

Preparation of Polypropylene-*graft*-Cardanol by Reactive Extrusion and Its Composite Material with Bamboo Powder

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ABSTRACT: The polypropylene-*graft*-cardanol was prepared by reactive extrusion, which is solvent-free melt process, continuous processing, and controllable over residence time. The effect of monomer and initiator concentration on grafting ratio, grafting efficiency, and melt flow index (MFI) was also studied. The yield was quantified by UV-vis spectrometer. The chemical structure was investigated by infrared spectroscopy and gel ratio. A possible mechanism was supposed. The particular structure of cardanol can retain the MFI value of matrix resins and prevent polypropylene (PP) from being decomposed.

The grafting ratio could be easily obtained from an experimental formula deduced from the linearity relationship between grafting ratio and MFI. The effect of cardanol grafted onto PP on the compatibility of PP and bamboo powder was studied by contact angle measurements, scanning electron microscopy, and tensile properties test. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1160–1167, 2010

Key words: poly(propylene) (PP); reactive extrusion; graft copolymers; composite

INTRODUCTION

Polypropylene (PP) is widely used in textiles, medical devices, automobiles, and many other products own to its low cost, superior chemical resistance, and proper mechanical properties. However, some inherent features of PP such as hydrophobicity and chemical inertness make PP poor in dyeability and surface modification and chemical functionalization.^{1–3} To increase the surface energy of PP, many approaches have been proposed so far, including using coupling agents^{4,5} and grafting modification.^{6–9} Because coupling agents can only react with the exterior of PP, grafting reaction is a practical technique to improve its dyeability, compatibility, and hydrophilicity. Among many grafting techniques such as in solution, melt phase, or solid-state process on polymer,^{6,7,10,11} the melt grafting, so called reactive extrusion has attracted increasing attention recently¹² because of the economical way of using the extruder for conducting chemical modification or polymerization reactions. Moreover, the merits of re-

active extrusion such as solvent-free melt process, continuous processing, and controllable over residence time¹³ have shown to be an efficient way for low cost production and processing methods, which enhance the commercial viability and cost competitiveness of these material. During the reactive extrusion, grafting reactions are generated by the action of peroxide. This process converts the low melt flow index (MFI) commodity resins to polymers with higher MFI (up to 100 times the original value)¹⁴ that has inferior mechanical properties.

Herein, we presented the preparation of polypropylene-*graft*-cardanol (PP-*g*-cardanol) by reactive extrusion. Cardanol (Scheme 1) is a main component of cashew nut shell liquid extracted from natural cashew shell.¹⁵ The unsaturated side chains containing double bonds can retain the MFI value of matrix resins. The phenyl hydroxyl of cardanol can stabilize radicals, maintain viscoelasticity, increase dyeability, compatibility, and hydrophilicity of PP. To make sure of the improvement of the surface energy of PP-*g*-cardanol, the compatibility of PP-*g*-cardanol and hydrophilic bamboo powder (BP) is evaluated.

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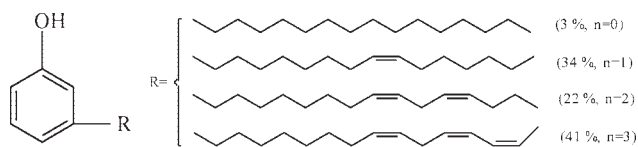
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EXPERIMENTAL

Materials

Isotactic polypropylene homopolymer powder (PPH-XD-045, MFI = 2.1–6.0 g/10 min) was purchased



Scheme 1 Chemical structure of cardanol.

from Shandong Kairi Chemical Industry, China. Cardanol was purchased from 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. It was dried in a dark room for a week before use. Other chemical reagents were purchased from local market.

Preparation of PP-g-cardanol

Precalculated amount of PP, cardanol, and DCP in ether were premixed in a high-speed disintegrating machine (JFW-A, China) at 2600 rpm/min under ambient condition. Then, the mixture was extruded by corotation, twin-screw extruder (Polylab Rheomix PTW24/28, Germany) at 180°C and at a screw rotational rate of 50 rpm/min. The extrudate was cooled through a water bath, followed by granulation. The coarse products were purified by dissolving them 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 at 80°C overnight.

Preparation of BP/PP-g-cardanol composite and BP/PP composite

The premixed mixture of BP and PP (3 : 7, mass ratio) in the presence (BP/PP-g-cardanol composite) and absence (BP/PP composite) of the cardanol and DCP was extruded by twin-screw extruder at 170–190°C and 50 rpm/min, then the extrusion products were calendered into the sheets of 0.5 mm thickness.

