Effect of multiwall carbon nanotubes on the phase separation of concentrated blends of poly[(α -methyl styrene)-co-acrylonitrile] and poly(methyl methacrylate) as studied by melt rheology and conductivity spectroscopy

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Abstract

Thermally induced phase separation in concentrated lower critical solution temperature (LCST) blends of poly[(α -methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (P α MSAN/PMMA) in presence of multiwall carbon nanotubes (MWNTs) with different surface characteristics ($\sim$ NH₂ functionalized and polyethylene modified) was monitored by modulated differential scanning calorimetry, melt rheology, conductivity spectroscopy and microscopic techniques. At a concentration of 2 wt%, the MWNTs clearly reduce the macromolecular mobility of the blend components and induce phase separation at lower temperatures as compared to the neat blends. Electron microscopic images revealed that phase separation resulted in a selective thermodynamically driven localization of both types of MWNTs in the P α MSAN phase whereas they were randomly distributed in the mono-phasic materials. Hence, a percolative MWNT network was formed at much lower concentrations as compared to those needed for percolation in the blend components. However, the significant changes in viscosity and elasticity of the blend components, brought about by the MWNTs, can also affect morphology development. This way, effective percolation in the blends can be hindered, as was observed for the 60/40 blend with polyethylene coated MWNTs (PE-MWNTs). Finally, a dramatic transition from an insulating one-phasic material at room temperature to a highly conductive material in the melt was induced by the phase separation.

Keywords: blends; carbon nanotubes; phase separation; percolation; rheology; electrical conductivity

1. Introduction

Phase separation of polymer blends involves a complex interplay between thermodynamics and kinetics. This complexity can be further amplified by the addition of nanoparticles as they can alter the free energy of the system and can lead to a redistribution of polymer molecules between the particle surface and the bulk, depending on the affinity of the polymers for the particles [1-4]. These phenomena can affect the miscibility window of the phases and the kinetics of phase separation. In addition, nanoparticles can impart intriguing properties to the blends such as morphological stability, electrical conductivity, structural integrity etc. Hence, the effect of nanoparticles on the compatibility and the phase separation process has been the subject of several experimental studies and simulations [1-14]. For example, Balazs and co-workers [9] found numerically that hard mobile nanoparticles with a preferential affinity for one of the components, slow down the coarsening of the domains in the late stages of spinodal decomposition whereas particles with no preferential adsorption do not affect the phase separation kinetics. In the latter scenario i.e. in absence of adsorption of polymer chains depletion forces become dominant and could lead to particle-particle aggregation and hence induce phase separation. In addition, the effect of nanoparticles on phase separation characteristics such as critical temperatures, kinetics and morphology development was reported to depend on the particle size, concentration and the interaction between the particle and the host matrix [2,3,4,12,15]. Hence, assessing the interaction between the nanoparticles and the components is essential to gain a thorough understanding of the thermodynamics and kinetics of phase separation.

In the recent past, phase separation has been explored with several techniques including differential scanning calorimetry (DSC), microscopy, light transmission, light scattering, electrical conductivity and rheology [11,16,17,18]. In DSC, phase separation can often be detected by means of an endothermic peak or kink in the heat flow curves [11,17,19]. In

addition, if the enthalpic effects of demixing are sufficiently large, the kinetics of demixing can be probed with modulated DSC [17]. Rheological measurements have been widely employed to study the phase behavior of blends through the changes in linear viscoelastic properties as the system evolves from a homogeneous through a metastable to the phase-separated regime [20]. In the latter regime, polymer blends exhibit pronounced elastic properties, long relaxation times and a failure of the time-temperature superposition [20,21,22]. In this context, the point of phase transition can be inferred both qualitatively and quantitatively from rheological measurements using one of the many fingerprints. The most widely used one is the observation of a shoulder in the storage modulus (G') – frequency curve that appears at low frequencies upon phase separation [20,21,22]. Similarly, Cole-Cole plots (η' as function of η'' or G' as function of G'') or relaxation spectra show an additional relaxation at low frequencies in phase separated systems [16]. Other representations such as isochronal plots of G' with temperature that show either a clear change in slope or an inflection (depending on the dynamic asymmetry of the components) in the vicinity of the transition point are also used to determine the phase separation temperature [20,23]. In addition, the time evolution of the dynamic moduli under isothermal conditions has been extensively investigated to correlate the viscoelastic response of the blends with the resulting morphology development after bringing the blend into the unstable region of the phase diagram [20,24,25,26]. For example, Kapnistos [20] and Polios [25] showed that the storage modulus increases with time during the early stage of spinodal decomposition and decreases in the later stages due to the breakup of the interconnected domains. Kim et al. [26] observed that both the storage and loss modulus increase initially, followed by a decrease at longer time scales due to the coarsening of the cocontinuous structures. Particularly in the case of particle-filled blends for which optical techniques can often not be used, rheological techniques can provide essential information about the phase separation characteristics [8,10-14]. However, in the case

of dynamically symmetric blends, rheology can only pick up signals when the correlation length of the concentration fluctuations is large enough [10,13].

The potential of carbon nanotubes (CNTs) as filler in polymeric nanocomposites has widely been explored owing to their extraordinary combination of properties (for recent reviews see refs. [27,28]). As a result of their large aspect ratio, they can form an interconnected network at relatively low concentrations. The abundance of π -electron clouds and the large specific surface area of CNTs facilitate interactions with the matrix polymers. Recently, it was shown that the adsorption of macromolecular chains on the surface of CNTs in a binary blend can be partially irreversible due to the high desorption energy [29]. Hence, it is rather interesting to investigate phase separation in presence of CNTs as the co-existence of macromolecular chains on the surface of the CNTs could alter the thermodynamics as well as the kinetics of phase separation. Moreover, the dispersion state of CNTs can be manipulated using phase separation as a tool leading to percolation at low CNT concentrations [30]. Although there are ample reports addressing structure-property relations in polymeric blends/composites containing CNTs ([27,28] and references therein), to our knowledge, the effect of CNTs on thermodynamics and kinetics of phase separation has only received limited attention [8,10].

Phase separation of the neat lower critical solution temperature (LCST) blend of poly[(α -methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (P α MSAN/PMMA) was extensively studied in the past [24,31,32]. In our earlier investigations [30,33], we studied the percolation of various types of MWNTs in P α MSAN/PMMA blends and assessed the potential of MWNTs for coalescence suppression in 85/15 P α MSAN/PMMA blends [30]. In the present study, we investigate in detail the phase separation in concentrated 40/60 and 60/40 P α MSAN/PMMA blends in presence of different types of MWNTs as the system transits from a homogeneous mono-phasic state via a metastable to the phase-separated state. First, the state of dispersion of the MWNTs in the blends before and after phase separation and the phase-separated morphology

will be discussed. Subsequently, the phase separation temperature and kinetics will be determined. Finally, the resulting electrical and rheological percolation of the MWNTs will be addressed.

