

양이온성 폴리프로필렌이 폴리프로필렌/폴리염화비닐 블렌드의 상용화에 미치는 영향

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Effect of Cationic Polypropylene on the Compatibility of Polypropylene/Poly(vinyl chloride) Blends

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Abstract: Graft copolymers were usually introduced to improve the compatibility and mechanical properties of polymer blends. In this paper, the effect of cationic vinyl monomer grafted polypropylene (FPP) with different grafting yields (GY) on mechanical properties of polypropylene (PP)/poly(vinyl chloride) (PVC) blends had been investigated. The results indicated that FPP could enhance compatibility of PP/PVC blend remarkably. The tensile strength and the impact strength of PP/PVC blends with a concentration of FPP (GY=16.78%) at 4 phr increased up to 18.10% and 74.67%, respectively. The viscosity of PP/PVC/FPP blends had been also investigated, and the results showed PP/PVC/FPP (80/20/4) blend was higher than that of other PP/PVC/FPP when FPP (GY=16.78%) was added. The SEM micrographs suggested that the compatibility of the PP/PVC blend was optimum when FPP (GY=16.78%) was added.

Keywords: cationic polypropylene, compatibility, PP/PVC blend, mechanical property, rheological property.

Introduction

To obtain new materials, polymer blending is a very attractive way, but most of the polymer blends are immiscible and/or incompatible because of high interfacial tension and, consequently, poor interface adhesion.^{1,2} However, the phenomenon of compatibility can be induced into an immiscible binary system by introducing a third component that will either interact chemically with both the phases or will have specific interaction with one phase and physical interaction with the other. The addition of a block or graft copolymer reduces the interfacial tension between the two phases, increases the surface area of the dispersed phase, promotes adhesion between the phase components, and stabilizes the dispersed phase morphology.³⁻¹⁰

The polyolefins and poly(vinyl chloride) (PVC) are two important classes of commercial polymers. Polypropylene (PP) has advantages such as excellent mechanical properties and chemical erosion resistance, and is widely used in various fields. PVC, an inexpensive polar polymer, is of high strength and fireproof. However, the striking difference between polarity of PP and PVC results in the low compatibility, and the interfacial adhesion between the phases strongly influenced the final properties of the materials.

Recently, the preparation of PP/PVC blends with excellent properties and the enhancement of their compatibilization by additives such as graft copolymer had been the focus of research interests all around the world.^{11,12} In this paper, the effect of cationic vinyl monomer grafted polypropylene (FPP) with different grafting yield on compatibility of PP/PVC (80/20) blends was investigated systematically. The measurements of SEM, rheological properties, tensile strength and impact strength indicated that the FPP could enhance compatibility of PP/PVC blend remarkably, and the compatibility of the PP/

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PVC/FPP (80/20/4) blend was optimal when FPP (GY=16.78%) was added. This paper also reports a new way to improve the poor compatibility of the reversed polar polymers. This research is worthwhile and the blend can be foreseen with a great prospect in the fields such as building materials, auto materials and piping materials.

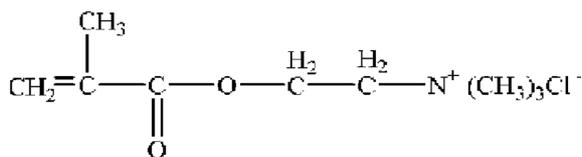
Experimental

Materials. Polypropylene (T30S), with a MFI (melt flow index) of 3.5 g/10 min, was purchased from Daqing Petroleum Chemical Corp. (Daqing, China). Suspension PVC (K=68) with an average polymerization degree of 1000 was supplied by Qilu Petrochemical Corp (Zibo, China). Methacryloxyethyltrimethyl ammonium chloride grafted PP (FPP) with grafting yields of 11.73%, 16.78%, 19.29%, 21.34% was self-prepared. Schematic structures of Methacryloxyethyltrimethyl ammonium chloride (METAC) was shown in Scheme 1. Grafting procedure as follow¹³:

The iPP granules (2.0 g) were swollen in styrene solution containing benzoyl peroxide (BPO), and then were immersed in METAC aqueous solution in a 250 mL four-neck round bottom flask with a condenser and a stirring device. The system was deoxygenated by bubbling nitrogen for 1 h. The grafting reaction was carried out by placing the reactor in a homemade electronically controlled temperature oil bath under a nitrogen atmosphere. The grafted PP was carefully washed with boiling water for 0.5 h removing METAC homo-polymer, and then were purified by Soxhlet extraction in acetone for 36 h in order to eliminate polystyrene (PSt), poly(styrene-co-METAC). Finally the purified samples were vacuum dried at 80 °C for 24 h. The grafting yield was calculated by the following equation:

$$\text{Grafting yield (GY)(\%)} = \frac{W_g - W_0}{W_0} \times 100$$

Where W_0 and W_g are the weights of the sample before and after grafting, respectively.



Scheme 1. Schematic structure of methacryloxyethyltrimethyl ammonium chloride (METAC).

Blend preparation. Before being blended, PVC and the processing additives were premixed in a high-speed mixer for 10 min at the mass ratio, PVC/tribasic lead sulphate/dibasic lead phosphite/stearic acid/paraffin (100/2/1/0.4, mass ratio). The mixtures was carried out at 180 °C in a two-roll mill (XKR-160, Zhanjiang Machine Co., Guangdong, China). PVC and FPP were blended for 2 min, and then blended with PP for 6 min. The blends were compressed into sheets with a hydraulic press at 180 °C and 10 MPa for 4 min, and then were cooled to room temperature.

Characterization. Tensile testing was performed on an LJ-500 N tensile test machine (Chengde Laboratory Instrument Works) at a speed of 10 mm/min according to ASTM standard test method. The notched Izod impact strength was measured with an X CJ-40 impact tester (Chengde Laboratory Instrument Works, Hebei, China) according to ASTM standard.

The melt viscosity of all blends under processing conditions was measured using a high-pressure capillary rheometer (model XLY-1) with a capillary die of 1 mm, and L/D ratio of 40. The experimental temperature was fixed at 180 °C with experimental loads of 200, 180, 160, 140, 120, and 100 kg/cm².

The cryofractured surfaces of all samples were characterized with a KYKY-1000B scanning electron microscope (Beijing Analytic Instrument Co., Ltd., China) operated at 15 kV. The specimens were immersed in liquid nitrogen for 5 min and then fractured. The fractured surfaces after proper drying were sputtered with a thin layer of carbon before scanning electron microscopy (SEM) examinations.

Results and Discussion

Characterization methods on compatibility of blends are often used such as T_g , cloud points, AFM, SEM, rheological properties, tensile strength and impact strength and so on. In this paper, we focus on the application performance of the blend such as rheological properties, tensile strength and impact strength, and SEM is used to characterize the compatibility from the micro morphology.

Tensile and Impact Strength. The tensile strength of the PP/PVC/FPP (80/20/4) blend was shown in Figure 1(a) when FPP with different grafting yield was added. Because of the poor inter-phase adhesion and high interfacial tension between the two phases, PP and PVC formed highly incompatible mixtures. The mechanical properties of these mixtures could be improved by the addition of FPP compatibilizer. Seen from

