

Preparation and Reaction Kinetics of Polypropylene-graft-Cardanol by Reactive Extrusion and Its Compatibilization on Polypropylene/Polystyrene

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ABSTRACT: Polypropylene-graft-cardanol (CAPP) was prepared by reactive extrusion with polypropylene (PP) and natural renewable cardanol, which improved the inherent defects of PP such as its chemical inertness and hydrophobicity. Moreover, the cardanol grafted onto PP resolved the degradation of PP during reactive extrusion and use. The effects of reactive extrusion on the change of the molecular structure of PP, the change in the free-radical concentration during processing, and the compatibilization of CAPP on the PP/polystyrene (PS) composite materials were examined in this study. The constants of the grafting reaction rate at the beginning of reactive extrusion were also deduced. The results show that cardanol was grafted onto PP, and the p- π conjugate system in cardanol was observed to stabilize free radicals. The grafting reaction rate (R_g) at the initial stage of the grafting reaction process was calculated through the equation $R_g = k_g[M\cdot][\text{Cardanol}]$, where k_g is the constant of the apparent grafting reaction rate and $[M\cdot]$ is the concentration of free radicals in the reaction system. k_g first increased with the growth of temperature and then began to decrease when the temperature exceeded the critical temperature of 200°C. The mechanical properties showed almost no change after the samples were aged for 72 h. This was due to CAPP, which changed PP/PS to a ductile material from a brittle one. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 39911.

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INTRODUCTION

Polypropylene (PP) is currently seen as one of the most important thermoplastics. However, PP is a nonpolar crystal polymer and thus has many disadvantages in cold resistance, size stability, dyeability, adhesion, printability, and tenacity at low temperatures. Because of the tertiary carbon atom in the PP structure, PP ages and degrades under heat, oxygen, and light during the processes of granulation making, storage, and application. Moreover, the use value and comprehensive physical and mechanical performances also decline. To improve the comprehensive performance of PP, many modification studies have been undertaken by scientists.^{1–6} In particular, the graft modification of reactive extrusion, which has advantages because of its solvent-free properties, continuity in the production process, and ease in reaction time manipulation, has shown remarkable results and thus aroused widespread interest.^{7–11} However, the tertiary carbon atom in the PP structure is prone to cause the molecular chain's β rupture and severe degradation during the reactive extrusion process. At the same time, some issues in

the modified products, such as effects on the anti-aging properties and low surface activity, still persist.

Reactive extrusion can achieve a controlled decrease in the viscosity in the PP melt,^{12,13} functionalization of PP,^{14–19} and so on. In the preparation of functionalized PP through reactive extrusion, PP functionalized by maleic anhydride was the earliest and most widely used modified product. Nevertheless, the low boiling point of maleic anhydride (202°C) combined with the high temperature (200–220°C) required for the grafting reaction of PP with maleic anhydride by reactive extrusion causes the maleic anhydride in the mixture to boil and continuously bubble during the grafting process. This seriously affects the properties of the product and thus the ensuing processing and application.²⁰ In addition, the high toxicity and easy sublimation of maleic anhydride can be harmful to the eyes of workers involved in the graft processing of the melt. There are, therefore, many limitations in the use of maleic anhydride grafted onto PP. Furthermore, polypropylene-graft-maleic anhydride (MAPP) usually reacts in the presence of the peroxide



Scheme 1. Chemical structure of cardanol.

initiator through free radicals. The primary radicals produced by the decomposition of the initiator capture the hydrogen in the PP molecular backbone and then generate macromolecular radicals. The macromolecular radicals not only graft maleic anhydride monomer but also cause their own β degradation.²¹

