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Microstructure and Mechanical Properties of Isotactic Polypropylene / Ploy (methyl methacrylate) Nanocomposite Prepared using Supercritical Carbon Dioxide

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Abstract: A novel composite comprising isotactic polypropylene (iPP) and poly (methyl methacrylate) (PMMA) was developed by using supercritical carbon dioxide (scCO₂), although they are usually immiscible and have phase-separated morphology. IPP and PMMA were blended at the nanometer level. The mechanical properties of iPP/PMMA composite such as dynamic viscoelasticity, yield stress, fracture stress and strain depended on composition of the composite.

1 Introduction

Blending of two or more polymers having different characteristic features might be one of important techniques to prepare a new material having a feature not found in any constituent polymer. In general, many polymer combinations are incompatible. Especially, amorphous polymer and semicrystalline polymer would not be well blended by the methods, because the amorphous polymer would be excluded from the crystalline regions during the crystalline-growth process [1].

As is well known, commercially available semicrystalline iPP is one of the most common polymers, but the versatility of iPP as an industrial material would be much more enhanced if another amorphous polymer could be blended in the amorphous phases of iPP. The present study is devoted to establish a new method to prepare a nanocomposite material of iPP with amorphous PMMA dispersed on nanometer scale in the amorphous phase of iPP. iPP and PMMA have quite different physical properties and cannot be well blended by the conventional method. In this method, scCO₂ is used as a processing medium to facilitate effective impregnation of methyl methacrylate monomer (MMA) into the amorphous phases of iPP and, subsequently, the impregnated MMA is allowed to polymerize radically, *in situ* [2].

2 Experimental

The iPP substrate, MMA, AIBN as an initiator were placed in a 50mL stainless steel vessel and sealed. Air in the vessel was replaced by CO₂. After the system reached to thermal equilibrium (35 °C), the vessel was pressurized upto a specific CO₂ pressure. The iPP substrate was soaked for 1 h. Then the vessel was repressurized upto last specific pressure, heated to the reaction temperature (80 °C), and held for 24 h. After the completion of the polymerization,

the vessel was cooled to 10 °C and gradually released to ambient pressure. The iPP/PMMA composite was dried *in vacuo* at room temperature after extraction with acetone for 24 h to remove unreacted reagents and the PMMA generated on the surface of the iPP/PMMA composite by using a Soxhlet extractor. The weight of PMMA which generated in iPP ground substance displayed it as weight increase rate (wt%) for the weight (100) of the ground substance sheet.

3 Results and discussion

Fig. 1 displays TEM micrographs of the solution blend of iPP/PMMA=100/100 (a) and the iPP/PMMA composite (104 wt%) (b). The dark portions in the micrographs are iPP domains and the light portions are PMMA domains. In the solution blend, large PMMA domains of micron scale were formed in iPP matrix. In the iPP/PMMA composite, on the other hand, PMMA domains are finely dispersed in iPP matrix on nanometer scale. Nevertheless, the crystalline lamellae of iPP can be clearly seen in the both blends when the micrographs are magnified, indicating that some portions of the original crystalline phases of iPP are preserved during the preparation process.

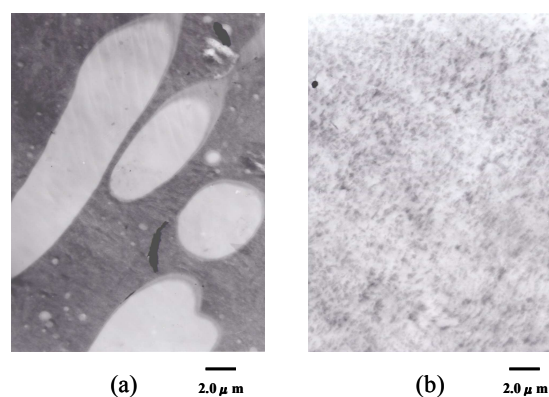


Fig. 1. TEM micrographs of solution blend 100/100 (a) and iPP/PMMA composite 104 wt% (b).

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Fig. 2 is plotted the scattering data in the form of the Lorenz-corrected SAXS intensity Iq^2 vs. scattering vector q . The iPP shows both the first- and second-order reflections, assigned to the long period corresponding to the sum of thickness of a crystalline layer iPPc and an amorphous layer iPPa in a crystalline lamella. The first- and second-order reflections are also observed in the solution blend because of macro-phase separation in the blend. In the iPP/PMMA composite 17 wt%, a shoulder appears in a q range around 0.3 nm^{-1} and it becomes a bump with increasing the weight of PMMA, the maximum of which is located at q of *ca.* 0.20 nm^{-1} in the iPP/PMMA composite 109 wt%. From these results, it would be speculated that PMMA was generated in the amorphous regions between crystalline lamellar.

