of remaining MWNTs 'agglomerates' as compared to the corresponding blends with unmodified MWNTs obtained from optical microscopic analysis. PyCHO modified MWNTs exhibit 3D MWNTs 'network' formation through 'nano-agglomerates' and 'individualized' MWNTs, which indicates 'preferential' localization of MWNTs in the ABS phase. Optical microscopic analysis indicates that D_{avg} values of MWNTs increase with increasing PA6 concentration. This finding is substantiated by the presence of 'nano-agglomerates' MWNTs present in the SAN [210, 211] as well as PA6 phases.

4.3.5 Influence of surface coverage of MWNTs by the organic modifier molecules on the crystallization behaviour of PA6 phase

Non-isothermal crystallization exotherms of PA6 phase of PA6/ABS blends with 5 wt% unmodified MWNTs are shown in Figure 4-38 (a) (crystallization exotherms for blends with Na-AHA modified MWNTs and PyCHO modified MWNTs are provided in Figure 5 of supplementary information). PA6 phase exhibits two exothermic peaks in the presence of unmodified MWNTs in PA6/ABS blends. Crystallization peak observed at higher temperature is due to the 'trans-crystalline lamellar' structure formation of PA6 phase, which is directly in contact with MWNTs surface [149]. Further, peak observed at lower temperature is associated with the bulk crystallization of PA6 phase in the presence of MWNTs. Ratio of the crystallization peak height at lower temperature (H_1) to the peak height at higher temperature (H₂) is determined in order to investigate the extent of 'interfacial crystallization' of PA6 in the presence of MWNTs [Figure 4-38 (b)]. Higher H₁/H₂ indicates lower fraction of 'trans-crystalline lamellar' structure, whereas lower value of H₁/H₂ indicates higher extent of 'interfacial crystallization'. This is presumably owing to higher 'available' surface of MWNTs for crystallization of the PA6 phase in addition to the lattice matching between MWNTs and PA6 crystallites. PA6/ABS blends with unmodified MWNTs and blends with Na-AHA modified MWNTs show H_1/H_2 values lower than the values exhibited by PA6/ABS blends with PyCHO modified MWNTs. Higher H₁/H₂ values indicate that the presence of PyCHO molecules on MWNTs surface, which suppresses the 'interfacial crystallization' of PA6 phase.

'Bulk crystallization' phenomenon of PA6 through heterogeneous nucleating action of MWNTs and 'trans crystalline lamellar' structure formation due to 'interfacial crystallization' are two competitive events, which are influenced by the finer molecular level dispersion of MWNTs and by the enhanced interaction of PA6 chains with the MWNTs surface. It has been established that the Na-AHA molecules are adsorbed on MWNTs surface during the modification step. However, 'melt-interfacial' reaction between NH₂ functionality of Na-AHA and COOH end groups of PA6 leads to the desorption of Na-AHA molecules from MWNTs surface. Desorption of Na-AHA molecules from MWNTs surface and effective 'debundling' of MWNTs in the presence of Na-AHA may lead to higher available MWNTs surface area, which subsequently manifest in an enhanced 'interfacial crystallization' of PA6 phase.



Figure 4-38 (a) Non-isothermal crystallization exotherms of PA6/ABS blends with 5 wt% unmodified MWNTs for varying blend compositions: 40/60, 45/55, 50/50, 55/45, 60/40, (b) crystallization peak height ratio of exothermic peak at lower temperature to exothermic peak at higher temperature (H_1/H_2) as a function of PA6 concentration in the blend indicating the competitive events of heterogeneous nucleated bulk crystallization and 'trans-crystalline' phase formation through 'interfacial crystallization' of PA6 phase in the presence of MWNTs.

4.3.6 'Interphase' formation through interaction between polymer phase and MWNTs surface

The variation of residual weight fraction of MWNTs at 500 °C with varying concentration of PA6 phase in PA6/ABS blends is shown in *Figure 4-39* (a). The experimentally observed residual weight at 500 °C (wherein the complete degradation of both the polymer phases has already occurred in nitrogen atmosphere) is higher than the concentration of MWNTs (5 wt%) present in the respective composites. It is also to be noted that MWNTs are thermally stable up to temperatures much higher than 500 °C in nitrogen atmosphere. PA6/ABS blends with unmodified MWNTs and Na-AHA modified MWNTs show higher residual weight as compared to the blends with PyCHO modified MWNTs.

The excess residual weight is an indication of the formation of the polymer 'interphase', which is strongly adhered to MWNTs surface, and thereby the 'interphase' layer could not be degraded even at 500 °C. Unmodified MWNTs may allow an effective wetting of MWNTs surface by the respective polymer phases. This leads to a higher fraction of 'interphase' layer in case of PA6/ABS blends with unmodified MWNTs, as polymer chains may interact easily with MWNTs in absence of any modifier molecules. However, polymer phases may be restricted from interacting with MWNTs surface due to the adsorption of modifier molecules when MWNTs are modified with organic modifiers, which may result in lower fraction of 'interphase' layer.

Interestingly, Na-AHA molecules may get 'desorbed' from MWNTs surface during the 'melt-interfacial' reaction between PA6 and Na-AHA molecules. This phenomenon may result in higher fraction of 'available' surface for polymer phases to interact, which may lead to the formation of higher 'interphase' layer. On the other hand, PyCHO molecules adsorbed on MWNTs surface may restrict the respective polymer phases from interacting strongly with MWNTs. Therefore, PA6/ABS blends with PyCHO modified MWNTs showed lower values of residual weight as compared to the corresponding blends with either unmodified or Na-AHA modified MWNTs. Polymer chains interact with MWNTs resulting in a coating or wrapping of MWNTs. During TGA heating scan, the polymer fraction degrades (between ~300 °C to ~400 °C) and the mass loss is attributed to polymer adsorbed on the MWNTs surface [26, 212, 213]. However, there may be a fraction of the polymer phase strongly adhered to the MWNTs surface that may not degrade even when bulk polymer phase has been thermally degraded. Therefore, mass of this thermally stable polymer fraction may be utilized as an effective tool to determine the nature and extent of polymer/MWNTs interaction based on remaining weight fraction after complete degradation of the polymeric phases.

Morgan et al. [214] found a thermally stable residue/char yield in case of PMMA/SiO₂ nanocomposites. The residue was attributed to polymer phase bound near silica particles, which may exhibit higher thermal stability than the bulk polymer phase that in turn could prevent release of evolved degradation products of polymeric phase and trapped the polymer phase resulting in thermally stable residue/char. Further, Baudouin et al. [215] have shown that polymer fraction strongly adsorbed on MWNTs surface could not be removed in spite of thorough washing and this polymer layer has been reported to represent multilayer adsorption owing to entanglements between adsorbed chains and non-adsorbed chains.

Further, onset of thermal degradation during TGA heating scan of the PA6/ABS blends with unmodified and modified MWNTs, as a function of PA6 concentration is shown in *Figure 4-39* (b). A gradual increase in onset of thermal degradation with increasing PA6 concentration for unmodified as well as modified MWNTs is observed. PA6/ABS blends with Na-AHA modified MWNTs exhibited overall lower onset of degradation temperature as compared to corresponding blends with unmodified MWNTs and PyCHO modified MWNTs. PA6/ABS blends with PyCHO modified MWNTs show higher values of onset of thermal degradation. The enhancement in thermal stability in the presence of PyCHO modified molecules might be due to overall enhanced aromaticity in the structure.

Various interactions between polymer phases, modifier molecules and MWNTs influence the 'interfacial crystallization' of PA6 phase on MWNTs surface, the 'interphase' formation and the DC electrical conductivity of the resultant composites. Unmodified MWNTs exhibit free MWNTs surface for polymer interaction, which has resulted in lower H_1/H_2 values and higher residual weight.



Figure 4-39 (a) Residual weight at 500 °C as a function of PA6 concentration (wt%) in the blends, indicating the formation of 'interphase' in the presence of various MWNTs, (b) variation in the 'onset of degradation' with increasing concentration of PA6 (wt%) in the blends.

However, PA6/ABS blends with unmodified MWNTs have exhibited lower DC electrical conductivity values due to highly 'agglomerated' structure of unmodified MWNTs with an exception of 60/40 (wt/wt) blend. 60/40 (wt/wt) PA6/ABS blend with unmodified MWNTs has exhibited high DC electrical conductivity value of $\sim 10^{-6}$ S/cm and has shown presence of high fraction of 'debundled' MWNTs. It is interesting to observe that PA6/ABS blends with Na-AHA modified MWNTs have shown significantly higher DC electrical conductivity values in spite of effective 'interfacial crystallization' and higher fraction of 'interphase' formation. This observation can be attributed to a refined 'network-like' structure formation of MWNTs in the presence of Na-AHA through effective 'debundling' of MWNTs as well as 'desorption' of Na-AHA molecules from MWNTs surface due to 'meltinterfacial' reaction. PA6/ABS blends with PyCHO modified MWNTs have exhibited higher DC electrical conductivity [with an exception of 40/60 (wt/wt) blend composition], lower extent of 'interfacial crystallization' and lower fraction of polymer 'interphase'. The presence of PyCHO molecules on the MWNTs surface may hinder the polymer chains from interacting effectively with the MWNTs. However, higher DC electrical conductivity values might be achieved through 'debundling' of MWNTs and effective charge transfer via 'conjugation'. It can thus be interpreted that the electrical conductivity of binary 'co-continuous' PA6/ABS blends with unmodified and modified MWNTs is significantly influenced with various interactions between polymer phases, modifier molecules and MWNTs.

The schematic of the probable interactions between the polymer phases with MWNTs and the modifiers when incorporated in the blends is shown *Figure 4-40*. MWNTs exhibit a highly 'agglomerated' state in absence of any surface modification. When the MWNTs are modified with Na-AHA, the Na-AHA molecules are adsorbed on MWNTs surface and lead to 'debundling' of MWNTs through electrostatic-like charge repulsion and steric stabilization [50]. However, the PyCHO molecules interact effectively with the MWNTs surface through ' π - π ' interaction. The presence of the PyCHO molecules adsorbed on the MWNTs has led to the effective debundling of MWNTs, probably due to the weakening of forces of attraction [103]. Further, when MWNTs are melt-blended with the polymers, the interaction between the polymer and the modified MWNTs influence the distribution and dispersion of the MWNTs in the respective polymeric phases. The 'melt-interfacial' reaction between the Na-AHA molecules and the PA6 polymer chains has resulted in the desorption of Na-AHA molecules from MWNTs surface, which manifests in higher 'available' MWNTs surface (which is supported by higher residual weight of composites and lower H₁/H₂ ratio obtained

from analysis of crystallization behaviour of PA6 phase). PyCHO molecules have facilitated the 'debundling' of MWNTs and further facilitated the charge transfer through 'conjugation' (which is supported by higher electrical conductivity values).



Figure 4-40 Schematic representation of the possible interactions existing between the organic modifiers and the MWNTs as well as between the modified MWNTs and the blend components PA6 and ABS resulting in the retention of a refined 'network-like' structure of MWNTs.

4.4 Evolution of phase morphology and 'network-like' structure of MWNTs in binary polymer blends during melt-mixing

4.4.1 Development of phase morphology: Effect of mixing time and the addition of modified MWNTs

Figure 4-41 [(a)–(l)] shows the SEM micrographs of 40/60 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs [*Figure 4-41* (a)–(d)], the corresponding blends with Na-AHA modified MWNTs (1:1, wt/wt) [*Figure 4-41* (e)–(h)] and the corresponding blends with PyCHO modified MWNTs (1:1, wt/wt) [*Figure 4-41* (i)–(l)] for varying melt-mixing time.

40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs show [*Figure 4-41* (a)–(d)] PA6 droplets dispersed in the ABS phase up to t = 5 minutes of melt-mixing, which further transforms to a 'co-continuous' morphology at t = 15 minutes of melt-mixing. Average diameters of dispersed PA6 phase have increased with increasing mixing time from ~3.55 µm for 1 minute, ~4.46 µm for 2 minutes and ~4.55 µm for 5 minutes of melt-mixing. 'Co-continuous' morphology is observed at 15th minute of melt-mixing with PA6 ligaments thickness of ~3.27 µm.

An earlier study showed that 40/60 PA6/ABS blend exhibited 'matrix-dispersed droplet' type morphology at the end of 15th minute of melt-mixing, wherein the major phase formed the matrix and the minor phase was dispersed in the form of droplets. It is proposed that the final morphology of 40/60 (wt/wt) PA6/ABS blends in the presence of unmodified MWNTs may be influenced by the variation of melt-viscosity of the constituent polymers, which may lead to the alteration of viscosity ratio in the corresponding blend in the presence of unmodified MWNTs. ABS phase exhibits significantly higher melt-viscosity as compared to the PA6 phase during melt-mixing. Further, the localization of unmodified MWNTs' phase. Thus, as the melt-mixing progresses, PA6 droplets might be deforming and developing a skeleton, which further results in a well-developed 'co-continuous' morphology at the end of 15th minute.

40/60 (wt/wt) PA6/ABS blends with Na-AHA modified MWNTs (1:1, wt/wt) [*Figure* 4-41 (e)–(h)] show that dispersed droplets of PA6 start elongating from t = 2 min of meltmixing, which further leads to the formation of 'continuous' phase at the end of 15 minutes of melt-mixing. Average diameter of 'dispersed' droplets is significantly higher as compared to the corresponding blend with unmodified MWNTs. Dispersed PA6 phase shows an average diameter of ~6.09 μ m for 1 minute, ~8.04 μ m for 2 minutes, ~14.6 μ m for 5 minutes and finally transforming to a 'co-continuous' phase morphology with the ligament thickness of ~7.16 μ m after 15 minutes of melt-mixing. The ligament size of the PA6 phase for 40/60 blends is increased in the presence of Na-AHA modified MWNTs as compared to the respective blends with unmodified MWNTs. This has also been observed over the entire 'cocontinuous range' for the PA6/ABS blends with Na-AHA modified MWNTs as compared to the blends with unmodified MWNTs at the end of 15th minute of melt-mixing. In the present context, it is observed that the PA6 droplets are elongated at a much earlier stage of meltmixing than that of the corresponding blend with unmodified MWNTs. It has also been found in earlier studies that in the presence of Na-AHA, the intrinsic viscosity of PA6 phase has decreased significantly due to the plasticization effect and/or chain scission of PA6 in the presence of Na-AHA. The final 'co-continuous' morphology exhibits 'concave' type of structure as compared to 'convex' type structure exhibited by the corresponding blends with unmodified MWNTs.

