



Viscosity-induced filler localisation in immiscible polymer blends



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ABSTRACT

The understanding of the localization of fillers in polymer blends is of primary importance for the production of polymer blends with controlled properties. In this paper, the effect of blend viscosity ratio on filler localization was investigated by preparing polypropylene (PP)/poly-ε-caprolactone (PCL) co-continuous blends with different viscosity ratios $K = \eta_{PCL}/\eta_{PP}$, varying from 0.06 to 14.7 and filled with carbon black particles (CB). Polymer phases were premixed before adding CB filler in order to avoid particles incorporation in the phase that melts first (i.e. PCL). The blend co-continuity was checked by solvent extraction technique. The filler localization was studied by different microscopies: Scanning Electron Microscopy, Transmission Electron Microscopy and Optical Microscopy. It was found that fillers located in the highest viscosity phase, whatever its chemical nature (PP or PCL). For viscosity ratio close to one, fillers were localized at the blend interface. These experimental observations were interpreted in terms of hydrodynamic forces acting on filler particles. These drag forces depend on phase viscosity and tend to extract fillers from the interface towards one of the polymer phase. So, fillers are extracted to the highest viscosity phase, applying the most important force. When viscosity ratio is close to one, the two forces balance each other, leading to a “stabilization” of the particles at the blend interface.

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1. Introduction

Filler localization in immiscible polymer blends has been the subject of extensive research during the last decade. Indeed, selective localization at the interface can be of practical interest. It allows for instance to significantly decrease the size of the dispersed phase or to induce specific properties at low filler contents like conductivity using the double percolation approach. The pioneering work of Sumita et al. [1,2] has shown that thermodynamics play an important role in filler location, through the wetting parameter ω defined as:

$$\omega_{A-B} = \frac{\gamma_{f-B} - \gamma_{f-A}}{\gamma_{A-B}} \quad (1)$$

where γ_{f-B} and γ_{f-A} are the surface tensions between fillers and, respectively, polymer B and polymer A. γ_{A-B} is the surface tension

between the two polymers. If $\omega > 1$, fillers will be located in polymer A. If $\omega < -1$, fillers will be selectively localized in polymer B. For other values, between -1 and 1 , fillers are localised at the interface of the blend. Nevertheless, in such high viscous media, the equilibrium state is not always reached and filler localization may differ from the thermodynamic considerations. Other parameters referred as “kinetic factors”, like blending procedure, hydrodynamics during mixing or phase rheology must also be taken into account [3–12]. Gubbels et al. [3–5] took advantage of the predominance of kinetics over thermodynamics to selectively localize CB fillers at the interface of polyethylene/polystyrene (PE/PS) blend. Their strategy consists in controlling the thermodynamically-driven migration of fillers, from the phase with which they less strongly interact (PS) and where they have been previously introduced through a premixing procedure towards the preferential one (PE), and stopping it when they accumulate at the blend interface [5]. Similarly, Goldel et al. highlighted carbon nanotube (CNT) transfer from poly(styrene-acrylonitrile) phase (SAN) in which they were premixed towards the better wetting polycarbonate phase (PC) [12]. Elias et al. [6–8]

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emphasized the importance of mixing procedure and thermodynamics on filler localization. Baudouin et al. [9–11] reported that in poly(ethylene-co-methyl acrylate)/polyamide (EMA/PA) blends, carbon nanotubes localization varies with mixing sequence. If the three components are added simultaneously in the mixing device, fillers are found to localize selectively at the blend interface, as predicted by thermodynamics. When they are first mixed with PA before addition of EMA phase, carbon nanotubes remain in the former phase after compounding, differing from thermodynamic expectation [10]. Most of the studies reported so far deal with the preferential localization of the filler in one phase, depending on the so called wetting parameter. Localization at the interface is either observed if a convenient range of the wetting parameter is chosen or seen as a temporary location when the filler moves from the thermodynamically unfavorable phase to the thermodynamically favoured one. Among all these kinetic parameters, the influence of the relative viscosity of the two phases is not clear and not systematically studied as acknowledged by Elias et al. [8]. Indeed, only few authors focused on the influence of phase viscosity on filler localization and unfortunately no definitive conclusion can be extracted [13–17]. Ibarra-Gomez et al. evidenced the influence of blend viscosity on CB fillers localization and consequently the electrical properties of the material [13]. This material consists in a blend of butadiene rubber (BR) and ethylene propylene diene monomer rubber (EPDM) and presents conductivity properties at low CB content due to the double percolation effect. However, the authors observed that, when the blend viscosity is increased, the double percolation effect is suppressed and the conductivity falls down. Feng et al. studied CB filled polypropylene/poly(methyl methacrylate) (PP/PMMA) blends, PP being the dispersed phase [14]. They report that fillers localize in the PMMA matrix phase when the viscosity ratio $K = \eta_d / \eta_m$ (dispersed phase viscosity over matrix viscosity) is near to one, as predicted by thermodynamics. By increasing PMMA viscosity, CB fillers localize at the interface or in the less viscous PP phase when the viscosity ratio further decreases. This is explained by the high viscosity of PMMA droplets which inhibits the diffusion of the particles inside them. Their results, corroborated by some other authors [15,16], disagree with those of Persson et al. [17] who studied blends of polyethylene/polyisobutylene (PE/PIB) filled with borate whiskers. In the former work, fillers are found to accumulate in the more viscous phase, whatever its chemical nature (PE or PIB). However, in the same study, their theory is contradicted by comparison with a polyamide/poly(styrene-co-acrylonitrile) (PA/SAN) blend in which fillers are localized in the PA less viscous phase. As a conclusion, the importance of phase viscosity has been recognized but is not yet fully understood.

