

Compatibilization of Polypropylene/Molecular Sieves Type 13X Based on Carboxyated Polypropylene

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ABSTRACT: Molecular sieves type 13X (13X) was selected as a filler of polypropylene (PP). The effect of carboxyated polypropylene (EPP) on mechanical properties, melting behavior, morphology and rheology behavior of PP/13X composites was studied. Mechanical properties tests showed that when 4% EPP added, the impact strength and tensile strength increased 65.6 and 4.6% than PP/13X composites, respectively. It was suggested that the EPP activated the heterogeneous nucleation centers on the filler surface, and made 13X dispersed in PP matrix homogeneously by POM. SEM

illustrated that EPP improved the adhesion and the compatibility between 13X and PP. Flow tests indicated that the EPP played the role of lubricant in PP/13X. All the investigations showed EPP was a true coupling agent for PP/13X composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 66–69, 2007

Key words: compatibilization; polypropylene; molecular sieves 13X; carboxyated polypropylene

INTRODUCTION

Various inorganic particles, such as montmorillonite, CaCO_3 , SiO_2 , TiO_2 , talc etc. are usually used as filler in the polymer matrix forming the inorganic/organic composites, to contribute to improving the crystallization, mechanical or rheological properties.^{1,2} Molecular sieves type 13X (13X) are crystalline aluminosilicate minerals and have high internal surface area due to the channels and pores, which are available for the adsorption of low weight molecules. 13X have been used in many industrial fields as catalysts, molecular sieves, adsorptive agents, ion exchange materials etc. They are also employed as an additive to provide antibacterial and flame retardant properties to polymers.^{3,4} The 13X are abundant and low-cost materials, which could be used as filler in polypropylene (PP) composites, however, 13X loading decreases the mechanical properties of PP because of poor interfacial interactions.

In our laboratory, it was found that the incorporation of carboxyated polypropylene (EPP) into PP/IFR composites results in the improvements of the compatibility between IFR particles and the polymer matrix.⁵ The purpose of the present work was to investigate the effects of EPP as a compatibilizer between PP and 13X.

EXPERIMENTAL

Materials

The PP [type T30S, $d = 0.901 \text{ g/cm}^3$] was supplied by Tian-Jin United Chemical (Tianjin, China). The 13X was supplied by FuChen Petrochemical Factory (Tianjin, China). EPP was prepared as reference,⁵ acid No. 0.088 mg KOH/g.

Equipment and analysis procedures

The tensile strengths were measured following the GB/T-1040-1992 standard by an LJ-3000N test apparatus, and the impact strengths were measured following the GB 1040 standard by an XCJ-40 test apparatus. The crystalline morphology of sample was captured by the camera DSC-V1 (SONY, Japan) observed on a XSZ-H polar optical microscope (POM) (Chongqing, China), with magnified 100 times. After being coated with gold, the morphology of the tensile fracture surfaces of the composites was observed with an Ammry 1000B scanning electron microscope (SEM). The rheological behavior was determined, using a XLY-II rheometer (Jilin, China), and the temperature was fixed at 190°C, with the experimental loads of 40, 60, 80, 100, 120, and 140 kg/cm².

Surface treatment of 13X

When xylene was heated to near boiling, EPP was added (EPP/xylene = 1 g/10 mL), after the EPP had dissolved completely added 13X, cooled with mixing

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TABLE I
Mechanical Properties of PP/13X/EPP Composites

Sample	PP/13X/ EPP	Tensile strength (MPa)	Impact strength (kJ m ⁻²)
A	100/0/0	38.07	3.58
B	100/6/0	35.80	3.43
C	99/6/1	36.20	3.75
D	98/6/2	37.32	4.46
E	97/6/3	37.89	5.40
F	96/6/4	37.46	6.21
G	95/6/5	35.55	5.17

round, filtrated, air-dried, and dried in a vacuum oven at 80°C for 10 h to get rid of xylene completely.

Preparation of the PP/13X/EPP composites

The composites were done at 170–180°C in a two-roll mill. After PP had melted, surface treated 13X was added, and the blending was carried out for 10 min; then the composites were removed for compression molding at 180°C for 3 min; finally, the composites were cooled to room temperature by cool pressing. After annealed at 70–80°C for 8 h, the specimen was operated on a ZHY-W almighty sample preparing machine.

Preparation of analysis samples

POM: The compression molded film sample was sandwiched between two cover glasses, and was kept on the hotplate at 200°C for 10 min to melt completely. Then the samples were transferred to a 200°C oven, and cooled naturally to 142°C, isothermal crystallized at 142°C for 2 h.

RESULTS AND DISCUSSION

Mechanical properties

Fan et al.⁶ have found that when 13X content was 6% the mechanical properties of PP/13X composites got to the optimal, based on titanate coupling agent. So here the PP/13X = 100/6 was chosen.

