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On the phase affinity of multi-walled carbon nanotubes in PMMA:LDPE immiscible polymer blends

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ABSTRACT

The localization of multi-walled carbon nanotubes (MWCNTs) in PMMA/LDPE blends was studied. Theoretical predictions suggested their preferential localization in the PMMA. Conversely, experimental work revealed that non-functionalized MWCNTs located in the LDPE, polymer first to melt. When the extrusion time is not long enough, the MWCNTs do not have the chance to further migrate to the thermodynamically most favourable phase. The evolution of a double percolation determined if the composite became semi-conductive. In that sense, two blends with PMMA to LDPE ratios of 80:20 and 20:80 containing 2 wt.% MWCNTs had electrical resistivity values in the order of 10^5 and 10^{12} Ω cm, respectively. Only in the 80:20 blend was the "effective" MWCNT concentration high enough such that electrical percolation was attained. However, bulk rheological properties were controlled by the major phase. Thus, 2 wt.% MWCNTs had a notable effect on the linear viscoelasticity at low frequencies of the 20:80 blend.

1. Introduction

Binary immiscible polymer blends may provide improved performance as compared to their separate constituents, since it is possible to take advantage of specific properties from one or both polymers. Moreover, composites of polymer blends and multi-walled carbon nanotubes (MWCNTs) are of special interest in a number of technological applications [1]. In this regard, their potential performance might be conditioned by the phase where the MWCNTs localize. The thermodynamic wetting parameter, based on the Young equation, has been largely used to successfully predict the selective localization of different filler particles (e.g. MWCNTs, carbon black, carbon fibers and nanoclays) in many immiscible polymer blends. Cardinaud and McNally [2] theoretically predicted and experimentally proved the preferential localization of MWCNTs in the PET phase of several PET/LDPE blends. The same result was achieved by Yesil et al. [3] for PET/HDPE and Goldel et al. [4] found that even minor differences in the wetting behavior were enough for MWCNTs with large aspect ratios to migrate to the more favorable PC phase in PC/SAN blends. Moreover, the wetting coefficient also proved to be successful at predicting the locations of three different silica nanoparticles in LDPE/PEO blends [5].

However, other parameters can govern the preferential localization of fillers. By way of example, Baudouin et al. [6] demonstrated that, in PA12/EA blends, partial irreversible adsorption of the polymer first to wet the MWCNTs (EA) can prevent their complete migration from the interface to the preferred PA12 phase. Zhao et al. [1] also reported that localization is greatly controlled by the mixing protocol employed. That is, when MWCNTs were premixed with PS and further blended with PVDF, more than 30 min was required for the filler to migrate to the thermodynamically preferred PVDF phase because the viscosity of this polymer at the mixing temperature was much higher than PS. Moreover, carbon black (CB) was found in the LDPE phase of a PMMA/LDPE blend, even though the wetting coefficient predicted that CB should locate to the PMMA phase for dispersion [7]. The authors again attributed this phenomenon to the higher viscosity of the PMMA phase.

With regard to nanocomposite characterization and properties, the electrical properties of polymer matrices containing CNTs have been the subject of a large number of research papers. Above the so-called electrical percolation threshold, the filler arrangement is such that electrical conductivity is allowed as continuous interconnected filler network is attained. In a binary immiscible

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polymer blend, the situation becomes much more complex, as the nanoparticles can localize in one phase, in another, in both or even at the interface. The double percolation theory explains that, in case of co-continuous morphology, the electrical percolation limit can be drastically reduced if the filler concentrates in the minor phase or, even better, at the interface [8]. The concept of double percolation, first reported by Sumita et al. [9] for blends filled with CB, provides a theoretical basis for electrical conductivity in immiscible polymer blends. This is turn has led to strategies to reduce the percolation threshold of conductive particles in the final nanocomposite to extremely low values [10,11].

With regard to rheological properties, double percolation does not guarantee a similar effect on the linear viscoelastic properties of the nanocomposite. In contrast to electrical conductivity, rheological percolation in immiscible polymer blends is only achieved if the percolated polymer constitutes the major phase or, at least, significantly contributes to the bulk rheology of the blend. A well-known example of the above mentioned improved performance derived from immiscible polymer blends would be the increased toughness of brittle matrices with rubbers or poly(olefin)s or, inversely, the promotion of enhanced tensile strength in elastomers filled with a brittle polymer [12]. Specifically, several reports have been devoted to blends with varying ratios of poly-(methyl methacrylate) (PMMA) and poly(ethylene)s (LDPE or HDPE). These polymers, which have traditionally been used as commodity plastics, have lately found application in the manufacture of products with high added value [12]. Very few studies have been reported on PMMA/PE blends filled with carbon-based conductive particles (e.g. carbon black, fibers or nanotubes). The published data is mainly composed of morphological characterization based on SEM/TEM observations which the authors use to justify electrical conductivity results based on double percolation theory or to try to reduce the electrical percolation threshold [9,10,13,14]. Moreover, very little attention has been paid to the linear viscoelasticity behaviour of these CNT filled blends. Only Hosseini Pour et al. [7] compared electrical and rheological percolation in a 50:50 PMMA:LDPE blend. However, to the best of our knowledge there has been no case where microscopy analysis and electrical conductivity measurements were used to give further support to a comprehensive rheological characterization, in terms of the effect of polymer ratio and selective CNT localization on the bulk viscoelastic properties. The present article, which explores the localization of MWCNTs in PMMA:LDPE blends, highlights the power of linear rheology as a characterization tool for nano-filled multiphase polymer blends. The results, which demonstrate that rheological percolation is only achieved if the polymer phase having a percolated filler network significantly contributes to the bulk rheology of the blend, were supported and validated by other more frequently used techniques (SEM, DSC and electrical conductivity measurements).