SEM micrographs for the corresponding 40/60 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs (1:1, wt/wt) are shown in *Figure 4-41* [(i)–(l)]. These blends show 'matrix-dispersed droplet' type morphology for the melt-mixing time up to t=15 mins. It is interesting to note that in spite of equivalent shear force experienced during melt-mixing, the 'matrix-dispersed droplet' type morphology did not transform to 'co-continuous' type after 15 minutes of melt-mixing. The melt-viscosity of the ABS phase is reported to decrease in the presence of PyCHO molecules, due to partial miscibility between PyCHO molecules and the ABS phase. Hence, along with the variation in the melt-viscosity ratio, a significant amount of MWNTs may even be migrated to ABS phase as well (or at the interface). These two counteracting factors may not yield a significant alteration of the viscosity ratio. The average diameter of the dispersed PA6 phase is found to be ~4.45 μ m for 1 minute, ~4.65 μ m for 2 minutes, ~4.55 μ m for 5 minutes, and ~3.6 μ m at the end of 15 minutes of melt-mixing.

SEM micrographs of 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt) melt-mixed for varying melt-mixing time are depicted in *Figure 4-42* [(a)–(l)]. SEM micrographs of blends with unmodified MWNTs melt-mixed for varying mixing time [*Figure 4-42* (a)–(d)] show the process of development of 'co-continuous' type of morphology from 'matrixdispersed droplet' type of morphology. Average diameter of dispersed droplets of ABS phase varies from ~3.58 μ m for 1 minute, ~8.21 μ m for 2 minutes, and ~10.35 μ m for 5 minutes (elongated droplets) to a co-continuous structure of ~3.63 μ m ligament thickness of PA6 phase at the end of 15 minutes melt-mixing. Unmodified MWNTs preferentially localize in the PA6 phase and with increasing mixing time the phase structure undergoes a transformation to a 'co-continuous' type. The transformation of 'matrix-dispersed droplet' to 'co-continuous' morphology in the presence of unmodified MWNTs may be related to the alteration of viscosity ratio as MWNTs may predominantly localized in the PA6 phase.



Figure 4-41 SEM micrographs of 40/60 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs melt-mixed for (a) 1 min, (b) 2 mins, (c) 5 mins and (d) 15 mins; the corresponding blends with Na-AHA modified MWNTs (1:1, wt/wt) melt-mixed for (e) 1 min, (f) 2 mins, (g) 5 mins, and (h) 15 mins; the corresponding blends with PyCHO modified MWNTs (1:1, wt/wt) melt-mixed for (i) 1 min, (j) 2 mins, (k) 5 mins, and (l) 15 mins [for (d) and (h) ABS phase was removed using THF, for remaining samples the PA6 phase was removed using formic acid] indicating variations in phase morphology with varying melt-mixing time and dispersion quality of MWNTs.



Figure 4-42 SEM micrographs of 60/40 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs melt-mixed for (a) 1 min, (b) 2 mins, (c) 5 mins and (d) 15 mins; the corresponding blends with Na-AHA modified MWNTs (1:1, wt/wt) melt-mixed for (e) 1 min, (f) 2 mins, (g) 5 mins, and (h) 15 mins; the corresponding blends with PyCHO modified MWNTs (1:1, wt/wt) melt-mixed for (i) 1 min, (j) 2 mins, (k) 5 mins, and (l) 15 mins [ABS phase was removed using THF] indicating variations in phase morphology with varying melt-mixing time and dispersion quality of MWNTs.

In case of 60/40 (wt/wt) PA6/ABS blends with Na-AHA modified MWNTs, meltmixed at varying mixing time [*Figure 4-42* (e)–(h)], the presence of elongated droplets (D_{avg} ~7.43 µm) was observed even at t=1 minute of melt-blending. Further, at 15th minute of meltmixing, the phase morphology exhibits a coarse 'co-continuous' morphology with PA6 ligament thickness of ~ 8.99 µm. MWNTs exhibit well-debundled structure in the presence of Na-AHA and also prefer to localize in the PA6 phase due to melt-interfacial reaction between the amine functionality of Na-AHA molecules and –COOH end groups of PA6 chains. Although the presence of Na-AHA results in the reduction of melt-viscosity of the PA6 phase, the extent of reduction is lower in case of 60/40 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs as compared to the corresponding 40/60 (wt/wt) PA6/ABS blend. Thus, the alteration of the melt-viscosity ratio may be related to the reduction of the meltviscosity of the phase due to plasticization effect and/or chain scission of PA6 along with the selective localization of MWNTs in the PA6 phase.

The corresponding blend with PyCHO modified MWNTs (1:1, wt/wt) show 'matrixdispersed droplet' structure at the 1st minute of melt-mixing ($D_{avg} \sim 6.89 \ \mu m$) [*Figure 4-42* (i)], dispersed droplets at the 2nd minute of melt-mixing ($D_{avg} \sim 9.55 \ \mu m$) [*Figure 4-42* (j)] and further, a well-developed 'co-continuous' morphology is observed at the 5th (ligament thickness ~6.15 \ \mum) and 15th minute (ligament thickness ~10.9 \ \mum) [*Figure 4-42* (k) and (l)]. The resulting co-continuous morphology may be the consequence of melt-viscosity ratio closer to unity [24] through the localization of higher fraction of PyCHO modified MWNTs in the ABS phase, compensating the effect of the decrease in melt-viscosity of ABS phase due to the presence of PyCHO molecules.

SEM micrographs of 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs and Na-AHA modified MWNTs (1:1, wt/wt) are shown in *Figure 4-43* [(a)–(f)], which indicate the extent of dispersion of MWNTs. It can be seen that the size of 'MWNTs rich phase' is decreased with increasing melt-mixing time in case of 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs [*Figure 4-43* (a)–(c)] as well as in case of 40/60 (wt/wt) PA6/ABS blends with blends with Na-AHA modified MWNTs [*Figure 4-43* (d)–(f)]. It can also be seen that beginning with a highly 'agglomerated' state, MWNTs distribute in the PA6 droplets and are seen to bridge between the PA6 and the ABS phase and are debundled effectively as compared to the corresponding blend with unmodified MNWTs.

High magnification SEM micrographs for the 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs (1:1, wt/wt) melt-mixed for 1 min respectively are depicted in *Figure 4-43* [(g)–(i)]. In the presence of unmodified MWNTs, the nanotubes are highly 'agglomerated' as shown in *Figure 4-43* (g). In case of Na-AHA modified MWNTs [*Figure 4-43* (h)] and PyCHO modified MWNTs [*Figure 4-43* (i)], MWNTs are seen in the form of debundled form and present in the ABS phase as well. *Figure 4-44* [(a)–(f)] exhibits the extent of dispersion of MWNTs in 60/40 (wt/wt) PA6/ABS blends with unmodified and modified MWNTs meltmixed for 2 minutes and 5 minutes. It can be observed from the micrographs that dispersion of MWNTs is improved from 2 minutes to 5 minutes irrespective of the blend composition. State of dispersion of MWNTs has been improved in the presence of organic modifiers, viz., Na-AHA and PyCHO, which is confirmed through AC electrical conductivity measurements as well (discussed later in subsequent sections).

Overall, it can be inferred that the infiltration/wetting of polymer chains into the MWNTs 'agglomerate' is insufficient at early stages of melt-mixing, thus, the majority fraction of unmodified MWNTs are observed as 'agglomerated' form. This is reflected in morphological investigations, which reveal 'matrix-dispersed droplet' type morphology and the presence of large 'MWNTs-rich' areas in either PA6 or ABS phase at lower mixing time. Further, as the melt-mixing progresses, unmodified MWNTs start dispersing in the PA6 phase, which leads to an increased melt-viscosity of the PA6 phase and subsequently leads to a well-developed 'co-continuous' morphology.

In the presence of novel organic modifiers: Na-AHA and PyCHO, an early development of 'co-continuous' phase morphology has been observed. The most refined phase structure is exhibited by the blends with unmodified MWNTs. In the presence of both the modifiers: viz. Na-AHA and PyCHO, the ligament thickness of PA6 phase is increased as well as the shape of the phase changes to 'convex' type from a 'concave' type co-continuous structure, which is an indication that these blend compositions are at or before the phase inversion region [54]. Plasticization and/or chain scission of the PA6 phase in the presence of Na-AHA and partial miscibility between ABS and PyCHO might also be the influencing during the development of 'co-continuous' morphology in the early stages of melt-mixing. Further, it would be interesting to investigate the influence of the formation of the percolative

'network-like' structure formation of MWNTs in the respective PA6/ABS blends with unmodified and modified MWNTs through electrical conductivity measurements.



Figure 4-43 SEM micrographs of 40/60 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs melt-mixed for (a) 1 min, (b) 2 mins, (c) 5 mins [PA6 phase was removed using formic acid]; 40/60 (wt/wt) PA6/ABS blends with 5 wt% Na-AHA modified MWNTs (1:1, wt/wt) melt-mixed for (d) 1 min, (e) 2 mins, (f) 5 mins [PA6 phase was removed using formic acid]; 40/60 (wt/wt) PA6/ABS blends melt-mixed for 1 min (g) with 5 wt% unmodified MWNTs, (h) the corresponding blend with Na-AHA modified MWNTs (1:1, wt/wt), (i) the corresponding blend with PyCHO modified MWNTs (1:1, wt/wt) [PA6 phase was removed using formic acid]. Reduction in size of 'MWNTs rich' phase in the presence of the modifier could be observed with varying extent of dispersion for unmodified and modified MWNTs.



Figure 4-44 SEM micrographs of 60/40 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs melt-mixed for (a) 2 minutes, (b) 5 minutes; 60/40 (wt/wt) PA6/ABS blends with 5 wt% Na-AHA modified MWNTs melt-mixed for (c) 2 minutes, (d) 5 minutes; 60/40 (wt/wt) PA6/ABS blends with 5 wt% PyCHO modified MWNTs melt-mixed for (e) 2 minutes, (f) 5 minutes. ABS phase has been removed using THF solvent. Influence of melt-mixing time and modification of MWNTs reveal the improved state of dispersion of MWNTs.

4.4.2 Crystallization behaviour and the variation in the glass transition temperature: Effect of mixing time and the influence of modified MWNTs

Crystallization behaviour of the PA6 phase in PA6/ABS blends with unmodified and modified MWNTs shows two crystallization exothermic peaks [*Figure 4-45* (a)–(d)], which are higher than the bulk crystallization temperature corresponding to pure PA6 as shown in *Figure 4-45* (a). Non-isothermal crystallization exotherms for PA6 phase of 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs are shown in *Figure 4-45* (b). Crystallization peak temperature observed at lower temperature indicating bulk crystallization phenomenon of PA6 (~191 °C) in the presence of unmodified MWNTs did not vary significantly. Crystallization temperature for the 'trans-crystalline lamellar' formation of PA6 increases with increasing mixing time from ~203 °C for 1 min to ~206 °C for 15 minutes of meltmixing. This might be due to the reduction of MWNTs 'agglomerate' size with increasing mixing time thereby PA6 chains interact and facilitate the 'trans-crystalline lamellar' structure formation.

Figure 4-45 (c) and (d) show the variation of crystallization peak intensity ratio (H_1/H_2) as a function of melt-mixing time. It can be seen from the plots that intensity peak ratio is decreased with increasing melt-mixing time in all the cases. This might be due to the fact that 'trans-crystalline structure' formation is favoured as a function of melt-mixing time in all the cases presumably due to improved 'wetting' of the nanotubes with PA6 phase. 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs lower H₁/H₂ values up to 5 minutes of melt-mixing as compared to the corresponding blends with Na-AHA or PyCHO modified MWNTs. 40/60 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs shows the lowest value for the crystallization peak intensity ratio (~ 0.78) at 15th minute of mixing. This may be explained in terms of enhancement in induction of a 'trans-crystalline' structure of PA6 in the presence of Na-AHA modified MWNTs. Presence of Na-AHA may preferentially drives MWNTs to the PA6 phase through 'melt-interfacial' reaction between the amine groups of Na-AHA and carboxylic acid end groups of PA6 phase. This may lead to desorption of Na-AHA molecules from MWNTs surface increasing the accessibility of MWNTs surface. The presence of Na-AHA molecules facilitates the debundling of MWNTs through electrostatic charge repulsion and steric stabilization during the initial modification

step [50]. More available MWNTs surface area through finer dispersion of Na-AHA modified MWNTs as compared to the unmodified MWNTs and desorption of Na-AHA molecules may significantly enhance the 'trans-crystalline' structure formation of PA6 phase. 40/60 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs show the presence of the second crystallization peak only after the 5th minute of mixing. This may be due to the effective surface coverage of MWNTs by PyCHO molecules, thereby decreased the accessibility of MWNTs surface for PA6 crystallization.

60/40 (wt/wt) blends with unmodified MWNTs show the lowest value of H₁/H₂ ratio [Figure 4-45 (d)]. Corresponding blends with Na-AHA modified MWNTs and PyCHO modified MWNTs show higher values of H₁/H₂. Effective wetting of MWNTs by the PA6 phase [due to comparable surface free energy values of PA6 (~36.5 mN/m at 260 °C) and MWNTs (~45.3 mN/m at 260 °C) and also the crystal lattice matching between PA6 chain and MWNTs], and higher surface area available due to the absence of adsorbed entity (viz., organic modifier) on the MWNTs surface for inducing the 'trans-crystalline' structure formation of PA6, might be the reasons for the enhanced magnitude of H₂ as compared to H₁ in case blends with unmodified MWNTs. H₁/H₂ values are higher as compared to the corresponding blends with unmodified MWNTs in case of 60/40 (wt/wt) PA6/ABS blends with Na-AHA modified MWNTs. This may be due to lower extent of chain-scission of PA6 polymer chains in the presence of Na-AHA in compared to 40/60(wt/wt) PA6/ABS blends with Na-AHA modified MWNTs. Further, in case of 60/40 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs; the 'trans-crystalline' phase formation may not be favoured presumably due to the surface coverage of MWNTs by the PyCHO molecules similar to that of 40/60 (wt/wt) PA6/ABS blends. Hence, it can be commented that the formation of 'translamellar' structure of PA6 has been favoured in the presence of good wetting of MWNTs with PA6 and higher accessibility of MWNTs surface (achieved through finer dispersion of MWNTs and desorption of modifier molecules) as a function of mixing time.