The mechanical properties of PP/13X/EPP composites were shown in Table I. As seen from Table I, composite B, addition of 6 g 13X in 100 g PP, because of the poor compatibility, the mechanical properties decreased obviously than pure PP. To improve the compatibility, part PP of the composites was substituted by EPP. It is can be seen in Table I, the mechanical properties produced a significant improvement by EPP, particularly for composite F, 4% EPP added, which met to the maximum value, the impact strength and tensile strength increased 65.6 and 4.6% than PP/13X composites, respectively. However, the mechanical property of the composite G was lower than that of E, indicating that a suitable

amount of EPP can improve the mechanical properties of PP/13X composites.

In a conclusion, mechanical properties of PP/13X composites can be improved by EPP evidently. It demonstrated that the compatibility between the 13X dispersed phase and the PP matrix phase was improved.

Morphology

The morphology is an important way to characterize the compatibility of the composites directly. Here it is investigated using POM and SEM.

Figure 1 was the POM of the composites PP/13X/EPP. As can be seen from Figure 1(a), with gloomy “cross” in the crystal, pure PP appeared as complete sphere crystal, the spherulites impinging on each other. According to Figure 1(b), the crystal morphology of the PP was greatly affected by the addition of 13X. As 13X added, the spherulites size decreased significantly and dispersed nonuniformly. The spherulites were large in the place where there were a few or no 13X, but small in the place where filler agglomerated. That might be the 13X served as seeds for spherulites growth in PP, resulted in the crystals grow on the surface of the 13X particles.

The effect of EPP on crystal morphology was shown in Figures 1(c) and 1(d). With the EPP content increased, the spherulites were uniform; its size distribution became narrow. Figure 1(d) illustrated that the 13X dispersed into the PP matrix homogeneously, and PP was crystallized over the 13X domain surface preferably. It was suggested that the EPP activated the heterogeneous nucleation centers on the filler surface, and improved the compatibility of 13X with PP.

(a) PP; (b) PP/13X/EPP = 100/6/0; (c) PP/13X/EPP = 98/6/2; (d) PP/13X/EPP = 96/6/4.

Figure 2 was the SEM of the tensile fracture surfaces of composites. It can be seen from Figure 2(a) (PP/13X composite), the interface between 13X and PP can be clearly observed, and the surface of the remaining holes appeared to be very smooth. This means that the adhesion was poor between 13X and PP. As EPP added [Fig. 2(b,c)], 13X dispersed homogeneously, and interface of 13X and the matrix became rough. It implied that EPP enhanced the matrix-filler interfacial adhesion, improved the dispersibility of the filler in the matrix, which in turn influenced the crystallization behavior of the PP matrix, and increased mechanical properties, as shown in the above section.

(a) PP/13X = 100/6; (b) PP/13X/EPP = 98/6/2; (c) PP/13X/EPP = 96/6/4.

Rheological behavior of composites

An XLY-II flow tester was used to investigate the rheological behavior of composites. A plot of appa-

