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# Specific Interactions and Reactive Coupling Induced Dispersion of Multiwall Carbon Nanotubes in Co continuous Polyamide6/Ionomer Blends

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**Summary:** An efficient strategy to achieve electrical conductivity in melt-mixed co-continuous blends is to restrict the conducting filler in a particular phase in the blends next to forming a percolated 'network-like' structure in that particular phase. However, strong inter-tube van der Waals' forces often lead to the aggregated structure leading to higher percolation threshold. In addition, the migration of the conducting filler during melt-mixing and the blending sequence significantly affect the bulk conductivity of the blends. SEM observation showed fine co-continuous structures associated with 50/50 blends of PA6/Surlyn with multiwall carbon nanotubes (MWNT). MWNT were localized in the vicinity of the ionic domains in the ionomer corresponding to a specific blending sequence when unmodified MWNT were used, however, in presence of Na-salt of 6-amino hexanoic acid (Na-AHA) modified MWNT, selective clustering was not observed may be due to the confinement of MWNT in the PA6 phase. To understand these complexities the electrical conductivity of melt-mixed blends of polyamide6/ionomer with MWNT was studied. However, it was observed that the blends with even 3 wt% unmodified MWNT showed insulating behaviour irrespective of the blending sequence adopted. In addition, the key role of a reactive modifier (Na-AHA) in facilitating uniform dispersion and subsequent 'network-like' formation by establishing specific interactions with MWNT was studied. It was found that the MWNT are selectively localized in the PA6 phase in the NA-AHA modified blends manifesting in higher electrical conductivity ($\sim 10^{-5}$ S/cm at 3 wt% MWNT) when using a specific blending sequence, due to melt-interfacial reaction between the $\sim NH_2$ functionality of Na-AHA and the $\sim COOH$ end groups of PA6. FTIR and Raman spectroscopic analysis also supported the existence of the specific interactions.

**Keywords:** blends; electrical conductivity; ionomers; MWNT; polyamide6

## Introduction

Blending of polymers is an important tool in developing new routes for obtaining materials with improved performances. However, most polymer blends are immiscible because of their high molecular weight and unfavourable interactions thus giving rise to multiphase structures. Among different strategies of polymer blend compatibilization the concept of reactive blending was shown to be most effective.[1] It is well established that promoting physical and/or chemical interactions between the blend components is an effective way of obtaining a blend with desired performances. Blends of polyamide6 (PA6) and poly (ethylene-methacrylic acid) copoly-

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mers (EMA) are such a type of blends which undergo a series of physico-chemical interactions resulting in intriguing blend properties which were observed to be profoundly dependent on the acid functionality of the copolymer.[2] Moreover, the use of polymers with few pendant ionic groups (ionomers) has the potential to exploit towards interesting blend properties and improving the compatibility with polar polymers.[3] Numerous literatures are known where polyethylene based ionomers have been used as compatibilizer in polyamide containing binary or ternary blends.[4–6] In addition, the dispersion of PA6 in EMA neutralized with metal ions was observed to be markedly better.[7]

Though there are evidences in the literature concerning the improvements in the physical and the mechanical properties of PA6 by blending with EMA[2] or EMA based ionomers,[7–9] the effect on the bulk electrical conductivity of the blends in presence of conducting fillers like multiwall carbon nanotubes (MWNT) has not received much attention. Hence this work has been undertaken in order to investigate the effect of MWNT on the bulk electrical conductivity of the blends of PA6 and EMA neutralized with sodium (Surlyn).

It is well established that the key factor in developing conducting polymer blends is to restrict the conducting filler into a specific phase by exploiting the concept of 'double-percolation'[10–12] next to formation of network-like structure at very low levels in that particular phase. However, this depends critically on the melt-rheology of each polymer phase and the difference in the affinity of fillers towards each blend components during processing.[13,14] In addition, redistribution and migration of conducting filler to the other phase during melt mixing often leads to higher percolation threshold in immiscible blends.[15]

Though, extensive efforts have been made in recent times to improve the compatibility between carbon nanotubes (CNT) and the polymer matrix by using different strategies like functionalization of CNT and subsequent covalent interaction to enhance the phase adhesion with the polymer matrix.[16,17] However, this route eventually disrupts the extended network of $\pi$-electrons of CNT thereby significantly affecting the intrinsic electrical conductivity associated with CNT. Alternatively, to avoid these adverse effects, several groups have also focused on non-covalent approaches[18–20] like the use of surfactants.[21–25] Unfortunately, the onset of decomposition of most of the surfactants is much lower than the processing temperatures of most of the polymers which limits its use in melt-mixing technique, which is otherwise technologically more viable. In addition to various strategies of improving the dispersion of CNT in the polymer matrix, the use of immidazolium salts,[26] conjugated polymers,[27] and ionomers[28] have also been investigated.