FTIR measurements

The purified samples were molded into thin films at 190°C and 1×10^6 Pa. Then, the films were analyzed by FTIR (Nicolet 5700, USA) to determine whether the cardanol was grafted onto PP.

UV-vis spectra measurements

The content of cardanol grafted on polymer was quantified by UV-vis spectrometer (TU-1900, Beijing Purkinge general instrument, China). Standard curve was decided by a series of cardanol standard solu-

tion at 273 nm and 90°C after dissolved in boiling 1-octane.

MFI test

A melt flow index tester (XRL-400A, Chengde precise instrument company, China) was performed at 190°C and under a pressure of 2.16 kg.

Gel fraction test

Certain amount of cardanol-grafted PP packed with 200-mesh copper net was extracted with refluxing xylene for 12 h in a soxhlet extractor, then the copper package was dried in a vacuum at 80°C for 24 h and weighed. The extraction was repeated until the weight of copper package did not change. The gel fraction was calculated from the following equation:

$$F_{\text{gel}} = \frac{M_R - (M_T - M_P)}{M_P} \times 100\%$$

where M_P is the weight of PP-g-cardanol (g), M_T is the total weight of polymer and copper net before extraction (g), and M_R is the total weight of residual polymer and copper net after extraction (g).

Contact angle measurements

The contact angle measurements of PP and purified PP-g-cardanol were conducted using a contact angle goniometer (SL200B, Solon Tech., Shanghai, China) at ambient temperature. All measurements were performed using the sessile drop method with drops of deionized water after about 10 s.

Tensile properties

Tensile specimens of the composites were cut off in the form of rectangular strips from the calendered plate, the dimensions of the specimens were 130 mm \times 10 mm. The tensile properties were tested on a universal testing machine, model LR5K (Lloyd, UK), at a crosshead speed of 5 cm/min. At least five specimens of each composite were tested and the medial values were reported.

Crystallinity measurements

Crystallinity was obtained by using a METTLER DSC822e Differential scanning calorimeter under nitrogen atmosphere at the cooling or heating rate of 10°C/min. The weights of all specimens were \sim 2–4 mg.

SEM

To evaluate the impregnation state of BP into PP, the tensile fracture surfaces were checked by the scanning electron microscopy (Field emission SEM, JEOL 7500 at 2 kV). The scanned surfaces were vacuum sputtered with platinum.

RESULTS AND DISCUSSION

Characterization of PP-g-cardanol

To investigate the formation of graft copolymer in the PP-g-cardanol in the process of reactive extrusion, both extrusion products of PP containing 0.2% DCP (dPP) and PP-g-cardanol were analyzed by FTIR. Figure 1 shows that the spectrum of PP-g-cardanol has similar absorption features to that of dPP. However, the PP-g-cardanol shows a significantly different IR spectrum: a new peak appears at 550–570 cm^{-1} , the absorption at 1625 cm^{-1} becomes stronger, and the absorption at 3400 cm^{-1} indicates the presence of phenyl hydroxyl group. The samples of FTIR have been purified before used, so these changes are accounted for the occurrence of a chemical reaction between cardanol and PP during the reactive extrusion. To support this further, Figure 1(b) shows the IR subtractive spectrum of PP-g-cardanol from dPP according to the formula of $A_s = A_g - (d_0/d_g)A_0$, where A_s is subtractive absorption, A_g and A_0 are the absorption of PP-g-cardanol and dPP, respectively, and d_g and d_0 are the film thickness of PP-g-cardanol and dPP, respectively. The characteristic absorptions of cardanol (e.g., 1630 cm^{-1} due to $\nu_{\text{C}=\text{C}}$ conjugated vibration of phenyl, 1370 cm^{-1} due to $\nu_{\text{C}-\text{O}}$ vibration of phenol, 985 cm^{-1} due to $\gamma_{-\text{C}=\text{C}=\text{C}-}$ vibration of cardanol side chains, 700 cm^{-1} due to out-of-plane bending of phenyl group and unsaturated side chains) confirm the grafting reaction.

During melt grafting extrusion initiated by peroxide, it is generally thought that main side reaction is β -decomposition of macromolecular tertiary carbon free radicals for PP and crosslinking for polyethylene.^{11,16–19} Gel fraction experiments of PP-g-cardanol are for the sake of testing the occurrence of crosslinking of cardanol grafted on the PP. Result showed that no gel was found in all of the samples. The unsaturated side chains of cardanol grafted onto PP did not crosslink during reactive extrusion because the rigid phenyl group of cardanol hinders the movement of unsaturated side chains, so it is possible to yield dimer or oligomer instead of crosslinked polymer.