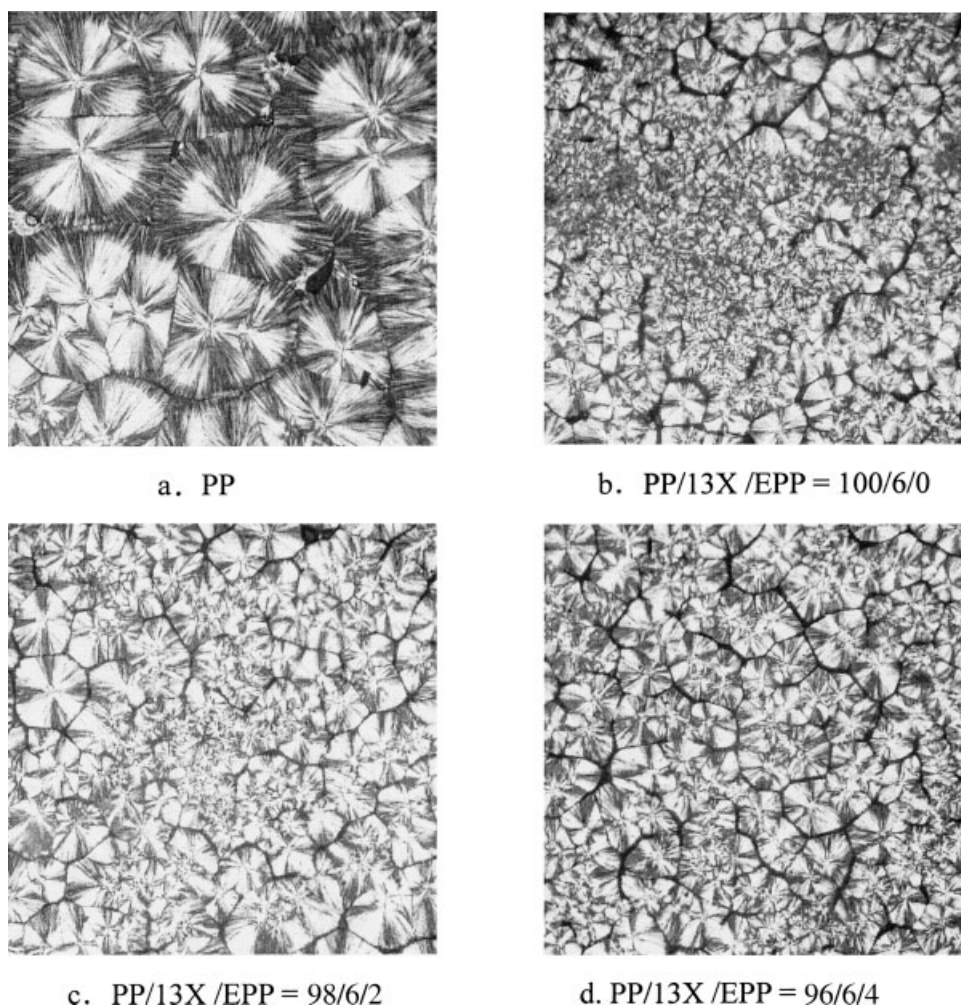


Figure 1 The POM of the composites PP/13X/EPP.

rent viscosity $\ln \eta_a$ versus shear rate $\ln \dot{\gamma}_w$ was given in Figure 3.

The η_a of PP/13X composite increased (Line A) compared with Pure PP (Line G), because 13X restricted PP molecular motion, thus imposed resistance to flow. With the addition of EPP the apparent viscosity of composites B, C, D, E, F decreased. Generally, the decrease in apparent viscosity indicates free molecular

motion of PP segments. Here the reasons could be that the EPP plays the role of a lubricant between PP and 13X, although a reduction in molecular weight of EPP⁵ by oxidizing reaction was one aspect. It represented a more homogeneous dispersion of 13X in the PP system, referring to the POM and the SEM micrographs.

In addition, the apparent viscosity of the composites decreased as the shear rate ($\ln \dot{\gamma}_w$) increased,

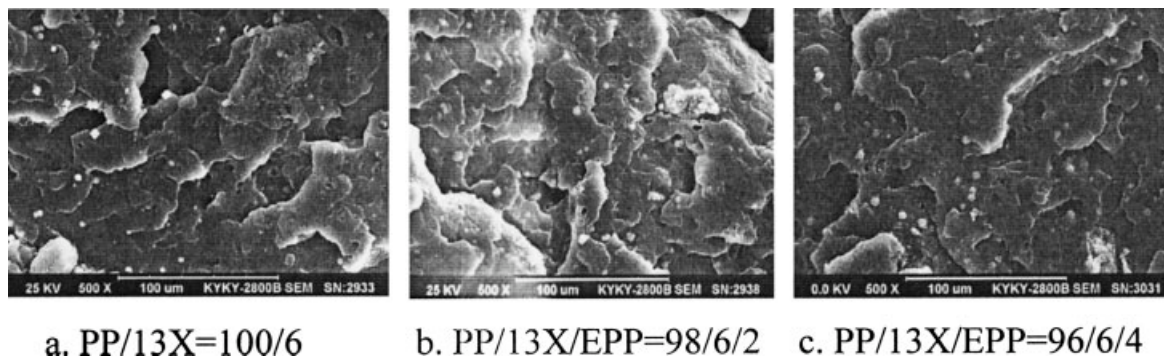


Figure 2 SEM of tensile fracture surfaces of PP/13X/EPP.

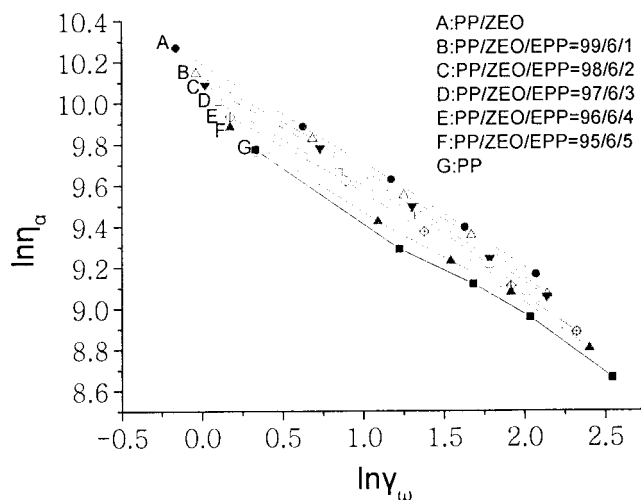


Figure 3 The rheological behavior of PP/13X/EPP (190°C).

demonstrating linearity, which implied that the melt is a pseudoplastic liquid and has good processibility.

CONCLUSIONS

Mechanical properties tests showed that 4% EPP added, the impact strength and the tensile strength

increased 65.6 and 4.6% than PP/13X composites, respectively, which illustrated that EPP reinforced the interaction between PP and 13X. POM results indicated that the addition of EPP enhanced the heterogeneous nucleation, and made 13X particles dispersed into the polymer matrix uniformly. The SEM gave the evidence that EPP improved the adhesion between 13X and PP. Flow tests indicated that the EPP played the role of lubricant between PP and 13X.

EPP was a true coupling agent for PP/13X composites, improved the interactions and the compatibility of PP and 13X.

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