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Selective localisation of multi walled carbon nanotubes in polypropylene/natural rubber blends to reduce the percolation threshold

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ABSTRACT

Polypropylene and natural rubber blends with multiwalled carbon nanotube (PP/NR + MWCNT nanocomposites) were prepared by melt mixing. The melt rheological behaviour of neat PP and PP/NR blends filled with different loadings (1, 3, 5, 7 wt%) of MWCNT was studied. The effect of PP/NR blends (with compositions, 80/20, 50/50, 20/80 by wt) on the rheological percolation threshold was investigated. It was found that blending PP with NR (80/20 and 50/50 composition) reduced the rheological percolation threshold from 5 wt% to 3 wt% MWCNT. The melt rheological behaviour of the MWCNT filled PP/NR blends was correlated with the morphology observations from high resolution transmission electron microscopic (HRTEM) images. In predicting the thermodynamically favoured location of MWCNT in PP/NR blend, the specific interaction of phospholipids in NR phase with MWCNTs was considered quantitatively. The MWCNTs were selectively localised in the NR phase. The percolation mechanism in MWCNT filled PP/NR blends was discussed and for each blend composition, the percolation mechanism was found to be different.

1. Introduction

Blending of polymers generate multi-component polymeric materials with improved properties and thereby, significantly expand the range of their applications. A recent trend in research of polymer blends is the study of the influence of nanofillers on various properties of immiscible blends. This area of research is of great significance as the blend morphology in these immiscible systems are greatly influenced by the filler distribution and dispersion. For instance, nanoclay [1–3] and graphene oxide sheets [4] are used as compatibilizing agent in polymer blends. The location of nanofiller in the blend components and state of dispersion of the nanofillers affect the dynamics of droplet break-up and coalescence of polymer phases [5]. It was reported prior that multiwalled carbon nanotube (MWCNT) could tune the blend morphology in immiscible polymer blends [6–9].

In polymer matrices, the conductive fillers such as carbon black, CNTs and graphene form continuous network structure only above a critical concentration. This critical concentration is known as percolation threshold. The high amount of filler needed to form the percolated network make the processing expensive and difficult. Researchers, to reduce the percolation threshold, cut down the cost of the final nanocomposite and ease the processing adopted different strategies. Dispersion of conductive fillers in immiscible polymer blend is one of the most accepted methods to reduce the percolation threshold [10–12]. Understanding and controlling of the localisation of these conductive nanofillers in polymer blends are the keys toward making new tailor-made materials [12–14]. The shape, size and aspect ratio of the fillers play a significant role on their localisation in melt mixed polymer blends. In immiscible blends with co-continuous morphology, the selective localisation of CNTs in one phase or partially at the interface could help to achieve a low percolation threshold due to the phenomenon called 'double percolation' [15]. According to Göldel et al. [13] thermodynamic stable localisation of high aspect ratio carbon nanotubes at the blend interface is expected to be unlikely. However, recently methods to control the localisation of MWCNT at the blend interface were reported to achieve ultra low percolation threshold [16,17].

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The blends of polypropylene and natural rubber (PP/NR) is an industrially important blend, especially in natural rubber producing countries where this thermoplastic elastomer (TPE) rubber can be used for myriad applications. The incorporation of nanofillers in PP/NR blends was previously reported by Bendjaouahdou and Bensaad [18]. They studied the role of organically modified montmorillonite (OMMT) in compatibilizing PP/NR blend. By considering the absence of significant literature on MWCNT filled PP/NR blends and their importance in electrical applications, the current study focuses on the reduced percolation threshold of MWCNTs in PP/NR blend compared to their corresponding homopolymer. The morphology of the blend in the presence of MWNTs was also assessed and was correlated with the rheological observations. It has been shown that dynamic frequency sweep of polymers and their blends gives detailed information on processing, dispersion state of nanofillers, and specific interactions between the nanofiller and the blend components [19–21]. Different studies on the rheological behaviours of polypropylene/MWCNTs nanocomposites were previously reported [22–25]. To the best of our knowledge the relationship between rheological percolation behaviour and morphology in MWCNT filled PP/NR blend has not received much attention.

In this study, PP/NR blends filled with MWCNT (with different MWCNT loading and blend ratios) were prepared using melt blending technique. The effect of PP/NR blend composition (80/20, 50/50, 20/80) on the rheological percolation threshold will be investigated. Recently, the role of non-rubber components in natural rubber (NR) such as phospholipids and proteins on the selective localisation of CNTs in polymer blends were investigated and it was found that the phospholipid can act as coupling agent in bonding the α-terminal of NR with the CNT surface through cation-π interactions [26–28]. The thermodynamically feasible location of MWCNT in PP/NR blend at processing temperature will be predicted quantitatively by considering this established cation-π interaction between the phospholipids in the NR and MWCNT and will be correlated with the rheological and morphological findings to suggest possible mechanism of percolation in various MWCNT filled blends.