To improve the grafting ratio by effectively reducing or preventing the degradation reaction, scientists have experimented with the addition of rare earth compounds²² and *N*-bromosuccinimide²³ during the reactive extrusion process. Unfortunately, the inhibition effect on degradation has been shown to be poor. Further studies have shown that conjugated molecules, such as styrene, have a promoting effect on the grafting reaction. Clearly, if phenolic compounds are linked to the PP molecular chain, PP will demonstrate surface activity and oxidative degradation resistance properties. Natural cardanol (a liquid extracted from the cashew nut shell) is a phenolic compound containing long unsaturated alkyl side chains²⁴ (Scheme 1). In theory, the unsaturated double bond in the long alkyl side chain would allow the grafting of cardanol onto the molecular chain of PP, whereas the benzene ring and phenolic hydroxyl group would play the role of antioxidants.²⁵

In this study, polypropylene-*graft*-cardanol (CAPP) was prepared through reactive extrusion. The change in the molecular structure after PP grafting was studied by NMR. The concentration variety of free radicals was quantitatively measured by electron paramagnetic resonance (EPR) in the grafting process, and the grafting reaction rate (R_g) of cardanol onto PP in the primary phase of reactive extrusion was calculated. The compatibilization of CAPP on a PP/polystyrene (PS) composite material was investigated. This research provides useful theoretic guidance for the practical application of grafting of cardanol onto PP through reactive extrusion. It was of great significance in increasing the surface chemical energy and improving the interfacial compatibility of PP.

EXPERIMENTAL

Materials

Isotactic PP homopolymer powder (PPH-XD-045, melt flow index = 2.1–6.0 g/10 min at 190°C and 2.16 kg) was purchased from Shandong Kairi Chemical Industry, Ltd., Co. (China). Cardanol was purchased from a local market and was used as the grafting monomer. It was used as received without further purification. The initiator, dicumyl peroxide (DCP), was supplied by Sinopharm Chemical Reagent Co. It was dried in a dark room for a week before use. MAPP was purchased from a local market, and its grafting ratio was 1.0–1.2%. Other chemical reagents were purchased from a local market.

Preparation of CAPPs

PP (200 g), cardanol (0–14 g, Table I) and DCP (0.4 g) in ether were premixed in a high-speed disintegrating machine (JFW-A,

Table I. Formulas of the CAPPs by Reactive Extrusion

Sample	CAPP ₀	CAPP ₁	CAPP ₃	CAPP ₅	CAPP ₇
PP (g)	200	200	200	200	200
DCP (g)	0.4	0.4	0.4	0.4	0.4
Cardanol (g)	0	2	6	10	14
Grafting ratio (%)	0	0.75	2.83	4.45	5.02

The number after CAPP means the portions of cardanol every 100 g PP used in the reactive extrusion.

China) at 2600 rpm under ambient conditions. Then, the mixture was extruded by corotation with a twin-screw extruder (Polylab Rheomix PTW24/28, HAAKE, Germany) at a screw rotation rate of 50 rpm and at a temperature of 170–190°C. The extrudate was cooled through a water bath, and this was followed by granulation. The coarse products were purified by their dissolution in refluxing xylene and precipitated into acetone under continuous stirring at room temperature to remove the unreacted monomer. The precipitate was filtered and rinsed with acetone and dried in a vacuum-drying oven at 80°C overnight. The coarse CAPPs used in the measurement of the grafting reaction kinetics were obtained by a Banbury mixer (Polylab OS, Haake, Germany) for different times and then purified with the same method as described previously.

Preparation of the PP/PS Composite Materials, PP, and CAPP₅ Sheets

PP and PS (mass ratio = 4:1) in the presence of 0, 5, 10, 15, and 20% CAPP or MAPP were extruded by corotation in a twin-screw extruder (Polylab Rheomix PTW24/28, Haake, Germany) at temperatures of 170–190°C and at a screw rotational rate of 50 rpm. Then, the extrusion materials were calendered into sheets with a thickness of 0.5 mm. The preparations of the PP and CAPP₅ sheets were same as that of the PP/PS composite materials.

¹³C-NMR Measurements

After the purified CAPP₅ was ground into powder of 200 mesh, the ¹³C-NMR spectrum was recorded on a Bruker Advance 400 WB wide-chamber, solid-state spectrometer (Germany) at a rotation rate of 10 kHz. The probe contacted the sample for 2 s at an interval of 3 s, and the total scanning times was 2000.