2. Experimental Part

2.1 Materials

Both poly- α -methylstyrene-co-acrylonitrile (P α MSAN, Luran KR2556) and polymethylmethacrylate (PMMA, Lucryl G77) were obtained from BASF. The blend P α MSAN-PMMA is miscible at low temperatures and the transition to a phase separated state is reported to occur at around 165 °C for blends containing 40 wt% P α MSAN and 175 °C for blends containing 60 wt% P α MSAN [31]. The characteristics of these polymers and the phase behavior of the neat blends have been extensively discussed in literature [31]. Two types of modified MWNTs were used in this study and were kindly provided by Nanocyl (SA, Belgium) [34]; the first type has an amine functionalisation (NH₂-MWNTs, NC3152, length: 600-700 nm, diameter: 9-10 nm, NH₂-functionalisation less than 0.5%); the second type (PE-MWNTs, NC9000, length: 1.2-1.5 μ m, diameter: 9-10 nm) is coated with an in-situ polymerized polyethylene (PE) layer and predispersed in high density polyethylene (HDPE). For functionalised MWNTs the surface free energy is of the order of 45 mN/m [35, 36]. The surface free energy at 220 °C is estimated to be 25.9 mN/m for PMMA and in the range of 27.4-34.5 mN/m for P α MSAN [30]. Hence, the NH₂-MWNTs are expected to be localized in the P α MSAN phase. Due to the non polar nature of PE [37], the PE-MWNTs might have a lower surface free energy and become more compatible with PMMA as compared to the NH₂-MWNTs. However, even for this type of MWNTs Pötschke et al. observed migration from the PE phase towards the PA phase with larger surface free energy [38] and Özdilek et al. observed selective localization of these MWNTs in the P α MSAN phase of PMMA-P α MSAN blends [33].

2.2 Preparation of the blends

Two sets of blends consisting of either 40 wt% or 60 wt% of P α MSAN in PMMA were prepared with or without MWNTs by melt-mixing using a 15cc DSM microcompounder at 200 °C (± 2 °C) with a rotational speed of 60 rpm for 20 min. All preparations were performed under nitrogen atmosphere in order to prevent oxidative degradation. It is important to note that the processing temperature of 200 °C is well above the cloud point of 165 °C for the 40/60 and 175 °C for the 60/40 P α MSAN/PMMA blends [31]. It was not possible to process them below their cloud point temperature due to limitations in the torque in the mini-extruder. The extrudate strands were melt-pressed at 160 °C (below the cloud point temperature) by means of a laboratory press (Collin). The melt-pressed samples of the neat blends were transparent and hence one-phasic.

2.3 Characterizations

Dynamic mechanical thermal analysis (DMTA) was performed using a Q800 (TA Instruments). Samples were prepared by compression molding disks of 0.85 mm thickness and cutting these to obtain the appropriate dimensions of 17x10 mm². A tensile force of 0.1 N preload was applied to the test specimen using a film tension clamp and dynamic oscillatory loading at a frequency of 10 Hz and with an amplitude of 0.05% strain was applied. Storage modulus (E') and $\tan \delta$ values were obtained during a temperature ramp of 3 °C/min. The change in slope in E' and the onset of the peak in $\tan \delta$ versus temperature curves were used to determine the T_g of the blends.

Modulated differential scanning calorimetry (MDSC) was carried out with a Q2000 (TA Instruments), using standard Al TZero pans containing 10 mg of sample. Before performing the experiments, the TZero, temperature, heat flow and heat capacity calibrations were performed with sapphire and indium standards. Temperature ramps from the homogeneous (120 °C) to the phase separated regime (260 °C) were performed to determine the phase separation temperature.

During the tests, the sample chamber was purged with nitrogen (50 ml/min). In DSC, the heat flow and hence the sensitivity can be increased by increasing the heating rate whereas lower heating rates result in an improved resolution of the heat flow peaks. Modulated DSC is an extension of standard DSC in which the applied temperature is modulated with a sine wave. In addition to the total heat flow signal, modulated DSC allows for the separation of the in-phase (reversing) and out-of-phase (non-reversing) parts of the heat flow signal, which can offer a combination of high sensitivity and high resolution [17]. In addition, quasi-isothermal MDSC measurements (with an average heating rate of 0°C) can be used to study the kinetics of phase separation [17]. Due to the absence of strong interactions such as hydrogen bonds, between P α MSAN and PMMA, their phase separation is accompanied by rather weak heat flow effects. Hence, a relatively high heating rate of 3 °C/min was found to be necessary to clearly pick up the phase separation. In addition to the constant average heating rate, the temperature was modulated with an amplitude of 2 °C and a period of 80 s.

The viscoelastic properties of the blends were studied using an AR2000ex stress-controlled rheometer (TA Instruments) with parallel plate geometry (25 mm diameter and 1 mm gap) under N₂ atmosphere. Isochronal dynamic temperature ramp measurements at a frequency of 0.1 rad/s, which is low enough to be in the terminal region [33], were performed from the homogeneous (120 °C) to the phase separated regime (220 °C) to determine the phase separation temperatures. Since low heating rates do not deteriorate sensitivity in rheology, a low heating rate of 0.3°C/min was selected to enable an accurate determination of the phase separation temperatures. The strain amplitude was within the linear viscoelastic region as determined *a priori*.

To investigate the kinetics of phase separation, 5 hour long time sweep experiments at an elevated temperature (220 °C) were performed at 1% strain and a frequency of 0.1 rad/s. G' showed almost time independent values after 5 hrs, reflecting completion of the phase

separation process. The resulting blend morphology and MWNT dispersion was characterized by small amplitude oscillatory measurements as a function of frequency.

Additional morphological analysis was performed by means of either field-emission gun (FEG) scanning electron microscopy (Philips XL30) or transmission electron microscopy (TEM, Philips CM 200 FEG). To investigate the dispersion of the MWNTs in the one-phasic blends, compression molded samples were cryofractured in liquid nitrogen and subsequently mounted on the SEM sample holder. The samples were gold sputtered to avoid charging. The phase separated samples were visualized with TEM since SEM did not provide sufficient contrast to distinguish the separate phases of PoMSAN and PMMA. For TEM, the compression molded samples (pressed at 160 °C in the one-phasic region) were first annealed at 220 °C for 5 hrs (to allow complete phase separation) and subsequently quenched to freeze the morphology. The samples were then sectioned by ultramicrotomy to thin lamellae (100 nm) and mounted on a Cu-TEM grid with holey carbon film.