2. Experimental section

2.1. Materials

Isotactic polypropylene (PP) (grade H350 FG, melt flow index = 38 g/10 min) used was supplied by Reliance India Ltd. Natural rubber (ISNR grade-5, Mn = 7.79 × l0^5) used was procured from Rubber Research Institute of India, Kottayam. The multi walled carbon nanotubes (MWCNT) with diameter 20–30 nm and length 15–30 μm, was supplied by Nanoshel, Punjab.

2.2. Sample preparation

Various composition of polypropylene and natural rubber (PP/NR) blends (80/20, 50/50, 20/80) were prepared by melt mixing technique using Brabender Plasticorder at 180 °C with a rotational speed of 60 rpm for 10 min. MWCNT filled PP/NR blends (PP/NR + MWCNT nanocomposites) were prepared by adding different MWCNT content (1, 3, 5, 7 wt%) during melt mixing in all of the blend compositions.

2.3. Characterization

Dynamic frequency sweep rheological analysis were carried out in stress controlled rheometer DHR3 (Discovery Hybrid Rheometer 3) from TA instruments. The measurements were performed in 25 mm parallel plates at 180 °C. The frequency varied from 100 to 0.1 rad/s. The micrographs of the samples were taken using Jeol JEM-2100 transmission electron microscope with an accelerating voltage of 200 keV. Ultrathin sections of bulk specimens (about 100 nm in thickness) were obtained by cryocutting with an ultramicrotome fitted with a diamond knife.

3. Results and discussion

A theoretical evaluation was done to find out the thermodynamically favoured localisation of MWCNT in the blend components (PP and NR). In polymer blends, the thermodynamic driving force behind the localisation of MWCNT preferentially in one phase is the minimisation of interfacial energy, as explained in other polymer blends filled with MWCNT [8,29]. The procedure adopted by Göldel et al. [29] has been used to determine the interfacial energy between two components in the ternary system. Both the harmonic-mean equation and geometric-mean equation were used to evaluate the interfacial energies.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left[\frac{\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}\right] \quad (1)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\sqrt{\gamma_1^d\gamma_2^d} + \sqrt{\gamma_1^p\gamma_2^p}\right) \quad (2)$$

where γ_1 and γ_2, are the surface free energy of the blend component 1 and 2 respectively, γ_1^d and γ_2^d are the dispersion parts of the surface energies of blend component 1 and 2 respectively and γ_1^p and γ_2^p are the polar parts of the surface energies of blend component 1 and 2 respectively. The values of the surface free energy of blend components and MWCNT were taken at 20 °C from the literature and is listed in Table 1. The surface free energy values determined from the contact angle measurement of NR cannot account the presence of phospholipids and is merely by the isoprene backbone. This is due the very small content (<1 wt%) of the phospholipids in NR and they are linked to the terminal chains of NR, i.e., they cannot migrate to the surface of the rubber sample. The effect of phospholipids on the interaction between NR and MWCNT can be quantitatively described by the use of corrected surface free energy values of NR. Hence, in order to predict the localisation of MWCNT in PP/NR blends, the corrected value of the surface free energy of NR as determined by Le et al. was used [26,28]. Surface free energy at processing temperature (180 °C) can be calculated by extrapolating the values at room temperature using the following equations [32,33],

$$K = \frac{11\gamma_o}{9T_c} \times \left(1 - \frac{T}{T_c}\right)^{\frac{11}{9}} \quad (3)$$

$$\gamma = \gamma_o \times \left(1 - \frac{T}{T_c}\right)^{\frac{11}{9}} \quad (4)$$

where K is the temperature correction factor, γ_o is the surface free energy at 0 °C, T_c is the critical temperature (T_c is 1000 K for polymers) and T is the temperature of the polymer. The surface free energies of blend components (PP and NR) and MWCNT at 180 °C

Table 1
The surface free energy and polarity of blend components and MWCNT.

Component	Surface free energy, mJ/m^2		Polarity, %
	At 20 °C	At 180 °C	
MWCNT	45.3 [Ref. [30]]	45.3	59
PP	29 [Ref. [31]]	21.19	0
Natural rubber	26 [Refs. [26,28]]	19.00	0