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Preparation of Polyolefin/Poly(methyl methacrylate) Pseudo-IPNs by Complicated Entanglement in Supercritical Carbon Dioxide

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Abstract: Polyolefin/Poly(methyl methacrylate) (PMMA) pseudo-interpenetrating polymer networks (IPNs) by complicated entanglement were prepared in supercritical carbon dioxide ($scCO_2$). The microstructure and mechanical properties of pseudo-IPNs were evaluated by small-angle X-ray scattering (SAXS) and dynamic viscoelastic analysis (DVA), respectively.

1 Introduction

Polyolefins such as polyethylene (PE) and polypropylene (PP) are considered to be the most important class of thermoplastics among all polymers because of their low cost, ease in processing, and wide range of technical properties and are therefore most widely being used. However, due to the difference in their structure, molecular weight, chain branching, and crystallinity, they are immiscible among themselves, as well as with other polymers. Most often these polymer blends have two different phases with poor adhesion between them at the interface, leading to lower mechanical properties.

A synthetic method for producing a new polymer composite using $scCO_2$ has been developed [1-3]. In this study, we prepared polyolefin/PMMA composites in $scCO_2$, and pseudo-IPNs with very improved mechanical properties were formed by the complicated entanglement of the amorphous chain of polyolefin and PMMA chain through controlling the mass gain of PMMA.

2 Experimental

The linear low density polyethylene (LLDPE) or isotactic polypropylene (iPP) substrate, methyl methacrylate (MMA), and 2,2′-Azobis(isobutyronitrile) (AIBN) were placed in a 50mL stainless steel vessel and sealed. Air in the vessel was replaced by CO_2. After the system reached thermal equilibrium (35°C), the vessel was pressurized up to a specific CO_2 pressure using a CO_2 delivery pump. The polyolefin substrate was soaked for 1 h. The vessel was then heated to the reaction temperature (80 °C), and held for 24 h to ensure that the polymerization of MMA was complete. The vessel was then cooled to 10 °C and gradually returned to ambient pressure. After extracting the sample with acetone for 24 h to remove unreacted reagents and the surface PMMA using a Soxhlet extractor, the Polyolefin/PMMA composite was dried in *vacuo* at room temperature. The mass gain was calculated using the following equation:

$$\text{Mass gain (wt\%)} = \frac{W_t - W_0}{W_0} \times 100$$

where W_0 is the initial weight of polyolefin substrate and W_t is the weight of polyolefin/PMMA composite sheet after drying.

3 Results and discussion

Fig. 1 shows the results on DVA curves of LLDPE and LLDPE/PMMA composites. In the LLDPE/PMMA composites, with increasing the mass gain of PMMA, new plateaus appeared, and the melting break temperature

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shifted to a higher temperature. Particularly, the LLDPE/PMMA composite 328 wt% shows a remarkable plateau that extended to 300 °C. In general, such plateaus are considered to be an effect of chemical cross-linking. But no cross-linking agents were added, and the polymer substrate wasn't cross-linked, too. We attribute these plateaus to the forming of pseudo -IPNs by the complicated entanglement of the amorphous chain of LLDPE and PMMA chain.

The thermal stability of LLDPE/PMMA pseudo -IPNs was evaluated by annealing the samples at 170 °C for 1min. In Fig. 2, the LLDPE/PMMA composite 117 wt% shows a poor storage modulus; while there is almost no change in the LLDPE/PMMA composite 328 wt% after annealing. This is because that in the LLDPE/PMMA composite that mass gain of PMMA is low, when the composite was annealed at a higher temperature than the melting temperature of LLDPE crystal, PMMA migrated by diffusion from the amorphous region of LLDPE, and the macroscopic domain structure was formed. While in the LLDPE/PMMA composite mass gain of PMMA is high, complicated entanglement between PMMA and amorphous chain of lamellar structure was formed, and PMMA couldn't easily migrate by diffusion from the amorphous region of LLDPE.

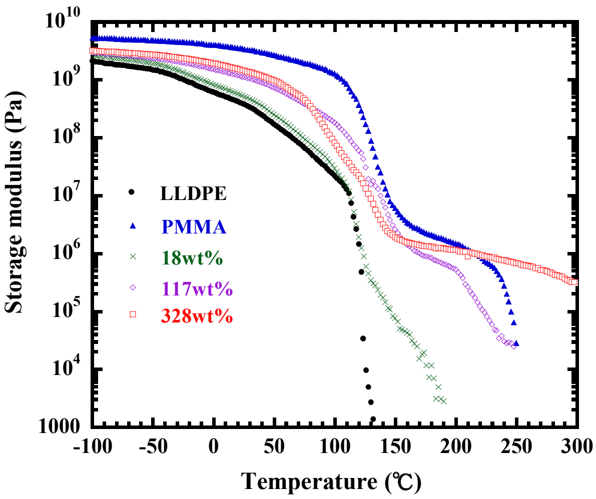

Fig. 1 Temperature dispersion curves of the storage modulus (E') of LLDPE and LLDPE/PMMA composites.

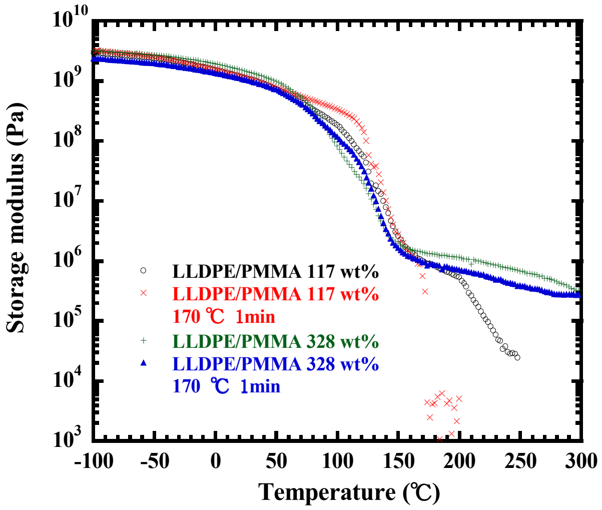

Fig. 2 Temperature dispersion curves of the storage modulus (E') of LLDPE/PMMA composites and LLDPE/PMMA composites after annealing at 170 °C for 1min.

Similarly, iPP/PMMA pseudo-IPNs also could be prepared using this method, and shows an enhanced storage modulus at a high temperature. The extent of storage modulus can be controlled by the mass gain of PMMA.

4 Conclusions and discussion

Polyolefin/PMMA pseudo-IPNs were prepared in $scCO_2$. These pseudo-IPNs are formed by the complicated entanglement of the amorphous chain of polyolefin and PMMA chain. The formation of pseudo-IPNs structures restricts the movement of the polyolefin and PMMA chains so that at temperatures beyond the polyolefin melting transition, this composite still remains a high storage modulus. Additionally, the extent of storage modulus can be controlled through controlling the mass gain of PMMA. Thus, new materials with an enhanced storage modulus at high temperatures can be developed.

5 Reference

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