Conductivity spectroscopy measurements were performed both at room temperature and at an elevated temperature of 220 °C on compression molded samples (16.5 mm diameter and 1.75 mm thickness) in the frequency range of 10^{-2} - 10^7 Hz using a Novocontrol Alpha high resolution dielectric analyzer. The instrument measures the complex impedance spectra of the sample. Complex conductivities were calculated from the complex impedance values by taking the sample geometry into account. In this work, the DC conductivity will be used to characterize the sample response. The latter is obtained from the real part of the complex conductivity at low frequencies, as described by Leys et al. [39]. For conductivity spectroscopy measurements at 220 °C, the samples were placed between two brass plates, separated by a circular Teflon spacer to maintain a fixed sample geometry in the melt state. The same spacer was used for all measurements in order to eliminate systematic errors in sample dimensions. A Novocontrol Quatro temperature controller, which uses nitrogen gas flow, was used to control the sample

temperature with an accuracy of 0.1 °C. Room temperature conductivities were measured for the miscible blends with both types of MWNTs. In addition, frequency scans were performed at a fixed temperature of 220 °C during phase separation for 5 hours. As each frequency scan took about 3 minutes, 100 such scans were performed.

3. Results and discussion

3.1 State of dispersion of MWNTs in the mono-phasic systems as probed by DMTA and FEG-SEM

To evaluate the effect of phase separation on the localization of MWNTs in the blends one should know their distribution in the mono-phasic blends, which are the starting materials for phase separation. As mentioned above, the blends were melt-mixed at 200 °C, which is well above the cloud point for both the 40/60 and 60/40 blends, but they were melt-pressed at a temperature in the one-phasic region (160 °C) prior to further characterizations. It is envisaged that this methodology (i.e. squeeze flow deformation) allows the phase separated domains (generated during melt mixing) to mix again or at least transform into micro heterogeneities [31]. The fact that the melt-pressed samples of the neat blends were transparent, suggests homogeneity. However, the nanocomposites were dark thus requiring more quantitative methods to assess homogeneity. Hence, the T_g of the melt-pressed samples was determined. It has been reported that DMTA can resolve separate T_g s of matrix and dispersed phase for domain sizes on the segmental level (order of 5-10 nm) [40]. In Fig. 1 the storage modulus and tan delta as a function of temperature are shown for neat blends and blends with PE-MWNTs or NH₂-MWNTs. It is evident from Fig. 1 that the melt-pressed blends indeed show a single T_g (one peak in tan δ versus temperature curves) confirming their homogeneity. A change in slope in the E' versus temperature curves (as indicated in Fig. 1) is evident at ~118 °C for 40/60 and ~120 °C for 60/40 neat P α MSAN/PMMA blends. The onset of the peak in the tan δ versus temperature

curves also coincides with these values. As expected, the T_g s of the blends are between those of the components (T_g of P α MSAN is ~ 124 °C and T_g of PMMA is ~ 109 °C) [31]. Furthermore, it can be seen from Fig. 1 that 1 wt% of MWNTs has a limited effect on the blend T_g whereas with 2 wt% NH₂-MWNTs the rise in T_g is substantial in both blends, essentially indicating reduced macromolecular chain mobility in presence of MWNTs in the composites. The reinforcement effects of MWNTs (especially in the glassy regions) can be judged from the values of the storage modulus (E') of the blends. All the blends investigated here, except for the 60/40 P α MSAN/PMMA blend with PE-MWNTs, displayed a substantial increase in the E' values (especially in the glassy region) in presence of MWNTs. For the 40/60 blends, PE-MWNTs at 1 wt% result in a slightly larger increase of E' as compared to NH₂-MWNTs at 1 wt%. This behaviour is in line with the expectations based on the longer length of the PE-MWNTs. The increase in the dynamic mechanical properties indicates a good dispersion and strong interactions between the MWNTs and the components of the blends. However, the nature of the interactions with the components can be strongly dependent upon the surface functionality of the MWNTs. The reduction of E' of the 60/40 blend with 1 wt% PE-MWNTs points to less good interactions between the MWNTs and the blend components in case of this system. The PE-MWNTs are coated with an in-situ polymerized PE layer and predispersed in HDPE. Presumably, the more polar nature of the NH₂-MWNTs can lead to specific/non-specific interactions with the major blend component P α MSAN (such as π - π interactions) in the 60/40 blends. The latter could possibly lead to better reinforcement of the blends due to a good dispersion.

Electron microscopy can provide further information on the state of dispersion of the MWNTs in the mono-phasic materials. The insets of Fig. 1 are FEG-SEM images of the cryofractured melt-pressed blends with 2 wt% NH₂-MWNTs. One can clearly observe a random

distribution of the MWNTs, appearing as white dots, representative of the conductive material in the bulk.

Fig. 1. Storage modulus and $\tan \delta$ as a function of temperature for P α MSAN/PMMA blends with NH_2 -MWNTs or PE-MWNTs a) 40/60; b) 60/40 (insets show the FEG-SEM images of the composites containing 2 wt% NH_2 -MWNTs).

3.2 State of dispersion of MWNTs and morphology of the phase-separated systems as probed by TEM

The blend morphology after phase separation and the corresponding dispersion of the MWNTs was studied by collecting TEM images of samples that were annealed for 5 hours at 220 °C, thus allowing phase separation to proceed until full completion. TEM images of P α MSAN/PMMA blends with different MWNTs at 2 wt% are shown in Fig. 2. Although the samples were not stained, the two components had sufficient contrast. The P α MSAN component appears dark while the PMMA appears bright in the bright-field TEM images. The 40/60 P α MSAN/PMMA blends in presence of MWNTs (at 2 wt%) show a cocontinuous morphology (see Fig. 2a-b). A similar morphology type was observed by other authors for the neat P α MSAN/PMMA blend with this composition, after annealing at 220 °C for either 10 minutes or 4 hours [31,41]. On the contrary, the 60/40 P α MSAN/PMMA blends containing either NH₂-MWNTs or PE-MWNTs exhibit a droplet-matrix type of morphology (see Fig. 2d-e). This morphology is completely different from that observed in literature for the neat 60/40 P α MSAN/PMMA blends for which cocontinuous morphologies were reported after 10 and 100 min of annealing [24,31]. This might indicate that the presence of MWNTs affects the morphology type obtained after phase separation. It is envisaged that selective localization of nanoparticles in the blends can alter the viscosity (or elasticity) ratio which can further significantly affect the resulting morphology. An estimation of these parameters can also shed light on the phase inversion concentration and will be discussed in more detail in Section 3.5. However, as morphology studies for neat 60/40 P α MSAN/PMMA blends in literature are limited to 100 min of annealing, the neat 60/40 blend was subjected here to the same annealing protocol as that used in the present work for the MWNT-containing blends. The neat blends also showed a droplet-matrix morphology after 5 hours of annealing (see Fig. 2c). This indicates the breakup of the initially formed cocontinuous structure into a droplet-matrix morphology,

irrespective of the presence of MWNTs. As can be seen in Figs. 2c-e, this formation of a droplet-matrix morphology by breakup rather than nucleation and growth of small droplets, can result in morphologies with a broad distribution of droplet sizes. When comparing Figs. 2d and 2e, clear differences in droplet size and droplet size distribution can be seen for blends with either 2 wt% NH₂-MWNTs or 2 wt% PE-MWNTs. This suggests the occurrence of breakup at different stages of the coarsening process, leading to largely different final morphologies. This aspect will further be investigated by studying the kinetics of phase separation (see Section 3.4.).