Figure 4-46 [(a)–(d)] shows the influence of localization and the state of 'agglomeration' of MWNTs on the glass transition temperature of ABS and PA6 phases, reflecting the extent segmental mobility in polymer chains at the T_g . As shown in *Figure 4-46* (a), the glass transition temperatures for ABS phase did not vary with increasing mixing time for 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs. Mixing time as well as non-covalent surface modification of MWNTs did not significantly influence the glass transition temperature of ABS phase in case

of 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs and Na-AHA modified MWNTs. However, in case of PyCHO modified MWNTs, T_g values are significantly lower as compared to the other cases at varying extent of mixing time. This observation indicates the plasticization action of PyCHO molecules, which even masks the influence of redistributed MWNTs in the ABS phase.

Figure 4-46 (b) shows the variation in T_g of ABS phase for 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs. T_g values of ABS have varied marginally in case of blends with unmodified MWNTs and Na-AHA modified MWNTs; however, in case of blends with PyCHO modified MWNTs, T_g values vary significantly as a function of mixing time. Lower fraction of MWNTs may be distributed in ABS phase due to higher concentration of PA6 phase (in case of unmodified MWNTs) and preferential localization of MWNTs in PA6 in the presence of Na-AHA modified MWNTs. However, finer dispersion of MWNTs in case of Na-AHA modified MWNTs is reflected in higher T_g values in case of blends with Na-AHA modified MWNTs in comparison to the corresponding blend with unmodified MWNTs. In case of 60/40 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs; an increase in T_g of ABS phase with increasing mixing time may be due to the migration of higher fraction of MWNTs in the ABS phase. On the other hand, T_g values of ABS in blends with PyCHO modified MWNTs.





Figure 4-45 Non-isothermal crystallization exothermic peaks of PA6 phase of 40/60 wt/wt PA6/ABS blends with (a) 5 wt% unmodified MWNTs, (b) Na-AHA modified MWNTs (1:1 wt/wt), (c) PyCHO modified MWNTs (1:1, wt/wt) and (d) crystallization peak height ratio of peak at lower temperature to the peak at higher temperature.



Figure 4-46 Variation in the glass transition temperature of ABS phase for 40/60 and 60/40 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs, Na-AHA modified MWNTs (1:1, wt/wt), PyCHO modified MWNTs (1:1, wt/wt), which indicates the fraction of MWNTs present in the ABS phase.

Glass transition temperature of the PA6 phase in case of 40/60 and 60/40 (wt/wt) PA6/ABS blends with unmodified and modified MWNTs are shown in *Figure 4-46* [(c)–(d)]. Glass transition temperature (T_g) of PA6 phase is higher in case of 40/60 (wt/wt) as compared to 60/40 (wt/wt) blends with unmodified and modified MWNTs. This might be the consequence of the higher relative fraction of MWNTs, which are localized in the PA6 phase in 40/60 (wt/wt) blends with unmodified or modified MWNTs as compared to 60/40 (wt/wt) blends with unmodified or modified MWNTs as compared to 60/40 (wt/wt) blends with unmodified or modified MWNTs is lower due to 60/40 (wt/wt) blends. In case of 60/40 (wt/wt) PA6/ABS blends, the fraction of PA6 taking part in the glass transition is higher as well as the relative fraction of the MWNTs is lower due to higher concentration of PA6 phase (60 wt%) for the same MWNTs concentration (5 wt%) as compared to the blends with 40 wt% of PA6.

4.4.3 Formation of 'network-like' structure and state of 'agglomeration' of MWNTs: Influence of mixing time

Variation in AC electrical conductivity as a function of frequency for 40/60 and 60/40 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs prepared at varying melt-mixing time is shown in *Figure 4-47* (a) and (b). *Figure 4-47* (c) and (d) exhibit the variation in the AC electrical conductivity with frequency for the corresponding blends with Na-AHA modified and [*Figure 4-47* (e) and (f)] PyCHO modified (1:1, wt/wt) MWNTs. It can be observed from the plots that in case of unmodified MWNTs, blends prepared at lower mixing time show non-conducting behaviour in both 40/60 (wt/wt) and 60/40 (wt/wt) PA6/ABS blends. On the other hand, 40/60 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs 'network-like' structure as compared to 60/40 (wt/wt) PA6/ABS blend.

In case of PA6/ABS blends with PyCHO modified MWNTs, blends show nonconducting behaviour at lower mixing time irrespective of the blend composition. With increasing mixing time, there is a transition from electrically insulating to electrically conducting behaviour of blends with PyCHO modified MWNTs (1:1, wt/wt). Electrical conductivity values obtained at the end of the 15^{th} minute are higher [40/60, ~7.55x10⁻⁵ S/cm; 60/40, ~2.6x10⁻⁴ S/cm] than the corresponding blends with unmodified [40/60, ~3.9x10⁻¹¹ S/cm; 60/40, ~4.36x10⁻⁶ S/cm] and blends with Na-AHA modified MWNTs [40/60, ~6.3x10⁻⁷ S/cm; 60/40, ~2.5x10⁻⁶ S/cm]. It can be seen from the plots that in the presence of the organic modifiers, the transition from electrically insulating to electrically conducting behaviour for the blends takes place at a lower mixing time as compared to the blends with unmodified MWNTs. 40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs remain insulating even after 15 minutes of melt-mixing; whereas corresponding blend with Na-AHA modified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt) showed electrically conducting behaviour right from t = 1 min and t = 5 mins respectively. In case of 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt) showed electrically conducting behaviour right from t = 1 min and t = 5 mins respectively. In case of 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs (1:1, wt/wt) and PyCHO modified MWNTs (1:1, wt/wt) show the electrically conducting behaviour at t = 2 mins and t = 5 mins respectively.

Table 4-8 Type of morphology and electrical conductivity values for 40/60 and 60/40 (wt/wt)PA6/ABS blends with 5 wt% unmodified MWNTs, Na-AHA modified MWNTs (1:1, wt/wt)and PyCHO modified MWNTs (1:1, wt/wt) prepared via varying the melt-mixing time ('M'stands for matrix; 'D' stands for 'dispersed droplet')

MWNTs type	Composition	Mixing time (min)	Morphology	Electrical conductivity (S/cm)	Composition	Mixing time (min)	Morphology	Electrical conductivity (S/cm)
Unmodified MWNTs (5 wt%)	40/60 (wt/wt) PA6/ABS	1	M = ABS, D =PA6	2.65x10 ⁻¹²	60/40 (wt/wt) PA6/ABS	1	M = PA6, D =ABS	6.2x10 ⁻¹²
		2	M = ABS, D =PA6	4.38x10 ⁻¹²		2	M = PA6, D =ABS	7.75x10 ⁻¹²
		5	M = ABS, D =PA6	7.89x10 ⁻¹²		5	M = PA6, D =ABS	3.64x10 ⁻¹²
		15	Co-continuous	3.9x10 ⁻¹¹		15	Co-continuous	4.36x10 ⁻⁶
Na-AHA modified MWNTs (1:1,wt/wt) (5 wt%)	40/60 (wt/wt) PA6/ABS	1	M = ABS, D =PA6	6.99x10 ⁻¹⁰	60/40 (wt/wt) PA6/ABS	1	M = PA6, D =ABS	1.11x10 ⁻¹¹
		2	M = ABS, D =PA6	7.61x10 ⁻¹⁰		2	M = PA6, D =ABS	1.89x10 ⁻¹¹
		5	M = ABS, D =PA6	1.09x10 ⁻⁸		5	Co-continuous	3.6x10 ⁻¹⁰
		15	Co-continuous	6.3x10 ⁻⁷		15	Co-continuous	2.5x10 ⁻⁶
PyCHO modified MWNTs (1:1,wt/wt) (5 wt%)	40/60 (wt/wt) PA6/ABS	1	M = ABS, D =PA6	5.47x10 ⁻¹³	60/40 (wt/wt) PA6/ABS	1	M = PA6, D =ABS	2.42x10 ⁻¹²
		2	M = ABS, D =PA6	1.63x10 ⁻¹²		2	M = PA6, D =ABS	4.07x10 ⁻⁷
		5	M = ABS, D =PA6	7.02x10 ⁻⁵		5	Co-continuous	2.46x10 ⁻⁴
		15	M = ABS, D =PA6	7.55x10 ⁻⁵		15	Co-continuous	2.6x10 ⁻⁴



Figure 4-47 Variation in AC electrical conductivity as a function of frequency for (a) 40/60 (wt/wt) and (b) 60/40 (wt/wt) PA6/ABS blends with 5 wt% unmodified MWNTs melt-mixed for 1 min, 2 mins, 5 mins and 15 mins; (c) 40/60 (wt/wt) and (d) 60/40 (wt/wt) PA6/ABS blends with 5 wt% Na-AHA modified MWNTs (1:1, wt/wt) melt-mixed for 1 min, 2 mins, 5 mins and 15 mins; (e) 40/60 (wt/wt) and (f) 60/40 (wt/wt) PA6/ABS blends with 5 wt% PyCHO modified MWNTs (1:1, wt/wt) melt-mixed for 1 min, 2 mins, 5 mins and 15 mins;

These observations definitely reflect the influence of the debundled state of dispersion of the MWNTs in the presence of modifiers and also the influence of the phase morphology development as a function of the melt-mixing time. PA6/ABS blends with PyCHO modified MWNTs exhibit higher electrical conductivity values as compared to the corresponding blends with unmodified MWNTs and Na-AHA modified MWNTs with increasing meltmixing time due to effective debundling of MWNTs in the presence of the organic modifier. It is to be noted that 40/60 (wt/wt) PA6/ABS blend shows 'matrix-dispersed droplets' morphology, wherein the conducting path might have been developed through the continuous ABS phase along with MWNTs present in the interface. All other blend compositions exhibit the double percolation phenomenon. Phase morphology at lower mixing time has been found to be 'matrix-dispersed droplet' type and with increasing mixing time it changes to elongated droplets and further to 'co-continuous' type of morphology with an exception of 40/60 (wt/wt) PA6/ABS blend with PyCHO modified MWNTs. Variation in electrical conductivity values shows non-conducting behaviour at lower melt-mixing time and with increasing duration of mixing the 'network-like' structure of MWNTs is formed. Hence, it can be commented that the MWNTs are accommodated in the elongated droplets and further in a well-developed 'co-continuous' phase, which results in a percolative 'network-like' structure formation of MWNTs [Table 4-8]. In the presence of modifiers, MWNTs are well-debundled; thus, facilitate the formation of 'network-like' structure formation of MWNTs.

- 4.5 Dispersion of non-covalently modified multiwalled carbon nanotubes in binary immiscible polymer blends: Effect of encapsulation of nanotubes with a conventional reactive compatibilizer
- 4.5.1 Morphological observations, extent of 'debundling' and surface coverage of MWNTs surface with SMA copolymer after encapsulation step

SMA encapsulated MWNTs were prepared with an intention to restrict/ localize MWNTs at the interface of PA6/ABS blend along with the reactive compatibilizer (SMA

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copolymer). In this context, Na-AHA and PyCHO modified MWNTs were utilized to enhance the interaction between SMA copolymer and the organic modifier. Further, SMA copolymer would also interact with PA6 chains (through reactive coupling) and ABS copolymer (via miscibility between SAN phase of ABS and SMA). These interactions may restrict the modified MWNTs at the interface of the blend. SMA encapsulated MWNTs were characterized via SEM observations, Raman spectroscopic analysis, and BET specific surface area analysis (*Figure 4-48*).

SMA encapsulation leads to a thicker layer on MWNTs surface [*Figure 4-48* (d)–(f)] irrespective of MWNTs type. The influence of organic modifier in 'debundling' MWNTs is observed along with entangled 'network-like' structure [*Figure 4-48* (b) and (c)]. However, the 'debundled' MWNTs could not be observed clearly after SMA encapsulation [*Figure 4-48* (e) and (f)]. TEM observations indicate the presence of SMA copolymer layer on MWNTs surface after encapsulation for unmodified and modified MWNTs, which is confirmed through an increased average diameter of MWNTs [for SMA encapsulated unmodified MWNTs ~19.7 nm; for SMA encapsulated Na-AHA modified MWNTs ~10.9 nm and for SMA encapsulated PyCHO modified MWNTs ~15.8 nm]. Na-AHA and PyCHO modified MWNTs show enhanced 'debundling' as compared to unmodified MWNTs. It is to be noted that the average diameter of MWNTs surface (for Na-AHA modified MWNTs ~13.2 nm and for PyCHO modified MWNTs ~13.5 nm as compared to unmodified MWNTs ~9.2 nm).

SMA encapsulated unmodified MWNTs exhibit the highest average diameter as compared to the modified MWNTs. This may be due to effective wrapping of MWNTs surface with SMA copolymer via ' π - π ' interaction between aromatic moiety in SMA copolymer and MWNTs surface. Further, SMA encapsulated modified MWNTs show lower average diameter values presumably through desorption of modifier molecules interacting with SMA copolymer chains. The average diameter value for SMA encapsulated Na-AHA modified MWNTs indicates significant 'desorption' of modifier molecules from MWNTs surface. Raman spectroscopic analysis (*Figure 4-49*) indicates that SMA encapsulation leads to a marginal shift in both D and G-band (characteristic peaks of MWNTs) for Na-AHA and PyCHO modified MWNTs (D-band peak shifted from ~1346 cm⁻¹ to ~1348.2 cm⁻¹, G-band peak shifted from ~1590.2 cm⁻¹ to ~1587.4 cm⁻¹ in the presence of Na-AHA; D-band peak shifted from ~1348.6 cm⁻¹ to ~1347.8 cm⁻¹, G-band peak shifted from ~1588.8 cm⁻¹ to ~1586.4 cm⁻¹ in the presence of PyCHO). Further, D and G-band remain unaffected for SMA encapsulated unmodified MWNTs (D-band peak shifted from ~1345 cm⁻¹ to ~1345.5 cm⁻¹, G-band peak shifted from ~1582 cm⁻¹ to ~1581.6 cm⁻¹).

