Creating Layers of Concentrated Inorganic Particles by Interdiffusion of Polyethylenes in Microlayers

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ABSTRACT: Interdiffusion of a polymer pair in microlayers was exploited to increase the concentration of inorganic particles in one of the components. When microlayers of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) were taken into the melt, greater mobility of linear LLDPE chains compared to branched LDPE chains caused the layer boundary to move in the direction of the more slowly diffusing chains in a manner similar to the Kirkendall effect in metals. This resulted in substantial shrinkage of the LLDPE layers and corresponding thickening of the LDPE layers. Adding a particulate in the LLDPE did not impede the process of interdiffusion in the melt, and the resultant shrinkage served to increase the particle concentration. For example, resistivity of initially nonconductive LLDPE layers containing nickel platelets decreased by 6 orders of magnitude into the semiconductor range after shrinkage concentrated the particles. The concentrating effect was also demonstrated with TiO_2 particles and talc platelets. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2877–2885, 1999

Key words: interdiffusion; microlayers; polyethylene; particle filler

INTRODUCTION

Coextrusion processes exist that make it possible to form two (or more) polymers into microlayered arrays with hundreds, sometimes thousands, of alternating layers with individual layer thicknesses on the order of microns or less.[1] Microlayering is an attractive approach for creating designed architectures from particulate-filled polymers.[2,3] If the particles are anisotropic, for example, platelets, flakes, tubes, or short fibers, the geometric constraints imposed by layer multiplying ensure orientation of the particles in the plane of the layers. If the filler is added for stiff-

ness, the toughness can also be enhanced by alternating a ductile layer to arrest cracks. Even more sophisticated applications of microlayering technology for creating filled polymer systems are possible. The ability of microlayering to "organize" conductive metal flakes was used to obtain highly anisotropic electrical properties.[4]

The stringent flow conditions required for microlayer coextrusion provide a rare opportunity to combine miscible polymers on a small scale with little or no mixing.[5–7] Heating into the melt state activates interdiffusion and the system gradually converts into a periodic gradient blend with compositional maxima and minima located at the centers of the initial layers. Although the diffusion coefficients of polymer chains are extremely low, the micron-size scale of the microlayers ensures significant compositional changes on the time scale of minutes or hours.

The compositional gradient is fixed by quenching to the solid state. If the components cocrystal-

lize isomorphically, systematic changes in the melting behavior make it possible to quantify the progress of interdiffusion. If the molecular weights are similar and the polydispersity is low enough, a single diffusion coefficient suffices in the analysis of the compositional gradient.[7] If these conditions do not apply, a diffusion model formulated for a polydisperse system reveals the role of different molecular weight species and enables extraction of diffusion coefficients for elementary chains.[8] The analysis demonstrates how interdiffusion of polyethylenes of normal molecular weight and molecular weight distribution can produce convective flow similar to the Kirkendall effect in metals. This occurs when highly mobile chains diffuse into a region of less mobile chains; the resulting osmotic pressure drives the bulk flow and causes the layer boundaries to move in the direction of the more slowly diffusing chains.[9,10]

The moving boundary in microlayers was demonstrated with a miscible high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) pair.[8] For this pair, most of the material interdiffused before there was significant movement of the boundaries. Although the polymers differed in average molecular weight and polydispersity, the mismatch of the component diffusional fluxes across the interface appeared only at longer times, being caused by the relative immobility of a small high-molecular-weight fraction of one of the components. The possibility arises that the moving boundary effect in microlayers can be exploited to create layered structures with highly concentrated inorganic particles. This might be achieved by filling the more mobile component with particulate and subsequently depleting the layer of polymer by interdiffusion.

In order to enhance the mismatch in diffusional fluxes and retain processability in the microlayer coextrusion process, a filled LLDPE and a conventional low-density polyethylene (LDPE) were used in the present study. It was anticipated that lower mobility of chains with long chain branches, compared to linear chains of normal molecular weight, would promote the moving boundary effect. Other experiments with a stationary boundary were required to demonstrate that particles acted as markers for the layer boundaries without significantly affecting interdiffusion. For this purpose, the filled LLDPE was combined with a miscible HDPE of similar molecular weight and molecular weight distribution. This HDPE did not have the high-molecular-

weight fraction that previously drove the moving boundary in microlayers of HDPE and LLDPE.[8]

EXPERIMENTAL

A LLDPE and a HDPE were provided by BP Chemicals, Ltd. The LLDPE comonomer was butene and the ethyl branch content was 20/1000 carbons. The LLDPE had a density of 0.922 g/cc, a molecular weight (M_w) of 118,000 g/mol, and a polydispersity of 4.2. The HDPE had a density of 0.954 g/cc, a M_w of about 76,000 g/mol, and a polydispersity of about 5.9. The molecular weight distributions provided by the manufacturer were well-approximated by a logarithmic normal distribution.[8] A LDPE (Quantum Petrothene NA 952,000) had a density of 0.923 g/cc. Melt blends of LLDPE with a 1 : 1 (wt/wt) ratio of HDPE or LDPE were prepared in the Haake rheomix mixing head at 200°C.