From the high resolution TEM images in the insets of Fig. 2 it is evident that both types of MWNTs are selectively localized in the P α MSAN phase of the blends, irrespective of the final morphology. It is worth pointing out at this stage that the localization of MWNTs in the PAMSAN phase is energetically favorable from a thermodynamic point of view (Section 2.1). The observed localization is thus a clear mandate to the fact that MWNTs migrate (or redistribute) to the more preferred phase during phase separation. This thermodynamically driven migration of MWNTs leads to an increase in their local concentration in a specific phase which facilitates their formation of network-like structures in the blends. In this context, dynamic frequency sweeps and electrical conductivity spectroscopy can be used as a probe to obtain further insight in the percolative network-like structure formation of MWNTs in the P α MSAN/PMMA blends (see Sections 3.5 and 3.6).

Fig. 2. TEM images of phase separated PaMSAN/PMMA blends a) 40/60 with 2 wt% NH₂-MWNTs; b) 40/60 with 2 wt% PE-MWNTs; c) 60/40 neat blends; d) 60/40 with 2 wt% NH₂-MWNTs; e) 60/40 with 2 wt% PE-MWNTs.

3.3 Effect of MWNTs on phase separation temperatures

The effect of nanoparticles on the phase separation temperature of LCST-type blends was extensively discussed by Ginzburg [4,6]. According to this model the total free energy of the system (blend with nanoparticles) depends on the polymer-polymer, particle-particle and polymer-particle interactions. Though this model describes the stability (or the free energy) of the homogeneous phase, it neglects the effect of particle ordering or segregation on the polymer-particle interactions. In the case of MWNTs, it is well understood that they are dispersed as an exfoliated network-like structure or in smaller bundles in a polymer matrix, where particle ordering is a common phenomenon even at very low concentrations. This is due to their high aspect ratio which facilitates the formation of a percolative network-like structure even at very low concentrations [27]. Interestingly, in the PaMSAN/PMMA blends the MWNTs were observed to be randomly distributed in the bulk in case of one-phasic materials (Figure 1)

whereas during phase separation the thermodynamic forces drive the MWNTs to migrate to their preferred phase, resulting in network-like structures (Fig. 2). It is envisaged that this preference of the MWNTs for one of the blend components and their redistribution in the blend, might affect the occurrence of phase separation. These effects are however not yet described by the available models. Hence, the effect of the presence of MWNTs in the blends on the phase separation temperatures is studied here in more detail.

3.3.1 As probed by MDSC

To determine the phase separation temperatures of neat P α MSAN/PMMA blends and blends filled with MWNTs, MDSC scans with a heating rate of 3 °C/min were performed. For the present blend, separation of the heat flow signal in the reversing and non-reversing contributions did not improve the sensitivity or resolution. Hence, the total heat flow is used to characterize phase separation. This total heat flow is similar to the heat flow that would be obtained in a standard DSC experiment. Heat flow curves for 60/40 P α MSAN/PMMA blends are shown in Fig. 3a. It can be seen from this figure that at the temperature at which phase separation is expected (175 °C), an endothermic peak starts in the heat flow signal. Similar endothermic peaks or kinks at the phase separation temperature were observed by others [11,17,19]. The relation between this endothermic peak and phase separation was confirmed by the absence of any peak in the second heating ramp of a phase-separated sample of which the morphology was frozen by quenching. At first glance, the neat 60/40 blend and the corresponding blends filled with PE-MWNTs or NH₂-MWNTs in Fig. 3a show a heat flow peak in the same temperature interval. To characterize and compare this in more detail, the extra heat flow originating from phase separation was calculated by subtracting the baseline (straight dashed lines in Fig. 3a). The thus obtained extra heat flow is plotted in Figs. 3b and 3c for 60/40 P α MSAN/PMMA and 40/60 P α MSAN/PMMA blends respectively. It can be seen that for all blends phase separation starts at about 160 °C and is completed at 220 °C, with a maximum at

187 °C and 183 °C for neat 60/40 and 40/60 blends respectively. The maxima (denoted as T_{DSC}) of all the blends investigated here are listed in Table 1. T_{DSC} is higher than the phase separation temperatures obtained by Laun et al. [31] from the optical appearance of the blends after 32 hours of annealing under isothermal conditions. This difference is caused by the fast heating rate in the present experiments [19]. The major conclusion from Figs. 3b and 3c is that the T_{DSC} temperatures at which the extra heat flow is maximum for 60/40 and 40/60 PαMSAN/PMMA blends are not affected by the presence of 1 wt% or 2 wt% PE-MWNTs or NH₂-MWNTs. Although the extra heat flow curves as shown in Figs. 3b and 3c could be obtained in a reproducible way, it appeared that the resolution was too low to accurately determine the onset temperature of phase separation. Hence, to determine the latter with a higher resolution, rheology experiments were performed at a lower heating rate (see next section).

Fig. 3. a) DSC curves obtained with a heating rate of 3°C/min. Curves are shifted vertically to enable comparisons. Straight dashed lines indicate the baselines; b) Smoothed extra heat flow due to phase separation for 60/40 blends with different concentrations and types of

MWNTs; c) Smoothed extra heat flow due to phase separation for 40/60 blends with different concentrations and types of MWNTs.

PαMSAN/PMMA blends	T_{DSC} (±1 °C)	T_{rheo from tanδ} (±1 °C)	T_s from FL (±1 °C)
40/60	183	173	215
40/60 + 1 wt% PE-MWNTs	183	171	216
40/60 + 1 wt% NH ₂ -MWNTs	183	173	215
40/60 + 2 wt% PE-MWNTs	184	--	
40/60 + 2 wt% NH ₂ -MWNTs	181	169	210
60/40	187	176	215
60/40 + 1 wt% PE-MWNTs	184	173	214
60/40 + 1 wt% NH ₂ -MWNTs	188	171	215
60/40 + 2 wt% PE-MWNTs	186	--	
60/40 + 2 wt% NH ₂ -MWNTs	186	167	210

Table 1 Comparing the critical phase separation temperature obtained from rheology (T_{rheo} and T_s) and differential scanning calorimetry (T_{DSC})