It is well realized that specific interactions like 'cation-$\pi$' coupled with melt-interfacial reaction induced dispersion can typically control the state of dispersion of MWNT in the PA6 matrix[29] as well as in binary blends of PA6 and acrylonitrile-butadiene-styrene (ABS).[15] In addition, we observed that owing to the specific interactions between the $Na^+$ ions in Surlyn and the extended $\pi$-electron clouds in MWNT, the tubes were mostly observed to be segregating in the vicinity of the ionic micro domains.[30] Hence, it becomes quite interesting to investigate the state of dispersion of MWNT in co-continuous blends of PA6 and Surlyn in presence of Na-salt of 6-amino hexanoic acid (Na-AHA). The state of dispersion of MWNT was assessed using AC electrical conductivity measurements and SEM analysis. The specific interactions were investigated using FTIR and Raman spectroscopic analysis.

## Experimental Part

### Materials and Sample Preparation

Polyamide 6 (PA6) with a zero shear viscosity of 180 Pa s at 260 °C was obtained from GSFC, Gujarat, India (Gujlon

M28RC, relative viscosity 2.8, $M_v$ is 38640 in 85% formic acid). The commercial grade of Surlyn ionomer resin, Surlyn 8320 was obtained from duPont, USA. It is a copolymer of ethylene and methacrylic acid (containing 9% acid where ~52% of the acid groups are neutralized to form sodium salt). CCVD synthesized thin multiwall carbon nanotubes (MWNT) were obtained from Nanocyl S. A. Belgium (NC 3100, purity >95%). 50/50 (wt/wt) blends of PA6/Surlyn and with MWNT were prepared by melt-mixing in a conical twin-screw extruder (Micro 5, DSM Research, Netherlands) at 260 °C with a rotational speed of 150 rpm for 15 min. The blends with Na-AHA modified MWNT were prepared under the same extrusion conditions. The detailed procedure to obtain Na-AHA and solid mixtures of Na-AHA modified MWNT is reported elsewhere.[29] Two different blending sequences were adopted during melt mixing. In blending sequence 1, MWNT (either purified or Na-AHA modified) were melt-mixed with PA6 for 10 min followed by the addition of Surlyn and was mixed for another 5 min. In blending sequence 2, MWNT (either purified or Na-AHA modified) were melt-mixed with Surlyn for 10 min followed by the addition of PA6 and was mixed for another 5 min. The blend compositions with their sample codes are listed in Table 1. Compression moulded sheets with a thickness of 0.2 mm were prepared from the extrudate strands at 230 °C. The samples used for dielectric measurements were cut from these sheets. The melt rheological response for pure PA6 at 260 °C and for Surlyn at 230 °C is shown in Figure 1a.

## Extraction Experiments and Scanning Electron Microscopy (SEM)

The cryofractured extrudate strands were selectively extracted with boiling xylene (to remove polyethylene phase of Surlyn) and also with formic acid (to remove the PA6 phase) to check the co-continuity of PA6/Surlyn blends with MWNT. It was found that the strands were remain intact in formic acid and was found to swell in boiling xylene, which indicated the co-continuous structure formation. Figure 1b shows the SEM micrograph of 50/50 blends of PA6/Surlyn with 3 wt% modified MWNT (S50MT3N50), which shows fine co-continuous structures. The state of dispersion of MWNT was also studied by SEM. The extruded strands were cryofractured using liquid nitrogen and were observed using a FEI Quanta 200.