The Zopaque RCL-9 TiO$_2$ had a mesh fineness of 325. The Supra talc platelets had an aspect ratio of 1–20 and a thickness of about 1–3 μm. Nickel flakes with an average thickness of 1 μm and an average aspect ratio of 10 were obtained from Novamet, Wyckoff, NJ. Fillers were blended with LLDPE in a twin-screw Haake extruder or with the Haake rheomix at 190°C. For microlayering, LLDPE was blended with 3 vol % TiO$_2$ (TiO$_2$–LLDPE), 5 and 20 vol % talc (5-talc–LLDPE and 20-talc–LLDPE, respectively), and 5 vol % nickel (Ni–LLDPE). Plaques of Ni-filled LLDPE with 5, 10, 15, and 20 vol % nickel were compression-molded at 190°C.

Microlayers with 32 alternating layers of HDPE and LLDPE (HDPE–LLDPE microlayers) or LDPE and LLDPE (LDPE–LLDPE microlayers) were extruded as a tape about 1 cm wide and 1 mm thick using the microlayer coextrusion system[2,3] and coextrusion conditions[8] described previously. The temperatures of the extruders were adjusted to obtain matched viscosities of the coextruded polymers. The extrusion rates were regulated to obtain a 1 : 1 ratio of the components.

A 6.6-mm circular disc was stamped from the center of the microlayer tape. Specimens this size fit snugly into the aluminum sample pan of the DSC and did not become distorted when melted. The pan lid was aligned with the extrusion direction to preserve sample orientation. To minimize the possibility of a two-phase melt, a temperature above the estimated UCST was chosen as the

Figure 1 Thermograms of the HDPE–LLDPE microlayer after it was taken to 200°C for the time indicated, compared to the thermogram of the HDPE–LLDPE melt blend and the thermogram of the HDPE–5-talc–LLDPE microlayer after 600 min at 200°C.

melt temperature for interdiffusion.[11] Specimens were heated in the Perkin–Elmer DSC-7 at a rate of 200°C/min, held at a temperature of 200°C for the desired time up to 3000 min. The choice of 40°C/min as the cooling rate was based on the cooling rate dependence of LDPE–LLDPE blend thermograms.[11] Zero minutes indicates that the specimen was taken to 200°C and cooled immediately.

The melt-treated specimen was removed from the DSC pan and halved normal to the extrusion direction. One of the halves was used for thermal analysis. The heating thermogram was obtained with a heating rate of 10°C/min. The other half was used for optical microscopy (OM). Sections about 10 μm thick were microtomed from the entire cross section with a cryogenic ultramicrotome. The layer morphology was viewed with transmission polarized light microscopy.

Microlayered and compression-molded specimens of nickel-filled LLDPE were prepared for conductivity measurements, as described previously.[4] The resistivity was taken from the slope of the linear voltage–current relationship.

RESULTS AND DISCUSSION

Microlayers of HDPE and LLDPE

A key indicator for miscibility and cocrystallization of polyethylenes with the broad molecular weight distribution and branching heterogeneity typical of commercial resins comes from a single melting peak. A monotonic shift in temperature and a linear change of enthalpy with composition define the specific melting characteristics and reveal the composition of a miscible, cocrystallizing polymer pair.[12–16] The single melting peak of the 1 : 1 blend, intermediate in melting temperature and enthalpy between those characteristic of the components (Fig. 1), provided evidence for miscibility and cocrystallization of the HDPE and LLDPE used in this study.