3.3.2. As probed by melt rheology

The effect of MWNTs on the phase separation temperature was also investigated rheologically by performing isochronal temperature ramp measurements with a heating rate of 0.3 °C/min at a fixed frequency of 0.1 rad/s and a strain amplitude in the linear viscoelastic region (determined *a priori*). This technique is widely used to determine the phase separation temperatures in complex systems (e.g. polymer blends with nanoparticles) as sample turbidity makes it rather difficult to determine the cloud point in such materials. In the blends investigated here only a limited interval of temperatures was studied in the homogeneous region due to the proximity of the LCST to T_g . As the system approaches the phase separation temperature the viscoelastic properties of the blend change substantially. A typical example illustrating the effects of phase separation is shown in Fig. 4a for the neat 60/40 PαMSAN/PMMA blend. At low temperatures the dynamic moduli (G' and G'') decrease with increasing temperature due to enhanced chain mobility. As the phase boundary is approached, competing forces (chain

mobility and thermodynamics) result in either a distinct slope change or an upturn in G' depending on the dynamic asymmetry of the blends (contrast in T_g) [20]. G'' exhibits a similar behavior however, with a phase lag (see Figure 4a). It should be noted though that apart from the dynamic asymmetry, the change in slope in G' is also very sensitive to the experimental conditions e.g. heating rate and frequency employed during the measurements and more importantly the interfacial tension in the generated two-phasic system [20]. Since the blends investigated here represent weak dynamic asymmetry, phase separation shows up as a slope change rather than a distinct peak in the curves of the dynamic moduli versus temperature. In this case, deducing the phase separation temperatures from the plots of $\tan\delta$ as a function of temperature appears to be more accurate since this variable shows a linear behavior (on log scale) in the pretransitional region and deviates from linearity upon phase separation. This deviation is quite prominent (Figs. 4d and 4e) in contrast to the slope change in G' versus temperature (Figs. 4b and 4c) and its occurrence will be referred to as the rheological phase separation temperature (T_{rheo}) in this paper.

Table 1 lists the phase separation temperatures obtained from temperature dependent $\tan\delta$ plots for the various blends investigated here. For the blends with 1 wt% MWNTs, the rheological data show limited effects of the MWNTs on the phase separation temperatures, although there is a tendency for a decrease of the phase separation temperature. However, for the blends with 2 wt% NH_2 -MWNTs, a clear reduction of the phase separation temperature can be observed. This decrease is more prominent in the case of the 60/40 P α MSAN/PMMA blends. It is noteworthy that for the blends with 2 wt% NH_2 -MWNTS a distinct effect of the MWNTs on the T_g of the blends was also present (Fig. 1), confirming the effect of the nanoparticles on the chain dynamics of the polymer components for these systems. A similar reduction of the phase separation temperatures was also observed for P α MSAN/PMMA blends containing thermally reduced graphene sheets [14]. Also in this case, the graphene sheets showed a preferential

localization in the P α MSAN phase after phase separation [14]. In that case, effects were however already clear at concentrations of 1wt%, which might be caused by the larger surface to volume area of platelets as compared to tubes. It is worth pointing out that the phase separation temperatures of the neat blends determined from the temperature ramp experiments, are still slightly higher than the cloud point temperatures, as found by Laun et al. [31]. This is most probably caused by the fact that the elastic contribution of concentration fluctuations in dynamically weakly asymmetric blends is small. Hence, a sufficient amount of interface has to be formed before the elasticity originating from the interface rather than concentration fluctuations can be picked up in the rheological signal.

In addition to the onset temperature of phase separation, the dynamic temperature measurements also allow to obtain the spinodal phase separation temperature (T_s) by using the theoretical approach of Fredrickson and Larson (FL) [23,42]. The theory yields the following expressions for the dynamic storage (G') and loss moduli (G''), respectively:

$$G' = \frac{k_B T \omega^2}{1920\pi} \left[\frac{1}{3} \left\{ \frac{R_{g1}^2}{\phi N_1} + \frac{R_{g2}^2}{(1-\phi)N_2} \right\} \right]^{1/2} \left[\frac{1}{\phi a_1^2 W_1} + \frac{1}{(1-\phi)a_2^2 W_2} \right]^2 [2(\chi_s - \chi)]^{-5/2} \quad (1)$$

$$G'' = \frac{k_B T \omega^2}{240\pi} \left[\frac{1}{3} \left\{ \frac{R_{g1}^2}{\phi N_1} + \frac{R_{g2}^2}{(1-\phi)N_2} \right\} \right]^{-1/2} \left[\frac{1}{\phi a_1^2 W_1} + \frac{1}{(1-\phi)a_2^2 W_2} \right] [2(\chi_s - \chi)]^{-1/2} \quad (2)$$

where, χ and χ_s designate the interaction parameter and the interaction parameter at the spinodal point respectively. R_{gi} denotes the radius of gyration of species i , N_i is the number of segments, W_i is the rate of motion of the subunit of length a_i (is of the order 10^9 - 10^{11} s $^{-1}$ for polymer melts). Assuming the following expression for the interaction parameter χ :

$$\chi = A + \frac{B}{T} \quad (3)$$

the following relation can be obtained:

$$\left(\frac{G''^2}{T G'} \right)^{2/3} = \frac{B}{C} \left(\frac{1}{T_s} - \frac{1}{T} \right) \quad (4)$$

where C is given by:

$$C = \left(\frac{45\pi}{k_B} \right)^{2/3} \left[\frac{a_1^2}{\phi} + \frac{a_2^2}{1-\phi} \right] \quad (5)$$

A linear relationship can be obtained by plotting $\left(\frac{G''^2}{TG'} \right)^{2/3}$ versus $\frac{1}{T}$ and the intercept with the horizontal axis yields the spinodal temperature T_s . A typical example illustrating the technique of obtaining the T_s from the FL plots is shown in Figure 4f for a 60/40 PαMSAN/PMMA blend. The T_s for the different blends investigated here are listed in Table 1. Similar to the results of the other techniques, the T_s is only lowered as compared to that of the neat blends in the case of blends with 2 wt% MWNTs. In summary, MWNTs (at 2 wt%) were observed to induce phase separation in both 40/60 and 60/40 PαMSAN/PMMA blends at lower temperatures as compared to the neat blends.

Fig. 4. a) Dynamic moduli as a function of temperature at 0.1 rad/s and 0.3 K/min for PαMSAN and neat 60/40 PαMSAN/PMMA blends; G' as a function of temperature at 0.1 rad/s and 0.3 K/min for b) 40/60; c) 60/40 PαMSAN/PMMA blends with different MWNTs; $\tan\delta$ as a function of temperature for d) 60/40; e) 40/60 PαMSAN/PMMA blends with different MWNTs; f) Fredrickson-Larson plots for the neat 60/40 blend.