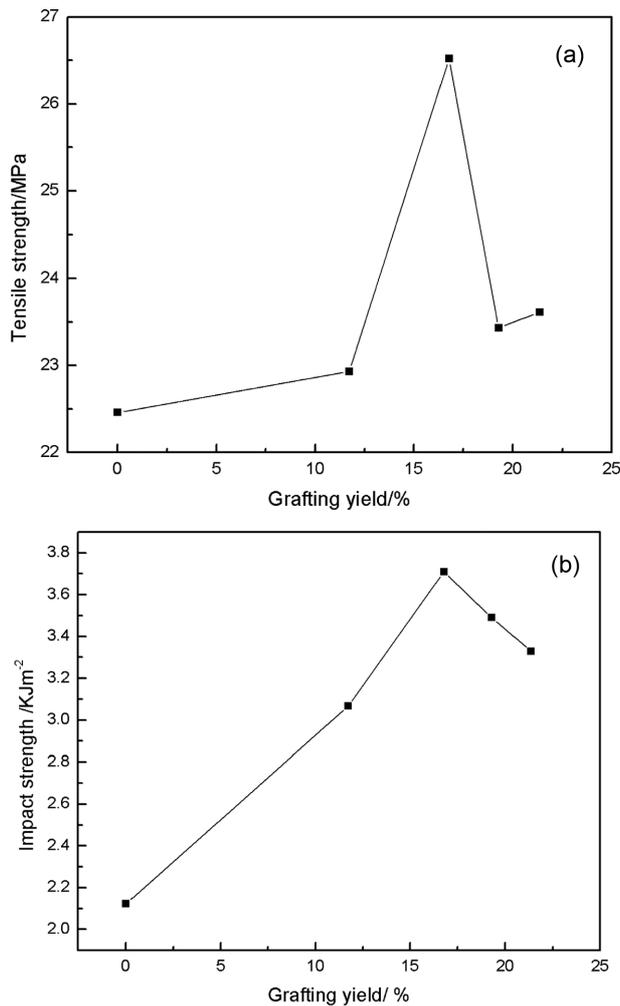


Figure 1. Mechanical properties of PP/PVC/FPP (80/20/4, wt%) blends when FPP with different grafting yield was added: (a) tensile strength; (b) impact strength.

Figure 1(a), the tensile strength increased with addition of compatibilizer. The tensile strength of PP/PVC blends with a concentration of FPP (GY=16.78%) at 4 phr increased up to 18.10%. However, a significant reduction in mechanical properties occurred when the grafting yield of FPP was beyond 16.78%. The results came from the change of compatibility between PP and PVC from the better to the worse. From theoretical point of view, firstly, FPP and PP phase formed eutectic. On the other hand, methenyl-hydrogen atom of PVC should interact with the ester carbonyl of METAC chains, and then form weak hydrogen bond,^{11,12,14} and ion-dipole interactions between the quaternary ammonium cation and PVC chains, as shown in Figure 2. In addition, according to Flory-Huggins quasi-lattice theory Huggins parameters $\chi_{PP/PVC/FPP}$ of the blends decreased because of addition of FPP, and the crit-

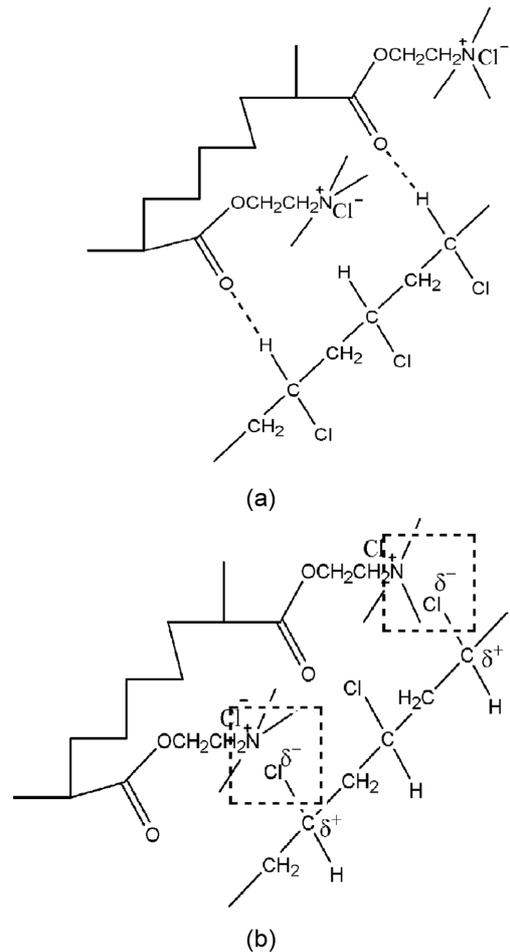


Figure 2. Interaction between groups-groups in blends: (a) weak hydrogen bond; (b) ion-dipole interactions.