The process of reactive extrusion involves the blending of certain amount of peroxides, cardanol, and PP. During melt extrusion of this mixture, the peroxide thermally decomposes to produce peroxy radicals (Scheme 2). These radicals can attack the car-

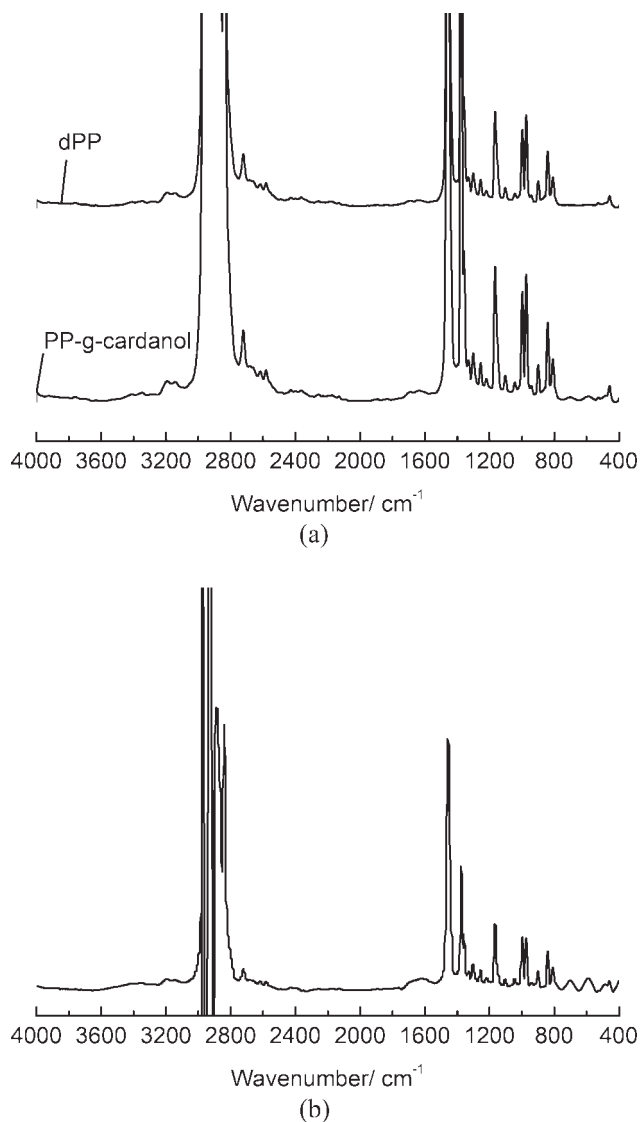
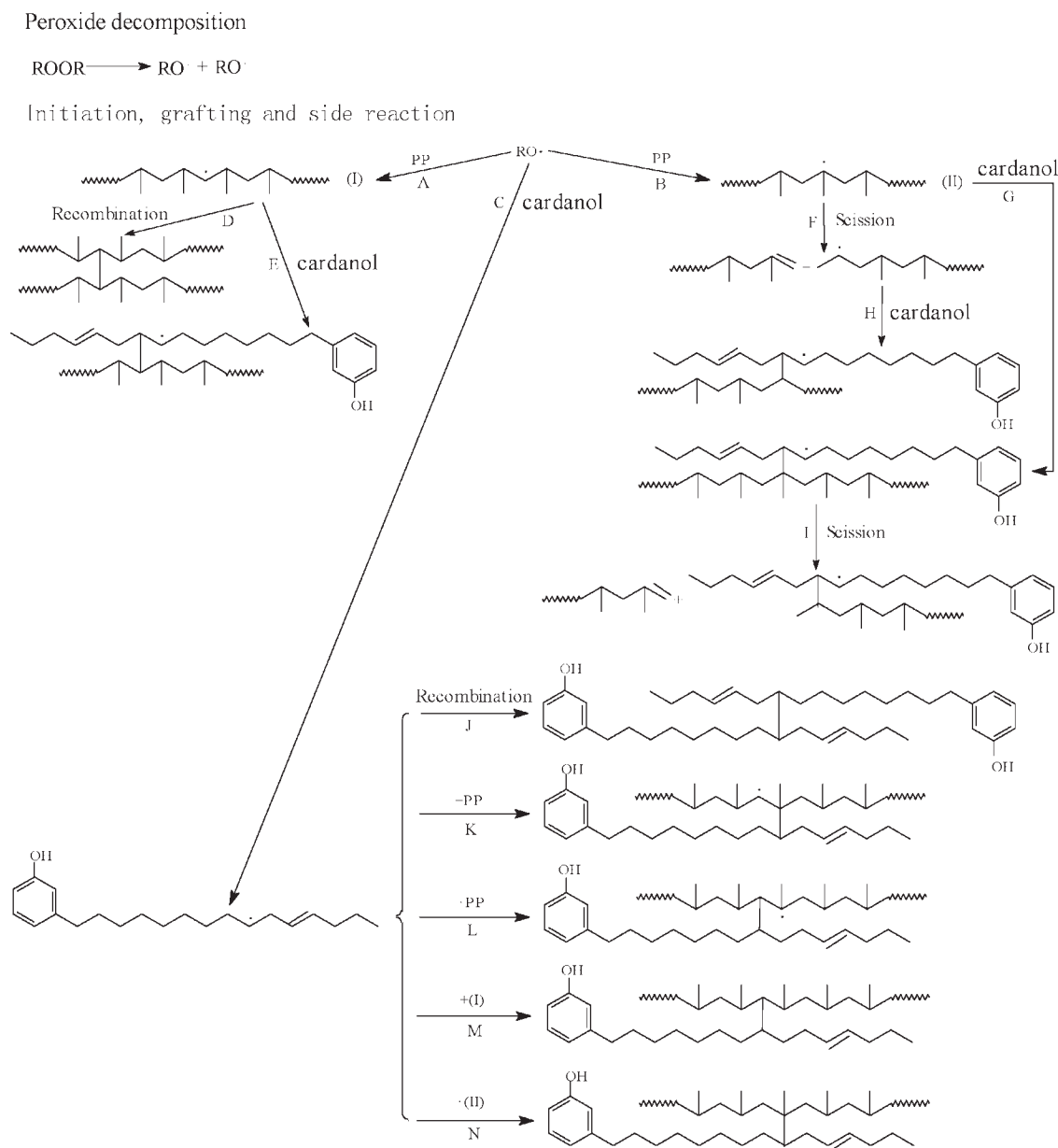