Grafting Ratio Measurements

The content of cardanol grafted onto the polymer was quantified by an ultraviolet–visible spectrometer (TU-1900, Beijing Purkinge General Instrument Co., Ltd., China). CAPP was dissolved in boiling *n*-octane and then kept in a 90°C water bath. The grafting ratio of CAPP was measured at a temperature of 90°C. A standard curve was decided by a series of cardanol standard solution at 273 nm and 90°C after dissolution in 1-octane.

Measurements of Free-Radical Concentration

The paramagnetic resonance tube loaded with the mixture of PP, DCP, and cardanol at different ratios was placed in an oil bath for 90 s at the same temperature as that used for Banbury mixing. The tube was immersed in liquid nitrogen and immediately quenched. Then, the EPR spectra were tested by a Bruker EMX EPR spectrometer with a diamond internal standard, and

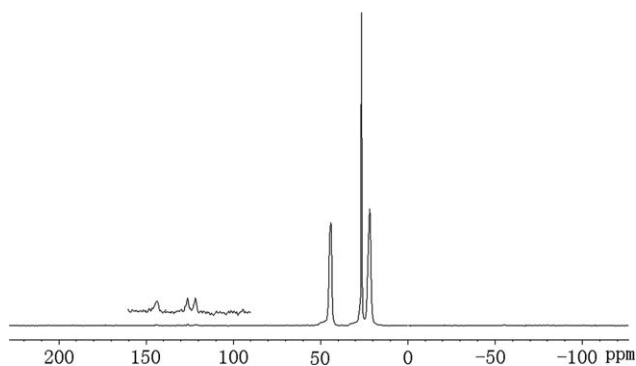


Figure 1. ^{13}C -NMR spectrum of CAPP₅.

the free-radical concentration of the reaction system was obtained by the dual integral of the EPR spectra.

Testing the Resistance Properties to Degradation of the PP and CAPP₅

The rolled sheets were cut into rectangular samples $130 \times 10 \text{ mm}^2$ and placed in an accelerated aging chamber with a mercury lamp for the aging experiments. With a LR5K universal testing machine (Lloyd British Co.), the yield strength, elongation at break, and tensile strength of the material were tested with a tensile rate of 5 cm/min and a preload of 5 N. Each kind of sample was tested in parallel five or more times, and the averages were obtained.

Scanning Electron Microscopy

To evaluate the compatibilization of CAPP on the PP/PS composite materials, the tensile fracture surfaces were checked by scanning electron microscopy (field emission, JEOL 7500 at 2 kV). The scanned surfaces were vacuum-sputtered with platinum.

RESULTS AND DISCUSSION

Characterization of PP-graft-Cardanol (CAPP)

Figure 1 shows the ^{13}C -NMR spectrum of CAPP₅ (grafting ratio = 4.45%). The resonance peaks at 21.6, 26.0, and 43.8 ppm corresponded to methyl, methylene, and methyldiene, respectively. Because of the low grafting ratio of the grafted product and the large molar mass of cardanol, the micro-environmental change of the grafted product was not obvious. After the process of amplification, three resonance absorption peaks were observed at 121.4, 126.0, and 144.0 ppm; these were undoubtedly the carbon resonance absorption peaks of cardanol's side-chain double bond and phenyl ring. The samples were purified before the ^{13}C -NMR test, and unreacted cardanol monomer was removed. The carbon resonance absorption spectrum of the phenyl ring indicated that cardanol was successfully grafted onto the main chain of PP. The result was the same as in the IR subtraction spectrum of CAPP₅ from CAPP₀.²⁵ The

increase in the hydrophilicity²⁵ and the introduction of the hydroxyl group and benzene ring were favorable for the reactivity of PP and compatibility with some other materials.

