



Phase structure, rheology and electrical conductivity of co-continuous polystyrene/polymethylmethacrylate blends filled with carbon black



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ABSTRACT

In this work the effect of carbon black concentration on the rheology, electrical conductivity and morphology development of PS/PMMA co-continuous blends during quiescent annealing is investigated. In the blends studied carbon black is preferentially localized in the PS. The specific interfacial length, which is taken as a measure of fineness of blends morphology, increases linearly with the carbon black content in the blends after melt mixing. However, significant suppression of the structure coarsening during annealing is observed in systems with more than 3 vol.% of carbon black, in which the filler structures induce pronounced flow restrictions. The final change in the flow behaviour of the blend induced by annealing is a result of competition between morphology coarsening and particle structure formation and it depends on the concentration of carbon black.

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1. Introduction

Polymer blends with co-continuous phase structure have a great potential to become materials with unique property profiles which cannot be obtained by using single polymers. However, there are crucial deficiencies which limit the application of co-continuous blends considerably. The interfacial area in co-continuous blends is usually large which together with low interfacial adhesion typical of immiscible blends results in unacceptable mechanical properties. Moreover, the phase structure of co-continuous blends is not stable and coarsens significantly during processing [1–6].

Also conductive polymer composites, i.e. systems consisting of an insulating polymer matrix and a conductive filler, have attracted great attention in recent decades as materials for antistatic packaging, electromagnetic shielding or sensing applications [7–9]. To produce materials with a desired level of electrical conductivity, the filler in concentrations distinctly above the percolation threshold has to be incorporated in the matrix. This, however, leads to a pronounced increase in composites viscosity and, thus, to a deteriorated processability [10]. At low filler concentration the percolating particle structures are not stable and they can be destroyed

by hydrodynamic stresses applied in mixing devices, which can result in a non-conductive material [11].

However, the addition of conductive fillers to the co-continuous immiscible polymer blend can limit to some extent the drawbacks of both materials mentioned above. Pronounced suppression of structure coarsening during annealing was observed in filled co-continuous blends with selective localization of the filler particles in one component or at the interface [12–14]. Simultaneously, the percolation threshold is reduced as the filler is not distributed homogeneously in the material [15–19]. This effect is known as double percolation. From this point of view conductive co-continuous polymer blends are promising multifunctional materials.

The localization of the filler particles is determined thermodynamically by the wetting behaviour of the components [20,21]. However, kinetic effects are important, too, as polymer blends after melt mixing are far away from the thermodynamic equilibrium [22]. Thus, the final distribution of the filler in the blend can be affected by the mixing sequence [23] or by the viscosity ratio of the polymers [24,25]. The incorporation of fillers into a co-continuous polymer blend leads often to a refinement of blends structure and to a suppression of coarsening during quiescent annealing. These changes in the morphology development are explained by an increase in the viscosity of the component containing the filler [12] or by the formation of particle structures preventing the motion of

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polymer chains [13,26]. If the filler is localized at the interface, immobilization of the interface by filler particles and reduction of interfacial tension are other plausible explanations (see Ref. [22] for more details).

In this work the effect of carbon black on the flow behaviour of PS/PMMA co-continuous blends is investigated. The PS/PMMA volume ratio of 1/1 is kept constant and the carbon black concentration varies up to 4.5 vol.%. Electron microscopy techniques are used to characterize the morphology development in the blends during quiescent annealing. Electrical conductivity measurements are performed to determine the percolation threshold of carbon black composites and to follow the particles aggregation during annealing. The results obtained from these two independent methods are used to explain the changes in rheology of the blends induced by quiescent annealing. The goal of the work is not to obtain systems with very low percolation threshold but to get an insight into relationships between rheology, structure and electrical properties of immiscible polymer blends with conductive filler.

2. Experimental

2.1. Materials and blends preparation

The blends investigated in this work consist of polymethylmethacrylate (PMMA) and polystyrene (PS). PMMA 7N with the density of 1.19 g cm^{-3} ($25 \text{ }^\circ\text{C}$) and the zero-shear viscosity of 41.0 kPa s ($200 \text{ }^\circ\text{C}$) was provided by Evonik Röhm. PS 158N with the density of 1.04 g cm^{-3} ($25 \text{ }^\circ\text{C}$) and the zero-shear viscosity of 16.2 kPa s ($200 \text{ }^\circ\text{C}$) was provided by Styrolution. A special conductive grade of carbon black (CB) Printex XE2 from Evonik Röhm, which is suitable for incorporation in thermoplastics, was used as filler. This high structured carbon black possesses a specific surface area of $900 \text{ m}^2 \text{ g}^{-1}$ measured by the BET-method and the density of 2.13 g cm^{-3} ($25 \text{ }^\circ\text{C}$).