This polymer pair approximately met the conditions for a stationary boundary during interdiffusion in microlayers. Without a prominent high-molecular-weight fraction in one polymer that could drive the Kirkendall effect, the flux of each component across the boundary would be about the same at all time periods. The process of interdiffusion of this polymer pair in microlayers as

Figure 2 Optical micrographs of the HDPE–5-talc–LLDPE microlayer after it was taken to 200°C for the time indicated.

monitored by the comparatively simple experimental method of melting behavior is shown with a series of thermograms obtained after the microlayer was held in the melt for a period of time (Fig. 1). Initially, the HDPE–LLDPE microlayer exhibited two melting peaks with maxima at 122.0 and 130.2°C, compared to those at 121.8 and 131.5°C for the LLDPE and HDPE resins, respectively. The close correspondence confirmed minimal mixing of the two polymers during coextrusion. The gradual convergence of the two melting peaks toward a single peak as the time in the melt increased reflected the progress of interdiffusion. A single peak with the same peak temperature, width, and enthalpy as the melting peak of the melt blend represented the interdiffusion endpoint of a homogeneous blend. This coincidence was observed after the microlayer was held in the melt for 600 min at 200°C (Fig. 1). Increasing the melt time to 3000 min produced only a barely detectable narrowing of the melting peak.

The thermogram of the microlayer with 5 vol % talc in the LLDPE layer also exhibited a single peak after 600 min in the melt at 200°C (Fig. 1). The correspondence in peak temperature, width, and enthalpy to the melting peak of the melt blend and to the melting peak of the HDPE–LLDPE microlayer after the same time in the melt at 200°C indicated that interdiffusion of the polymer components proceeded essentially to the endpoint of a homogeneous blend in the presence of talc particles.

The talc particles easily identified the LLDPE layers in optical micrographs of sections cut from the HDPE–5-talc–LLDPE microlayer (Fig. 2). The thickness of the layers defined by the talc particles did not change after 600 min in the melt at 200°C.

Even when a single melting peak in the DSC thermogram indicated that movement of LLDPE and HDPE chains across the interface had produced a homogeneous blend, the talc particles continued to mark the original LLDPE layers. With no net flux of one component across the boundary, there was no driving force for movement of the particles.

Microlayers of LDPE and LLDPE

Creating a net flux of polymer out of the filled layer in order to shrink the layer and concentrate the particles required a polymer pair with specific characteristics. The combination of filled LLDPE with unfilled LDPE met the requirements that the polymers be miscible in the melt in order to interdiffuse, have molecular weights different enough to create a moving boundary, and viscosities similar enough to process into good microlayers. Adding TiO_2 made the LLDPE layers easily distinguishable in the optical microscope. Before interdiffusion had an effect, the filled and unfilled layers had approximately the same thicknesses, as expected for the coextruded 1 : 1 composition [Fig. 3(a)]. However, after 600 min at 200°C, the filled layers were distinctly thinner than initially [Fig. 3(b)], indicating that LLDPE chains had diffused into the LDPE layers more rapidly than vice versa. The net flux of LLDPE caused the filled layers to shrink and forced the particles closer together.

Interdiffusion of LDPE and LLDPE at 200°C was demonstrated by following the DSC thermogram after a microlayer of the unfilled polymers had been in the melt for various periods of time. Initially, the microlayer exhibited endothermic melting peaks at 111.0 and 121.2°C, which corre-

Figure 3 Optical micrographs of the LDPE–TiO$_2$–LLDPE microlayer after it was taken to 200°C for the time indicated.

sponded to the component melting peaks at 110.6 and 120.8°C, respectively (Fig. 4). A third peak gradually appeared in the thermogram; and after 3000 min in the melt, the thermogram closely resembled that of the melt blend with the same composition. The complex melting behavior, with three distinct endothermic peaks, probably reflected phase separation during cooling with superimposed effects of crystallization kinetics.[11] Nevertheless, the change in the microlayer thermogram definitively showed that the polymers interdiffused; moreover, coincidence of the thermograms of the interdiffused microlayer and the melt blend signified that interdiffusion for 3000 min approached the same degree of mixing as melt blending.

The microlayer interdiffusion experiment was repeated with LLDPE that contained 5 and 20 vol % talc. After 3000 min in the melt at 200°C, melting thermograms of these microlayers also exhibited the three endothermic peaks that characterized thermograms of the melt blend and the

Figure 4 Thermograms of the LDPE/LLDPE microlayer after it was taken to 200°C for the time indicated compared to the thermogram of the LDPE/LLDPE melt blend.

Figure 5 Thermograms of the LDPE/LLDPE microlayer, the LDPE–5-talc–LLDPE microlayer and the LDPE–20-talc–LLDPE microlayer, all after 3000 min at 200°C, compared to the thermogram of the LDPE/LLDPE melt blend.

interdiffused LDPE–LLDPE microlayer (Fig. 5). The similarities confirmed a high degree of interdiffusion in the presence of talc particles.