In the present paper, a better understanding of the role of phase viscosity on filler localization in immiscible co-continuous blends is targeted. CB filled co-continuous polypropylene (PP)/poly- ϵ -caprolactone (PCL) blends with a wide range of viscosity ratio are prepared (from $K = 0.06$ where the matrix is much more viscous than the minor phase to $K = 14.7$ where the matrix is less viscous than the minor phase). K is defined as the viscosity of the minor phase (PCL) over the viscosity of the major phase (PP). To the best of our knowledge no systematic study of the viscosity ratio over such a large range has been reported in the literature. By mixing first the two polymeric phases before addition of the fillers, it is possible to avoid their incorporation in the phase that melts first (the one with the lowest melting point) during early stages of the mixing. This mixing procedure has not been widely used in the literature and allows direct observation of the influence of phase viscosity, since the filler is not prewetted by any of the components of the blend. One might note that this mixing procedure can be easily transferred in an industrial plant.

2. Materials and methods

2.1. Materials

Four polypropylenes with different melt flow indices (PP 100-GA1 called “PP4” from Ineos, PP 040 G1E called “PP3”, PP 080 G2M called “PP2” and PP 099 K2M called “PP1” from Repsol) and three polycaprolactones with different molecular weights (Capa 6800 called “PCL3”, Capa 6500 called “PCL2” and Capa 6400 called “PCL1” from Perstorp) were used in this work (Table 1). As filler, carbon black Sterling MT (called “CB”) provided by Cabot with particle size in the range of 200–400 nm was used (Table 2). The chemical stability of both polymers has been checked over one hour and no significant evolution of the viscosity could be detected.

2.2. Sample preparation

The blends were prepared using a Thermo Haake MiniLab Rheomex CTW5 micro compounder with corotative screws. This device contains a circulation band that allows controlling mixing time. In this work, we studied PP/PCL blends with different viscosity ratios but same composition of 60% wt PP, 40% wt PCL (corresponding to 64/36 v/v according to polymer densities at room temperature) to which were added 17 phr wt CB. The mixing procedure included two steps. The two polymeric materials were first molten and mixed together in the compounder at 200 °C during 10 min. Then, carbon black fillers were dispersed into the blend and mixing was carried out for 10 additional minutes before extrusion. This procedure avoided pre-wetting of particles by the polymeric phase that melts first, i.e. PCL phase (T_m of PP is around 160 °C and T_m of PCL is around 60 °C) as encountered when polymers and CB are introduced at the same time. The screw speed was kept constant at 20 revolutions per minute (rpm), leading to an apparent shear of about 70 s⁻¹, according to the supplier of the micro compounder. After extrusion, the samples were moulded in plates of 25 mm diameter and 1 mm thickness using a hot press at 200 °C. Samples were molten during 5 min before compression at 8 tons during 1 min. The compression step was realized as quickly as possible to limit coalescence phenomenon in the blend.

In order to investigate filler localization, blends with various viscosity ratios K , were prepared by selecting different PP/PCL

Table 1
Main characteristics of polymers used in this work.

Polymers	Commercial name	Supplier	Melt flow index at 230 °C (g/10 min)	Zero shear viscosity (Pa s) at 200 °C	Viscosity at 70 s ⁻¹ (Pa s) and 200 °C
PP1	PP 099 K2M	Repsol	55	99	70
PP2	PP 080 G2M	Repsol	20	323	173
PP3	PP 040 G1E	Repsol	3	3331	301
PP4	PP 100-GA1	Ineos	0.9	10,593	693
PCL1	Capa 6400	Perstorp	40	44	41
PCL2	Capa 6500	Perstorp	7	218	194
PCL3	Capa 6800	Perstorp	3	1545	1027

Table 2
Main characteristics of carbon black fillers used in this work.

Commercial name	Supplier	Surface area (m ² /g)	Oil absorption number (DBP; ml/100 g)	Primary particle size (nm)
Carbon black Sterling MT	Cabot	7	34	250/462

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