Preparation of Nanometer Dispersed Semicrystalline/Amorphous Polymer Pseudo-interpenetrating Network Using Supercritical Carbon Dioxide as a Swelling Agent

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Novel linear low-density polyethylene/poly(methyl methacrylate) (LLDPE/PMMA) pseudo-interpenetrating polymer networks (IPNs) were prepared using supercritical CO_2 as a swelling agent. These pseudo-IPNs were formed by the complicated entanglement of the amorphous chain of LLDPE and PMMA chains through controlling the mass gain of PMMA. Small-angle X-ray scattering (SAXS) measurement showed that LLDPE and PMMA were blended at the nanometer level. The thermodynamic miscibility and thermal stability of pseudo-IPNs were evaluated by dynamic viscoelastic analyzer (DVA) and SAXS. The results showed that the LLDPE and PMMA were somewhat thermodynamically miscible, and the structure of LLDPE/PMMA composite with a high mass gain was not easily broken when annealed at temperatures higher than T_m of LLDPE ($T_{m,LLDPE}$). DVA also showed that they retain high storage modului at temperatures beyond the LLDPE melting transition. Further, the extent of the storage modulus can be controlled through controlling the mass gain of PMMA.

The blending of two or more polymers with different characteristics is one of the most important techniques used to prepare new materials with novel features not found in any current constituent polymer. In general, the miscibility of different polymers is so limited that conventional methods such as melt processing or casting from solution are difficult. A synthetic method for producing new polymer composites using supercritical carbon dioxide (scCO₂) as a swelling agent has been developed by Watkins and McCarthy.[1] Both the monomer and initiator are dissolved in scCO₂, then impregnated into the polymer substrate, and subsequently polymerized. Since then, a number of composites using different polymer systems have been produced by this methodology,[2–5] and we, too, have prepared new polymer composites.[6–9]

Phase dispersion crosslinking synergism, or synthesis of interpenetrating polymer networks (IPNs), is an effective method for improving the properties of polymeric materials. Several groups have prepared semi-IPNs using scCO₂. Han et al. showed that semi-IPNs of crosslinked poly(methyl methacrylate) (PMMA) within a silicone rubber matrix and crosslinked polystyrene in a polypropylene matrix could be prepared in scCO₂.[10,11] Howdle et al. prepared semi-IPNs of ultrahigh-molecular-weight polyethylene (UHMWPE) with PMMA-co-poly(ethylene glycol) dimethacrylate (PEGDMA) through scCO₂ facilitated impregnation of MMA and ethylene glycol dimethacrylate (EGDMA) monomers into UHMWPE, and this composite remains mechanically strong even at temperatures above the melting temperature (T_m) of UHMWPE.[4] These

composites have all been extended to the preparation of semi-IPNs by incorporating crosslinking agents or IPNs if the substrate is a crosslinked polymer. In this paper, we describe the preparation of linear low-density polyethylene (LLDPE)/PMMA pseudo-IPNs using scCO₂ as a swelling agent, where the term "pseudo-IPNs" is used because there is no real chemical crosslinking in LLDPE/PMMA composites. The pseudo-IPNs were formed by the complicated entanglement of the amorphous chain of LLDPE and PMMA chains through controlling the mass gain of PMMA using scCO₂, a technique not found in a literature survey. This work aimed to: (1) prepare LLDPE/PMMA pseudo-IPNs with nanometer dispersion, (2) prove the formation of LLDPE/PMMA pseudo-IPNs, (3) study the features of the pseudo-IPNs using scCO₂.

