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Partially miscible polystyrene/polymethylphenylsiloxane blends for nanocomposites

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Abstract The potential of polystyrene/polymethylphenylsiloxane (PS/PMPS) blends as a matrix for nanocomposites is investigated. It was proven by dynamic rheometry and conductivity measurements that PMPS effectively disperses carbon nanotubes, as was already known for polydimethylsiloxane (PDMS). The phase behaviour of PS/PMPS blends was investigated using differential scanning calorimetry or modulated temperature differential scanning calorimetry. The blends were found to exhibit partial miscibility, in contrast to the known immiscible behaviour of PS/PDMS blends. A miscibility window exists for PS/PMPS blends containing less than approximately 10 wt% PMPS.

Keywords Partial miscibility · Nanocomposites · Percolation threshold · Polysiloxanes

Introduction

Nanocomposites have become increasingly important over the last 20 years [1]. A promising application lies in the field of electromagnetic shielding and antistatics, where cheap and lightweight conducting materials play an important role (e.g. for coatings [2]). The level of electrical conductivity required for these applications can not be provided by traditional polymers, since most are insulators. One alternative is the use of (expensive) intrinsically conducting polymers that typically form a conjugated system [3]. A more attractive alternative is the addition of a low degree of conductive filler to a less expensive conventional polymer, yielding a conductive composite material. The use of carbon nanotubes (CNTs) to create conducting or semiconducting nanocomposites has been the subject of many studies [1, 4–9]. In order to transfer the beneficial intrinsic properties of the CNTs such as their high conductivity to the bulk of the nanocomposite, it is vital that the CNTs form a three dimensional percolating network through the polymer matrix. Therefore, a good dispersion of the CNTs in the polymer matrix is crucial and often requires specialised techniques, since their low reactivity and natural occurrence in bundles makes unfunctionalised CNTs insoluble in most materials [6, 10]. Thus, lowering the percolation threshold, defined as the lowest amount of filler material resulting in the formation of a percolating network, is an important aim since the nanofiller is often much more expensive than the polymer matrix.

In a recent study by Beigbeder et al. [11], polydimethylsiloxane (PDMS) was found to easily disperse multi-walled carbon nanotubes by mechanical mixing. This constitutes a significant simplification in terms of sample preparation, possibly eliminating the need for complex dispersion methods such as latex technology [12] or CNT functionalization [10]. Because of its low glass-transition temperature, low surface energy, and high thermal stability, PDMS is a desirable blend component [13, 14]. One blend system containing PDMS that received much attention in

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literature is with polystyrene (PS), often in combination with PS-b-PDMS block copolymers as compatibilizer due to the strong immiscibility of the two components, which leads to problems regarding the morphological stability. [13, 15–20]. The use of compatibilizers to stabilize the PS/PDMS interface can improve the stability, but complicates the blend preparation. Furthermore, compatibilization using block copolymers is not straightforward. Chuai et al. [17] investigated the effect of the compatibilizer molar mass (M_n) on different blend compositions and noted that the phase size decreased when the relative amount of compatibilizer increased, although only low percentages of compatibilizer showed this effect. Despite promising results, the especially low miscibility with PS coupled with its high mobility makes PDMS a challenging component to incorporate in blends.

In this article, polymethylphenylsiloxane (PMPS) is tested as an alternative for blending with PS (see Fig. 1 for structures). The basis of its chemical structure is the same as for PDMS: a flexible Si–O backbone, but one of the methyl sidegroups is replaced by a phenyl ring. This change in chemical structure may give rise to a better interaction with PS. As the phase behaviour of PS/PMPS blends is not known, a comparative study is performed by thermal analysis in order to determine whether PS/PMPS blends could be used for nanocomposites. The dispersive qualities of PMPS are further investigated by conductivity measurements and dynamic rheometry.