Grafting Reaction Kinetics and Apparent Grafting Reaction Rate Constant (k_g) of CAPP₅

The initiator, DCP, decomposed under the heat of the Banbury mixer and subsequently triggered the grafting reaction. The grafting reaction corresponded to the free-radical polymerization mechanism as follows:²⁶

$$R_g = k_g [M] \cdot [\text{Cardanol}] \quad (1)$$

where R_g is the grafting reaction rate in the initial phase, $[M \cdot]$ is the concentration of free radicals in the reaction system as measured directly by EPR, and $[\text{Cardanol}]$ is the concentration of cardanol.

The homopolymerization of cardanol was considered an unnecessary concern on the basis of the following two arguments:

1. The gelation rate in the grafting reaction was zero,²⁵ which indicated an absence of homopolymerization. We thus deduced that the reaction among cardanol was not very lively because the concentration of cardanol was low and the cardanol molecule was still quite large. In particular, the rigid benzene ring was especially effective in limiting the diffusion of molecules and therefore decreasing the contact opportunities among cardanol.
2. Although the 5% cardanol in xylene was refluxed for 46 h in the presence of 0.2% DCP, the viscosity of solution remained almost unaffected. Table II shows the viscosity ratio (determined by the Ubbelohde viscometer method) at different reaction times. Cardanol was observed to diffuse faster in xylene than in the PP melt. However, even after it had reacted for 46 h, the viscosity had still only increased by 5%. Therefore, the probability of homopolymerization in cardanol was very low.

Free radicals are extremely unstable and have a short lifetime at room temperature. However, this became especially different as the characteristic absorption peaks in the EPR spectra were still observed with CAPPs that had been kept at room temperature for 10 days (Figure 2). $[M \cdot]$ was seen to increase with a growing concentration of cardanol. This indicated a close relationship with both the oxidative polymerization (Scheme 2) at the side chain of cardanol and the stabilization of free radicals (Scheme 3) through the $p-\pi$ conjugated system formed between the hydroxyl group and the benzene ring in cardanol. According to the results of EPR, the free-radical concentration in the system that contained the initiator was much higher than in the system without initiator (Table III). Therefore, the free radicals in the

Table II. Thermal Polymerization of the Dilute Cardanol Solutions

Reactive time (h)	0	1.5	3.5	6	10	15.5	24	31	40	46
Time of outflow (s)	158.1	161.4	162.6	163.5	164.2	164.3	164.4	164.9	166.2	166.9
Viscosity ratio	—	1.02	1.03	1.03	1.04	1.04	1.04	1.04	1.05	1.05

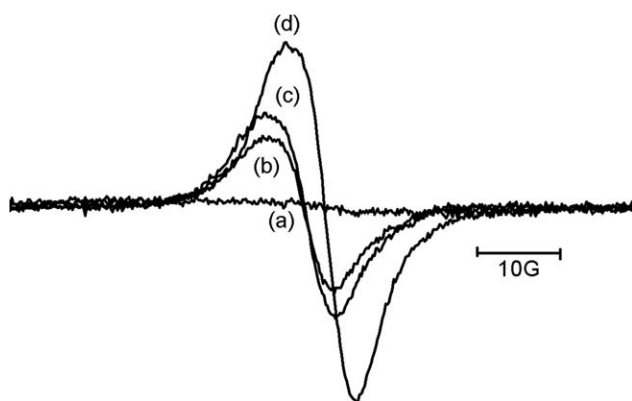
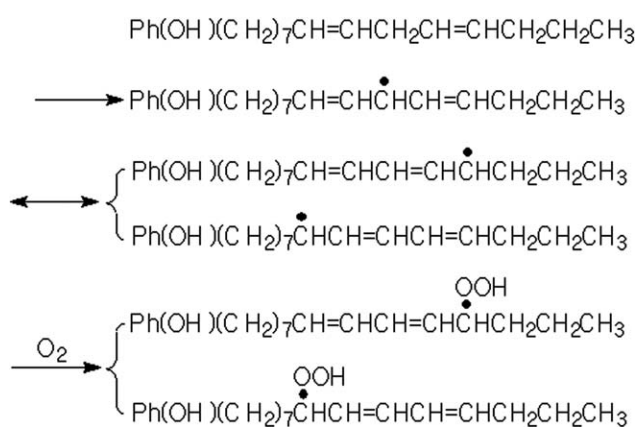