ical $\chi_{CPP/PVC}$ is almost invariant, so $\chi_{PP/PVC/FPP}$ is trend to $\chi_{CPP/PVC}$, the compatibility of two phase increased.¹⁵ These reasons have the abilities to improve compatibility of PP and PVC, and deduce the increasing of the tensile strength of the blends. However, as the grafting yield of FPP increased, the number of quaternary ammonium cations increased, they might be grouped together because of electrostatic interaction. Additionally, the quaternary ammonium groups acted nucleation agent, and promoted the PP crystallization,¹³ which possible induced the phase separation of PP/PVC blend, so the addition of FPP with higher grafting yield was not favorable to increase the tensile strength of the blends.

The effect of FPP with different grafting yield on the impact strength was shown in Figure 1(b). It was given that the impact strength of PP/PVC blend increased up to 74.67% when FPP (GY=16.78%) was added and then decreased remarkably. The reasons were the same as mentioned above. It should be

stressed that morphology was a key to determine mechanical properties of blends. The final morphology was strongly dependent on the processing conditions, the amounts and grafting yield of the FPP. The effects of FPP on the morphologies of PP/PVC blends would be discussed in next section.

Processing Characteristics. The complex viscosities of PP/PVC/ (80/20) blends were showed in Figure (3) when FPP with different grafting yield was added. There are good linearities of $\text{Ln}\eta_a$ versus $\text{Ln}\dot{\gamma}_w$ in studied range, which was the same as power law. The rheological behavior of the blends was typical pseudoplastic fluid characteristics. The rheological properties of the blends were found to be changing dramatically with the addition of FPP components. The viscosity of PP/PVC/FPP (80/20/4) blends reached a maximum value when FPP (GY=16.78%) was added. The results also indicated an improvement of compatibility resulted from the FPP compatibilizer, which was capable of interaction with both PP and PVC. And as grafting yield of FPP was over 16.78%, the viscosity of PP/PVC/FPP blends decreased. The possible explanation is that the addition of FPP with polar groups, which formed eutectic with PP; At the same time, as above mentioned, methenyl-hydrogen atom of PVC should interact with the ester carbonyl of METAC chains, and then form weak hydrogen bond;^{11,12,14} ion-dipole interactions between the quaternary ammonium cation and PVC chains, and thus result in forming entanglement between the molecular chains of PP and PVC. In a word, these reasons enhanced the interaction of two phases in the blends, and thus increased the resistance of

movement of chains in melt blends, therefore the viscosity of PP/PVC/FPP blends was higher than that of PP/PVC blend. As FPP with higher grafting yield was added, the number and density of quaternary ammonium ion increased, which could lead to agglomeration between the ions of side chain, the compatibility of the blend system decreased, and thus apparent viscosity decreased sharply. At the same time, as the load increased, the apparent melt viscosity decreased, which was the same as the rheological behavior of polymer melts.¹⁶

Morphology. Figure 4 showed the morphology of PP/PVC/FPP (80/20/4, wt%) blends observed by SEM when FPP with different grafting yield was added. The PP/PVC blend exhibited spherical phase domains of PVC and weak interfacial adhesion, surrounded by the continuous PP phase as shown in Figure 4(a). The SEM micrographs of PP/PVC blends suggested that the minor-phase particle size of the dispersed phase decreased when FPP was added. The partial miscibility between the PP and PVC was observed to increase as the grafting yield of FPP increased, and up to optimal when FPP (GY=16.78%) was added (Figure 4(c)). The change of morphology could improve the mechanical properties of the PP/PVC due to the decrease minor-phase particle size (phase PVC) and the increase of compatibilization at the polymer/polymer interface. But as FPP with higher grafting yield was added, the size of dispersed particles did not decrease, and indicated that FPP (GY=16.78%) was sufficient to occupy the interface between PP and PVC (Figure 4(c)). As a result, FPP with higher grafting yield remained in the bulk and did not