Figure 1 (a) IR spectra of dPP and PP-g-cardanol. (b) IR subtractive spectrum of PP-g-cardanol from dPP.

danol side chains (C) and the polymeric PP chains¹⁷ (A and B). However, the σ -bond energy of PP polymeric chains is higher than the π -bond of cardanol side chains. Moreover, there exist conjugated carbon-carbon double bonds between C_{11} and C_{13} in partial cardanol side chains (Scheme 1), so the activation energy of cardanol is lower than that of PP and it is easy to yield primary radicals along route C. The order of reactivity of the radicals is reverse with that of monomers,²⁰ thus PP radicals possess stronger propagation ability than the cardanol ones. The diffusion of cardanol primary radicals is restricted by the spacial obstruct of phenyl group. Therefore, cardanol primary radicals can only initiate the circumambient monomers or couple with circumambient radicals. Secondary carbon radicals (I) of PP either combine or initiate cardanol side chains and yield chain radicals. Tertiary carbon radicals (II) of PP are prone to scissor



Scheme 2 Proposed reaction mechanism of PP-g-cardanol.

and reset to yield inert secondary carbon radical and alkenes (F, I). Free radical polymerization experiences three stages, that is, slow initiation, fast propagation, and rapid termination, so initiation velocity determines reactive velocity. Reaction B is easier than reaction A because the activation energy of tertiary carbon is much lower than secondary carbon. In conclusion, reactive extrusion of PP-g-cardanol mainly goes along route B, C, J, and N because cardanol monomer and PP third carbon radical are more active than cardanol radical and PP.

Effect of monomer and initiator concentration on grafting ratio and grafting efficiency

To quantify the grafting degree of PP-g-cardanol, effect of monomer and initiator concentration on

grafting ratio (the mass ratio of grafted cardanol to PP) and grafting efficient (the mass ratio of grafted cardanol to the total reacted and unreacted monomers) was investigated (Figs. 2 and 3). Figure 2 shows that grafting ratio increases to the value of 5.20% and then declines slightly when the weight of cardanol exceeds 7 g/100 g PP in the presence of 0.2% DCP, whereas grafting efficiency increases rapidly to 94.3% when the weight of cardanol is up to 3 g/100 g PP then drops afterward. The trends of grafting ratio and grafting efficiency affected by initiator concentration are accordant (Fig. 3). It is interesting that 0.61% grafting ratio is detected in the extrusive blending of 7 g cardanol and 100 g PP even without initiator because a little cardanol radicals were generated in the thermal and high-speed