## AC Conductivity

The AC conductivity measurements were performed on the compression molded samples (across the thickness) in the frequency range between $10^{-2}$ and $10^{7}$ Hz using Alpha high-resolution analyzer coupled to a Novocontrol interface (broad band dielectric analyzer). The samples were placed between two gold electrodes that were pressed together with a screw. The DC conductivity of the samples was determined from the AC conductivity plots in the region of low-frequency plateau by fitting power law equation ($\sigma_{ac} = \sigma_{dc} + A\omega^n$, $0 < n < 1$).[31]

## FTIR and Raman Spectroscopy

FTIR spectroscopic analysis was carried out with compression-moulded films using

**Table 1.**
Sample codes and compositions of PA6/Surlyn blends with MWNT.

| Sample code | PA6 (wt%) | Surlyn (wt%) | Purified MWNT (wt%) | Na-AHA modified MWNT (wt%) | Blending Sequence |
|---|---|---|---|---|---|
| N50S50 | 50 | 50 | – | – | – |
| N50T3S50 | 50 | 50 | 3 | – | 1 |
| S50T3N50 | 50 | 50 | 3 | – | 2 |
| N50MT3S50 | 50 | 50 | – | 3 | 1 |
| S50MT3N50 | 50 | 50 | – | 3 | 2 |

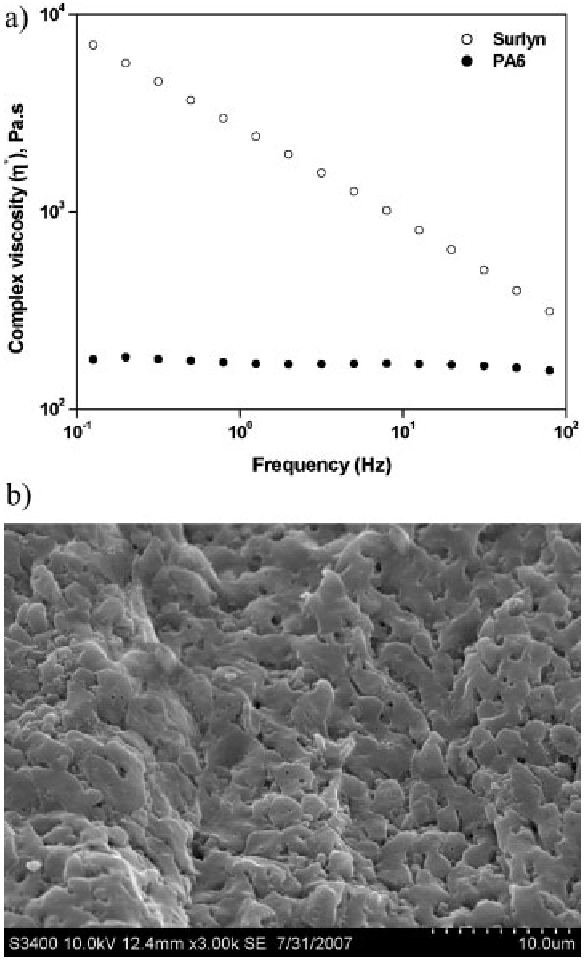

***Figure 1.***
(a): Melt rheology of PA6 and Surlyn; (b) SEM micrograph of cryofractured and formic acid etched surfaces of S50MT3N50.

Nicolet, MAGNA 550 at room temperature in the scanning range of 400 to 4000 $cm^{-1}$. Raman spectroscopy was performed using a Jobin Yovon (HR 800 micro-Raman) on extrudate strands over a scanning range of 200 to 2000 $cm^{-1}$ with an incident laser excitation wavelength of 514 nm.

## Results and Discussions

### SEM Investigations: State of Dispersion of MWNT

In order to investigate the state of dispersion of MWNT in the blends we carried out SEM of cryofractured samples of blends of PA6/Surlyn with MWNT as shown in Figure 2. Figure 2a depicts the SEM of cryofractured surfaces of 50/50 blends of PA6 and Surlyn.

Figure 2b-c shows the SEM of cryofractured surfaces of blends with MWNT. Interestingly, selective clustering of MWNT in the vicinity of the ionic domains (encircled region) was observed possibly associated with the Surlyn phase. In addition, the tubes were also found in the other phase of the blends as observed from the SEM micrographs.