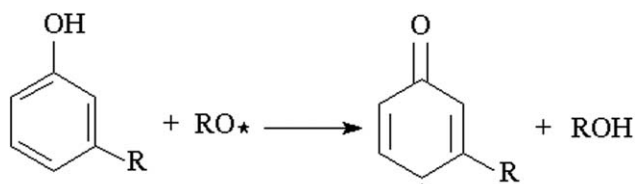
Figure 2. EPR spectra of CAPPs containing cardanol at concentrations of (a) 0, (b) 1, (c) 3, and (d) 5%.



Scheme 2. Polymerization among cardanol in the presence of oxide.

CAPP system, including the radicals triggered by heat, oxygen, and the initiator, could only remain constant because of the stabilization of the p- π conjugated system in cardanol.

Figure 3 shows the relationship between the grafting ratio of CAPP₅ at different reaction temperatures and the reaction time in the mixer. The figures suggest a linear relationship between the grafting ratio and the reaction time at the initial stage. Meanwhile, R_g during the initial phase could be determined from the curve slope and was calculated at the early reaction stage. At the later reaction stage, the vibration of R_g tended to



Scheme 3. Stabilization of conjugated p- π to radicals.

slow with the growth of the reaction time because the monomer of cardanol decreased. The graft monomer had good compatibility with the polymer. The grafting reaction could, therefore, be controlled primarily through chemistry. With increases in the reaction temperature and initiator decomposition rate, higher free-radical concentrations formed in local areas and subsequently accelerated the reaction rate.

k_g could be obtained from eq. (1) and the EPR test results (Table III). The results suggest that k_g first increased with rising temperature and then decreased after the critical reaction temperature (200°C) was exceeded because of depolymerization. Nonetheless, the reaction was still fast, as the high temperature maintained the free-radical concentration at a high level.

Resistance Properties to Degradation of PP and CAPP₅

Cardanol grafted onto PP was beneficial to the resistance properties to degradation. Table IV shows the resistance properties to degradation of CAPP₅ compared to the initial PP before and after aging in the accelerated aging chamber with a mercury lamp. The inherent microscopic damage in CAPP₅ resulted in a lower yielding strength than in PP. The short chain branches of cardanol in CAPP₅ increased the intermolecular distance, decreased the intermolecular forces, and reduced the entanglement points. The tensile strength decreased consequently. The crosslinking between the side chains of cardanol grafted onto PP increased the elongation at break of PP to $837 \pm 13\%$. It was significant that the mechanical properties of CAPP₅ had almost no change after 72 h of aging. However, the mechanical properties of PP decreased dramatically after it was aged for 72 h. We concluded that CAPP possessed a better resistance to degradation than did the initial PP.

Compatibilization of CAPP₅ on the PP/PS Composite Material

Plastic alloys attract great attention as they can not only maintain the excellent performance of existing components but also

Table III. Summary of the Reaction Temperatures and $[M]$, R_g , $[C]$, and k_g Values for Reactive Extrusion

Sample	Temperature (°C)	$10^{-13}[M]$ (number of spins/g)	$10^4 R_g$ (g g ⁻¹ s ⁻¹)	Mass fraction of cardanol to PP (%)	$10^{-8}k_g$ (g/mol)
CAPP ₅	170	1.56	1.31	7	0.72
CAPP ₅	180	1.56	1.87	7	1.03
CAPP ₅	190	1.88	2.58	7	1.18
CAPP ₅	200	2.06	2.93	7	1.22
CAPP ₅	210	3.02	3.48	7	0.99
Cardanol	190	0.82	—	—	—