'G-band' of MWNTs is broad and complex due to multiple walls present in MWNTs [216]. Further, any shift in the tangential 'G-band' corresponds to an interaction through transfer of electrons between the modifier molecules and MWNTs [217, 218]. This observation indicates that SMA copolymer establishes an interaction with modified MWNTs surface during the 'encapsulation' step, which may exert hydrostatic pressure on MWNTs surface. A similar observation has been reported for SMA encapsulated SWNTs earlier [219].

The ratio of intensity of 'D-band' peak to the 'G-band' peak (I_D/I_G) is a measure of the extent of ordered graphitic structure associated with the respective MWNTs [220]. In this context a lower value of I_D/I_G of MWNTs also signifies a lower fraction of 'agglomerated' structure of MWNTs [178, 200]. Figure 1 depicts that SMA encapsulation results in a lower I_D/I_G value irrespective of the type of MWNTs. However, the value is significantly lower in case of Na-AHA and PyCHO modified MWNTs, which also suggests a higher extent of interaction between SMA and the organically modified MWNTs. It is to be noted that I_D/I_G ratio is significantly decreased for Na-AHA and PyCHO modified MWNTs.

Decreased values of I_D/I_G ratio in case of Na-AHA and PyCHO modified MWNTs suggested an improved 'debundling' of modified MWNTs (I_D/I_G for unmodified MWNTs ~1.18; for Na-AHA modified MWNTs ~0.96 and PyCHO modified MWNTs ~0.75). Raman spectroscopic analysis indicates further 'debundling' of MWNTs in the presence of SMA copolymer molecules, which is reflected in decreased I_D/I_G values (I_D/I_G for SMA encapsulated unmodified MWNTs ~1.1; for SMA encapsulated Na-AHA modified MWNTs ~0.8 and SMA encapsulated PyCHO modified MWNTs ~0.63).



Figure 4-48 Characterization of SMA encapsulated unmodified MWNTs (1:1, wt/wt), SMA encapsulated Na-AHA modified MWNTs (1:1:1, wt/wt/wt), SMA encapsulated PyCHO modified MWNTs (1:1:1, wt/wt/wt) and the corresponding MWNTs without SMA encapsulation through SEM and TEM observations and average diameter determined from TEM observations.

	Unmodified MWNTs	Na-AHA modified MWNTs	PyCHO modified MWNTs	
Raman	700 600 1345 ~ 1582 400 1000 1500 2000 Wavenumber (cm ⁻¹)	360 340 320 300 200 200 200 200 200 200 1500 200 Wavenumber (cm ⁻¹)	400 PyCHO modified MWNTs - 1348.6 ~ 1588.8 - 1348.6 ~ 1588.8 - 1000 1500 2000 Wavenumber (cm ⁻¹)	
spectroscopic	SMA encapsulated	SMA encapsulated	SMA encapsulated	
analysis	Unmodified MWNTs	Na-AHA modified MWNTs	PyCHO modified MWNTs	
	600 500 500 500 500 500 500 500	350 SMA encapsulated Na-AHA modified MWNTs ~ 1348.2 ~ 1587.4 1000 1500 2000 Wavenumber (cm ⁻¹)	600 SMA encapsulated PyCHO modified MWNTs 500 - 1347.8 - 1347.8 - 1586.4 - 1000 1500 - 2000 Wavenumber (cm ⁻¹)	
	Unmodified MWNTs	Na-AHA modified MWNTs	PyCHO modified MWNTs	
	~1.18	~0.96	~0.75	
I_D/I_G	SMA encapsulated	SMA encapsulated	SMA encapsulated	
	Unmodified MWNTs	Na-AHA modified MWNTs	PyCHO modified MWNTs	
	~1.1	~0.8	~0.63	
	Unmodified MWNTs	Na-AHA modified MWNTs	PyCHO modified MWNTs	
Surface Area	~269.9	~40.7	~40.4	
(BET)	SMA encapsulated	SMA encapsulated	SMA encapsulated	
(in m [*] /g)	Unmodified MWNTs	Na-AHA modified MWNTs	PyCHO modified MWNTs	
	~84	~29.5	~11.3	

Figure 4-49 Characterization of SMA encapsulated unmodified MWNTs (1:1, wt/wt), SMA encapsulated Na-AHA modified MWNTs (1:1:1, wt/wt/wt), SMA encapsulated PyCHO modified MWNTs (1:1:1, wt/wt/wt) and the corresponding MWNTs without SMA encapsulation through Raman spectroscopic spectra and (I_D/I_G), and specific surface area determined through BET analysis.

SMA encapsulation leads to a lower surface area irrespective of the type of MWNTs, which indicates that SMA copolymer adsorbs on the MWNTs surface. Further, modification of MWNTs with NA-AHA and PyCHO molecules manifests in a decreased surface area of MWNTs due to the adsorbed modifier molecules on MWNTs surface (specific surface area for unmodified MWNTs ~269.9 m²/g; Na-AHA modified MWNTs is ~40.7 m²/g and for PyCHO modified MWNTs is ~40.4 m²/g). It is also interesting to note that SMA encapsulation leads to a much lower value of specific surface area in case of PyCHO

modified MWNTs (~11.3 m²/g) as compared to both unmodified MWNTs (~84 m²/g) and Na-AHA modified MWNTs (~29.5 m²/g).

BET analysis revealed that average surface area is lower for SMA encapsulated Na-AHA modified MWNTs (~29.5 m²/g) and SMA encapsulated PyCHO modified MWNTs (~11.3 m²/g) as compared to SMA unmodified MWNTs (~84 m²/g). However, surface area values exhibited by unmodified and modified MWNTs without SMA encapsulation are higher than the corresponding MWNTs encapsulated with SMA (unmodified MWNTs ~269.9 m²/g; Na-AHA modified MWNTs ~40.7 m²/g and PyCHO modified MWNTs ~40.4 m²/g as given in [204]). Thus, it is confirmed that SMA encapsulation of MWNTs leads to effective surface coverage of MWNTs with SMA copolymer and modification step with organic modifier results in enhanced 'debundling' of MWNTs irrespective of encapsulation step with SMA copolymer.

4.5.2 Investigation of SMA copolymer mediated 'melt-interfacial' reaction

Figure 4-50 (a) shows the FTIR spectra for neat PA6/ABS blends with 5wt% SMA copolymer. Sample codes and composition details are provided in *Table 4-9*. Characteristic peaks at ~1704 cm⁻¹ and ~1770 cm⁻¹ indicate 'imide' bond formation through 'reactive coupling' in the presence of SMA copolymer [101, 221]. Characteristic peaks at ~1859 cm⁻¹ and ~1782 cm⁻¹ correspond to an unreacted MA fraction [222]. A characteristic peak observed at ~700 cm⁻¹ in FTIR spectra suggests the presence of styrene moiety [223].*Figure 4-50* (b) shows the FTIR spectra of neat PA6, PA6 and ABS blends with 5 wt% SMA encapsulated unmodified MWNTs of varying blend composition. In addition, the presence of the characteristic peaks at ~1710 and ~1778 cm⁻¹ confirms 'imide' bond formation through 'melt-interfacial' reaction between amine end group of PA6 and anhydride functionality of SMA copolymer.

Figure 4-50 (c) shows FTIR spectra for PA6/ABS blends with SMA encapsulated Na-AHA modified MWNTs. The imide peaks (at ~1725 cm⁻¹ and at ~1782 cm⁻¹) indicate 'melt-interfacial' reaction in the presence of SMA copolymer. *Figure 4-50* (d) shows the FTIR spectra for PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs. Peaks at ~1741 cm⁻¹ and ~1781 cm⁻¹ indicate the presence of imide peaks. Unreacted anhydride

fraction is indicated through the peak at ~1860 cm^{-1} in PA6/ABS blends with SMA or SMA encapsulated MWNTs.

Sample	Codes
Polyamide 6	Ν
Acrylonitrile-butadiene-styrene	А
Thin purified MWNTs	Т
PA6/ABS blends with SMA	S _m
PA6/ABS blends with SMA encapsulated unmodified MWNTs (1:1, wt/wt)	$N_x A_{(100-x)} SE5T5$ 'x'= 40,45,50,55, 60 wt%
PA6/ABS blends with SMA encapsulated MWNTs modified with Na-AHA (SMA:MWNTs:Na-AHA; 1:1:1, wt/wt/wt)	N _x A _(100-x) SE5M5 'x'= 40,45,50,55, 60 wt%
PA6/ABS blends with SMA encapsulated MWNTs modified with PyCHO (SMA:MWNTs:PyCHO; 1:1:1, wt/wt/wt)	N _x A _(100-x) SE5Py5 'x'= 40,45,50,55, 60 wt%

Table 4-9 Sample codes with their composition for PA6/ABS blends with MWNTs


Figure 4-50 FTIR spectra for PA6/ABS blends of varying blend composition 40/60 – 60/40 (wt/wt) with (a) SMA (N_xA_ySm5), (b) SMA encapsulated unmodified MWNTs (1:1, wt/wt) (N_xA_ySE5T5), (c) SMA encapsulated Na-AHA modified MWNTs (1:1:1, wt/wt/wt) (N_xA_ySE5M5) and (d) SMA encapsulated PyCHO modified MWNTs (1:1:1, wt/wt/wt) (N_xA_ySE5Py5).



Figure 4-51 Normalized intensity of imide peak at ~1736 cm⁻¹ with respect to the intensity of C-C stretching peak at ~1115 cm⁻¹ as a function of PA6 concentration (wt%).

Figure 4-51 shows the variation of normalized imide peak intensity as a function of concentration of PA6 phase in case of PA6/ABS blend with SMA, PA6/ABS blend with SMA encapsulated unmodified MWNTs, SMA encapsulated Na-AHA modified MWNTs and SMA encapsulated PyCHO modified MWNTs. Normalized intensity of 'imide' peak shows lower values in case of PA6/ABS blends with SMA encapsulated Na-AHA modified MWNTs (in the range of $\sim 0.46 - \sim 0.56$) as compared to the corresponding blends with SMA, blends with SMA encapsulated unmodified and SMA encapsulated PyCHO modified MWNTs, which exhibit normalized amide peak intensity ~1.0. Lower value of normalized imide peak intensity ratio in case of SMA encapsulated Na-AHA modified MWNTs may indicate lower extent of 'melt-interfacial' reaction between -NH2 functionality of PA6 and maleic anhydride functionality of SMA copolymer. The normalized peak intensity of amide peak was increased with increasing concentration of PA6 in PA6/ABS blend with Na-AHA modified MWNTs. Increase in amide peak indicated increasing extent of 'melt-interfacial' reaction between Na-AHA molecules and PA6 phase. Therefore, it is likely that a fraction of -NH₂ end groups of PA6 may be consumed in 'melt-interfacial' reaction with -COOH functionality of Na-AHA, which further may not take part in 'melt-interfacial' reaction between -NH2 end groups PA6 molecules and maleic anhydride functionality of SMA copolymer.

4.5.3 Phase morphological features on incorporation of SMA encapsulated unmodified/ modified MWNTs in PA6/ABS blends

Morphological features of PA6/ABS blends of varying blend composition [40/60, 45/55, 50/50, 55/45 and 60/40 (wt/wt)] with 5 wt% SMA encapsulated unmodified MWNTs, the corresponding blends with SMA encapsulated Na-AHA modified MWNTs and SMA encapsulated PyCHO modified MWNTs are depicted in *Figure 4-52* (a)–(e), *Figure 4-52* (f)–(j) and *Figure 4-52* (k)–(o) respectively. Ligament thickness values in case of 'co-continuous' type morphology and the values of 'average diameter' in case of 'matrix-dispersed droplets' type morphology are provided in *Table 4-10*.

Blends with SMA encapsulated unmodified MWNTs show dispersed droplets of PA6 in 40/60 PA6/ABS (wt/wt) of $D_{avg} \sim 2.19 \mu m$, transform to 'co-continuous' type morphology with ligament thickness of ABS phase of ~6.56 μm in 45/55 PA6/ABS (wt/wt). Further, a phase inversion with ABS droplets of $D_{avg} \sim 2.03 \mu m$ is observed in 50/50 PA6/ABS (wt/wt)

and in 55/45 PA6/ABS (wt/wt) with the corresponding D_{avg} of ~1.18 µm [Figure 4-52 (a)–(e) and Table 4-10]. Subsequently, transforming to a 'co-continuous' type morphology with ligament thickness of ABS phase of ~7.79 µm in 60/40 PA6/ABS (wt/wt). However, PA6/ABS blends with Na-AHA modified MWNTs encapsulated with SMA [Figure 4-52 (f)-(j) and *Table 4-10*] show higher ligament thickness as compared to the corresponding blends with SMA encapsulated unmodified MWNTs (~12.5 µm for 45/55, wt/wt; ~11.7 µm for 50/50, wt/wt), which further transforms to a 'matrix-dispersed droplet' type morphology in 55/45 PA6/ABS (wt/wt) with D_{avg} of ~1.5 µm and 60/40 PA6/ABS (wt/wt) with D_{avg} of ~2.1 µm. Further, PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs [Figure 4-52 (k)-(o) and Table 4-10] show 'co-continuous' morphology with an exception of 40/60 (wt/wt) blend composition ($D_{avg} \sim 0.50 \ \mu m$). The ligament thickness values of the PA6 phase in case of 45/55 PA6/ABS (wt/wt) is observed to be ~5.66 µm, for 50/50 (wt/wt) PA6/ABS it is ~8.82 μ m, for 55/45 (wt/wt) the value is ~7.22 μ m and for 60/40 (wt/wt) it is observed to be ~5.48 µm. However, blends with unmodified and Na-AHA/PyCHO modified MWNTs without SMA copolymer have exhibited 'co-continuous' morphology with an exception of 40/60 (wt/wt) blend with PyCHO modified MWNTs. The ligament thickness has been observed in the range of ~3.3 µm to ~3.6 µm for PA6/ABS blends with unmodified MWNTs, ~7.2 µm to ~9 µm for PA6/ABS blends with Na-AHA modified MWNTs and ~5.1 µm- $\sim 10.9 \,\mu m$ for PA6/ABS blends with PyCHO modified MWNTs.