The optical micrographs in Figure 6 show the

LDPE–5-talc–LLDPE microlayer after it was in the melt at 200°C for various periods of time. Initially, the filled and unfilled layers had approximately the same thicknesses as expected for the 1 : 1 composi-

Figure 6 Optical micrographs of the LDPE–5-talc–LLDPE microlayer after it was taken to 200°C for the time indicated.

Figure 7 Change in the average layer thicknesses of the LDPE–5-talc–LLDPE microlayer with time in the melt at 200°C.

tion. After 60 min in the melt, the filled LLDPE layers were noticeably thinner and the LDPE layers were noticeably thicker due to the net flux of LLDPE chains. The filled layers continued to shrink as the melt time increased. A similar decrease in thickness occurred with LLDPE layers that initially contained 20 vol % talc.

After 3000 min in the melt, the average LLDPE layer thickness decreased from 32 to 8 μm as the LDPE layer thickness increased from 32 to 54 μm (Fig. 7). Correspondingly, the talc concentration would have increased by a factor of 3.5 to 17.5 vol %. Because layer thicknesses did not reach a leveling off point within the time scale of the experiments, further concentration of the talc particles probably could have been achieved with longer melt times.

The filler particles were not uniformly distributed in the shrunken LLDPE layers. As the initially homogeneous filled layers shrank, they acquired a distinct concentration of oriented talc particles at the boundaries. The effect was evident after 60 min in the melt and increased in prominence at 600 min as the filled LLDPE layers shrank further [Fig. 6]. However, after 3000 min, the concentrated particles appeared homogeneously distributed in the thin LLDPE layers. The phenomenon is easily understood. Particles drifted in the hydrodynamic flow that resulted from the mismatch in diffusional fluxes of the components. The diffusional fluxes, proportional to the composition gradient, had a maximum at the layer boundaries. Approaching the center of the layer, the diffusional fluxes gradually vanished due to the periodic symmetry of the system.

Changes in the particle distribution reflected the time dependence of the composition gradient. At short times, primarily, the boundary regions were affected. With time, the gradient gradually broadened, increasing the depth of the layer affected by interdiffusion, until layer homogeneity marked the end point.

Microlayers of LDPE and LLDPE with a Conducting Filler

The opportunities for layered structures with concentrated inorganic particles was explored further with an electrically conducting particle. The effect of nickel content on volume resistivity of LLDPE is shown in Figure 8. Compression-molded specimens with low metal content were almost nonconductive. However, at a critical volume fraction, about 15%, the resistivity fell sharply to 10^3–10^4 ohm cm. Assuming that this corresponded to a percolation threshold, the value of 15 vol % was at the lower limit of the range for spherical particles, 15–35 vol %.[17,18] The higher specific surface area of nickel platelets compared to spheres, which increased the probability of particle–particle contacts, probably accounted for the low percolation threshold.[19,20]

The in-plane resistivity of the LDPE–Ni-LLDPE microlayer with 5 vol % nickel was about 10^{10} ohm cm, comparable to the resistivity of compression-molded LLDPE with a nickel content below the

Figure 8 Logarithm of the volume resistivity versus filler content of compression-molded nickel-filled LLDPE. In-plane resistivity of the LDPE–Ni–LLDPE microlayer after 5 min and 600 min in the melt at 200°C is indicated.

Figure 9 Optical micrographs of the LDPE–Ni–LLDPE microlayer after it was taken to 200°C for the time indicated.

percolation threshold. Taking the microlayer into the melt for 600 min decreased the in-plane resistivity by about 6 orders of magnitude to 10^3–10^4 ohm cm, a value that put it above the percolation threshold. The transitional behavior resulted from shrinkage of the LLDPE layers. The thickness of the Ni-filled LLDPE layers decreased by about a factor of 2 after 600 min in the melt (Fig. 9). Correspondingly, the average nickel concentration in the LLDPE layers would have increased to about 10 vol %. This value was below the percolation threshold. The low resistivity of the filled layers probably reflected concentration of oriented nickel particles at the boundaries. Here, the concentration easily could have exceeded the percolation threshold. The resistivity of the specimen was highly anisotropic. In the cross-plane direction, it was essentially nonconductive.

This example illustrates the potential of microlayer coextrusion as a vehicle for combining polymers and inorganics into designed microstructures with unique properties or property combinations. Previous publications demonstrated the capacity to orient anisotropic particles and organize them into layers. This study extends the options to include concentration of particles by thermal manipulation of the microlayer. Other possibilities are imaginable for microprocessing polymeric materials with specific mechanical, optical, electrical, or barrier properties.

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