Materials and techniques

Commercial polystyrene (PS, M_n 66400 g/mol, melt index 14), polydimethylsiloxane (PDMS, M_n 24000 g/mol) and polymethylphenylsiloxane (PMPS 710® 500 centistokes fluid) were obtained from Aldrich. Multiwall carbon nanotubes (MWNTs), synthesized by catalytic vapour deposition or CVD, with an average length of 1.5 µm and an average diameter of 9.5 nm were obtained from Nanocyl (commercial NC7000 thin MWNT grade). PMPS nanocomposites were prepared by shearing (6500 RPM) PMPS and an amount of CNTs using an Ika T25 basic Ultra-Turrax high shear mixer. Due to the very low quantities of CNTs involved, preparation of PMPS nanocomposites with loadings lower than 0.05 wt% were prepared by dilution of a 0.05 wt% composition. Unless stated otherwise, blend systems were annealed for 5 h at 120 °C before thermal analysis. PS/PMPS blend nanocomposites were prepared using a DSM Xplore 15 ml Micro-Compounder lab scale twin screw extruder for solvent-free bulk sample preparation. Extrusion was performed at 160 °C after a residence time of 15 min with a shear of 170 RPM.

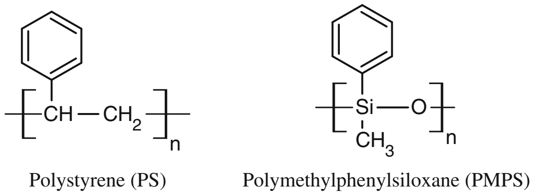

Fig. 1 Molecular structures of PS and PMPS

Conventional and modulated temperature differential scanning calorimetry (MTDSC) measurements were performed on a TA instruments Q2000 Tzero DSC with a liquid nitrogen cooling system or refrigerated cooling system, using helium or nitrogen as purge gas, respectively. Conventional DSC experiments were performed at 10 K min^{-1}. For all modulated experiments, the same heating rate (2.5 K min^{-1}) and modulation (amplitude 0.5 K and period 60 s) were used.

Small angle oscillatory shear rheometry (*dynamic rheometry*) experiments were performed on a TA Instruments AR-G2 rheometer fitted with a 25-mm stainless steel cone-and-plate geometry (cone angle 4°). Frequency sweep experiments were conducted at 30 °C using strain amplitude of 0.1, 0.5 or 1% for the PMPS nanocomposites, and at 200 °C using a strain amplitude of 0.25% for the blend systems. By performing a strain sweep at 1 Hz in advance, it was made sure that the frequency sweeps were conducted within the linear viscoelastic region of the samples.

Four-point and two-point conductivity measurements were carried out at 25 °C using an Agilent 34401A 6.5 digit multimeter on a known sample volume in the case of PMPS nanocomposites. Measurements were performed directly on the surface of the films for PS/PMPS blend nanocomposites. The contact between the sample and the measuring device was improved by the use of a colloidal graphite paste (Cat#12660) provided by Electron Microscopy Science.

Results and discussion

Because PMPS is a much less studied siloxane polymer compared to PDMS, in a first step their thermal properties are examined and compared. Next, the dispersion quality of CNT in PMPS is investigated. A third step is the study of the PS/PMPS blend phase behaviour, followed by the study of the PS/PMPS blend nanocomposites.

Pure siloxanes

In order to get a general idea of the thermal transitions of PMPS, conventional DSC is used. While PDMS is semicrystalline, PMPS is a completely amorphous polymer (see Fig. 2). Clearly, the flexibility of PMPS is reduced as compared to PDMS because of the bulky phenyl side group, which results in a higher T_g (from about −128 °C for PDMS to about −57 °C for PMPS) and inhibits crystallization. Despite this, the long Si–O bond still makes the PMPS chain very flexible and its T_g is still low enough to be in the melt state at room temperature.