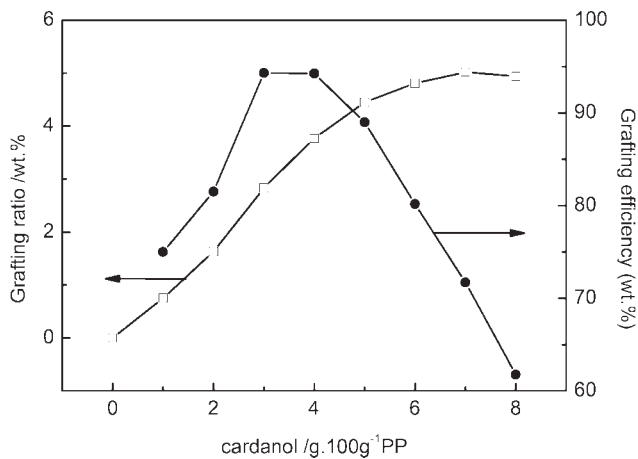


Figure 2 Effect of monomer concentration on grafting ratio and grafting efficiency using 0.2 g DCP every 100 g PP.

shearing action. It is much easier for DCP to initiate. Small quantity of initiator (0.1 wt %) makes grafting ratio increase to 3.99%. A small quantity of DCP radicals mainly initiate cardanol along C. Grafting ratio maintains at a value of 4.7% in the range of 0.2–0.4 g DCP/100 g PP when more DCP can initiate reaction B and coupled by M and N except for reaction C. If the initiator increases to 0.5%, superfluous radicals do not combine with cardanol radicals but initiate G and F so grafting ratio increases further.

Effect of monomer and initiator concentration on melt flow index

MFI is related to molecular weight, branching degree, and crosslinking degree. Without cardanol, PP polymeric chains are attacked by DCP radicals along route B and F, which causes the decreasing of molecular weight and the increasing of MFI from 3.49 to 18.23 g/10 min (Fig. 4). However, MFI decreases to 6.72 g/10 min immediately in the pres-

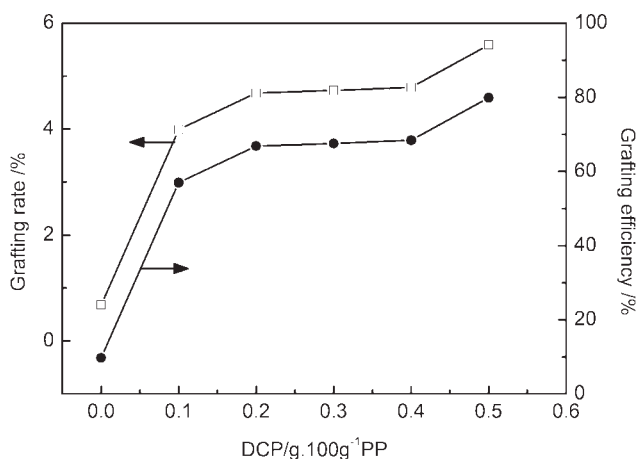


Figure 3 Effect of DCP concentration on grafting ratio and grafting efficiency using 7 g cardanol every 100 g PP.

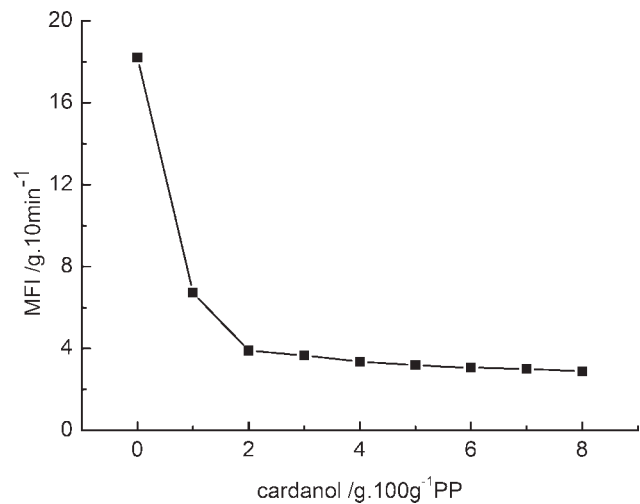


Figure 4 Effect of monomer concentration on melt flow index using 0.2 g DCP every 100 g PP.

ence of 1 wt % cardanol. The following two reasons account for this phenomenon: first, initiation velocity decides dominant reaction and reactive velocity. The initiation velocity of cardanol is faster than that of PP in the reactive copolymer blending. DCP initiates cardanol first and the decomposition probability of PP decreases. Second, PP radicals are prone to couple with cardanol radicals even if grafting reaction is along route B. MFI goes back to the level of virgin PP (3.49 g/10 min) when cardanol increases to 3% and then maintains a slowly decreasing trend. If only reactive extrusion blending contains 7% cardanol, MFI values are less than virgin PP no matter how much initiator is added (Fig. 5). MFI value reaches minimum when a little DCP (1 %) makes reaction to go along route C, J, and N. It is obvious for PP to decompose when DCP increases from 0.1 to 0.2% and from 0.4 to 0.5%. MFI increases slightly when DCP concentration is between 0.2 and 0.4%