3.4 Phase separation kinetics as probed by timesweep measurements

First, it was attempted to follow the phase separation kinetics at 220°C by means of MDSC, similar to the work of Dreezen et al. [17]. However, the change in heat capacity during phase separation was too limited for this system to obtain reliable information. Alternatively the kinetics was studied by means of rheology, more specifically time sweep experiments were performed with a fixed frequency (0.1 rad/s) and strain (1%) after a stepwise increase in temperature from room temperature to 220 °C. It has been reported that at this temperature, both the neat blends (40/60 and 60/40 PαMSAN/PMMA) phase separate by spinodal decomposition [31]. It is envisaged that during the early stages of spinodal decomposition, G' rises due to an increase in both concentration fluctuations and specific interfacial area. However, in the late stages of spinodal decomposition, G' decreases due to interfacial tension driven coarsening or breakup of the cocontinuous structure to a droplet-matrix structure [20,24,25,26] until steady state conditions are reached [24]. Fig. 5a shows the time evolution of G' for neat 40/60 and 60/40 PαMSAN/PMMA blends. It is evident from Fig. 5a that for both blends, only the signals from the late stages of spinodal decomposition could be picked up i.e. the interfacial tension driven

coarsening of co-continuous structures. Similar observations were also reported by Vinckier and Laun [24]. The curves of the dynamic moduli versus time do not allow for a differentiation between a cocontinuous morphology, as observed for the 40/60 blend or a droplet-matrix type of morphology, as observed for the 60/40 blend. This indicates that breakup of the cocontinuous structure occurs only after rather long annealing times, at which the structure has already substantially coarsened and the interfacial area is not too much reduced by the transition to spherical droplets. The difference in the absolute value of the dynamic modulus of 60/40 versus 40/60 P α MSAN/PMMA blends should not be interpreted as a manifestation of differences in phase structure, as it is known that P α MSAN is more elastic than PMMA [31].

The evolution of the dynamic modulus during phase separation changes dramatically in the blends in presence of MWNTs, as can be seen in Figs. 5b-e. For the 40/60 blends with a cocontinuous structure, the reduction in dynamic modulus as a function of time can only be noticed for the blend with a concentration of NH₂-MWNTs as low as 0.5 wt% (see Fig. 5g). Interestingly, even for this blend, the dynamic modulus starts to increase as a function of time after about 10 min. For blends with larger concentrations of MWNTs, G' increases as a function of time during the complete annealing experiment of 5 hours (see Fig. 5b). With increasing concentration of MWNTs, a corresponding increase of the dynamic modulus is found. For the highest concentration of MWNTs, moduli that are about 500 times larger than that of the neat blend are obtained. Based on the morphology of the blends containing 2 wt% MWNTs (Figs. 2a and 2b), this large increase in storage modulus can not originate from the slightly increased interfacial area due to the finer morphology as compared to that of the neat blend. In addition, it is not expected that MWNTs can increase the interfacial tension of the blend to such a large extent that it could explain this large storage modulus. However, it is known that adding fillers of nanoscopic dimensions to polymers can increase the elasticity of the material significantly, particularly above the percolation threshold of the filler. The percolation thresholds of NH₂-

MWNTs and PE-MWNTs in the P α MSAN phase are $\sim 2\text{-}3$ wt% [30] and $\sim 0.5\text{-}1$ wt% [33] respectively. Hence, the thermodynamically driven migration of MWNTs to the P α MSAN phase during phase separation is expected to increase their effective concentration. This effective rise in the concentration is by a factor of ~ 2.5 in the 40/60 blends, which results in concentrations well above the percolation threshold of both MWNTs in P α MSAN. Consequently, the network of MWNTs is also expected to increase the melt elasticity of the blends as compared to that of the neat blends and can presumably mask the microstructural developments which otherwise can be judged from the time evolution of G' . Moreover, at an elevated temperature the dynamic percolation of MWNTs plays a dominant role in the formation of a 'network-like' structure in the composites. To gain insight, G' as a function of time was monitored for the filled P α MSAN homopolymer with 2 wt% NH₂-MWNTs (see Fig. 5e). Interestingly, the P α MSAN/PMMA blends with only 0.5 wt% of MWNTs exhibit significantly higher G' values as compared to P α MSAN with 2 wt% NH₂-MWNTs although the effective concentration of NH₂-MWNTs in the P α MSAN phase of the blend is expected to be only 1.25 wt%. This clearly shows that the effects on the blend storage modulus of phase separation induced localization of NH₂-MWNTs in one of the blend phases exceeds the mere concentration effect. This could partially be caused by a reduction of the morphological coarsening, which allows for a larger amount of interface in the MWNT-filled blend as compared to the neat blend. However, these effects are not sufficient to explain the significant increase in G' . Based on the TEM images in Fig. 2b, it can be concluded that the presence of the PMMA domains, well dispersed throughout the polymer blend, drives the MWNTs towards the center of the P α MSAN domains (energetically favored phase), thereby further facilitating the formation of a percolative MWNT network. It is worth noting that PE-MWNTs percolate better in P α MSAN ($\sim 0.5 - 1$ wt%) as compared to NH₂-MWNTs. This early onset of percolation can be related to the filler dimensions. The length of PE-MWNTs is higher

than that of NH₂-MWNTs by a factor two. Hence, a larger storage modulus is also obtained for the blend with 2 wt% PE-MWNTs as compared to that with 2 wt% of NH₂-MWNTs (Figure 5b).

Finally, Fig. 5 shows that despite the fast increase of the modulus at short time scales, it takes much longer time to reach a steady state in the blends with MWNTs; in the neat blends, it takes less than 150 min for G' to reach its saturated stage (Fig. 5a) whereas it takes more than 200 min for blends with 2 wt% MWNTs (Fig. 5b). Two different scenarios have been identified that can affect the process of phase separation in presence of nanoparticles [5-6]. In one case in which nanoparticles move randomly throughout the system it is envisaged that the domain growth is disturbed and this phenomenon is often termed as ‘weak coupling’. In contrast, if the nanoparticles are thermodynamically driven to a specific phase, often termed as ‘strong coupling’, the domain growth is believed to be slowed down instead of arrested. In our case the latter scenario i.e. ‘strong coupling’ is believed to be the dominant mechanism affecting phase separation. However, the slow dynamics of MWNTs in these high viscous polymer melts, will also lead to slow structural reorganizations of the MWNT network, which could cause a gradual but very slow increase of the storage modulus with time, as observed in Fig. 5.

In the 60/40 blends, that are characterized by spinodal decomposition into a cocontinuous structure, followed by breakup of this structure into a droplet-matrix type of morphology, a slightly different evolution of the storage modulus is obtained in some cases. For the blends with NH₂-MWNTs (Fig. 5d), an increase of the storage modulus with time can be observed for the two concentrations of MWNTs. Moreover, the values of G' are of the same order of magnitude as those of 40/60 P α MSAN/PMMA blends (Fig. 5b). Similar to those blends, the large values of G' point to the formation of percolated MWNT networks. However, for the 60/40 blend with 2 wt% of PE-MWNTs, a clear decrease of the storage modulus at short annealing times is observed and a reversal of the evolution of G' only occurs after about 25 minutes. This blend also shows a remarkably lower value of the storage modulus as compared to the other blends. It

can be noted here that this blend is also the only one for which the elastic modulus E' of the one-phasic blend in the glassy region showed lower values as compared to that of the neat blend (Fig. 1), indicating weak interactions and/or less good dispersion of the PE-MWNTs in this blend. Based on an effective concentration of PE-MWNTs of 3.3 wt% in the 60/40 P α MSAN/PMMA blend, percolation of the nanotubes and large values of G' would be expected. However, the absence thereof suggests that MWNT network formation is clearly prohibited, which allows coarsening to proceed much further, resulting in larger droplets, as is confirmed by the TEM images in Figs. 2c-e. The kinetics of fibril breakup processes is closely related with the interfacial tension, but also matrix viscosity and elasticity play a role [43]. Hence, to understand the effects of the different MWNTs on the fibril breakup process, the effects of these MWNTs on the rheology of the blend components should be known. This will be discussed in more detail in Section 3.5.