Fig. 3 shows temperature dispersion curves of the loss tangent ($\tan \delta$) for original iPP, PMMA, solution blend and iPP/PMMA composite. The solution blend showed the peaks of glass transition temperature (T_g) of iPP and PMMA and T_m of iPP. This also confirms presence of macro-phase separation in the solution blend. In contrast, among the peaks that were showed in the iPP/PMMA composites, the peak that arises from the $T_{g,iPP}$ shifts to the high temperature, and the peak that arises from the $T_{g,PMMA}$ shifts to the low temperature. These two peaks indicated that iPP and PMMA were blended thermodynamically to some extent.

Table. 1 shows results of tensile test at 20°C . In the solution blend, a macro-phase separation was induced because iPP and PMMA are incompatible with each other. As for the macro-phase separated structure, a disadvantageous effect on the mechanical properties usually occurred. However, yield stress of all iPP/PMMA composite is considerably higher than that of iPP. Fracture stress of iPP/PMMA composite is also increased comparing to iPP. Therefore, PMMA generated in the amorphous regions at nanometer size affected significantly the mechanical properties of iPP/PMMA composite. And these mechanical properties of iPP/PMMA composite can be controlled with the mass gain of PMMA.

4 Conclusions

We have succeeded in obtaining iPP/PMMA composite using scCO_2 . iPP and PMMA that generated in the amorphous region of iPP were blended at the nanometer level. PMMA affected significantly yield stress, fracture stress and fracture strain of iPP/PMMA composite. And these mechanical properties of iPP/PMMA composite can

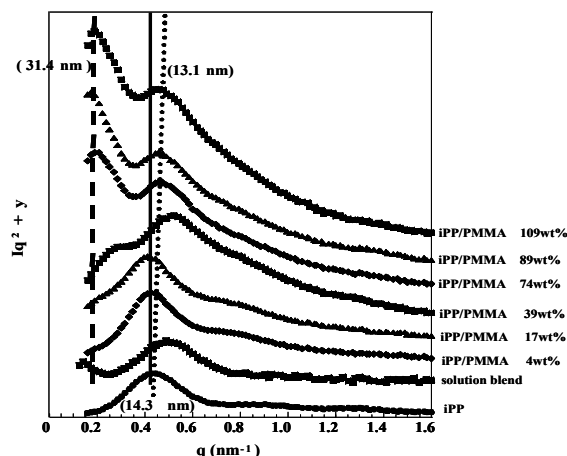


Fig. 2. Plots of Lorenz-corrected SAXS intensity Iq^2 vs. q of iPP, solution blend and iPP/PMMA composites.

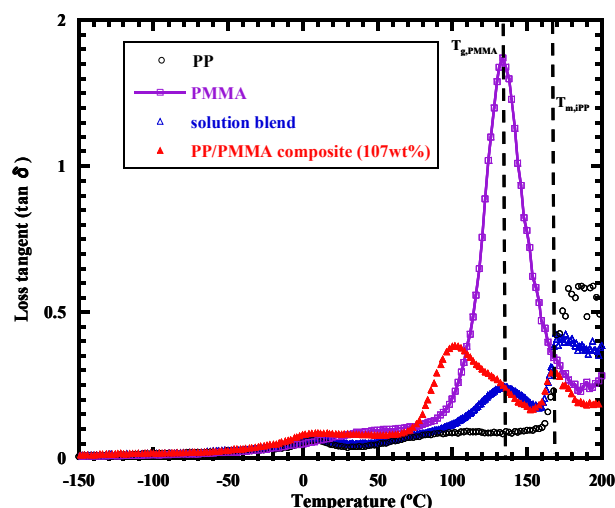


Fig. 3. Temperature dispersion curves of the loss tangent ($\tan \delta$) for original iPP, PMMA, solution blend and iPP/PMMA composite (mass gain: 107 wt%).

Table. 1 Results of tensile test.

Sample name	Yield stress (MPa)	Fracture stress (MPa)	Fracture strain (%)
PP	31	30	1290
iPP/PMMA composite (17 wt%)	34	36	1000
iPP/PMMA composite (28 wt%)	37	35	860
iPP/PMMA composite (59 wt%)	38	33	90
iPP/PMMA composite (74 wt%)	38	33	55
iPP/PMMA composite (109 wt%)	38	34	30
solution blend	—	27	4
PMMA	—	42	5

be controlled with the mass gain of PMMA.

5 Reference

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