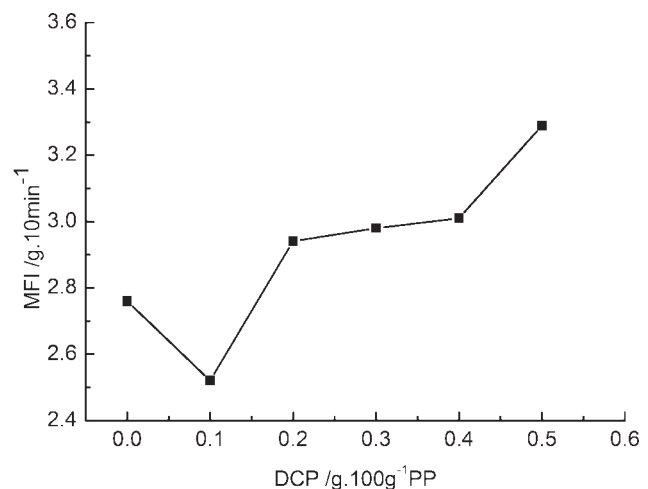


Figure 5 Effect of initiator concentration on melt flow index using 7 g cardanol every 100 g PP.

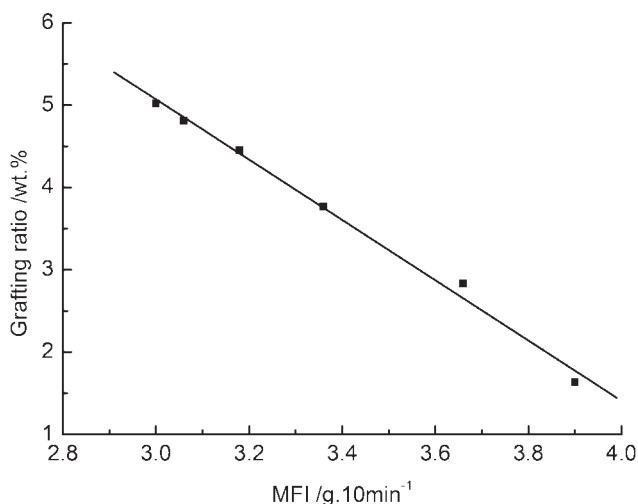


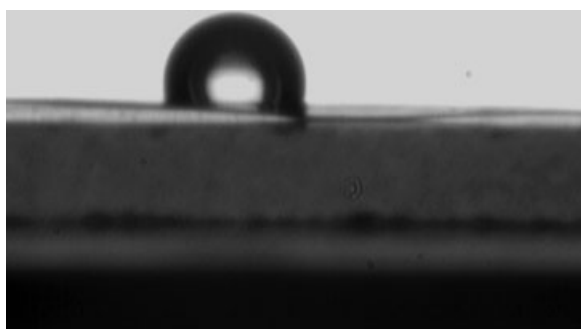
Figure 6 Linearity relationship between grafting ratio and MFI ($3 < \text{MFI} < 4$).

because the concentration of cardanol radicals does not change any more while PP radicals are captured before decomposition. When DCP concentration increased to 0.5%, abundant PP radicals without combination decompose along F and I. Therefore, it is appropriate to fix 0.2 g DCP to every 100 g PP to

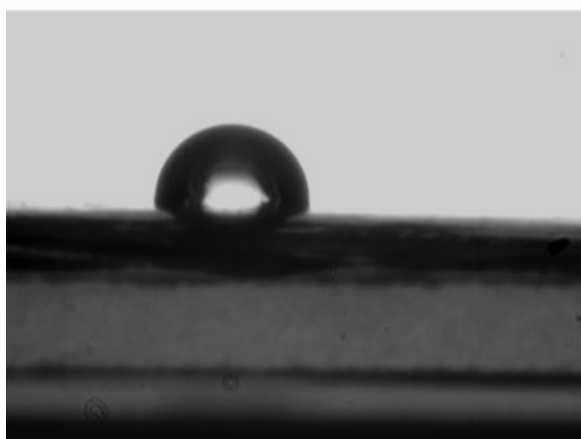
increase grafting ratio and decrease decomposition degree.

Relationship between grafting ratio and melt flow index

It is a problem to quantify the grafting degree of functionalized PP all the time. The measurement of MFI is an easy method. The value of MFI shows that polymer viscosity is correlated to branching extent of polymer for the functionalized PP at some shear rate. Can the grafting degree of functionalized PP be obtained by MFI measurement? Figure 4 shows that grafting ratio and MFI keep linearity correlation (Fig. 6) in certain extent when DCP concentration is 0.2 g/100 g PP, that is, grafting ratio = $16.06 - 3.66 \times \text{MFI}$ ($3 < \text{MFI} < 4$), in which relative coefficient R is 99.66% and standard deviation SD is 0.1205.