Phase morphology development during melt-mixing depends on factors such as meltmixing time, blend composition, viscosity ratio and presence of compatibilizer [115]. Presence of reactive compatibilizer reduces the interfacial tension, which may lead to 'cocontinuous' structure via suppressing 'droplet break-up' [24]. However, reactive compatibilizer also increases interfacial adhesion and interfacial viscosity through 'meltinterfacial' reaction. This phenomenon may alter the 'melt-viscosity' ratio in case of PA6/ABS blends in the presence of SMA copolymer. Further, SMA encapsulated unmodified MWNTs may localize in either of the polymer phases or at the interface owning to possible interactions between SMA copolymer and polymer blend components. A majority fraction of MWNTs may localize in the ABS phase in 40/60 (wt/wt) PA6/ABS blend with SMA encapsulated unmodified MWNTs due to miscibility between SMA and SAN phase of ABS. PA6 phase may form 'dispersed droplets' due to the suppressed coalescence of PA6 droplets in the presence of SMA copolymer. A higher fraction of MWNTs fraction may localize in the PA6 phase as the concentration of PA6 phase increases, which may lead to an enhancement in melt-viscosity of the PA6 phase. This suggests that the 'melt-interfacial' reaction and localization/migration of MWNTs to various phases occurring simultaneously during meltmixing influences the phase morphology development. 50/50 and 55/45 (wt/wt) blends with SMA encapsulated unmodified MWNTs show a refined 'matrix-dispersed droplet' type morphology, whereas 60/40 (wt/w) blend with SMA encapsulated unmodified MWNTs shows a 'co-continuous' type of morphology.

Chain scission/plasticization of PA6 phase in the presence of Na-AHA leading to decreased molecular weight of PA6 phase is observed earlier. Presence of elongated PA6 droplets in ABS phase confirms the reduction in melt-viscosity of PA6 in 40/60 PA6/ABS blend with SMA encapsulated Na-AHA modified MWNTs. Increased PA6 concentration may facilitate the localization of MWNTs in the PA6 phase via 'melt-interfacial' reaction between -NH₂ of Na-AHA and -COOH end group of PA6 chain and/or -NH₂ of Na-AHA and MA functionality of SMA. MWNTs in general may escape from the SMA phase irrespective of the type of MWNTs (unmodified or modified) during melt-mixing due to thermodynamic factor. Further, increase in PA6 concentration leads to a 'phase inversion', which may be a consequence of facilitated 'droplet-breakup' owing to stabilization of phase morphology in the presence of SMA copolymer. SMA encapsulated PyCHO modified MWNTs may preferably localize in the ABS phase in absence of adequate PA6 phase. Thus, as PA6 phase concentration increases, a higher fraction of MWNTs may localize in the PA6 phase. Selective distribution of MWNTs in PA6 is likely to result in an increased meltviscosity of the PA6 phase, which results in a well-developed 'co-continuous' type morphology.

When MWNTs are encapsulated with a reactive compatibilizer, the probability of MWNTs to reside at the interface is significantly higher. However, during the 'simultaneous' melt-mixing protocol, as all components are fed into the barrel at once, the probability of SMA encapsulated MWNTs staying in the ABS phase is also significant. SMA molecules interact with PA6 phase through 'melt-interfacial' reaction, which involves a reaction between MA functionality of SMA and the amine functionality of PA6 phase. Hence, it is speculated that melt-viscosity of both blend components will be altered in the presence of SMA copolymer and MWNTs, which will influence the phase morphology of the resultant composite. In brief, various events occurring during 'simultaneous' melt-mixing such as 'reactive compatibilization' due to SMA copolymer, interaction between modifier molecules

adsorbed on MWNTs and SMA molecules, MWNTs escaping from SMA encapsulation to the PA6 phase during melt-mixing influence the type of phase morphology of PA6/ABS blends with SMA encapsulated unmodified and modified MWNTs.



Figure 4-52 SEM micrographs of (a) 40/60, (b) 45/55, (c) 50/50, (d) 55/45, (e) 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated unmodified MWNTs 1:1 (wt/wt); (f) 40/60, (g) 45/55, (h) 50/50, (i) 55/45, (j) 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated Na-AHA modified MWNTs 1:1:1 (wt/wt/wt); (k) 40/60, (l) 45/55, (m) 50/50, (n) 55/45, (o) 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs 1:1:1 (wt/wt/wt), for (a), (f) and (k) PA6 phase was removed using formic acid and for remaining blend compositions ABS phase was removed using THF.

4.5.4 Dispersion and localization of SMA encapsulated MWNTs in blend components

Figure 4-53 (a)–(f) show TEM micrographs of 40/60 (wt/wt) PA6/ABS blends with SMA encapsulated unmodified MWNTs [*Figure 4-53* (a)–(b)], SMA encapsulated Na-AHA modified MWNTs [*Figure 4-53* (c)–(d)] and the corresponding blends with SMA encapsulated PyCHO modified MWNTs [*Figure 4-53* (e)–(f)]. Micrographs of 40/60 (wt/wt) blends with SMA encapsulated unmodified MWNTs show presence of a majority fraction of 'agglomerated' MWNTs localized in PA6 phase as well as at the interface. However, a 'dispersed' fraction of MWNTs is also present in the SAN phase of ABS. Figure 6 (c) and (d) exhibit 'network' of finely dispersed MWNTs present in both the polymer phases as well as at the interface of 40/60 (wt/wt) PA6/ABS blend with SMA encapsulated Na-AHA modified MWNTs. TEM micrographs from *Figure 4-53* (e) and (f) show the presence of 'nano-agglomerates' and 'debundled' MWNTs in PA6, ABS phases and also at the interface.

TEM micrographs of 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated unmodified MWNTs [*Figure 4-54* (a) and (b)], SMA encapsulated Na-AHA modified MWNTs [*Figure 4-54* (c) and (d)] and SMA encapsulated PyCHO modified MWNTs [*Figure 4-54* (e) and (f)] are shown in *Figure 4-54*. Micrographs in *Figure 4-54* (a) and (b) show that MWNTs are distributed in both PA6 and ABS phases, further MWNTs exhibit 'agglomerated' structure in case of blends with SMA encapsulated unmodified MWNTs. TEM micrograph of 60/40 (wt/wt) PA6/ABS blend with SMA encapsulated Na-AHA modified MWNTs not only shows preferential localization of MWNTs in the PA6 phase [*Figure 4-54* (c) and (d)], but also exhibits a fraction of MWNTs distributed in the ABS phase as well as the interface. The corresponding blend with SMA encapsulated PyCHO modified MWNTs [*Figure 4-54* (e) and (f)] shows selective localization of MWNTs. This may be attributed to ' π - π ' interaction between SAN part of ABS and PyCHO modified MWNTs.

40/60 (wt/wt) PA6/ABS blends with unmodified MWNTs showed highly 'agglomerated' MWNTs present in both PA6 and ABS phases. MWNTs were finely dispersed; 'individualized' MWNTs present in both the phases and also at the interface in the corresponding blend with Na-AHA modified MWNTs.



Figure 4-53 TEM images of microtome sections (thickness ~60 nm) of 40/60 (wt/wt) PA6/ABS blend with (a) SMA encapsulated unmodified MWNTs 1:1 (wt/wt), (b) SMA encapsulated Na-AHA modified MWNTs 1:1:1 (wt/wt/wt) and (c) SMA encapsulated PyCHO modified MWNTs 1:1:1 (wt/wt/wt) where the ABS phase has been stained by OsO₄.



Figure 4-54 TEM images of microtome sections (thickness ~60 nm) of 60/40 (wt/wt) PA6/ABS blend with (a) SMA encapsulated unmodified MWNTs 1:1 (wt/wt), (b) SMA encapsulated Na-AHA modified MWNTs 1:1:1 (wt/wt/wt) and (c) SMA encapsulated PyCHO modified MWNTs 1:1:1 (wt/wt/wt) where the ABS phase has been stained by OsO₄.

Na-AHA modified MWNTs were observed as 'bridges' between the phases. PyCHO modified MWNTs were present in the form of 'nano-agglomerates' and were present in both the phases and at the interface. 60/40 (wt/wt) PA6/ABS blends with unmodified MWNTs and Na-AHA modified MWNTs showed a higher fraction of 'individualized' MWNTs; whereas blend with PyCHO modified MWNTs showed a presence of smaller 'nano-agglomerates' of MWNTs present in both PA6 and ABS phases as well as at the interface. A fraction of MWNTs is present at the interface of PA6/ABS blend in the presence of SMA encapsulated unmodified and modified MWNTs, which is higher as compared to the corresponding blends with unmodified/ modified MWNTs in absence of SMA copolymer.

4.5.5 Non-isothermal crystallization behaviour of PA6 phase: Influence of interactions between modifier molecules, SMA copolymer and MWNTs surface

Crystallization exotherms of PA6/ABS blends with SMA encapsulated unmodified MWNTs are shown in *Figure 4-55* (a). Two crystallization peaks are observed in all blend compositions, which indicates 'heterogeneous nucleation' effect due to MWNTs. In order to determine the extent of 'heterogeneous nucleation' in the presence of SMA encapsulated MWNTs, a ratio of crystallization peak heights [height of peak at lower temperature (H₁)/ height of peak at higher temperature (H₂)] is calculated. H₁/H₂ ratio is an indication of the relative extent of two types of crystallization processes taking place simultaneously.

Figure 4-55 (b) shows the variation of H_1/H_2 as a function of blends composition for PA6/ABS blends with SMA encapsulated unmodified MWNTs, SMA encapsulated Na-AHA modified MWNTs, and SMA encapsulated PyCHO modified MWNTs along with the corresponding blends with non-encapsulated unmodified/ modified MWNTs. H_1/H_2 varies with blend composition as well as with the type of MWNTs in case of blends with SMA encapsulated MWNTs. Further, the corresponding blends without SMA encapsulation show lower H_1/H_2 values. Lower H_1/H_2 values are observed in case of SMA encapsulated Na-AHA modified MWNTs. Further, H_1/H_2 values are comparable in case of blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs in absence of SMA copolymer.

Crystallization exotherms of the PA6/ABS blends with various MWNTs show split in crystallization peak (at ~196 °C and ~208 °C) due to the heterogeneous nucleation mechanism caused by MWNTs [19, 149]. H₁/H₂ has been used as a qualitative tool to study the availability of the free surface area, where 'interfacial' crystallization can be induced [149]. In case of unmodified MWNTs and SMA copolymer, the free surface area available for nucleation of the PA6 chains may be lower due to highly 'agglomerated' nature of unmodified MWNTs and the 'surface wrapping' of nanotubes with the SMA molecules. In the presence of Na-AHA modified MWNTs, it is likely that a fraction modifier molecule is 'desorbed' from the MWNTs surface. This phenomenon may result in a relatively higher 'free' surface of MWNTs, which may act as 'heterogeneous' nucleation sites. In case of PyCHO molecules interacting with MWNTs, the effective surface area coverage of MWNTs may lead to lowering of the available surface area thus, the 'interfacial crystallization' may be retarded [224]. Intensity of the crystallization peak at higher temperature increased with improved state of dispersion of MWNTs [149].



Figure 4-55 (a) Crystallization exotherms obtained from DSC for PA6/ABS blends with SMA encapsulated unmodified MWNTs (1:1, wt/wt) (N_xA_ySE5T5) and (b) crystallization peak height ratio (H_{lower}/H_{higher}) for PA6/ABS blends with SMA encapsulated MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs of varied blend composition (40/60–60/40, wt/wt) and the corresponding blends without SMA copolymer.

When H_1/H_2 value is high, it indicates lower extent of 'interfacial crystallization' and when H_1/H_2 value is low, it shows enhanced 'interfacial crystallization' of PA6 phase in the presence of MWNTs. SMA encapsulated PyCHO modified MWNTs exhibit lower specific surface area (~11.3 m²/g) as compared to SMA encapsulated Na-AHA modified MWNTs (specific surface area of ~29.5 m²/g). It is important to note that specific surface area values are comparable for Na-AHA modified MWNTs and PyCHO modified MWNTs (specific area value is ~40 m^2/g) in absence of SMA copolymer. This observation substantiates the possibility of 'desorption' of Na-AHA molecules as they participate in 'melt-interfacial' reaction with SMA copolymer.