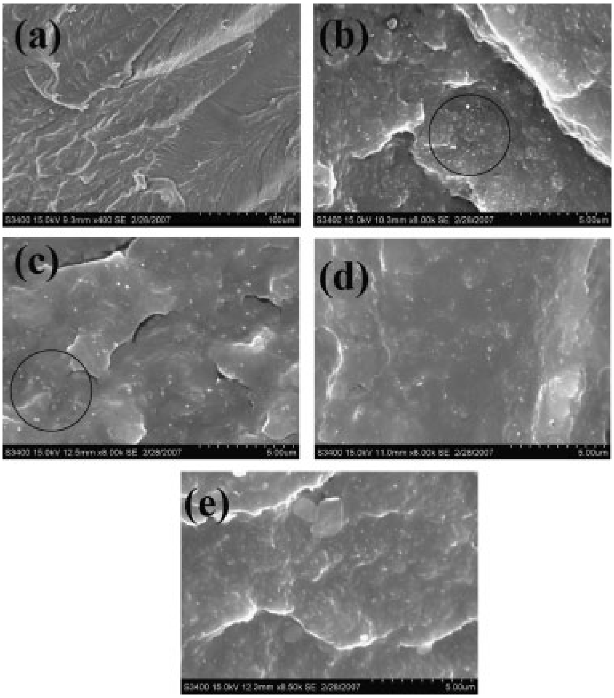

***Figure 2.***
SEM of (a) N50S50, b) N50T3S50, c) S50T3N50, d) N50MT3S50, e) S50MT3N50.

Even if extraction experiments and the SEM micrograph of the etched sample (Figure 1b) revealed the co-continuous structures associated with 50/50 PA6/Surlyn with MWNT, the SEM micrographs of the cryofractured strands do not reveal different phases of PA6 and Surlyn. In this context it is to be pointed out that selective clustering of MWNT in the vicinity of ionic micro domains was also observed in Surlyn/MWNT composites.[30] The selective clustering of MWNT was attributed to the specific interaction between $Na^+$ ionic moieties in Surlyn and MWNT during melt-mixing.

It may be proposed that MWNT are dispersed mostly in Surlyn phase due to the existence of specific interaction along with there is a possibility of migration of MWNT in the PA6 phase due to the melt-viscosity factor if blending sequence 1 or 2 has been adopted. However, in presence of Na-AHA, blending sequence 1 may lead to the confinement of MWNT in the PA6 phase due to the specific interaction involved between MWNT and NA-AHA, which may be true even when blending sequence 2 has been adopted.

More explicitly, in presence of Na-AHA the tubes may be driven to the interface of the blends governed by the competitiveness of the above factors. Interestingly, on carefully looking at the SEM micrograph of the cryofractured and formic acid etched surfaces of blends with Na-AHA modified MWNT related to a specific blending sequence (blending sequence 1), we observed that the majority of the tubes were locked right at the interface of the PA6/Surlyn blends (see Figure 3).

It is well understood that specific interactions existing between $Na^+$ moieties of Surlyn and MWNT and the reactive coupling between acid end groups of PA6 and amine functionality of Na-AHA restricts the tubes at the interface during melt mixing.

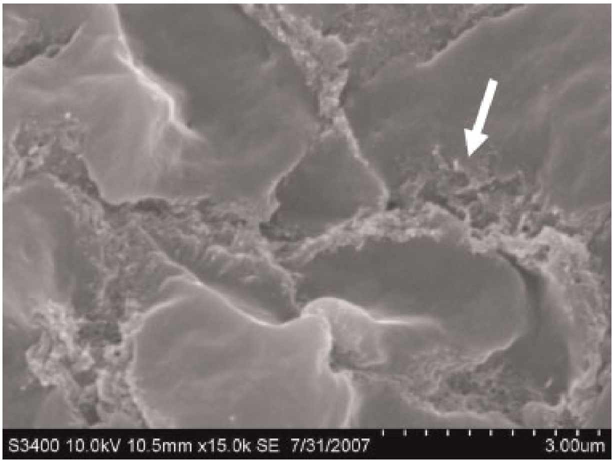

***Figure 3.***
SEM of N50MT3S50 showing the localization of MWNT at the interface of co-continuous blends of PA6 and Surlyn.