Fig. 5. Time evolution of G' at 0.1rad/s and with 1% strain for a) neat 40/60 and 60/40 blends; b) 40/60 blends with MWNTs; c) 60/40 blends with NH₂-MWNTs; d) 60/40 blends with PE-MWNTs; e) filled homopolymers versus phase separated systems.

In summary, the phase separation process facilitates the increase in effective concentration of MWNTs in one phase of the blends and the viscoelastic properties are dominated by the network of MWNTs rather than the concentration fluctuations.

3.5 Percolation and effects of MWNTs on the phase inversion concentration

The changes in the viscosity (and elasticity) ratios due to selective filling above a critical value can affect the phase inversion concentration and the evolution of cocontinuous structures by means of fibril breakup processes [43,44]. Fig. 6 compares the complex viscosity (η^*) and G' at ω_{eval} (0.039 rad/s) for the components with MWNTs. The zero shear viscosities of P α MSAN and PMMA at 220 °C are 10550 Pas and 6065 Pas respectively. It is evident from Fig. 6a that the effective increase in η^* and G' of P α MSAN in case of PE-MWNTs is quite significant in contrast to NH₂-MWNTs, particularly above the percolation threshold of the filler. For instance at 2 wt% PE-MWNTs, the effective rise in η^* ($\eta^*_{\text{P}\alpha\text{MSAN/PE-MWNTs}}$: 2.3E8 Pa s; $\eta^*_{\text{P}\alpha\text{MSAN/NH}_2\text{-MWNTs}}$: 16070 Pa s) and G' ($G'_{\text{P}\alpha\text{MSAN/PE-MWNTs}}$: 7679 Pa; $G'_{\text{P}\alpha\text{MSAN/NH}_2\text{-MWNTs}}$: 60.3 Pa) of the P α MSAN phase is several orders of magnitude higher as compared to NH₂-MWNTs. This can be attributed to the larger length of the PE-MWNTs which facilitates the formation of a percolated network.

However, if filler dimensions would be the only factor, similar behavior would be expected for the PMMA phase (see Fig. 6b). On the contrary, in PMMA a higher percolation threshold for PE-MWNTs and lower values of viscosity and elasticity as compared to NH_2 -MWNTs were observed. The $-\text{NH}_2$ functional moieties on the MWNT surface can presumably interact with the $-\text{O}-\text{C}=\text{O}$ of PMMA [45] leading to better dispersion. Hence, the rheological percolation threshold is governed by a complex interplay between the intrinsic characteristics of the nanoparticles and the extent of interaction between the nanoparticles and the polymer matrix. In the case of 60/40 P α MSAN/PMMA blends, the selective localization of the MWNTs in the P α MSAN matrix phase after phase separation caused a substantial increase in the viscosity and elasticity of this phase, especially in the case of PE-MWNTs. This change in the rheological behavior has resulted in a coarser morphology and inhibited percolation of the MWNTs. In this context, conductivity spectroscopy measurements will provide additional information on the formation and destruction of the MWNT network in the blends during phase separation (see Section 3.6).

Fig. 6. Complex viscosity (η^*) and G' at ω_{eval} (0.039 rad/s) of (a) P α MSAN with different MWNTs; b) PMMA with different MWNTs.

To show the effects of phase separation on the formation of percolative MWNT networks in the different blends more clearly, their linear viscoelastic behavior with MWNTs after the complete phase separation i.e. after 5 hrs at 220 °C is shown in Fig. 7. G' at low frequencies becomes almost independent of the test frequency above a critical concentration of MWNTs which is a typical solid-like response of the nanocomposites. It has been reported that interconnected structures of anisometric fillers result in a yield stress [27] and a plateau in G' and G'' manifesting the transition from 'liquid-like' to 'solid-like' elastic behavior in the filled blends. The G' as a function of frequency for 40/60 blends with different MWNTs are shown in Fig. 7a-b respectively. A plateau in the low frequency regime in G' is observed at 0.5 wt % MWNTs in 40/60 cocontinuous blends, irrespective of their type (Figs. 7a-b). Similar observations were made above 1 wt% in 60/40 blends with NH₂-MWNTs (Fig. 7c). However, for 60/40 blends with PE-MWNTs the linear viscoelastic behavior remains almost unaffected with increasing concentration of MWNTs (Fig. 7d).

Fig. 7. G' as a function of frequency for (a) 40/60 blends with NH_2 -MWNTs; b) 40/60 blends with PE-MWNTs; c) 60/40 blends with NH_2 -MWNTs; d) 60/40 blends with PE-MWNTs.

The phase separation process significantly affects the overall state of dispersion of MWNTs, which can further affect the viscosity and elasticity ratios in the blends. This, in its turn, has an effect on the blend morphology and hence its viscoelasticity. A quantitative estimation of the additional viscoelasticity of the blend after phase separation can help in predicting the phase inversion concentration (ϕ_{PI}). We followed the procedure adopted by Steinmann et al. [44] to estimate ϕ_{PI} .

The extra contribution to G' due to selective filling at a given evaluation frequency (ω_{eval} , 0.039 rad/s) can be estimated from the following relations:

$$G'_{\text{extra}} = G'_{\text{blend}} - G'_{\text{mix}} \quad (10)$$

$$G'_{\text{mix}} = \phi_{\text{PaMSAN}} G'_{\text{PaMSAN}} + (1 - \phi_{\text{PaMSAN}}) G'_{\text{PMMA}} \quad (11)$$

In Fig. 8, the extra G' of the blends are plotted as a function of volume fraction of the PaMSAN phase. G'_{extra} increases from both sides and meet at a maximum, manifesting the ϕ_{PI} (Figure 8a). For neat blends, the maximum occurs at 60 wt% PaMSAN. According to this criterion, the ϕ_{PI} shifted towards lower content of PaMSAN due to selective filling (see Fig. 8b). In earlier investigations [30,33], we observed that the interconnected domains start developing in the blends even at 15 wt% dispersed phase (of PaMSAN) in presence of PE-MWNTs and NH_2 -MWNTs (see insets of Fig. 8b). It is envisaged that for neat blends, the co-continuous structures that are formed at lower concentrations of the minor phase are the thinnest and are destroyed. However, selective filling retards the fibril break-up process. It is worth pointing out that interfacial tension driven coalescence does not destroy the co-continuous structures but rather leads to coarsening of the domains. The kinetics of the fibril break-up process is strongly influenced by interfacial tension and matrix viscosity (or elasticity). Above a critical value of the viscosity (or elasticity) ratio the interconnected domains can break up completely into droplet-matrix type of morphology; often characterized by a bimodal distribution of the droplets [46]. These factors lead to a shift in the phase inversion concentration and the onset of co-continuity. Similar observations were reported for SMA compatibilized PA6/(PPE/PS) blends [46]. In case of filled blends, especially with large aspect ratio fillers, the effective changes in viscosity (and elasticity) ratio dominate the overall kinetics of the fibril break-up process as their contribution to interfacial tension (effective) is not significant unlike for compatibilizers at the interface [47].