Table 4-10 Comparison of the morphology of the samples for PA6/ABS blends of varied
blend composition with SMA encapsulated MWNTs, Na-AHA modified MWNTs and PyCHO
modified MWNTs

MWNTs type	Composition	Morphology	Droplet size (D _{avg}) / ligament thickness (L _{avg})
SMA encap. MWNTs 1:1 (wt/wt)	N40A60SE5T5	M = PA6, D = ABS	$D_{avg} = 2.19$
	N45A55SE5T5	Co-continuous	$L_{avg} = 6.56$
	N50A50SE5T5	M = ABS, D = PA6	$D_{avg}=2.035$
	N55A45SE5T5	M = ABS, D = PA6	$D_{avg} = 1.175$
	N60A40SE5T5	Co-continuous	$L_{avg}=7.79$
SMA encap. Na- AHA mod. MWNTs 1:1:1 (wt/wt/wt)	N40A60SE5M5	M = PA6, D = ABS	Elongated droplets
	N45A55SE5M5	Co-continuous	$L_{avg} = 12.5$
	N50A50SE5M5	Co-continuous	$L_{avg} = 11.67$
	N55A45SE5M5	M = ABS, D = PA6	$D_{avg} = 1.48$
	N60A40SE5M5	M = ABS, D = PA6	$D_{avg} = 2.08$
SMA encap. PyCHO mod. MWNTs 1:1 (wt/wt)	N40A60SE5Py5	M = PA6, D = ABS	$D_{avg} = 0.50$
	N45A55SE5Py5	Co-continuous	$L_{avg} = 5.66$
	N50A50SE5Py5	Co-continuous	$L_{avg} = 8.82$
	N55A45SE5Py5	Co-continuous	$L_{avg} = 7.22$
	N60A40SE5Py5	Co-continuous	$L_{avg}=5.48$

Table 4-11 Storage modulus values in the glassy as well as the rubbery region, and glass transition temperatures of PA6 and ABS in the blends and blends with SMA encapsulated MWNTs (MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs) obtained by dynamic mechanical thermal analysis

	Storage modulus (GPa)		T _g (°C) (from	
			tan delta peak)	
Sample	Glassy region (25 °C)	Rubbery region (140 °C)	PA6	ABS
PA6	4.4	0.715	54.2	_
ABS	3.27	0.086	_	128.1
N60A40	4.42	0.356	54.9	115.1
N60A40SE5T5	5.19	0.096	65.8	126.5
N60A40SE5M5	6.4	0.425	62.8	122
N60A40SE5Py5	3.1	0.316	64.4	109
N40A60	4.64	0.515	63.2	129.4
N40A60SE5T5	3.8	0.465	66.7	126.8
N40A60SE5M5	4.2	0.368	64.5	125
N40A60SE5Py5	3.02	0.283	46.2	116

4.5.6 Influence of SMA encapsulation on the extent of 'interphase' formation

Figure 4-56 (a) shows TGA plots of PA6/ABS blends with SMA encapsulated unmodified MWNTs. The residual weight is determined at 500 °C in case of PA6/ABS blends with SMA encapsulated unmodified and modified MWNTs. It is to be noted that thermal degradation of both the polymer phases has been completed at temperature lower than 500 °C. *Figure 4-56* (b) exhibits a plot of residual weight versus concentration of PA6

phase for PA6/ABS blends with SMA encapsulated unmodified/modified MWNTs and the corresponding blends with unmodified/modified MWNTs. Figure 4-56 (c) shows the variation in onset of thermal degradation as a function of concentration of PA6 phase for PA6/ABS blends with SMA encapsulated unmodified/modified MWNTs and the corresponding blends with unmodified/modified MWNTs. PA6/ABS blends with SMA encapsulated unmodified/modified MWNTs show residual weight equivalent or higher than MWNTs fraction (5 wt%) present in the respective blend. Further, the values observed are lower as compared to the corresponding blends with unmodified/modified MWNTs without SMA copolymer. The onset of degradation observed in case of blends with SMA encapsulated unmodified/modified MWNTs is lower as compared to the corresponding blend with unmodified/modified MWNTs without SMA copolymer. Further, PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs exhibit higher onset of thermal degradation as compared to SMA encapsulated unmodified and SMA encapsulated Na-AHA modified MWNTs. Blends with SMA encapsulated Na-AHA modified MWNTs show significantly lower onset of degradation, whereas the corresponding blends with SMA encapsulated unmodified MWNTs exhibit marginal decrease in onset of degradation.

The residual weight observed at 500 °C indicates MWNTs fraction (5 wt%) and the 'interphase' formed due to the polymer phase, which is strongly adhered to MWNTs surface. The 'interphase' is not thermally degraded even after complete degradation of bulk polymer phase [26, 213]. An 'interphase' is formed through effective wetting of MWNTs with the respective polymer phase. SMA encapsulation step results in wrapping of MWNTs with SMA copolymer, which is confirmed through TEM observation. SMA copolymer retards the wetting of MWNTs by blend components and exhibits degradation behaviour similar to the 'bulk' polymer phase. Therefore, 'interphase' formation becomes difficult, which is reflected in lower residual weight in case of PA6/ABS blends with SMA encapsulated unmodified/ modified MWNTs. Whereas, blends with unmodified/ modified MWNTs without SMA copolymer exhibit higher 'interphase' formation, presumably due to effective 'wetting' of MWNTs surface.

An enhanced onset of thermal degradation indicates higher thermal stability of PA6/ABS blends with various MWNTs. The presence of SMA copolymer may introduce additional aromaticity in the structure; therefore it may result in increased onset of thermal degradation. The onset of degradation may also be influenced in the presence of organic

modifier molecules through interactions between SMA copolymer, MWNTs, modifier molecules and polymer phases. Na-AHA molecules lead to chain scission of PA6 phase resulting in decreased molecular weight of the respective phase. This phenomenon may manifest in a decrease in onset of thermal degradation of the blends with SMA encapsulated Na-AHA modified MWNTs. Further, PyCHO molecules introduce additional aromaticity in the structure along with SMA copolymer. This is reflected in significantly increased onset of thermal degradation. Overall, the presence of SMA copolymer influences various interactions between MWNTs, modifier molecules and polymer phases, which are subsequently reflected in the extent of 'interphase' formation in various blends.



Figure 4-56 (a) TGA plot of PA6/ABS blends of varying blend compositions (40/60, 45/55, 50/50, 55/45 and 60/40, wt/wt) with 5 wt% SMA encapsulated unmodified MWNTs. (Heating scan was carried out from room temperature to 800 °C in nitrogen atmosphere.) (b) residual weight at 500 °C as a function of PA6 concentration (wt%) in the blends, indicating the formation of 'interphase' in the presence of various MWNTs, (c) variation in the 'onset of degradation' with increasing concentration of PA6 (wt%) inPA6/ABS blends with unmodified MWNTs, Na-AHA modified MWNTs, PyCHO modified MWNTs.

4.5.7 Formation of 'rheological' network and segmental motion of the various phases: Influence of SMA encapsulation, modification with organic modifiers and blend composition

Variation in complex viscosity as a function of frequency for 40/60 and 60/40 (wt/wt) PA6/ABS neat blends, blends with SMA, blends with SMA encapsulated MWNTs (unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs) is depicted in *Figure 4-57* (a) and (b) respectively. *Figure 4-57* (a) shows that complex viscosity of 40/60 (wt/wt) PA6/ABS blend increases in the presence of SMA copolymer. Further, 40/60 (wt/wt) PA6/ABS blend with SMA encapsulated unmodified and SMA encapsulated Na-AHA modified MWNTs show marginally higher complex viscosity; whereas complex viscosity decreases for the corresponding blend with SMA encapsulated PyCHO modified MWNTs. 60/40 (wt/wt) PA6/ABS blend exhibits significant increase in complex viscosity in the presence of SMA copolymer. Further, the corresponding blends show an enhanced complex viscosity for blends with SMA encapsulated unmodified MWNTs, blends with SMA encapsulated Na-AHA modified MWNTs.

Complex viscosity values at lower frequencies are considered as a tool to investigate the 'liquid-like' to 'solid-like' transition in the presence of MWNTs due to the formation of 'rheological' network through an increased complex viscosity value. Complex viscosity values at the low frequencies are higher in the presence of SMA encapsulated MWNTs as compared to the values obtained in case of neat blends and blend with only SMA copolymer, which indicates the 'stiffening' effect of MWNTs. *Figure 4-57* (c) and (d) show variation in complex viscosity values at 0.1 rad/s for 40/60 and 60/40 (wt/wt) PA6/ABS blend and blend with MWNTs in presence and absence of SMA copolymer respectively. 40/60 (wt/wt) PA6/ABS neat blend shows a marginal increase in complex viscosity in the presence of SMA copolymer. Blends with SMA encapsulated unmodified MWNTs do not show any appreciable increase as compared to the corresponding blend without SMA copolymer for both 40/60 and 60/40 (wt/wt) PA6/ABS blends. However, blends with SMA encapsulated Na-AHA modified MWNTs. Blend with SMA encapsulated or marginally higher complex viscosity value as compared to the corresponding blend with Na-AHA modified MWNTs. Blend with SMA encapsulated

PyCHO modified MWNTs exhibits lower complex viscosity with respect to the corresponding blend with PyCHO modified MWNTs.

Enhancement in complex viscosity in case of blends with Na-AHA modified MWNTs and SMA encapsulated Na-AHA modified MWNTs may be due to the 'melt-interfacial' reaction and/or the formation of refined 'network-like' structure of MWNTs. Lower complex viscosity values in case of blends with PyCHO modified MWNTs and SMA encapsulated PyCHO modified MWNTs may be due to 'miscibility' between PyCHO molecules and SAN phase of ABS of PA6/ABS blends. An addition of compatibilizer to a polymer blend leads to enhanced melt-viscosity of the blend through 'melt-interfacial reaction' between the maleic anhydride functionality of SMA and amine end groups of PA6 chains [101]. The presence of modifier leads to 'debundling' of MWNTs, which results in a refined 'network-like' structure of MWNTs in PA6/ABS blends and subsequently leads to an enhanced complex viscosity. However, variation in melt-viscosity in the present case suggests that it is a complex interplay of interactions between SMA copolymer, modifier molecules, MWNTs and the various polymer phases.

Figure 4-58 (a) and (b) show the variation of tan δ as a function of temperature for 40/60 (wt/wt) and 60/40 (wt/wt) PA6/ABS blends with unmodified and modified MWNTs respectively. Figure 4-58 (c) and (d) exhibit the variation of tan δ as a function of temperature for 40/60 (wt/wt) and 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated unmodified and modified MWNTs respectively. 40/60 (wt/wt) PA6/ABS blend [Figure 4-58 (a) and *Table 4-11*] shows higher storage modulus (~4.64 GPa at 25 °C) values as compared to the individual blend components (PA6, ~4.4 GPa and ABS, ~3.27 at 25 °C) especially in the glassy (at 25 °C) region. Further, an increase in storage modulus values in the glassy region and the rubbery region are observed in the presence of 40/60 (wt/wt) PA6/ABS blends, for blends with unmodified MWNTs (~5.8 GPa at 25 °C, 0.4 GPa at 140 °C) and for blends with Na-AHA modified MWNTs (~5.3 GPa at 25 °C, ~0.9 GPa at 140 °C). However, 40/60 blend with PyCHO modified MWNTs showed a marginal decrease of storage modulus (~3.76 GPa in glassy region, at 25 °C and ~0.43 GPa in rubbery region, at 140 °C). Further, 60/40 (wt/wt) PA6/ABS blends exhibit marginally higher storage modulus (~4.42 GPa at 25 ^oC) as compared to the individual blend components (PA6, ~4.4 GPa and ABS ~3.27 GPa at 25 °C) Incorporation of unmodified MWNTs has resulted in marginal variation in the storage modulus (~4.2 GPa at 25 °C) as compared to the corresponding neat blend (~4.4 GPa at 25

^oC). Whereas, for 60/40 (wt/wt) PA6/ABS blend with Na-AHA modified MWNTs and PyCHO modified MWNTs, the storage moduli values have increased to ~4.8 GPa at 25 ^oC in both the cases.

40/60 (wt/wt) blends with SMA encapsulated MWNTs, SMA encapsulated Na-AHA modified MWNTs and SMA encapsulated PyCHO modified MWNTs show decreased storage moduli (~3.8, ~4.2 and ~3.02 GPa in glassy region at ~25 °C respectively) as compared to the corresponding neat blend (~4.64 GPa in glassy region) as shown in Figure 4-58 (c). However, 60/40 (wt/wt) blend exhibits higher storage modulus in the presence of SMA encapsulated Na-AHA modified MWNTs (~6.4 GPa in glassy region at ~25 °C) as compared to the corresponding blend with SMA encapsulated unmodified MWNTs (~5.2 GPa in glassy region at ~25 °C). However, the corresponding blend with SMA encapsulated PyCHO modified MWNTs shows a lower storage modulus ~3.12 GPa in the glassy region (at ~25 °C) [Figure 4-58 (d)]. Further, storage moduli observed in rubbery region at ~140 °C indicate higher value in case of 60/40 (wt/wt) blend with SMA encapsulated Na-AHA modified MWNTs (~0.42 GPa) as compared to the corresponding blend with SMA encapsulated unmodified MWNTs (~0.1 GPa) and SMA encapsulated PyCHO modified MWNTs (~0.32 GPa). Increase in storage moduli values may be due to improved state of dispersion of MWNTs in the presence of modifier molecules and/or 'melt-interfacial' reaction between compatibilizer and PA6 phase. Lower storage moduli values in the presence of PyCHO molecules may be due to the 'miscibility' between the SAN phase of ABS and PyCHO molecules.

Table 4-11 shows that the tan delta peak (corresponding to T_g of PA6 phase) for PA6 phase shifts to higher temperature in the presence of ABS phase for both the blend compositions: 40/60 [~63.2 °C] and 60/40 (wt/wt) [~59.4 °C] PA6/ABS blend. 40/60 (wt/wt) PA6/ABS blend with unmodified MWNTs shows the T_g of PA6 phase at ~66.6 °C, the corresponding blend with Na-AHA modified MWNTs shows at ~75.1 °C and the corresponding blend with PyCHO modified MWNTs shows at ~62.9 °C. 60/40 (wt/wt) blend with unmodified MWNTs at ~58.8 °C and the corresponding blend with PyCHO modified MWNTs at ~54.9 °C. T_g of ABS phase in case of 40/60 (wt/wt) PA6 blends with unmodified MWNTs is shown at ~128.3 °C, in case of the corresponding blend with Na-AHA modified MWNTs is shown at ~128.3 °C.

MWNTs the T_g is observed at ~126.5 °C and for the corresponding blend with PyCHO modified MWNTs the corresponding T_g is observed at ~122.6 °C.