Pseudo-IPNs of LLDPE with PMMA prepared through scCO₂ facilitated impregnation of MMA monomer into LLDPE, where it was subsequently polymerized in situ.[18] The mass gain of PMMA could be controlled by modulating the initial pressure of CO₂, and a series of LLDPE/PMMA composites with mass gains of 0–450 wt % were prepared. In previous studies, LLDPE/PMMA composites were prepared using different compatibilizers,[12–14] but these composites display phase separation on the micron scale and do not offer desirable mechanical properties. In this study, PMMA was generated in the amorphous region of LLDPE, wherein PMMA and LLDPE were blended at the nanometer level. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) analyses showed that the addition of PMMA did not affect the crystallinity and crystal forms of LLDPE. The microstructure of the LLDPE/PMMA composite can be investigated by small-angle X-ray scattering (SAXS). SAXS is a powerful tool for probing the detailed microstructure of semicrystalline/amorphous composites.[6,9] The morphological parameters in the lamellar level, such as the long period, can be deduced from the one-dimensional correlation function or the interphase distribution function. Figure 1a shows the Lorentz-corrected SAXS profiles of original LLDPE and LLDPE/PMMA composites. In the original LLDPE, the scattering vector q of the peak top was $0.390 \, nm^{-1}$ (calculated 16.1 nm Bragg spacing). This peak was due to the long period of the lamellar structure.[15,16] In the LLDPE/PMMA composite, enhanced scattering intensity was observed through the lower scattering vector q ($q < 0.3 \, nm^{-1}$), while the peak from the long period of LLDPE became progressively weaker with increasing mass of PMMA. This enhanced scattering intensity was not observed for the original LLDPE. The enhanced scattering intensity of the LLDPE/PMMA composite depended on the mass gain, which is consistent with the generation of small-angle scattering from extensive disruption of the crystalline
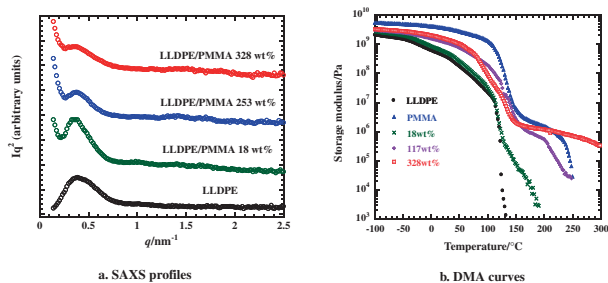
Figure 1. Correspoding relationship between microstructure and macroscopical mechanical properties of LLDPE/PMMA composites.

Figure 2. Temperature dispersion curves of the loss tangent (tan δ) for LLDPE, PMMA, and LLDPE/PMMA composites.

layer upon incorporation of PMMA into the polymer composites.

The dynamic viscoelastic analyzer (DVA) is a sensitive instrument that measures the mechanical response of materials by monitoring property changes with respect to temperature and/or frequency of oscillation. In Figure 1b, the results for DVA are represented as a function of temperature for original LLDPE and LLDPE/PMMA composites. The temperature dependencies of the storage modulus (E') of LLDPE alone show features characteristic of a semicrystalline polymer: a slow decrease in E' throughout the temperature region between -20 and $120\,°C$. At $T \approx 120\,°C$, the crystalline phase of LLDPE melts, which is seen as a marked decrease in the modulus. In the LLDPE/PMMA composites, with increasing mass of PMMA, new plateaus appeared, and the melting break temperature shifted to a higher temperature. In particular, the LLDPE/PMMA composite at 328 wt % shows a remarkable plateau that extends to 300 °C. In general, such plateaus are considered to be an effect of crosslinking but no crosslinking agents were added and the polymer substrate was not crosslinked either. Therefore, we attribute these plateaus to the formation of pseudo-IPNs by a complicated entanglement of the amorphous chain of LLDPE and PMMA chains. To support this explanation, we evaluated the thermodynamic miscibility and thermal stability of pseudo-IPNs.

The thermodynamic miscibility of LLDPE and PMMA was evaluated by DVA. Figure 2 shows the temperature dispersion curves of the loss tangent (tan δ) for LLDPE, PMMA, and the LLDPE/PMMA composites. For LLDPE, the α-relaxation peak appeared at ca. $-20\,°C$ corresponding to the T_g of the amorphous LLDPE chain ($T_{g,LLDPE}$). For PMMA, the α-relaxation peak appeared at ca. $140\,°C$, which corresponds to the T_g of the PMMA chain ($T_{g,PMMA}$). The LLDPE/PMMA composite showed the three peaks which correspond to $T_{g,LLDPE}$, $T_{g,PMMA}$, and the T_m of LLDPE ($T_{m,LLDPE}$). The two peaks corresponding to $T_{g,LLDPE}$ and $T_{g,PMMA}$ are shifted with respect to each other: with the $T_{g,LLDPE}$ peak shifted toward a higher temperature and the $T_{g,PMMA}$ peak shifted toward a lower temperature. Further, the extent of shift increased with increasing mass of PMMA. These results imply that, using this method, the LLDPE and PMMA polymers were somewhat thermodynamically miscible.[17]