Prior to processing all materials were dried at $80 \text{ }^\circ\text{C}$ in a vacuum oven for at least 16 h. The PS/PMMA blends filled with CB were prepared by a two-step melt mixing procedure. In the first step CB was dispersed in one blend component yielding a high concentrated premixture, which was in the second step diluted with the second polymer to the desired CB concentration. These blends are denoted as (PS/CB)/PMMA and (PMMA/CB)/PS with the composition of the premixture given in the bracket. Additionally a blend PS/PMMA/CB prepared by direct mixing was investigated, i.e. both polymers and CB were fed simultaneously into a chamber of an internal mixer. In all cases the melt mixing took place in a kneader PolyDrive 557–8310 from Haake at $200 \text{ }^\circ\text{C}$ and a rotation speed of 60 min^{-1} for 8 min. The PS/PMMA volume ratio of 1 was kept constant in all blends prepared and the final concentration of CB was varied between 0 and 4.5 vol.%. After mixing the materials were granulated and compression moulded in a hot press at $200 \text{ }^\circ\text{C}$ for 2 min without pressure and 2 min at 200 bar.

All the CB concentrations given in the paper are real values estimated by a thermogravimetric analysis in nitrogen atmosphere at a heating rate of 10 K min^{-1} using a TGA Q5000 from TA Instruments.

2.2. Rheological and electrical characterization

Viscoelastic properties of premixtures and blends prior and after annealing ($200 \text{ }^\circ\text{C}$, 70 min) were investigated using a stress controlled shear rheometer Gemini from Malvern Instruments with plate–plate geometry (diameter 25 mm, gap 2 mm). The frequency sweeps were performed in the linear viscoelastic regime at the temperature of $200 \text{ }^\circ\text{C}$ and the stress amplitude of 200 Pa in the

range from 0.01 to 100 rad s^{-1} from low to high frequencies. At least two measurements on different samples were performed. If not given by error bars, the variation coefficients of the quantities measured were smaller than 3%. The direct current electrical conductivity of the blends in the molten state during the annealing was measured directly in the rheometer using a Picoammeter 6487 from Keithley as a source of the constant voltage of 1 V and a unit measuring the current flow through the specimen. A detailed description of the setup used can be found in Ref. [27].

2.3. Electron microscopy

The phase structure and carbon black distribution in the blends were examined by transmission electron microscopy (TEM). Sections of 60 nm thickness were cut at a speed of 0.5 mm s^{-1} at room temperature using an ultramicrotome Ultratome III from LKB equipped with a diamond knife. The sections were collected on copper grids (300 mesh) and analysed without staining in a Tecnai G2 Spirit Twin 12, FEI, at an acceleration voltage of 120 kV.

The scanning electron microscopy (SEM) was employed in order to visualize large areas of materials sufficient for reasonable image analysis. To obtain smooth surfaces the specimens were cut at room temperature using an ultramicrotome U2 from Reichert with a glass knife. The PMMA was selectively etched by glacial acetic acid at $60 \text{ }^\circ\text{C}$ for 1 h. The etched specimens were washed with ethanol in an ultrasonic bath for 40 min and after drying covered with a thin layer of gold using Sputter Coater S150B from Edwards. Finally the blends morphology was observed in a scanning electron microscope LEO 435VP from Leica equipped with a secondary electrons detector at an acceleration voltage of 10 kV.

The fineness of the co-continuous morphologies observed in the studied blends was characterized by the specific interfacial length L defined as a length of the interface per unit area (Eq. (1)).

$$L = \frac{1}{A} \sum_i l_i \quad (1)$$

In Eq. (1) $\sum_i l_i$ is the sum of interfacial lengths detected in the micrograph of a cut surface and A is the total area of the micrograph. As insufficient contrast did not allow direct automatic image analysis of the micrographs (Fig. 1a), the interfaces were manually redrawn on a transparent sheet which was digitalized as a binary picture (Fig. 1b). Finally the interfacial lengths were detected and evaluated automatically using the image analysis freeware JMicroVision (Nicholas Roduit, version 1.2.7). Five SEM micrographs of the same magnification from different places of two different specimens were evaluated for every material. Average values of the parameter L and standard deviations characterizing the spatial variation of structure fineness were calculated. Thus, the total areas analysed varied between approx. $6500 \text{ } \mu\text{m}^2$ for blends with fine morphology (high magnification micrographs) and $645000 \text{ } \mu\text{m}^2$ for blends with coarse morphology (low magnification micrographs).

3. Results and discussion

The localization of filler particles in immiscible polymer blends can be predicted by the wetting parameter ω_{12} according to Young's equation (Eq. (2)):

$$\omega_{12} = \frac{\gamma_{CB-PS} - \gamma_{CB-PMMA}}{\gamma_{PS-PMMA}} \quad (2)$$

where γ_{i-j} stands for interfacial tension between given blends components. Depending on the value of ω_{12} , carbon black tends to be localized in PS ($\omega_{12} < -1$), in PMMA ($\omega_{12} > 1$) or at the interface ($-1 < \omega_{12} < 1$). The interfacial tension between components is

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