Figure 4-57 Variation of complex viscosity with frequency for (a) 40/60 (wt/wt) PA6/ABS blends and (b) 60/40 (wt/wt) PA6/ABS blends; where, PA6 (1), PA6/ABS blends (N_xA_y) (2) and blends with SMA (N_xA_ySm5) (3), PA6/ABS blends with SMA encapsulated MWNTs [unmodified MWNTs, N_xA_ySE5T5; Na-AHA modified MWNTs, N_xA_ySE5M5 and PyCHO modified MWNTs, N_xA_ySE5Py5] (4–6) and ABS (7); variation of complex viscosity values observed at 0.1 rad/s for neat blends, blends with SMA encapsulated unmodified MWNTs, blends with SMA encapsulated Na-AHA modified MWNTs and SMA encapsulated PyCHO modified MWNTs along with complex viscosity values of corresponding blends with unmodified MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs for (c) 40/60 (wt/wt) PA6/ABS blends and (d) 60/40 (wt/wt) PA6/ABS blends.



Figure 4-58 Variation of tan delta with temperature obtained from DMTA analysis for (a) 40/60 (wt/wt) and (b) 60/40(wt/wt) PA6/ABS blends with unmodified MWNTs (N_xA_yT5), Na-AHA modified MWNTs (N_xA_yM5) and PyCHO modified MWNTs (N_xA_yPy5); (c) 40/60 (wt/wt) and (d) 60/40(wt/wt) PA6/ABS blends with SMA encapsulated unmodified MWNTs (N_xA_ySE5T5), Na-AHA modified MWNTs (N_xA_ySE5M5) and PyCHO modified MWNTs ($N_xA_ySE5Py5$).

Further, T_g of the SAN part of ABS for 60/40 (wt/wt) PA6/ABS blend with unmodified MWNTs is observed at ~121.5 °C, the corresponding blend with Na-AHA modified MWNTs is shown at ~120.3 °C and the blend with PyCHO modified MWNTs is depicted at ~118.9 °C. PA6 phase of 40/60 (w/wt) PA6/ABS blend shows a higher glass transition temperature as compared to 60/40 (wt/wt) PA6/ABS blend with unmodified and modified MWNTs. 40/60 (wt/wt) PA6/ABS blend with SMA encapsulated unmodified MWNTs shows the T_g of PA6 phase at ~66.7 °C, the corresponding blend with SMA encapsulated Na-AHA modified MWNTs shows at ~64.5 °C and the corresponding blend with SMA encapsulated PyCHO modified MWNTs depicts at ~46.2 °C. Glass transition temperature of the SAN phase of ABS in case of 40/60 (wt/wt) PA6 blends with SMA encapsulated unmodified MWNTs is observed at ~126.8 °C, in case of the corresponding blend with SMA encapsulated with Na-AHA modified MWNTs is shown at ~125 °C and for the corresponding blend with SMA encapsulated PyCHO modified MWNTs is exhibited at ~109 °C.

60/40 (wt/wt) PA6/ABS blend with SMA encapsulated unmodified and modified MWNTs exhibit higher T_g values of PA6 phase as compared to the corresponding blend with unmodified and modified MWNTs without SMA copolymer. On the other hand, T_g value of the SAN phase of ABS in case of 60/40 blend with SMA encapsulated unmodified and SMA encapsulated Na-AHA modified MWNTs are higher as compared to the corresponding blends with unmodified and modified MWNTs. However, 60/40 PA6/ABS blend with SMA encapsulated PyCHO modified MWNTs exhibits a lower glass transition temperature corresponding to the SAN phase (of ABS) as compared to the corresponding blend with PyCHO modified MWNTs. T_g values of SAN phase for 60/40 (wt/wt) PA6/ABS blend with SMA encapsulated unmodified MWNTs is depicted at ~126.5 °C, the corresponding blend with SMA encapsulated Na-AHA modified MWNTs is shown at ~122 °C and the blend with SMA encapsulated PyCHO modified MWNTs is observed at ~109 °C.

This observation may indicate a 'restricted' segmental mobility of PA6 chains due to the presence of a majority fraction of MWNTs localized in the PA6 phase. Similarly, SAN phase of ABS of 40/60 (wt/wt) PA6/ABS blends with unmodified and modified MWNTs exhibits higher glass transition temperature as compared to the SAN phase of 60/40 (wt/wt) PA6/ABS blends with unmodified and modified MWNTs, which may be attributed to lower extent of 're-distribution' of MWNTs to the ABS phase in case of 60/40 blends. Localization of MWNTs depending on the blend composition may lead to a variation in glass transition temperatures of the corresponding polymer phases. Further, the presence of SMA copolymer introduces an additional restriction in polymer chain segmental mobility, which may significantly alter the polymer chain dynamics [225].

4.5.8 Formation of 'network-like' structure of MWNTs: Effect of SMA encapsulation, modification with organic modifiers and blend composition

Variation in AC electrical conductivity as a function of frequency and the corresponding DC electrical conductivity as a function of concentration of PA6 phase for blends with SMA encapsulated unmodified/ modified MWNTs and the corresponding blends with unmodified/ modified MWNTs are shown in *Figure 4-59* (a)–(f) respectively. *Figure 4-59* (a) depicts that blends with SMA encapsulated unmodified MWNTs show a 'non-conducting' behaviour irrespective of the blend composition. PA6/ABS blends with unmodified MWNTs showed DC electrical conductivity values in the range of 10^{-11} – 10^{-6} S/cm, and the DC electrical conductivity value increases with increasing PA6 concentration in the blend. Whilst, PA6/ABS blends with SMA encapsulated unmodified MWNTs exhibit electrically insulating behaviour irrespective of the blend composition [*Figure 4-59* (b)].

PA6/ABS blends with 5 wt% SMA encapsulated Na-AHA modified MWNTs exhibit significantly higher electrical conductivity values [$\sim 10^{-9}$ to $\sim 10^{-7}$ S/cm] for the entire blend composition range as compared to the corresponding blends with SMA encapsulated unmodified MWNTs [$\sim 10^{-11}$ S/cm] as shown in *Figure 4-59* (c). PA6/ABS blends with Na-AHA modified MWNTs [$\sim 10^{-7}$ - 10^{-6} S/cm], showed higher electrical conductivity (~ 2 orders of magnitude) as compared to the blends with SMA encapsulated Na-AHA modified MWNTs ($\sim 10^{-9}$ - 10^{-8} S/cm) [*Figure 4-59* (d)].

40/60 (wt/wt) PA6/ABS blend with 5 wt% SMA encapsulated PyCHO modified MWNTs shows an insulating behaviour, whereas remaining blend compositions viz. 45/55, 50/50, 55/45 and 60/40 (wt/wt) PA6/ABS demonstrate enhanced electrical conductivity values [$\sim 10^{-8}$ – 10^{-4} S/cm] as shown in *Figure 4-59* (e). In the presence of PyCHO modified MWNTs without SMA copolymer, PA6/ABS blends showed electrical conductivity values in the range of $\sim 10^{-5}$ – 10^{-4} S/cm, while PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs exhibit electrical conductivity values in the range of $\sim 10^{-5}$ – 10^{-4} S/cm, while PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs exhibit electrical conductivity values in the range of $\sim 10^{-12}$ to $\sim 10^{-3}$ S/cm, which increase with increasing PA6 concentration in the blend [*Figure 4-59* (f)].

MWNTs are effectively 'debundled' in the presence of Na-AHA molecules through 'steric stabilization' and 'electrostatic charge repulsion' mechanism [50]. Therefore, PA6/ABS blends with Na-AHA modified MWNTs showed significantly higher electrical conductivity as compared to the corresponding blends with unmodified MWNTs. However, a layer of SMA copolymer on MWNTs surface may result in lower electrical conductivity values of the resultant composites [58]. SMA copolymer interacts with MWNTs surface through the styrene part. This is reflected in lower electrical conductivity values of PA6/ABS blends with SMA encapsulated Na-AHA modified MWNTs as compared to the blends with Na-AHA modified MWNTs confirming the partial wrapping of the surface of MWNTs with SMA copolymer. Moreover, electrically conducting behaviour of these composites indicates a possibility that some of the Na-AHA molecules may get 'desorbed' from MWNTs surface during 'melt-interfacial' reaction between SMA copolymer and PA6 molecules. On the other hand, PyCHO molecules may effectively cover MWNTs surface through strong ' π - π ' stacking interaction with MWNTs [226, 227]. This phenomenon may hinder SMA copolymer from wrapping MWNTs surface effectively. Further, PyCHO molecules facilitate electrical conduction through 'conjugation' phenomenon. SMA encapsulating layer or any molecules present on MWNTs may also affect the nucleation ability of nanotubes, which has been already discussed in the earlier section.

Figure 4-60 shows a schematic for proposed interactions between SMA copolymer, MWNTs and modifier molecules for SMA encapsulated PyCHO modified MWNTs. PyCHO molecules may interact with nanotube surface as well as the SMA molecules. The presence of aromatic molecules near to the surface of MWNTs may affect the state of dispersion of MWNTs. SMA encapsulation of MWNTs resulted in non-conducting blend samples, due to a polymer wrapping on nanotubes surface. Whilst, in case of PyCHO modified MWNTs, which were encapsulated by SMA copolymer; a fraction of the nanotubes most likely may localize at the interface due to an interaction between the SMA and PyCHO molecules, which in turn may drive the ternary entity at the interface of PA6/ABS blend. Also, the similarity of the chemical structure between polyaromatic molecule PyCHO and MWNTs might be a strong reason of the retainment of the original MWNTs structure and thus, the presence of SMA copolymer could not result in the decrease in the electrical conductivity of the PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs.



Figure 4-59 AC electrical conductivity as a function of frequency for PA6/ABS blends of varying blend compositions (40/60 – 60/40, wt/wt) with SMA encapsulated: (a) unmodified MWNTs (1:1, wt/wt) (N_xA_ySE5T5), (c) Na-AHA modified MWNTs (1:1:1, wt/wt/wt) (N_xA_ySE5M5) and (e) PyCHO modified MWNTs (1:1:1, wt/wt/wt) (N_xA_ySE5Py5); DC electrical conductivity values for SMA encapsulated unmodified MWNTs (b), SMA encapsulated Na-AHA modified MWNTs (d) and SMA encapsulated PyCHO modified MWNTs (f) along with the corresponding DC electrical conductivity values of blends without SMA copolymer.



Figure 4-60 Schematic for probable polymer-nanotube interaction in case of SMA encapsulated MWNTs [MWNTs, Na-AHA modified MWNTs and PyCHO modified MWNTs], complex interplay of various factors such as the interaction between the MWNTs, blend components (through hydrophobic interactions, π - π interaction), processing parameters, blend composition.

If a nanotube has a parallel orientation to the interface during melt-mixing at the interface, then the transfer rate between phases is lower and hence, the probability of the nanotube to be confined at the interface of the blend is likely to be higher [141]. Na-AHA modified MWNTs show effective debundling, hence 'well-debundled'/'individualized' MWNTs may localize at the interface when encapsulated with SMA and may get confined at the interface. Due to broadening of the interface in the presence of a compatibilizer, the re-distribution of MWNTs in ABS phase may not be possible.

Further, Gotovac et al. [228] investigated the adsorption of polycyclic aromatic molecules on the SWNTs and showed that in the presence of the polycyclic aromatic molecules, nanotubes became stiffer. In addition, PyCHO molecules are likely to alter the

radial flexibility of a number of aromatic rings in the tube structure resulting in hardening of the RBM mode. Thus, the probability of nanotube being parallel to the interface and subsequently to localize at the interface may be higher when MWNTs surface is modified with Na-AHA/PyCHO modifier.

Chapter 5: Summary, conclusions and future scope

State of dispersion of MWNTs in PA6/ABS blends has been studied extensively to investigate the influence of dispersion media, blend composition, surface modification with non-covalent organic modifiers, and presence of the compatibilizer.

5.1 State of dispersion of multiwall carbon nanotubes investigating influence of organic modifiers and dispersion media

The aim of this study was to investigate the state of dispersion of unmodified and modified MWNTs in corresponding dispersions. Optical microscopic analysis showed lower primary 'agglomerate' size of MWNTs for modified MWNTs as compared to the unmodified MWNTs [D_{avg} value for unmodified MWNTs ~107.9 µm; D_{avg} value for SDS modified MWNTs ~44 µm, D_{avg} value for Na-AHA modified MWNTs ~49 µm and D_{avg} value for PyCHO modified MWNTs ~69.2 µm]. MWNTs dispersions exhibited improved 'debundling' of MWNTs with increasing ultrasonication time and in the presence of organic modifiers. However, limited debundling has been achieved in case of unmodified MWNTs. Modified MWNTs exhibited higher concentration of 'individualized' MWNTs as compared to unmodified MWNTs, which was confirmed through higher UV-vis absorbance values and

lower I_D/I_G ratio determined by Raman spectroscopic analysis as compared to values exhibited by the corresponding dispersions with unmodified MWNTs.

Dispersion of MWNTs was improved in case of Na-AHA modified MWNTs as compared to MWNTs modified with either SDS or PyCHO. Dispersions of MWNTs in various organic media exhibited varied primary 'agglomerate' size of MWNTs for unmodified MWNTs. PyCHO modified MWNTs exhibited lower value of D_{avg} as compared to unmodified MWNTs irrespective of the dispersion media. Higher UV-vis absorbance values exhibited by PyCHO modified MWNTs as compared to unmodified MWNTs indicate effective 'debundling' of MWNTs irrespective of the dispersion media. Further, 'dispersibility' of MWNTs in aqueous or organic media has been found to be a function of various solvent parameters. Therefore, it has been inferred that multiple factors should be considered in order to study the 'dispersibility' of MWNTs.

5.2 Dispersion, migration and 'network-like' structure formation of MWNTs in 'co-continuous' PA6/ABS blends

'Simultaneous' melt-mixing protocol has resulted in the distribution of MWNTs in both the phases depending upon the concentration of the PA6 phase in case of PA6/ABS blends. Higher concentration of PA6 phase in the blends has led to higher fraction of MWNTs in the PA6 phase, which has resulted in a well-developed 'network-like' structure of MWNTs. The UV-vis spectroscopic analysis, TGA analysis and solution experiments showed the extent of localization of MWNTs in the ABS phase, especially the effect of modification of MWNTs with Na-AHA molecules, which has resulted in higher concentration of MWNTs localized in the ABS phase. The presence of Na-AHA molecules has resulted in chain scission of PA6 phase, which was confirmed through intrinsic viscosity measurements and analyzing normalized torque values. In brief, the non-covalent modification of MWNTs by an organic molecule – Na-AHA has resulted in the effective debundling of MWNTs and enhanced interaction with the PA6 phase; however it cannot prevent the localization of the MWNTs in the ABS phase owing to the 'simultaneous' melt-mixing protocol.