PMPS nanocomposites

Where PDMS is known to disperse CNTs, making it a potential blend component for double percolated systems, this has not been documented for PMPS. Evidence of good CNT dispersion by PMPS is found through dynamic rheometry, as seen in Fig. 3. The pure polymer melt behaviour is visco-elastic (not shown), meaning that at lower frequencies a more liquid like behaviour is found (phase angle δ close to 90°) whereas at higher frequencies the behaviour approaches that of an elastic solid (δ close to 0°). PMPS nanocomposites clearly deviate from this classical case, as an elastic response is found at low frequencies for the investigated loadings of 0.1 and 0.5 wt%, apparent as a low phase angle, in combination with a high and almost frequency independent storage modulus G' (see Fig. 3). This is often referred to as solid-like behaviour and can be explained by the formation of a percolating CNT network. It has been found before for both CNTs- and nanoclay-based nanocomposites [21–23]. When at low oscillation frequencies this CNT network is probed, an elastic response is generated by the CNTs. A larger amount of CNTs leads to a denser network, indicated by a lower phase angle and the much higher G' values of the 0.5 wt% compared to the 0.1 wt% nanocomposite. Taking these rheological results into account, which indicate the formation of a mechanically percolating network, a similar trend would be expected for the electrical percolation. The performed conductivity measurements do indeed show that relatively high values are found when CNTs are mixed through PMPS, but all the directly prepared compositions seem to be above the percolation threshold. Therefore, samples of 0.025, 0.02 and 0.01 wt% were prepared by dilution of the 0.05 wt% system. As below 0.02 wt% the conductivity could no longer be measured by the experimental setup, this indicates that the percolation limit is approximately 0.02 wt% or even lower (see Fig. 4). Because an experimental value for pure PMPS was not accessible, and since no conductivity data on PMPS are available in literature, the literature value of 2.5×10^{-14} S m^{-1} for pure PDMS is given for comparison [24]. Note that the latter is still ca. 10^9 times lower than the lowest value of Fig. 4 for 0.02 wt% CNT.

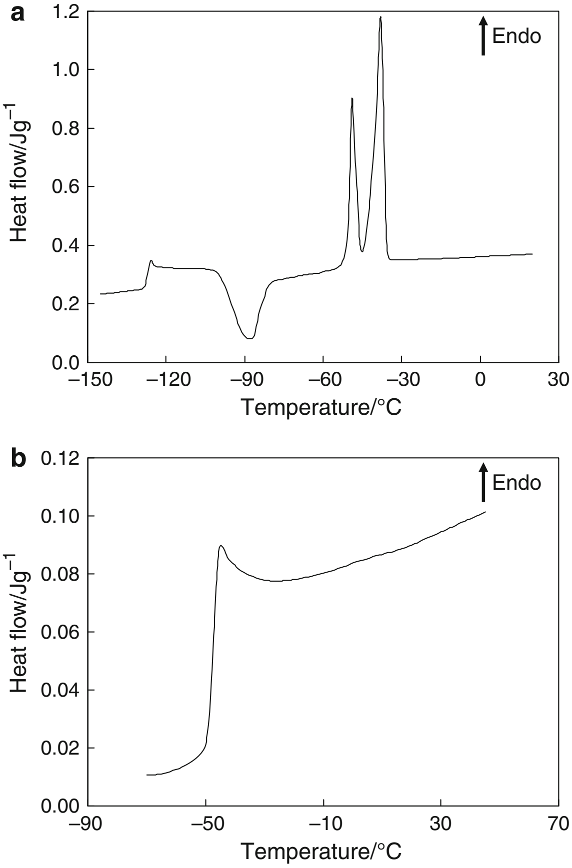

Fig. 2 DSC thermograms of pristine PDMS (**a**) and PMPS (**b**), showing the semicrystalline nature of PDMS and the amorphous nature of PMPS

Phase behaviour of PS/PMPS blends

Blends of PS/PMPS were prepared with 50/50, 70/30, 80/20 and 90/10 composition (wt%/wt%). Higher siloxane amounts were not analysed extensively due to the liquid behaviour of the siloxanes used in this study, making these compositions useless as a nanocomposite matrix. A first observation is the transparency of the 90/10 composition which is an indication of homogeneity, pointing towards (partial) miscibility of PMPS and PS. Partial miscibility