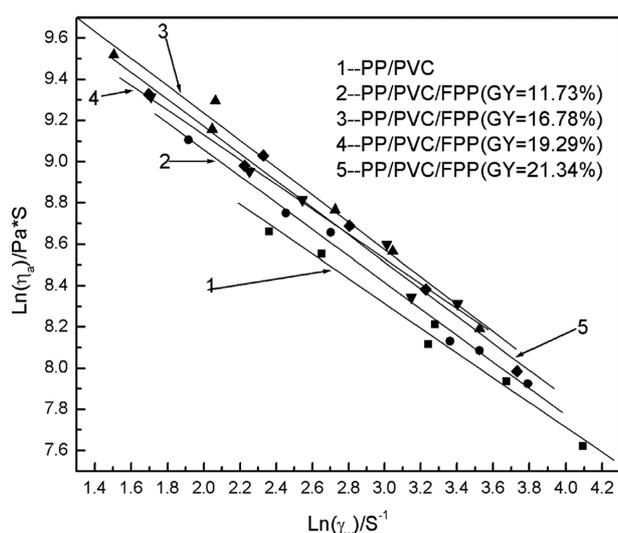


Figure 3. Rheological behaviour of PP/PVC/FPP (80/20/4) when FPP with different grafting yield was added.

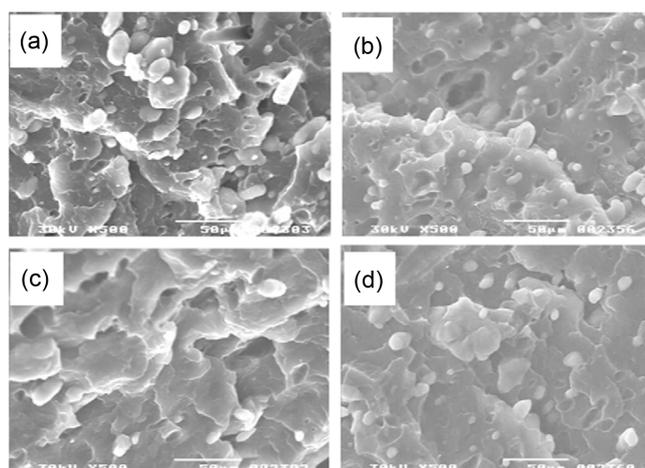


Figure 4. SEM micrographs of the fractured surfaces of PP/PVC/FPP (80/20/4) when FPP with different grafting yields was added: (a) PP/PVC; (b) PP/PVC/FPP (GY=11.73%); (c) PP/PVC/FPP (GY= 16.78%); (d) PP/PVC/FPP (GY=21.33%).

contribute to the reduction of interfacial tension, which would not cause further reduction in minor-phase particle size (Figure 4(d)). The mixing thermodynamics and the kinetics controlled the decrease in the average minor-phase particle size, in which the miscibility was increasing, and did not further discuss in the paper. The SEM micrographs demonstrate that coalescence was suppressed by addition of the compatibilizer, and it is in accordance with the mechanical and rheological result, suggesting the formation of an interfacial compatibilizer.

Conclusions

In this paper, the cationic polymeric compatibilizer with different grafting yield was successfully applied to the PP/PVC blend and improved the compatibility of PP/PVC blend. The results demonstrated that cationic vinyl monomer grafted polypropylene (FPP) enhanced tensile strength and impact strength significantly in comparison with PP/PVC blends, and optimal when FPP (GY=16.78%) was added. The tensile strength and impact strength of the blends reached the maximum value when FPP (GY=16.78%) was added and then decreased as the grafting yield of FPP increased. The PP/PVC/FPP (GY=16.78%) blends had the higher viscosity than that of other PP/PVC/FPP blends, and the viscosity of PP/PVC/FPP blends decreased when FPP with higher grafting yield was added.

The prepared blends had the two-phase morphology shown by the SEM micrographs. The PVC spherical droplets of the minor phase dispersed in PP continuous matrix phase as FPP components were added, and optimal when FPP (GY=16.78%) was added. The SEM micrographs supported that FPP enhanced the compatibility of the PP/PVC blend.

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