5.3 Influence of non-covalent modification on the state of dispersion of multiwall carbon nanotubes in co-continuous binary polymer blends

Raman spectroscopic analysis and FTIR analysis of Na-AHA modified MWNTs has indicated enhanced interaction between the modifier molecules and MWNTs. Further, the decrease in I_D/I_G ratio and primary MWNTs 'agglomerate' size in the presence of modifiers revealed an effective 'debundling' of the MWNTs after modification step. Presence of modifier molecules has resulted in effective break-up of MWNTs 'agglomerates' in PA6/ABS blends as well, which was supported by optical microscopic analysis. Morphological observations have indicated that localization of MWNTs influenced the transformation from 'matrix-dispersed droplet' type morphology to 'co-continuous' type morphology through variation in 'melt-viscosity' ratio. Further, ligament size of PA6 phase has increased in the presence of modifier molecules, which has resulted in accommodation of higher fraction of MWNTs in the PA6 phase with refined MWNTs 'network'. TEM observations showed presence of 'nano-agglomerated' and 'individualized' MWNTs in case of modified MWNTs. MWNTs are localized in both PA6 and ABS phases and a fraction of MWNTs was also localized at the interface in case of blends with modified MWNTs.

PA6/ABS blends with unmodified MWNTs showed DC electrical conductivity values between ~ 10^{-11} – 10^{-6} S/cm, whereas the DC electrical conductivity value has increased with increase in PA6 phase concentration. Blends with Na-AHA modified MWNTs have exhibited higher DC electrical conductivity values in the range of ~ 10^{-7} – 10^{-6} S/cm and the corresponding blends with PyCHO modified MWNTs have shown values between the range of ~ 10^{-5} – 10^{-4} S/cm, which marginally varied on the basis of PA6 concentration. Ratio of the crystallization peak height at lower temperature (H₁) to the peak height at higher temperature (H₂) has strongly indicated that higher surface area might be 'available' in the presence of Na-AHA modified MWNTs through 'desorption' of Na-AHA molecules during 'meltinterfacial' reaction with the PA6 phase as well as due to higher extent of 'debundling' of MWNTs. 'Melt-interfacial' reaction has also been found to be a driving force for MWNTs to preferentially localize in the PA6 phase. On the other hand, effective surface coverage of MWNTs surface by PyCHO molecules has led to suppressed 'interfacial crystallization' of PA6 phase on MWNTs surface. 'Interphase formation' further substantiated the phenomenon of enhanced interaction between MWNTs and PA6 in the presence of Na-AHA through higher residual weight obtained in case of composites with Na-AHA modified MWNTs. Although PA6/ABS blends with PyCHO modified MWNTs have exhibited lower residual weight in TGA analysis as compared to the corresponding blends with Na-AHA modified MWNTs, the presence of 'interphase' was suggested as the residual weight of 10–12 % was observed at 500 °C.

5.4 Evolution of phase morphology and 'network-like' structure of multiwall carbon nanotubes in binary polymer blends during melt-mixing

This study revealed that phase morphology development of the PA6/ABS blends with MWNTs has been significantly influenced by the melt-mixing time. 'Matrix-dispersed droplet' type morphology was exhibited at the early stages of melt-mixing, which further transformed to a well-developed 'co-continuous' type of morphology for the PA6/ABS blends with unmodified and Na-AHA/PyCHO modified MWNTs; with an exception of 40/60 (wt/wt) PA6/ABS blends with PyCHO modified MWNTs. Droplets of dispersed phase were elongated with increasing mixing time and further resulted in the formation of a 'co-continuous' structure. In case of 40/60 (wt/wt) PA6/ABS blend with PyCHO modified MWNTs, the 'network-like' structure might have developed through the connectivity of MWNTs present in the matrix and the fraction present at the interface. Variation in the phase morphology was influenced by the melt-mixing time, shear stress exerted by the respective blend components, and the melt-viscosity ratio.

In the presence of organic modifiers: Na-AHA and PyCHO, MWNTs have exhibited 'well-debundled' structure. Formation of the 'network-like' structure of unmodified MWNTs was found to be difficult and it was also found to be dependent on the blend composition. However, PA6/ABS blends with Na-AHA modified MWNTs and PyCHO modified MWNTs have exhibited electrically conducting behaviour from the early stage of melt-mixing. In the presence of the modifier, formation of 'network-like' structure was found to be influenced by the melt-mixing time and blend composition. Non-isothermal crystallization behaviour of

PA6 phase showed that the interaction between MWNTs and the PA6 chains was enhanced with increasing mixing time. The formation of 'trans-crystalline lamellar' structure was facilitated in case of unmodified MWNTs through availability of free surface area (with the matching of crystal lattice of PA6 chain and MWNTs) of MWNTs to induce the 'interfacial' crystallization. On the other hand, the presence of the adsorbed modifier molecules on the nanotube surface has adversely affected the formation of 'trans-crystalline' lamellar structure.

5.5 Dispersion of non-covalently modified multiwalled carbon nanotubes in binary immiscible polymer blends: Effect of encapsulation of nanotubes with a conventional reactive compatibilizer

A shift in Raman 'D-band' peak and 'G-band' peak has indicated an enhanced interaction between SMA molecules and MWNTs surface. Lower specific surface area of MWNTs in case of SMA encapsulated Na-AHA modified MWNTs (specific surface area is ~29.5 m^2/g) and SMA encapsulated PyCHO modified MWNTs (specific surface area is ~11.3 m^2/g) as compared to the SMA encapsulated unmodified MWNTs having specific surface area of ~84 m²/g confirms the wrapping of MWNTs with SMA copolymer. Normalized imide peak ratio has depicted that extent of 'melt-interfacial' reaction between SMA copolymer and PA6 chains is lower in case of blends with SMA encapsulated Na-AHA modified MWNTs as compared to the corresponding blends with SMA encapsulated unmodified MWNTs and SMA encapsulated PyCHO modified MWNTs. This finding substantiated that 'meltinterfacial' reaction between PA6 and Na-AHA consumes a fraction of 'functional' groups, which may not contribute to 'melt-interfacial' reaction between SMA copolymer and PA6. Enhanced storage moduli as well as Tg values of PA6 and ABS phases in case of SMA encapsulated Na-AHA modified MWNTs indicate improved interaction between SMA copolymer, modifier molecule, MWNTs and the various polymer phases, which may result in 'effective' stress-transfer between polymer phase and MWNTs. Lower values of H₁/H₂ in case of blends with SMA encapsulated Na-AHA modified MWNTs (~1.36 - ~1.4) with respect to the corresponding blends with either SMA encapsulated unmodified MWNTs (~1.61-2.33) or SMA encapsulated PyCHO modified MWNTs (~2.32 - ~2.32) strongly indicate higher extent of 'interfacial crystallization' of PA6 phase on MWNTs. This finding, therefore suggests the 'desorption' of Na-AHA molecules from MWNTs surface through 'melt-interfacial' reaction between Na-AHA and SMA copolymer.

SEM observation showed the transformation of phase morphology from 'matrixdispersed droplets' type to 'co-continuous' type in case of 40/60 to 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated unmodified MWNTs and SMA encapsulated Na-AHA modified MWNTs. PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs exhibited 'co-continuous' type morphology with an exception of 40/60 (wt/wt) PA6/ABS blend. Variation in the phase morphology is likely to be a result of alteration of 'meltviscosity' ratio through 'preferential localization' of MWNTs and/or 'melt-interfacial' reaction between SMA copolymer and PA6 phase.

MWNTs 'network', 'nano-agglomerates' are observed in case of PA6/ABS blend with SMA encapsulated unmodified MWNTs. Blends with SMA encapsulated Na-AHA modified MWNTs show 'individualized' MWNTs in PA6 and SAN part of ABS phase. 40/60 and 60/40 (wt/wt) PA6/ABS blends with SMA encapsulated PyCHO modified MWNTs show 'nano-agglomerates' of MWNTs preferentially localized in the SAN phase. A fraction of MWNTs is localized at the interface of the blend in all the cases. Effective wrapping of unmodified MWNTs with SMA copolymer results in an electrically insulating behaviour of blends with SMA encapsulated unmodified MWNTs over the entire composition range. Interactions between modifier molecules, MWNTs and SMA copolymer influence the electrical conductivity behaviour of PA6/ABS blends with SMA encapsulated modified MWNTs. Blends with SMA encapsulated Na-AHA modified MWNTs exhibited DC electrical conductivity in the range of $\sim 10^{-9}$ to $\sim 10^{-8}$ S/cm over the entire blend composition range presumably through 'desorption' of Na-AHA molecules adsorbed on MWNTs surface during the 'melt-interfacial' reaction with SMA copolymer. Moreover, surface coverage of MWNTs with PyCHO molecules has resulted in DC electrical conductivity in the range of $\sim 10^{-12}$ S/cm to $\sim 10^{-4}$ S/cm for the corresponding blends with SMA encapsulated PvCHO modified MWNTs, where 40/60 (wt/wt) blend showed electrically insulating behaviour. In brief, this study shows a complex interplay of various phenomena in developing MWNTs based electrically conducting PA6/ABS blends in the presence of organically modified MWNTs and a reactive compatibilizer.

5.6 Conclusion

The exhaustive studies from Section 4.1 to Section 4.5 have established an explicit understanding of various factors influencing the dispersion of MWNTs in PA6/ABS blends. Based on which, it may be concluded that the dispersion state and confinement of MWNTs in immiscible, binary blends of PA6 and ABS have been influenced by various interactions between the modifier molecules, MWNTs, reactive compatibilizer and respective polymer phases. MWNTs' 'network-like' structure in the blend was influenced by 'selective' localization of a higher population of MWNTs specifically in one phase of the blend as well as by the formation of 'nano-agglomerated' and 'individualized' MWNTs.

5.7 Future scope

This work has provided important insights to various issues in connection with the dispersion of MWNTs in aqueous or organic media and in PA6/ABS blends along with an exhaustive analysis of various interactions between the modifier molecules, reactive compatibilizer, MWNTs and the respective polymer phases. The study can be further extended to analyze following aspects of MWNTs dispersion:

- The extent of dispersion and the stability of the MWNTs dispersions of unmodified and modified MWNTs may be investigated utilizing a mixture of organic media. Further, to determine the dispersion of these unmodified and modified MWNTs in melt-mixed PA6/ABS blends.
- MWNTs may be extracted from the PA6/ABS phases and the 'interphase' formation on the MWNTs surface may be investigated extensively via TEM observations and TGA analysis.
- Experimental investigation of the fraction of MWNTs localized at the interface of PA6/ABS blend can be carried out.

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- Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Influence of non-covalent modification on dispersion state of multiwalled carbon nanotubes in melt-mixed immiscible polymer blends", ACS Applied Materials and Interfaces, (2014) 6 11054–11067.
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- Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Evolution of phase morphology and 'network-like' structure of multiwall carbon nanotubes in binary polymer blends during melt-mixing", Article in Press, *DOI: 10.1002/pen.23897* (Polymer Engineering and Science, 2014).
- 4. **Amrita V. Poyekar**, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Dispersion of non-covalently modified multiwalled carbon nanotubes in binary immiscible polymer blends: Effect of encapsulation with a conventional reactive compatibilizer", Under preparation.
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- B. F. Jogi, Arup R. Bhattacharyya, Amrita V. Poyekar, Petra Pötschke, George P. Simon, Satish Kumar, "Multiwall carbon nanotubes mediated novel compatibilization route in binary blends of polyamide6 and acrylonitrile butadiene styrene copolymer", Article in Press, DOI: 10.1002/pen.23905 (Polymer Engineering and Science, 2014).

Conference presentations and posters

- Paper: Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon "Interfacial localization of multiwall carbon nanotubes in polyamide6 and acrylonitrile butadiene styrene co-polymer blends in the presence of a reactive compatibilizer", 28th International Conference of Polymer Processing Society (PPS–28), 2012, Pattaya, Thailand.
- Poster: Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Comparative study of state of dispersion of multiwall carbon nanotubes in presence of noncovalent modifiers in suspensions and in the blends of polyamide6 and acrylonitrile butadiene styrene copolymer", Asian Workshop on Polymer Processing (AWPP) – 2013, Goa, India.
- Poster: <u>Best Poster Award (Second)</u>, Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Formation and Refinement of Multiwall Carbon Nanotubes 'Network-like' Structure in Polyamide6 and Acrylonitrile Butadiene Styrene Copolymer Blends: Influence of Melt-mixing Time", Polymer Processing Society – Asia Australasia Conference – 2013, Mumbai, India.
- Poster: Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Non-covalent modification of the Multiwall Carbon Nanotubes by Polyaromatic Molecule to Prepare Conducting Composites", 2013, 3rd Federation of Asian Polymer Societies (FAPS), Polymer Congress and Macro – 2013, IISc, Bangalore, India.
- Poster: <u>Best Poster Award</u>, Amrita V. Poyekar, Arup R. Bhattacharyya, Ajay S. Panwar and George P. Simon, "Conducting Composites of multiwall carbon nanotubes involving cocontinuous blends of polyamide 6 and acrylonitrile butadiene styrene" at International Symposium on Advances in Nanomaterials (ANM 2010), 2010, Kolkata, India.
- Poster: Amrita V. Poyekar, Arup R. Bhattacharyya, Amrita Talapatra, Rupesh A. Khare, Ajit R. Kulkarni, "Optimization of Processing parameters influencing AC electrical conductivity of PA6/ABS+MWNT composites", 2009, 25th Annual Meeting of Polymer Processing Society (PPS-25), 2009, Goa, India.
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