



Localization of micro and nano- silica particles in a high interfacial tension poly(lactic acid)/low density polyethylene system



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ABSTRACT

This work studies the effects of thermodynamic and kinetic parameters on the localization and migration of spherical micro- and nano-silica particles in the high interfacial tension blend system of poly (lactic acid), (PLA)/low density polyethylene (LDPE). The surface modification of micro-silica particles from a high to a low energy surface was carried out by the grafting of (2-Dodecen-1-yl) succinic anhydride to the surface of micro-silica particles using a new gas-phase reaction approach. The surface modification was confirmed by X-ray photoelectron spectroscopy analysis and surface energy measurements. Young's model predicts that the thermodynamic equilibrium localization of unmodified and modified silica particles in PLA/LDPE blends should be in the PLA phase and at the PLA-LDPE interface, respectively. Scanning electron microscopy results confirm that when unmodified micro- or nano-silica particles are added to a PLA/LDPE melt, the silica particles are selectively localized in the PLA phase even in the blend sample with only 5 vol.% of PLA. However, the modified micro-silica particles were found to be located principally in the LDPE phase. The influence of kinetic parameters was imposed by premixing modified and unmodified micro-silica particles with a high viscosity LDPE phase (H-LDPE). In that case both silica types remain in the H-LDPE phase independent of shear rate and mixing time. When the viscosity of the LDPE phase is reduced, unmodified and modified micro-silica migrate to their thermodynamically predicted locations in the PLA phase and at the PLA-LDPE interface respectively. In the case of unmodified nano-silica particles premixed in the H-LDPE phase, individual well dispersed nano-silica particles migrate to the PLA phase while aggregates remain in the H-LDPE phase. These results have important implications in the field of nanocomposites and indicate that the localization of well-dispersed nanoparticles in a high interfacial tension multiphase system will not likely be influenced by kinetic effects. Kinetic effects are much more dominant in micro-scale silica systems and the kinetic effects are found to depend on a film-draining mechanism at the PLA-LDPE interface region.

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1. Introduction

Micro- and nano-particles dispersed in multiphase polymer systems have received significant attention as they can provide a wider range of mechanical and/or electrical properties as compared with those based on a single polymer matrix. Controlling the localization of the particles into specific phases or at the interface is one of the key parameters in achieving property control in such multiphase systems [1–7]. It has been shown that the localization of solid particles in a dispersed rubbery phase not only increases the dispersed phase size [8,9], but also dramatically suppresses the energy dissipation mechanisms [1]. The localization of solid

particles in the dispersed phase at high solid contents was found to promote the continuity development through the formation of a 3D network of the particles encapsulated by the dispersed phase [10]. The localization of solid particles in the matrix phase can reduce the dispersed phase size by diminishing coalescence through the formation of a physical barrier between the dispersed phase droplets as well as through an increase in the matrix viscosity [11–13]. The localization of solid particles at the interface has also been reported to decrease the dispersed phase size by a solid barrier mechanism [14] and can even enhance the interfacial interactions between polymeric phases [15–18]. In conductive polymer blends, it has been found that the localization of solid particles in either phase of a co-continuous system can significantly reduce the conductivity threshold [2,6]. This latter phenomenon is known as double percolation [6,19]. The lowest electrical percolation threshold can

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be achieved when the conductive particles are localized at the interface of co-continuous polymeric phases [5].

It is apparent that, in addition to the dispersion of solid particles [4,20], controlling the localization of solid inclusions in a multi-phase polymer system is crucial to achieving the desired mechanical and/or electrical properties. Despite the numerous studies in the literature on this subject, a comprehensive understanding of the parameters and mechanisms governing micro- and nano-solid particle migration and localization in multiphase polymer systems is lacking.

Among the few mechanisms that have been proposed to explain the migration of solid particles in multiphase polymer systems, shear induced migration is the most mentioned mechanism [12,21,22]. In this case, the migration of solid particles is assumed to be controlled only by the hydrodynamic forces and the particles are transferred to the other phase as soon as they collide with the interface. The frequency of collision between mono-dispersed particles can be estimated as [12]:

$$C = \frac{8}{\pi} \dot{\gamma} \phi \quad (1)$$

Where $\dot{\gamma}$ and ϕ are the shear rate and the volume fraction of the particles respectively. This mechanism, however, does not explain the trapping of solid particles at the interface reported in some previous studies [23,24]. The Slim Fast mechanism was proposed by Goldel et al. [25] to explain the effect of aspect ratio on the migration of solid particles at the interface. Some authors [12,21] also suggested that the trapping of solid particles between two colliding dispersed phase droplets can transfer solid particles from the matrix phase to the dispersed phase. Although each of these mechanisms may explain a part of the migration and localization process, they do not provide an overall picture of the surface energy/thermodynamics of the migration process versus the effects of important kinetic parameters such as viscosity, mixing strategy and the particle size of solid inclusions. In a previous study from this group [23], the migration and localization of micro- and nano-silica particles in low interfacial tension blends of poly(lactic acid), PLA, and poly(butylene adipate-co-terephthalate), PBAT, were studied in detail and it was shown that the film draining step, between silica particles and the interface, and the migration velocity at the interface are limiting factors that can cause a non-equilibrium localization of silica particles.