## AC Electrical Conductivity: Role of Specific Interactions

AC electrical conductivity measurements were carried out for the blends of PA6/Surlyn with MWNT in order to evaluate the frequency dependent electrical conductivity and are depicted in Figure 4a. The bulk conductivity of Surlyn, PA6 and 50/50 blends of PA6/Surlyn increases with increase in frequency as expected for insulating materials. The investigation of the effect of blending sequence on the bulk conductivity of the blends indicated that both blends with even 3wt% MWNT showed insulating behaviour. If one assumes that the conductivity in co-continuous blends is governed by 'double percolation' phenomenon then one could expect the conductivity of co-continuous 50/50 PA6/Surlyn blends with 1 wt% MWNT to be similar as that of 2 wt% MWNT filled Surlyn composites or 3 wt% MWNT filled PA6 composites should be similar as that of 50/50 PA6/Surlyn with 1.5 wt% MWNT composites. It is well understood that the agglomeration of MWNT and migration/redistribution of MWNT during melt mixing may prevent the formation of network-like structure in a specific phase in the blends.

It is well realized that strong inter-tube van der Waals' forces inhibit the uniform dispersion and network-like structure formation of MWNT in the polymer matrix. Hence, higher loadings of MWNT are required to reach the desired percolation threshold. It is believed that the filler usually restricts in the low viscous phase in co-continuous blends. In our case as the viscosity of the PA6 phase is much lower as compared to Surlyn (see Figure 1a), the tubes are expected to restrict in the PA6 phase in co-continuous blends of PA6 and Surlyn. At the same time the tubes are even expected to establish specific interactions with the $Na^+$ ionic moieties present in Surlyn. This would possibly lead to a situation where the tubes would migrate to the other phase or redistribute during melt mixing.

In order to overcome this complexity we employed a reactive modifier (Na-AHA) which is expected to establish 'cation- $\pi$' type of interaction between $Na^+$ of Na-AHA and $\pi$-electron clouds of MWNT and would involve in melt interfacial reactions between amine functionality of Na-AHA and the acid end groups of PA6 thereby restrict the MWNT in a specific phase during melt mixing.

The effect of blending sequence on the bulk electrical conductivity of the blends can be observed from Figure 4a. A dramatic