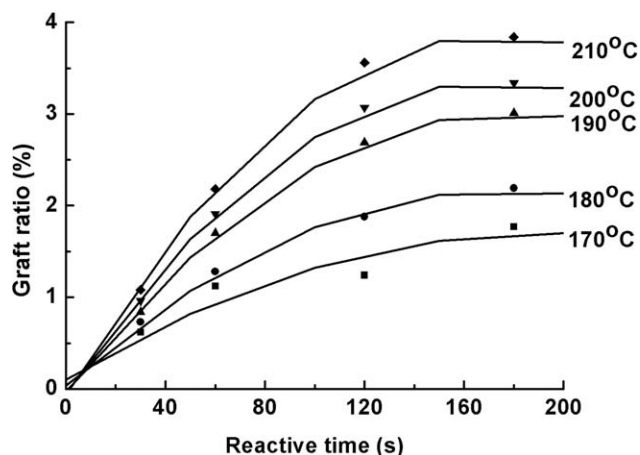


Figure 3. Grafting ratios of CAPP₅ versus the reaction time at different temperatures.

improve the performance deficiencies of the respective polymer. However, most blends are thermodynamically immiscible; the interfacial tension between the two phases is large and interfacial bonds are weak, leading to poor dispersion and poor mechanical properties of the blend. The compatibilizer can reduce the interfacial energy of the two phases, which promotes phase dispersion, improve the adhesive strength of phase interface and stabilize the morphological structure. The CAPP contains graft side chains with polar phenolic hydroxyl groups and a benzene ring. So, does such a graft product have the compatibilizing effect on aromatic/lipid class polymer blends? For this reason, the tensile properties and morphology of PP/PS in the

presence of CAPP were investigated to explore the compatibilizing effect of CAPP on these two kinds of thermodynamically incompatible systems. Moreover, the compatibilization of CAPP on PP/PS was compared with that of MAPP.

Because of the rigidity of the benzene ring in PS, the blends had high Young's modulus values (Figure 4). The appropriate amount of the compatibilizer, CAPP (the amount of compatibilizer was less than 10 parts), contributed to the dispersion of PS in PP. The granularity of the dispersed phase was moderate, and the phase interface had a strong interaction force. Thus, the Young's modulus and tensile strength (Figure 4) were both greater than those of the PP/PS blends in the absence of CAPP. When the amount of CAPP compatibilizer was greater than 10 parts, the crystals of PP and PS were destroyed by the cardanol groups, and consequently, the tensile strength decreased. The polar carboxyl groups and nonpolar PP and PS in the presence of MAPP showed poor compatibility; this decreased the Young's modulus and tensile strength of the blend.

The tensile fracture surface [Figure 5(a)] of the sample from PP/PS was smooth, with almost no deformation; this indicated typical brittle fracture. The tensile fracture surfaces of the sample from the PP/PS/CAPP blends [5% mass ratio; Figure 5(b)] showed a significant yield with an elongated matrix that stretched into filaments before breaking; therefore, this situation belonged to typical ductile fracture. It is worth noting that many voids were observed between the PS and PP matrix in the ductile fracturing of PP/PS/CAPP. The generation of these voids made the blend release the static tensile stress of the crack tips by its own interfacial debonding in the fracture process. This

Table IV. Resistance Properties to Degradation of PP and CAPP₅

Sample	PP	CAPP ₅	PP	CAPP ₅
Aging time (h)	0	0	72	72
Yield strength (MPa)	54.5 ± 0.78	27.7 ± 0.47	16.92 ± 0.33	29.57 ± 0.41
Tensile strength (MPa)	54.56 ± 0.78	40.62 ± 0.69	16.95 ± 0.23	38.16 ± 0.39
Elongation at break (%)	41 ± 1	837 ± 13	2 ± 0	773 ± 11