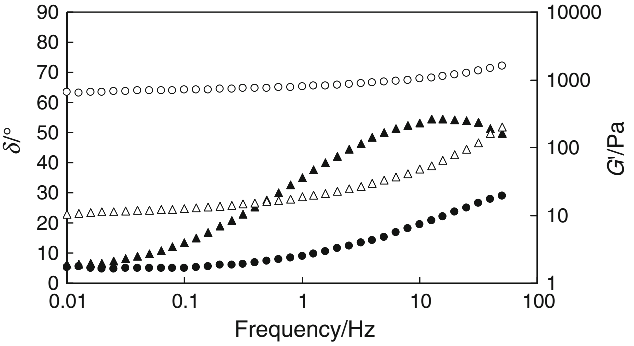

Fig. 3 Rheometry measurements at 30 °C for the PMPS nanocomposites with a 0.1 wt% (*filled* and *open triangles*) and 0.5 wt% (*filled* and *open circles*) CNT loading. The δ and G' values are indicated by *filled* and *open symbols*, respectively

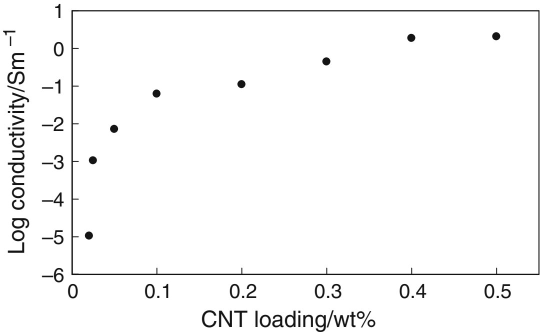

Fig. 4 Conductivity measurements at 25 °C of the prepared PMPS/CNT nanocomposites

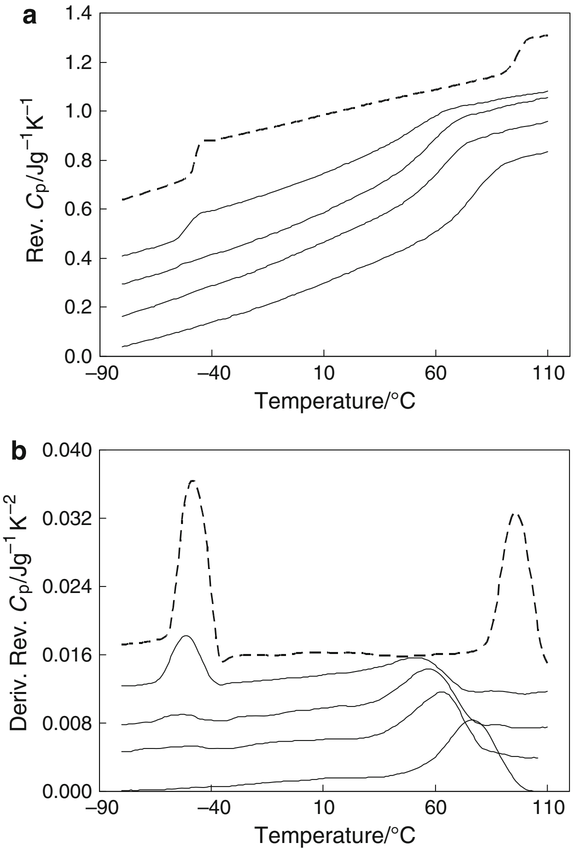

Fig. 5 MTDSC thermograms showing the Rev. C_p (**a**) and derivative signal (**b**) of, from *top* to *bottom*, 50/50, 70/30, 80/20 and 90/10 PS/PMPS blend in a heating cycle after annealing. In both figures, a simulated unmixed 50/50 composition is displayed as a *dashed line* for comparative purposes. For clarity the curves were shifted *vertically*