PLA/PE blends are of interest in the study of solid particle localization since they provide the case of a model high interfacial tension system. In addition, the blending of PLA with PE has been shown to improve the elongation at break and impact properties of PLA considerably [26,27]. For instant, Anderson and Hillmyer [27] found that the addition of 20 wt.% of PE and 5 wt.% of PLA-PE, as the compatibilizer, significantly increased the impact strength of PLA from 20 J/m to 760 J/m.

The main objective of this paper is to study the effect of thermodynamic and kinetic parameters on the migration and localization of spherical micro- and nano-silica particles in PLA/LDPE blends. The effect of the surface energy of polymer components as well as the surface energy of micro-silica particles on the localization of the silica particles will be studied. Moreover, the effect of mixing strategy, viscosity of the LDPE phase, the particle size of silica and shear rate of mixing on the localization of silica particles will be evaluated.

2. Experimental

2.1. Materials

PLA 2003D (Natureworks, Cargil) with 4% D-isomer and a melt

flow index of 6 g/10 min was purchased from NatureWorks LLC. Two types of LDPE (133A and 100.BW) with melt flow indices of 0.25 g/10 min and 2 g/10 min were purchased from Dow Chemicals and ExxonMobil and will be referred to hereafter as H-LDPE and L-LDPE respectively. (2-Dodecen-1-yl) succinic anhydride was purchased from Sigma–Aldrich and was used as received. Spherical micro- and nano-silica particles, SEAHOSTAR KE-P30 and KE-P10, with hydroxyl content of 1 mmol/g were received from Nippon Shokubai, Japan. The average diameters of the individual spherical particles for micro- and nano-silica are 300 nm and 100 nm respectively. All the materials were dried under vacuum at 60 °C overnight before being used in the experiments.

2.2. Surface modification of micro-silica particles

A new gas-phase reaction approach was used to modify the surface of micro-silica particles which eliminates the need of using a solvent and the precautions required for controlling the solvent moisture content. To this aim, 3 g of micro-silica powder was placed on a mesh in a desiccator containing 1 g of (2-Dodecen-1-yl) succinic anhydride at the bottom of the desiccator. After applying a vacuum using a vacuum pump, the desiccator was placed in an oven at 160 °C. After the reaction time, the desiccator was removed from the oven and cooled in the air. In order to remove the unreacted (2-Dodecen-1-yl) succinic anhydride, the silica powder was washed six times with acetone using a washing cycle of three days, followed by centrifugal separation of the particles. Finally the obtained powder was dried in a vacuum oven at 60 °C overnight. The unmodified micro-silica and modified micro-silica particles will be referred as U-micro-silica and M-micro-silica respectively in the rest of the paper.

2.3. Surface energy measurements and interfacial tensions

The surface energy of PLA and unmodified silica were examined in a previous study [23]. To measure the surface energy of L-LDPE and H-LDPE at room temperature, thin sheets of the polymers were prepared by compression moulding. Ethanol and distilled water were used to remove any contamination from the surface of the sheets. Finally, the sheets were dried at 60 °C for 6 h in a vacuum oven. The surface energy was then determined by measuring the contact angles of water, glycerol and diiodomethane, as liquid probes, on the polymer sheets. The Owens–Wendt [28] approach was used to determine the surface energy as well as its dispersive and polar components. The pendant drop technique was used to measure the surface energies of L-LDPE and H-LDPE at the processing temperature. The apparatus and the operation description can be found elsewhere [29]. The melt densities of L-LDPE and H-LDPE at 180 °C were measured as 0.75 g/cm³ using a high pressure piston-type dilatometer (PVT100, ThermoHaak). To determine the surface energy of modified-silica particles, a film of M-micro-silica was formed by casting a suspension of 1 wt.% of M-micro-silica in acetone. The film is a layer of about 20 μm thick that is formed on a substrate so it can keep its integrity. The surface energy of M-micro-silica at room temperature was determined using the contact angle method. The test procedure was the same as the one described for H-LDPE and L-LDPE. The surface energy of M-micro-silica at the processing temperature was estimated using the thermal coefficient of −0.1 mN/m reported for hydrophobic silica in the literature [22,30]. The interfacial tensions between PLA/LDPE, PLA/M-micro-silica and LDPE/M-micro-silica were calculated using the Harmonic Mean approach [31]:

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