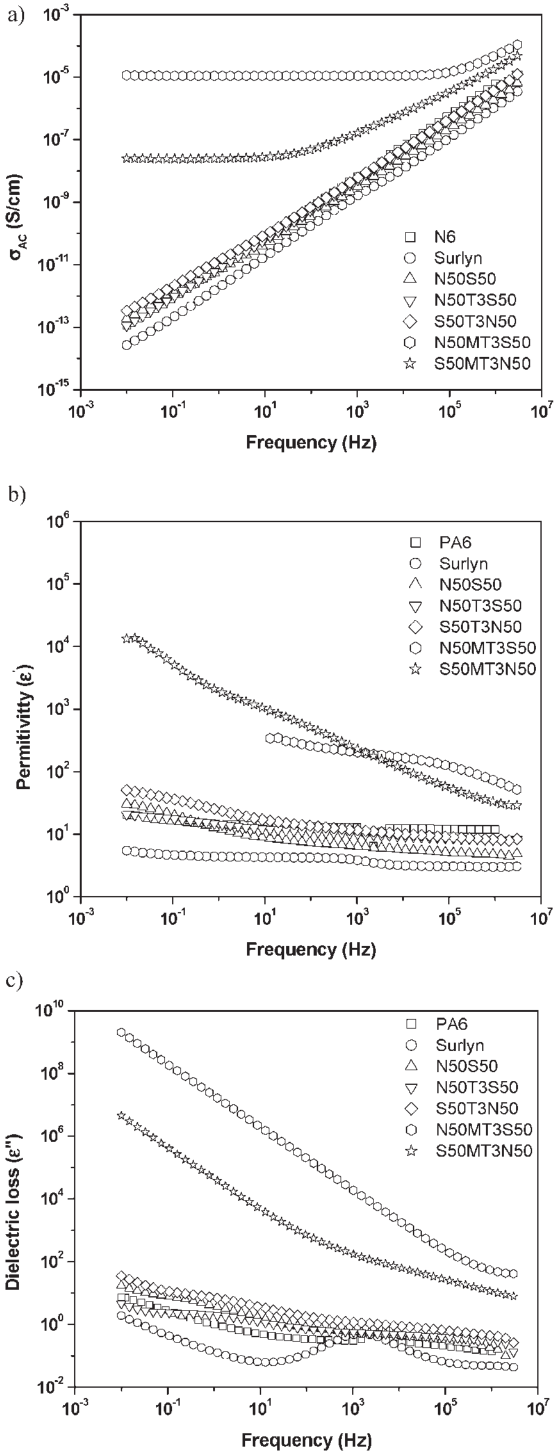

***Figure 4.***
(a) AC conductivity versus frequency plots, (b) permittivity versus frequency plots and (c) Dielectric loss spectra for PA6/Surlyn blends with MWNT.

response (nearly 7 orders of magnitude higher as compared to the neat blends) in the electrical conductivity in the blends is observed at 3 wt% with an increase in the cross over frequency ($\omega_c = 37500$ Hz) for blending sequence 1 where the MWNT was initially mixed with PA6 followed by Surlyn. The improved bulk conductivity in the blends related to a specific blending sequence can be attributed to the melt interfacial reactions next to the specific interactions involved during melt mixing.

The dielectric properties of the blends with MWNT are shown in Figures 4b&4c. Due to high AC conductivity in the sample (N50MT3S50), it was not possible to measure reasonable values of $\varepsilon'$ in the blends. However, it can be clearly seen that for pure PA6, Surlyn and 50/50 blends of PA6/Surlyn the $\varepsilon'$ values are nearly constant. Even with the blends with 3 wt% MWNT no significant changes in the $\varepsilon'$ values are observed whereas blends with Na-AHA modified MWNT show a significant different behaviour. Here $\varepsilon'$ is observed to decrease with increase in frequency. Two types of loss have been identified in polymers, the dipole-segmental loss and dipole group loss.[32] The appearance of loss is associated with the mobility of the polymer chains in the amorphous parts. It is believed that polar substituents in the side chains gives rise to dipole group loss which may also occur below the glass transition temperature of the polymer since the relaxation time for such groups is smaller than the main chain segments and hence they retain their mobility even at lower temperature where the segments in the main chain are practically immobile.[32] They manifest in an inflection in $\varepsilon'$ and a peak in the $\varepsilon''$ plots which can be clearly seen for neat Surlyn and PA6 in our case. It is also evident that below percolation threshold the $\varepsilon'$ values are nearly constant and there are small changes in $\varepsilon''$ values but show significantly different behaviour above percolation. At higher loading of MWNT, the restriction in the mobility of the chains is believed to be a dominant factor governing the $\varepsilon''$ values manifesting in significantly different behaviour for blends with 3 wt% (1:1, MWNT:Na-AHA).

## Specific interactions: FTIR and Raman Spectroscopic Analysis

Figure 5a shows the FTIR spectra for pure Surlyn and blends of PA6/Surlyn with MWNT. One can clearly observe the carbonyl stretch at ~1698 $\text{cm}^{-1}$ in pure Surlyn. Interestingly, we observe a strong peak shift corresponding to carbonyl group vibration for PA6/Surlyn blends with MWNT, which is presumably due to the existence of 'cation-$\pi$' type of interaction between the $Na^+$ ionic moieties in Surlyn and $\pi$ electron clouds of MWNT. An additional peak at ~1635 $\text{cm}^{-1}$ is also observed prominently in 50/50 PA6/Surlyn blends manifesting the reactive coupling between acid groups of Surlyn and the amine functionality of PA6 during melt mixing. One can even observe a weak shoulder at ~1635 $\text{cm}^{-1}$ in blends with MWNT. In blends with Na-AHA modified MWNT, the melt-interfacial reaction between acid groups of PA6 and amine functionality of Na-AHA occurs in addition to the reactive coupling between acid groups of Surlyn and the amine functionality of PA6. Hence it is difficult to differentiate the peaks corresponding to this vibrational stretch. In order to further investigate the specific interactions existing between Surlyn and MWNT and between Na-AHA modified MWNT and PA6 we also carried out Raman spectroscopic analysis. The MWNT used in this study show two strong Raman bands at ~1341 $\text{cm}^{-1}$ and ~1574 $\text{cm}^{-1}$ corresponding to tangential D and G bands respectively (See Figure 5b). Raman spectroscopic analysis (Figure 5b) further supports the interactions existing between the sodium ion in Surlyn ($Na^+$) and the $\pi$-electron cloud of MWNT manifesting in strong up-shifts in both G-band and D-band of MWNT in the composites. The effect of blending sequence can also be observed from Figure 4b. Interestingly, the maximum shift is observed in the blends with blending sequence 1 where in Na-AHA