The thermal stability of LLDPE/PMMA composites was evaluated by the following method. LLDPE/PMMA composites with different mass gains of PMMA were annealed at 170 °C for
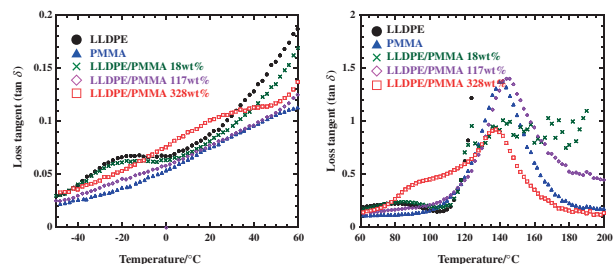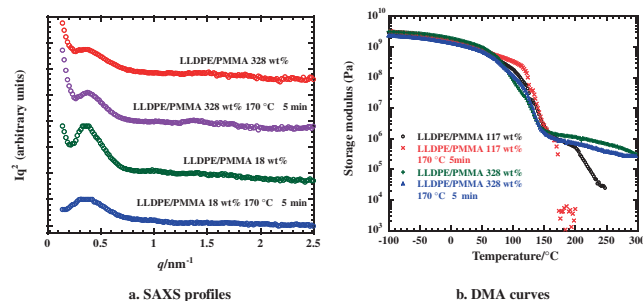

Figure 3. Correspoding relationship between microstructure and macroscopical mechanical properties of LLDPE/PMMA composites after annealing at 170 °C for 5 min.

5 min, and their microstructure and mechanical properties were investigated by SAXS and DVA, respectively. The results are shown in Figure 3. After annealing at 170 °C for 5 min, a new peak was observed in the LLDPE/PMMA composite of 18 wt %, which was derived from LLDPE. In contrast, the LLDPE/PMMA composite of 328 wt % showed almost no changes. The reason for this difference in behavior is that when the LLDPE/PMMA composite with a low mass gain of PMMA was annealed at a temperature higher than $T_{m,LLDPE}$, PMMA migrated by diffusion from the amorphous region of LLDPE and a macroscopic domain structure was formed. On the contrary, when the mass gain of PMMA was high, a complicated entanglement between PMMA and the amorphous chains of the lamellar structure was formed, so PMMA could not easily migrate by diffusion from the amorphous region of LLDPE. Therefore, the nanostructure of this composite was retained after annealing. The results of DVA are in accord with SAXS data. The LLDPE/PMMA composite at 18 wt % annealed at 170 °C was not studied because its melting break is below 170 °C. In contrast, the LLDPE/PMMA composite at 117 wt % could be used to evaluate the thermal stability. After annealing at 170 °C for 5 min, the LLDPE/PMMA composite at 117 wt % showed a poor storage modulus while there was almost no change in the LLDPE/PMMA composite at 328 wt %. To further confirm the thermal stability, a longer annealing time and different temperatures are necessary, and this is the subject of ongoing investigations.

On the basis of the results for thermodynamic miscibility and thermal stability, the mechanism of formation for pseudo-IPNs is shown in Figure 4. In LLDPE/PMMA composites with a low mass gain, the generated PMMA is dispersed in the amorphous region of LLDPE. When annealed at temperatures
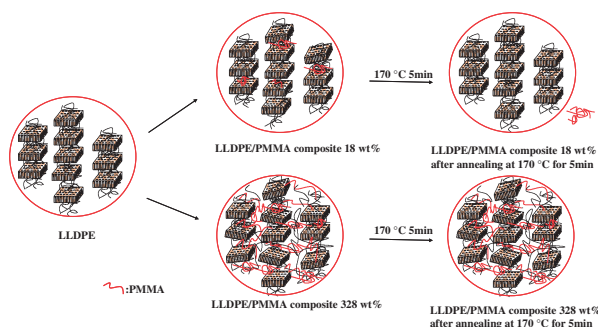
Figure 4. The forming mechanism of LLDPE/PMMA pseudo-IPNs.

higher than $T_{m,LLDPE}$, the PMMA migrates by diffusion from the amorphous region of LLDPE and pseudo-IPNs are not formed. In LLDPE/PMMA composites with a high mass gain, the generated PMMA forms a new successive phase and entangles with the amorphous chain of LLDPE. This structure is not easily broken when annealed at temperatures higher than $T_{m,LLDPE}$, so and pseudo-IPNs are formed. It should be pointed out that there is no distinct boundary between low and high mass gain. Pseudo-IPNs are gradually formed with increasing mass gain of PMMA.

In summary, we have demonstrated that LLDPE/PMMA pseudo-IPNs with nanometer dispersion can be prepared in scCO$_2$. These pseudo-IPNs are formed by the complicated entanglement of the amorphous chain of LLDPE and PMMA chains. The formation of pseudo-IPNs structures restricts the movement of the LLDPE and PMMA chains so that at temperatures beyond the LLDPE melting transition, this composite retains a high storage modulus. It was also demonstrated that through controlling the mass gain of PMMA, the extent of the storage modulus can be controlled. Thus, new pseudo-IPN materials with enhanced mechanical properties can be developed by tuning synthesis conditions such as the ratio of the blending polymer and the type of polyolefin and blending polymer.

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