was indeed confirmed by MTDSC measurements, since for the 90/10 composition only one T_g step is visible, whereas for a completely immiscible system two T_g's, corresponding to pure PMPS (−47 °C) and pure PS (100 °C) would be expected (see Fig. 5). The visible T_g step has decreased from the usual PS value of around 100 °C to around 77 °C. This points towards a plasticizing effect of PMPS on PS, which is expected for a miscible polymer blend system composed of a high and low T_g component. Looking at the heat capacity signal, the 80/20 composition seems to display the same behaviour, having no visible T_g for a PMPS-rich phase and a single T_g for a PS-rich phase that has decreased further to about 63 °C. The more sensitive derivative signal, however, shows that a T_g is observed near −47 °C, indicating a small fraction of an almost pure PMPS-rich phase. For the 70/30 composition, the T_g at −47 °C is more pronounced with a larger peak in the derivative signal. While for the 90/10 composition all the PMPS present was dissolved in PS, effectively plasticizing this component, two phases are thus observed for the 80/20 and 70/30 compositions. This corresponds to the behaviour expected for a partially miscible system, where the two separate phases contain both components, but in different ratios. A 50/50 PS/PMPS blend is also shown in Fig. 5 as well as a simulated unmixed 50/50 composition obtained by addition of the thermograms of both pure components divided by two. It can be seen that both T_g's, and especially that of the PS-rich phase have broadened compared to the unmixed simulation, and an interphase is formed. Compared to the compositions of lower PMPS content, a clear T_g is now visible for the PMPS-rich phase, whereas the T_g of the PS-rich phase is substantially broadened primarily due to an important interphase region. In summary, there is a clear T_g evolution for the PS-rich phase, as depicted in Fig. 6, while the PMPS-rich phase appears to have a constant T_g near that of pure PMPS. Above 80 wt% PS, the T_g evolution of the PS-rich phase corresponds well with the T_g as predicted by the Couchman equation for a homogeneous blend [25, 26]. At lower wt% PS, the T_g evolves towards a constant level. This further confirms the partial miscibility of PS and PMPS. Although of lesser interest for this work, the 10/90 and 30/70 compositions were included to get a more complete view of the phase behaviour. For some ratios accurate determination of the T_g proved difficult due to the broadness of the transition.

For comparative purposes PS/PDMS blends with similar compositions were also prepared. As expected based on literature, all compositions of PS/PDMS blends show completely immiscible behaviour, with two separate T_g's for PDMS and PS at the same temperatures as found for the pure materials (see Fig. 7). Also, the melting peak of PDMS in the blend is completely similar to that of pure PDMS. This is indicative for an immiscible system.

PS/PMPS blend nanocomposites

Having proven that the PS/PMPS systems show partial miscibility, and that PMPS effectively disperses CNTs, blend nanocomposites were examined. First, CNTs were

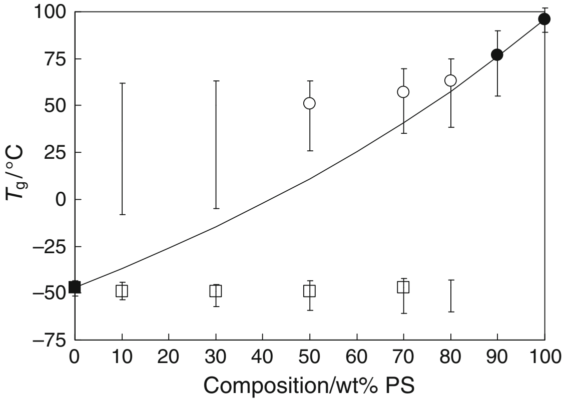

Fig. 6 T_g evolution of the PS-rich (*filled and open circles*) and PMPS-rich (*filled and open squares*) phases in the examined PS/PMPS blends, with onset and endpoint of transition indicated with *error bars*. Homogeneous and heterogeneous systems are depicted with *filled* and *open symbols*, respectively. When only onset and endpoint are given, accurate determination of the T_g was impossible. The curve depicts the T_g evolution in case of homogeneous blends predicted by the Couchman equation [25, 26]