2. Experimental

2.1. Materials

The polymers used in this study were: a) poly(methyl methacrylate) (PMMA) Plexiglas 6 N, from Evonik Industries (an amorphous thermoplastic moulding compound, with $T_g = 99$ °C, MVR at 230 °C/3.8 kg = 12 cm^3/10min, and melt density = 1.10 g/cm^3); b) low density polyethylene (LDPE) LD605BA, from ExxonMobil (a general purpose LDPE grade, with $T_m = 108$ °C, MFI at 190 °C/2.16 kg = 6.5 g/10min, and melt density = 0.76 g/cm^3). Non-functionalized multi-walled carbon nanotubes (MWCNTs) NC7000, from Nanocyl S.A, Belgium were used. They are produced via a catalytic carbon vapor deposition (CCVD) process, have average diameter and length of 9.5 nm and 1.5 μm, respectively, and surface area between 250 and 300 m^2/g.

2.2. Composite blend preparation

In the first instance, blends of PMMA and LDPE in varying weight proportions of 100:0, 80:20, 60:40, 50:50, 40:60, 20:80 and 0:100 with a constant MWCNT concentration of 2 wt.% were prepared. The formulations for all composite materials prepared are listed in Table 1. Prior to melt mixing both polymers were subjected to cryo-milling, with liquid N_2 in a Freezer/Mill SPEX machine. The fine powder obtained assisted more intimate mixing with the MWCNTs before feeding to the extruder. After milling, all powders were subjected to vacuum drying at 50 °C overnight.

Neat blends (i.e without MWCNTs) were also prepared and used as reference samples. The compounding of all blends was conducted in a co-rotating twin-screw micro-extruder within the interval 180–220 °C, a Thermo-Haake MiniLab II, at 120 rpm and a mixing time of 5 min. As can be seen from Table 1, the extrusion temperature was progressively decreased with increasing LDPE content, to minimize possible degradation.

In a second set of experiments, two further sets of composites were prepared based on PMMA:LDPE ratios of 80:20 and 20:80, but with varying MWCNT concentration of 0.2, 0.5, 1, 2, 3.5 and 5 wt%. Test specimens were prepared by injection molding using a Thermo-Haake MiniJet II, under 800 bar and for 15 s, see Table 1 for parameters used. Two types of specimens were obtained: a) 25 mm diameter x 1.6 mm thickness disks, for dynamic shear rheology and b) 80 mm × 10 mm × 4 mm bars, for volume electrical resistivity measurements and SEM observations.

2.3. Blend and composite characterisation

The linear viscoelastic properties were evaluated with a controlled-stress rheometer, a Thermo-Haake MARS III equipped with an air convection oven, at a constant temperature of 180 °C, using smooth plate-plate geometry (25 mm diameter, 1.4 mm gap). The measurement temperature and time were optimized in order to prevent samples from thermal degradation. Firstly, for every sample, dynamic shear stress sweeps, at 1 Hz, were carried out, in order to determine the limit of linear viscoelasticity (LVE). Then, frequency sweep tests were performed between 0.1 and 100 rad/s, at stress values within the LVE regime. At least 3 replicates for each sample were studied.

Differential Scanning Calorimetry (DSC) was conducted on all materials to determine the thermal properties using a Mettler Toledo DSC1 calorimeter with ~10 mg samples placed in aluminium pans, under N_2 gas purge flow. The samples were firstly heated up to 220 °C and kept for 5 min in order to erase the thermal history. Then, they were subjected to cooling down to 20 °C, followed by heating up to 220 °C, both scans at a rate of 10 K/min.

The volume electrical resistivity of the composite materials was determined using 30 mm × 10 mm x 4 mm bar specimens with a Keithley 6517B-Electrometer, employing a “two-point probe” method [15]. With this approach, two copper strips were glued on

Table 1
PMMA/LDPE volume percentages and processing (extrusion, injection and molding) temperatures for every blend ratio studied.

PMMA:LDPE wt. ratio	100:0	80:20	60:40	50:50	40:60	20:80	0:100
vol.% PMMA	100	73.43	50.89	40.86	31.54	14.73	0
vol.% LDPE	0	26.57	49.11	59.14	68.46	85.27	100
Extrusion T (°C)	220	200	195	195	190	185	180
Melt injection T (°C)	225	205	205	205	195	190	190
Molding T (°C)	100	90	90	80	75	75	75