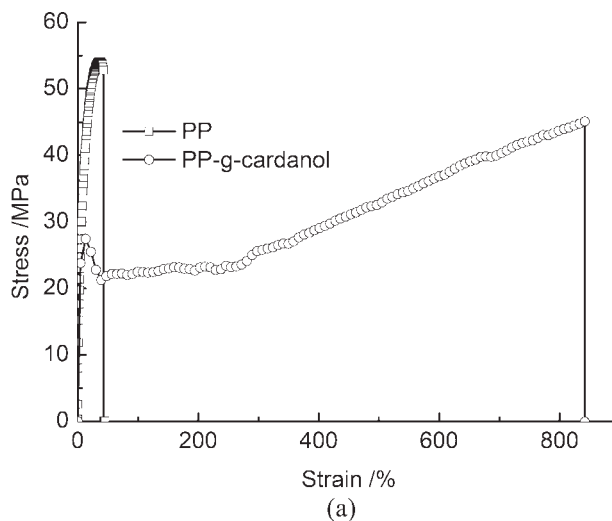


(a)

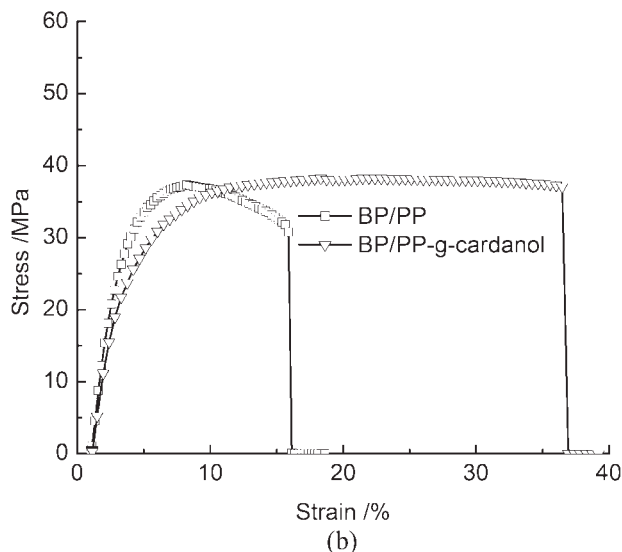


(b)

Figure 7 (a) Contact angle image of neat PP. (b) Contact angle image of PP-g-cardanol.



(a)



(b)

Figure 8 (a) Tensile curves of PP and PP-g-cardanol. (b) Tensile curves of BP/PP composite and BP/PP-g-cardanol composite.

TABLE I
Tensile Properties and Crystallinity

Samples	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Crystallinity (%)
PP	1005 ± 24	54.5 ± 0.30	41 ± 2	48.20
PP-g-cardanol	808 ± 28	45.1 ± 0.98	846 ± 23	47.22
BP/PP	1498 ± 55	31.43 ± 1.07	16 ± 1	24.79
BP/PP-g-cardanol	1226 ± 61	31.49 ± 1.49	37 ± 1	24.49

Contact angle measurement

Measurement of water contact angle gives a good estimate of the polarity of the polymer films. The measured images of the water drop are illustrated in Figure 7(a,b). Water contact angle of PP shows to be hydrophobic. The grafting reaction of cardanol onto PP gives rise to the decrease of contact angle. The average value of eight measurements at various points of PP is 104° and the value of PP-g-cardanol is 91°. Although the results of contact angle of PP-g-cardanol show that it is hydrophobic, the decrease of contact angle and the introduction of phenyl group and phenolic hydroxyl group are helpful to improve the reactivity and compatibility with other components.

Tensile properties

PP is a kind of crystal polymer, so it possessed high tensile strength and low elongation at break as showed in Figure 8(a). The grafting reaction results in the increase of elongation at break because of the breakage of crystal structure (Table I) of PP and chain entanglement of cardanol and PP. Moreover, the grafted product exhibited typical curve of crystalline polymer containing strain hardening because of recrystallization and chain entanglement. Figure 8(b) and Table I show that there are not evident difference in Young's moduli and tensile strength between BP/PP composite and BP/PP-g-cardanol composite. However, the elongation at break of BP/PP-g-cardanol composite is 2.4 times to that of BP/PP composite. The increase of elongation at break can be attributed to the grafting reaction and enhanced interfacial action between the BP and grafted PP, which result in a more efficient transfer of stress along the modified interface. In the case of BP/PP composite, the poor interfacial action between BP and PP leads to microcrack formation under loading and therefore reduces the elongation at break.