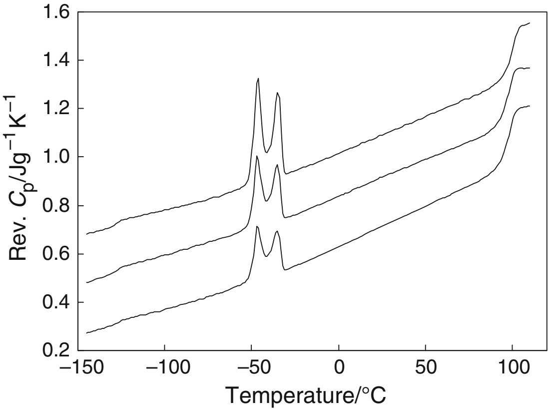

Fig. 7 MTDSC heat capacity plots (Rev. C_p) showing from top to bottom 70/30, 80/20 and 90/10 PS/PDMS blend compositions in a heating cycle after annealing

added to PMPS, yielding PMPS masterbatches of 1 or 5 wt% loading. These PMPS masterbatches were then blended with PS in different ratios using a lab-scale extruder. The chosen ratios were 90/10, 85/15 and 80/20. A CNT composite with a pure PS matrix, containing 5 wt% CNTs, was extruded for comparison. The CNT dispersion in the blend systems was examined using dynamic rheometry. Due to the method of preparation, different blend ratios give rise to different CNT loadings. For all systems the lower CNT loadings (0.1–0.2 wt%) give viscous liquid behaviour, with δ values close to 90° at low frequency and a frequency-dependent G' (see Fig. 8). All blends prepared with the 5 wt% PMPS masterbatch, resulting in CNT loadings of 0.5–1 wt%, show solid-like behaviour at low frequency:

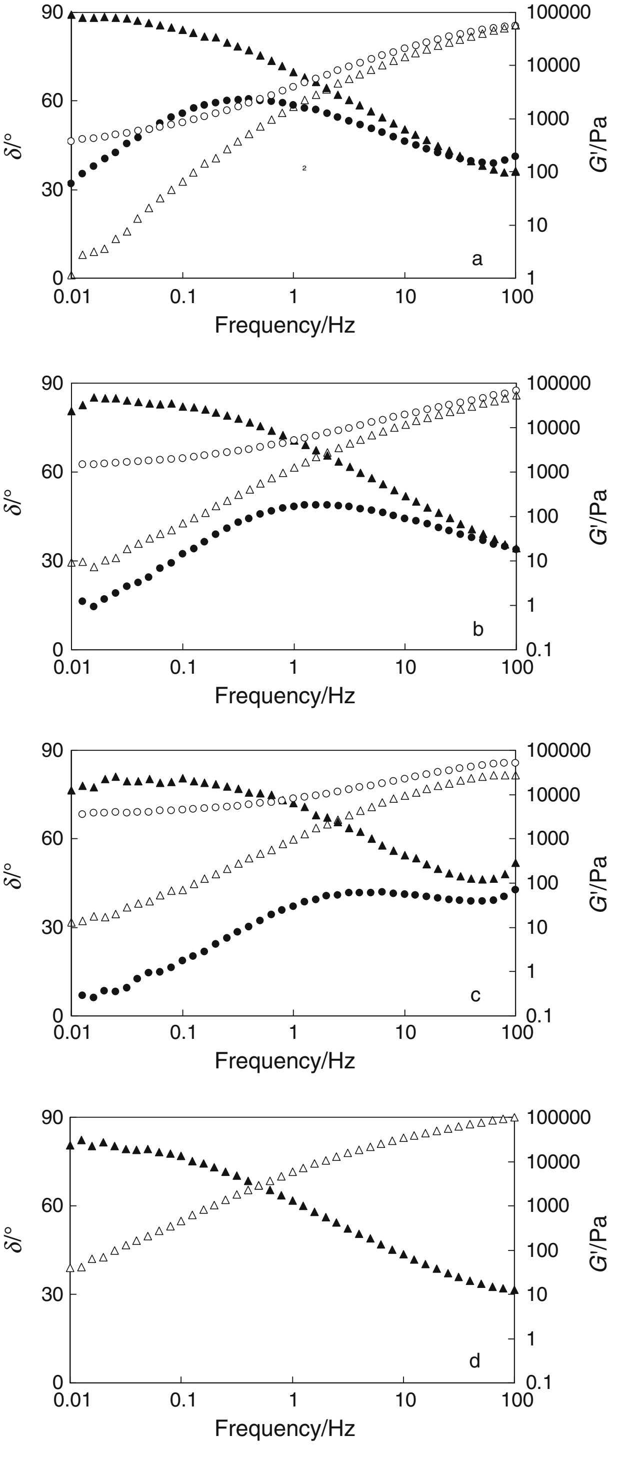

Fig. 8 Dynamic rheometry results at 200 °C for PS/PMPS blend nanocomposites: **a** 90/10 blend with 0.1 wt% (*filled* and *open triangles*) and 0.5 wt% (*filled* and *open circles*) CNT, **b** 85/15 blend with 0.15 wt% (*filled* and *open triangles*) and 0.75 wt% (*filled* and *open circles*) CNT, **c** 80/20 blend with 0.2 wt% (*filled* and *open triangles*) and 1 wt% (*filled* and *open circles*) CNT, and **d** 100% PS with 5 wt% CNT (*filled* and *open triangles*). δ and G' are indicated by *filled* and *open symbols*, respectively

low δ values and an almost frequency independent G' are noted, pointing towards a percolating CNT network. If the G' values at 0.01 Hz are compared, it can be seen that the effect of this percolating network is greatest for the 80/20 system (G': 3537 Pa), followed by the 85/15 system (G': 1459 Pa) and the 90/10 system (G': 373 Pa). This solid-like behaviour due to CNT percolation is completely absent for the composite based on pure PS with 5 wt% CNTs, even though the loading is five times higher than that of the percolated 80/20 blend, showing the positive effect of the PMPS for the dispersion of the CNTs in PS.

Surprisingly, no conductivity was measured for any of the PS/PMPS blends studied above, indicating the absence of electrical percolation. As the setup was successfully used to measure the conductivity of the PMPS nanocomposites, it would seem that there is an unknown effect hindering electrical percolation even though mechanical percolation is clearly present. It has been observed before that the rheological percolation threshold is lower than the electrical percolation threshold [7, 27], explained by the shorter CNT–CNT distance required for electron tunneling compared to the distance required to restrain polymer chain movement. In this case, it is possible that the loadings used so far are insufficient for conductivity. Nevertheless, the inverse situation, where electrical percolation precedes rheological percolation has also been reported, although for a different polymer system where a surfactant is used to incorporate CNTs (latex method) [28]. Further research with regard to this behaviour is going on.

Conclusions

In this study, the potential use of PS/PMPS blends for nanocomposites was studied. Similar to PDMS, PMPS easily disperses CNTs, as was shown by dynamic rheometry and conductivity measurements. Based on MTDSC measurements, PMPS was found to be partially miscible with PS, unlike PDMS which is strongly immiscible with PS. A miscibility window exists for PS/PMPS blends containing less than approximately 10 wt% PMPS.

PS/PMPS blends can thus lead to homogeneous as well as phase-separated systems with phases that are more compatible than in the case of completely immiscible components. This allows for the easy preparation of CNT-containing PMPS/PS blends, since there is no need for block copolymers to compatibilize the system.

Based on these results, PS/PMPS blends of different blend ratios were used to prepare CNT nanocomposites by extrusion. While this resulted in mechanically percolated systems for blends containing 0.5–1 wt% of CNTs, no electrical percolation was seen. The reason for this discrepancy is hitherto unknown and requires further study. If electrical percolation can be achieved, easy dispersion of CNTs in PMPS may be used as an elegant preparation method for CNT nanocomposites based on PS or other polymers.

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