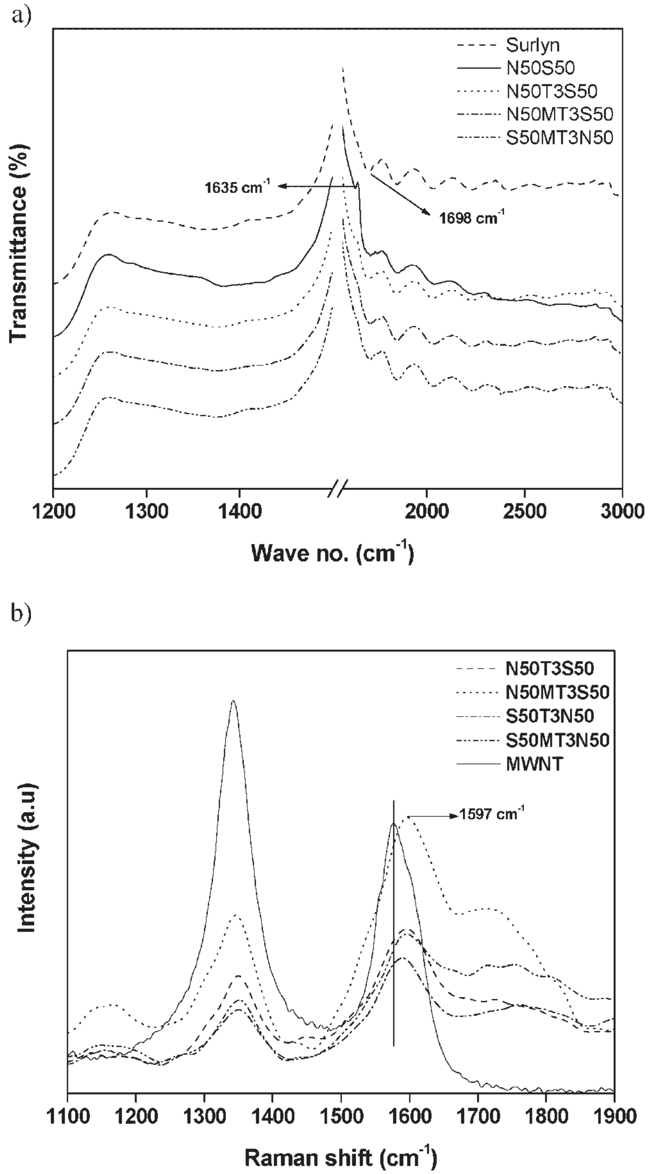

***Figure 5.***
(a) FTIR and (b) Raman spectra for PA6/Surlyn blends with MWNT.

modified tubes were initially mixed with PA6 followed by Surlyn. Moreover, the intensity of G bands in the blends with MWNT is observed to be higher as compared to purified MWNT manifesting the existence of specific interactions. The strong band corresponding to the carbonyl group at ~ 1698 cm$^{-1}$ also appears as shoulder in the blends of PA6/Surlyn with MWNT.

## Conclusions

MWNT were observed in the vicinity of the ionic domains in the Surlyn phase in the

PA6/Surlyn blends owing to the specific interactions where as in case of blends with Na-AHA modified MWNT, the clustering phenomenon could not be observed. Specific interactions induced dispersion of MWNT has been observed to facilitate uniform dispersion of MWNT in melt-mixed co-continuous blends of PA6 and Surlyn which was manifested in AC electrical conductivity measurements. The bulk electrical conductivity of the blends was observed to be significantly dependent on the blending sequence adopted during melt mixing. In addition, FTIR and Raman spectroscopic analysis revealed the existence of the specific interactions.

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