Fig. 8. Evaluation of the elastic criterion maximum of G' at $\omega_{\text{eval}} = 0.039 \text{ rad/s}$ at 220°C dependent on the volume fraction of the P α MSAN phase of the blends a) for neat blends; b) for blends with MWNTs (inset showing the corresponding morphologies for blends with NH₂-MWNTs).

3.6 Electrical conductivity: selective localization of MWNTs

It is evident from the TEM images that irrespective of their type, MWNTs migrate to the P α MSAN phase during phase separation, driven by thermodynamic forces. Such selective distribution results in MWNT-rich domains in the blends which preset an alternative strategy for more effective percolation. To investigate this, electrical conductivity spectroscopy measurements were performed on the blends with MWNTs, both before phase separation (i.e at room temperature, Fig. 9a) and during phase separation at an elevated temperature (220°C) (Fig. 9b). Interestingly, irrespective of their type, both 40/60 and 60/40 P α MSAN/PMMA blends with 2 wt% MWNTs show insulating properties at room temperature (i.e when the blends are homogeneous, see Fig. 9a), which, later on reveal an increase in the melt conductivity (at 220°C) by several orders of magnitude (see Fig. 9b). At an elevated temperature, the blends phase separate and allow MWNTs to migrate to the P α MSAN phase. Such migration of MWNTs during the phase separation leads to an increase in their local concentrations which assists in the formation of a percolative network-like structure as manifested from the plateau (dc conductivity).

As a general observation, the 40/60 P α MSAN/PMMA blends which show co-continuous morphologies have reasonably good electrical conductivities in the melt. Among the 40/60 blends, the one with 2 wt% PE-MWNTs has a conductivity which is two orders of magnitude higher than that of the NH₂-MWNTs filled one. The higher conductivity of the 40/60 P α MSAN/PMMA blend with PE-MWNTs is in agreement with its larger storage modulus (Fig. 5) and can be explained on the basis of the larger length of the PE-MWNTs as compared to NH₂-

MWNTs. In the case of 60/40 P α MSAN/PMMA blends, the one with 2wt% NH₂-MWNTs shows an impressive increase in conductivity during phase separation, reaching a final conductivity higher than 10⁻³ S/cm. The 60/40 P α MSAN/PMMA blend with PE-MWNTs exhibits much lower conductivity which, instead of increasing, even slightly decreases as the phase separation proceeds (see inset of Fig. 9b). A close look at the time scales revealed that the time scale of the decrease in conductivity is in reasonably good agreement with the time scale of the decrease in G' during time-sweep experiments (see inset of Fig. 9b). As already discussed in Section 3.5, a plausible explanation for both the low value of conductivity and its slight decrease during phase separation of the 60/40 sample with 2 wt% PE-MWNTs is the less pronounced network build up of PE-MWNTs and the more pronounced coarsening.

Fig. 9. Electrical conductivities (σ , S/cm) of the 60/40 and 40/60 blends with 2wt% MWNTs: a) before phase separation at 25°C; b) during phase separation for 5 hours at 220°C (inset showing the magnified view (as indicated) of the evolution of conductivity with time for 60/40 blends with 2wt% PE- MWNTs and also comparing the evolution of G' with time for this particular composition).

A cartoon (Fig. 10) further illustrates how phase separation in polymeric blends can be used as a template to increase the effective concentration of MWNTs which otherwise is difficult from processing viewpoint. Processing polymer nanocomposites involving higher fractions of MWNTs becomes practically very difficult as, most often, the end to end distance (R) of a flexible polymer chain is greater than the surface to surface distance between two MWNTs (van der Waals' distance). The MWNTs which are randomly dispersed in a mono-phasic system, migrate or re-distribute upon phase separation driven by thermodynamic forces. This leads to transition from insulating materials at room temperature (one-phasic) to a highly conducting material in the melt (two-phasic) as a result of phase separation. By quenching such morphologies, a highly conductive material with controlled phase microstructures can be developed.

Fig. 10. Cartoon illustrating the effect of MWNTs on the resulting morphology of the blends during phase separation (the grey regions indicate the P α MSAN phase; the white regions represent the PMMA phase; hairy like structures represent MWNTs).

4. Conclusions

Thermally induced phase separation in 40/60 and 60/40 LCST-type blends of poly[(α -methyl styrene)-co-acrylonitrile]/poly(methyl methacrylate) (P α MSAN/PMMA) were monitored in the presence of surface functionalised multiwall carbon nanotubes (MWNTs) by differential

scanning calorimetry, melt rheology, conductivity spectroscopy and microscopic techniques. The temperature interval in which phase separation occurred is independent of the type and amount of MWNTs added. The evolution of dynamic moduli (G') as a function of temperature was used as a probe to investigate the structural development as the system transits from the mono-phasic to the bi-phasic regime. The rheological phase separation temperature (T_{rheo}) was observed to be shifted to lower temperatures for 60/40 and 40/60 blends filled with MWNTs.

The phase separation kinetics was investigated in presence of two different types of MWNTs by isochronal time-sweep measurements at a deep quench depth in the unstable region. The evolution of the viscoelastic properties was dominated by the network formation of MWNTs after their selective localization in the P α MSAN phase and did not reveal the time dependence of the phase separation process.

Electron microscopic images revealed that the phase separation resulted in selective localization of MWNTs in the P α MSAN phase of the blends which were initially randomly distributed in the mono-phasic materials. This led to significant changes in the viscosity (and the elasticity) ratios in the blends which further resulted in a shift in the phase inversion concentration towards lower P α MSAN content. The resulting morphology of the blends was found to be strongly governed by the type of MWNTs which in turn, affected the overall state of dispersion of MWNTs, more specifically the 'network-like' structure. This was supported by both time sweep experiments and conductivity spectroscopy measurements.

The phase separation induced selective localization of MWNTs in the blends also resulted in a dramatic transition from an insulating one-phasic material at room temperature to a highly conducting material in the melt. By quenching such morphologies, effective percolation of MWNTs can be achieved at room temperature in contrast to filled homopolymers or mono-phasic materials.

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