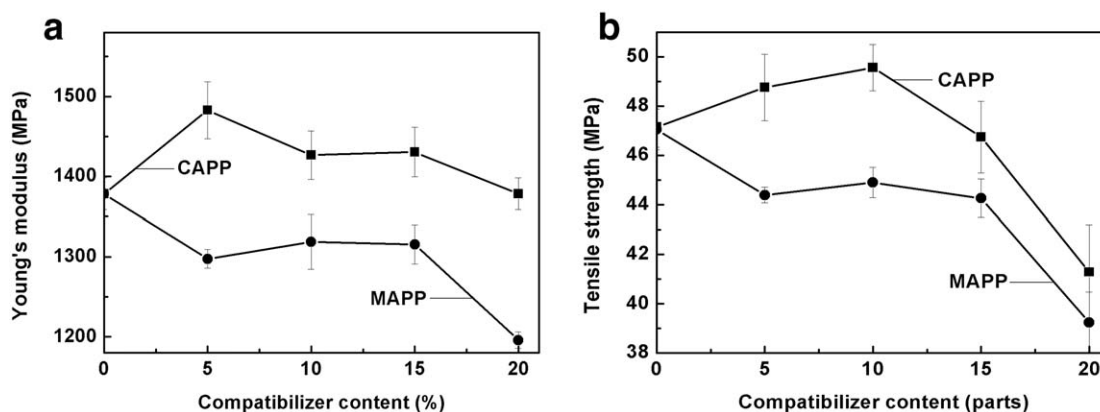


Figure 4. Mechanical properties of the PP/PS composite materials.

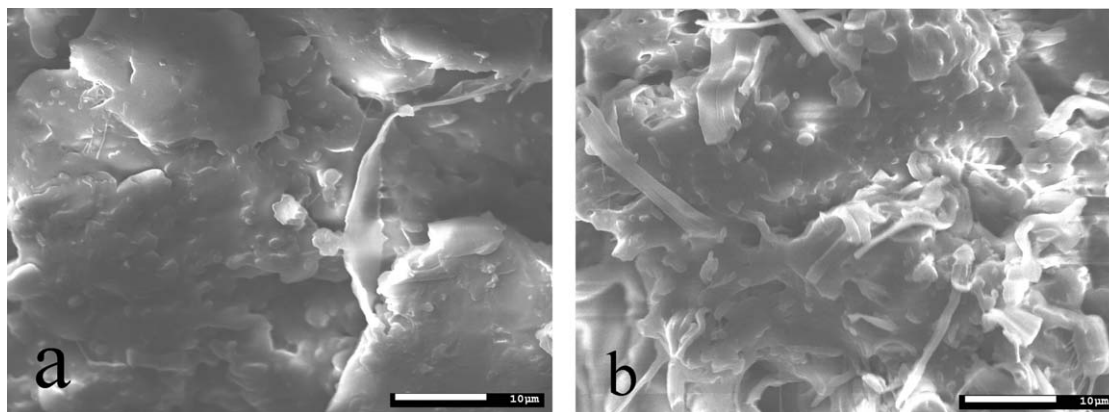


Figure 5. Morphologies of the tensile fracture surfaces of (a) PP/PS and (b) PP/PS/CAPP.

created the conditions for the shear yielding of the matrix and thereby improved the tensile properties of the blend.

CONCLUSIONS

CAPPs were prepared successfully by the reactive extrusion method with a twin-screw extruder to graft cardanol onto the main chain of PP. The carbon resonance absorption peaks of cardanol's side-chain double bond and phenyl ring at 121.4, 126.0, and 144.0 ppm were observed in the ^{13}C -NMR of CAPP₅. The p- π conjugate system in cardanol stabilized the free radicals and effectively inhibited the degradation of the PP chain.

R_g at the initial stage of the grafting reaction process was calculated through eq. (1). k_g first increased with increasing temperature and began to decrease when the temperature exceeded the critical temperature of 200°C.

CAPP possessed better resistance properties to degradation than the initial PP. This was because CAPP in the composite materials caused PP/PS to change to a ductile material from a brittle one. The compatibilization of CAPP was superior to that of MAPP.

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