SEM analysis

The tensile fracture surfaces were observed by SEM (Fig. 9). Micrograph shows that many voids and unbroken bamboo fibers exist on the BP/PP compos-

ite fracture surface [Fig. 9(a)]. It indicates poor adhesion between BP and PP. The poor adhesion of BP and PP is a consequence of the chemical nature of these materials: the BP is hydrophilic, whereas PP is hydrophobic. Cardanol grafted onto PP can act as a compatibilizer in BP/PP-g-cardanol composite as cardanol can be bonded to the hydroxyl group on the BP surface, resulting in an improved interfacial adhesion between BP and PP. Evidence of improved adhesion between BP and PP-g-cardanol was found

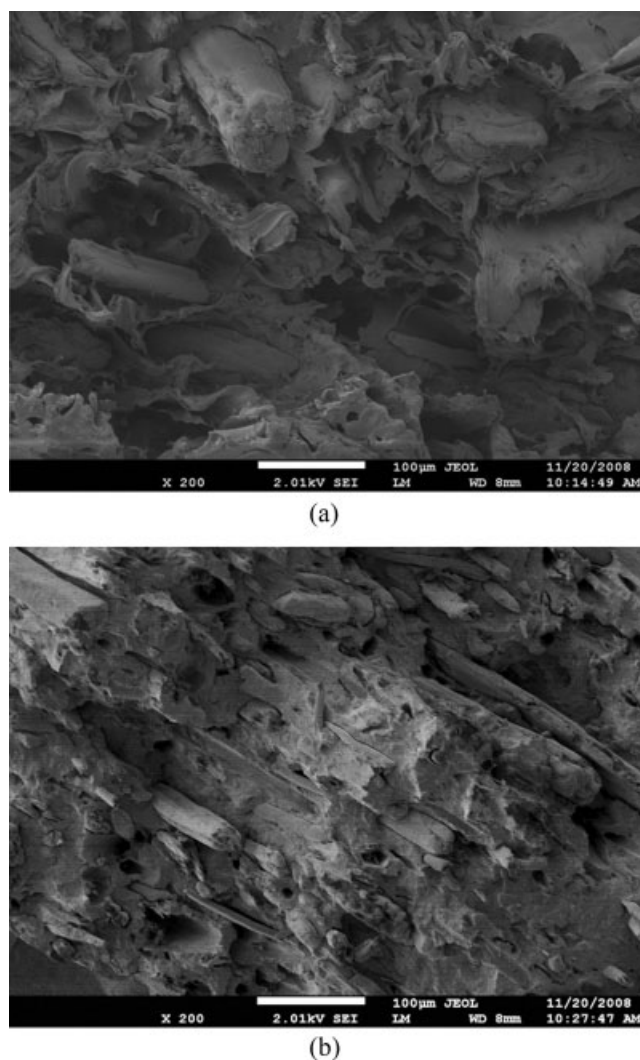


Figure 9 (a) SEM micrograph of BP/PP composite. (b) SEM micrograph of BP/PP-g-cardanol composite.

from the fracture surface of tensile sample [Fig. 9(b)]. In the fracture surface, most of bamboo fibers are still well embedded into the PP-g-cardanol matrix. In addition, the fracture surface shows a more "brittle" texture, with extensive fractured fiber and less pullout bamboo fiber, compared with the BP/PP composite on which more pullout bamboo fibers were seen.

CONCLUSIONS

PP-g-cardanol was prepared by reactive extrusion in the presence of initiator of DCP. Characteristic absorptions of cardanol were shown in the FTIR of grafting product. This confirms that cardanol was grafted onto PP chains successfully. No gel in extrusive processing suggested that the cardanol themselves did not crosslink. The optimal proportion of reactive blending was 7 g cardanol, 0.2 g DCP, and 100 g PP to increase grafting ratio and decrease decomposition when DCP radicals mainly initiated the unsaturated side chains of cardanol. In reactive extrusion blending, cardanol monomers and PP radicals are prone to react along the route of cardanol primary radicals coupling with cardanol radicals or PP tertiary carbon radicals. UV-vis testing was used to quantify the grafting degree of PP. The experimental formula was put forward to simplify the grafting quantification, by which grafting degree could be calculated from MFI which is easy to get. Grafting reaction decreased the hydrophobicity of PP, and the BP/PP-g-cardanol composite exhibits better tensile properties and compatibility than BP/

PP composite because cardanol grafted on the PP can effectively modify the surface energy of PP.

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