A novel grafting-modified waste rubber powder as filler in natural rubber vulcanizates

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ABSTRACT: Polycardanol was synthesized from cardanol, paraformaldehyde, p-toluenesulfonic acid, phosphoric acid (H_3PO_4), and phosphorus pentoxide (P_2O_5) via a two-step process. Results indicated that polycardanol is an acid with high molecular weight and can be self-crosslinked at high temperature. A modified WRP (MWRP) grafted by long chain can be obtained from the reaction between WRP and polycardanol. The sulfur content of MWRP is 0.27%, which is lower than that of WRP by 0.47%. The oxygen content of MWRP is higher by 13% than that of WRP. The phosphorus content of MWRP reaches 5.25%. The water contact angle of MWRP is 91.5°, whereas that of WRP is 123.7°. The properties of the WRP/NR and MWRP/NR composites were also investigated. MWRP/NR possesses higher tensile strength than WRP/NR because of the enhanced interfacial interaction between MWRP and the NR matrix. Post-treatment is also conducive for MWRP/NR to improve its tensile strength at high MWRP content. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42993.

INTRODUCTION

The rapid development of the automobile industry in recent years has resulted in a significant global problem: the disposal of worn-out tires. Tires have a stable three-dimensional network that makes them insoluble, infusible, and difficult to recycle. Researchers have exerted considerable effort to conduct studies on recycling worn-out tires.[1–3]

A feasible method for recycling waste rubber is to convert this material into waste rubber powder (WRP) and use it as filler or replacement for raw rubber.[4–10] However, the incorporation of WRP into rubber or plastic matrix makes the property of the entire system poor because of the incompatibility between WRP and the polymer matrix. Currently, modifying WRP involves two methods. One method is to break the sulfur crosslink bonds by mechanochemical method,[11–14] biodesulfurization,[15–17] microwave,[18–20] or ultrasound.[21,22] Lu et al.[14] used solid-state mechanochemical milling to devulcanize post-vulcanized fluoroelastomer scraps. After milling, the sol fraction of the ground fluoroelastomer increased from its original 1.4% to 19.8%. Li et al.[15] modified WRP using biodesulfurization, thereby decreasing the sulfur content and increasing the reactive sites on the WRP surface. Scuracchio et al.[18] performed thermogravimetric analysis to understand the effect of microwave treatment on the ground tire rubber structure. The increase of microwave treatment time resulted in the thermo-oxidation peak of the main rubber chains disappearing gradually. Nevertheless, the desulfurization process is accompanied by the degradation of the rubber backbone, which is not conducive in improving the mechanical properties of the final material.

The other method of modifying WRP is to improve the physico-chemical properties of the WRP surface, either through acid treating,[8,23] coating method,[24,25] or grafting method.[26–28] Colom et al.[23] applied sulfuric acid to modify reused tire particles, resulting in the appearance of a rough surface. Moreover, 30% hydrogen peroxide solution and various concentrations of nitric acid were used to modify WRP.[8] The results showed that waste rubber particles grafted using maleated polypropylene (MAPP) can generate strong interaction with polypropylene (PP).[25] WRP was also grafted using polystyrene via styrene free radical polymerization initiated by thermal initiators.[26] Grafting efficiency in this approach is affected by numerous factors, including initiator mass, reaction time, and polymerization temperature.

The preceding discussion highlighted that the methods in modifying WRP have their respective advantages and disadvantages. Therefore, we can maximize the advantages of the aforementioned methods to generate a new, modified WRP (MWRP)
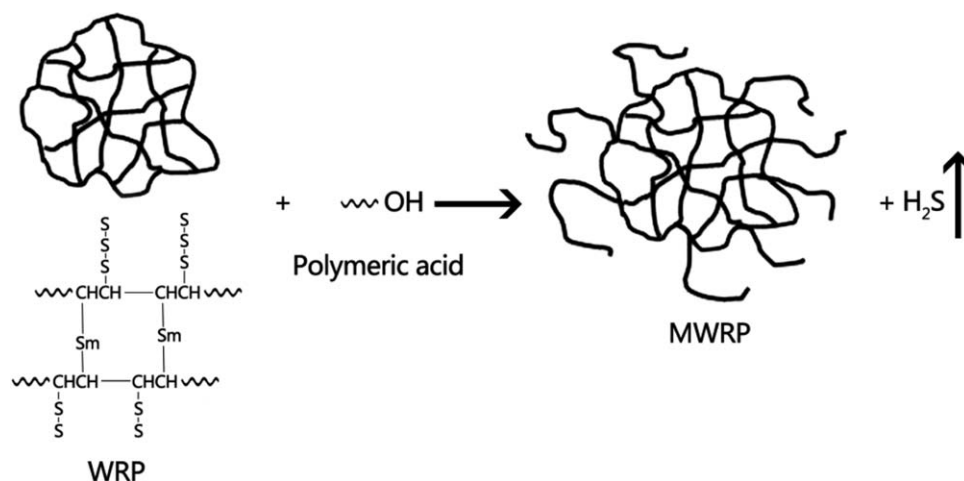
Figure 1. Schematic diagram of MWRP preparation.

that considers desulfurization and grafting. Evidently, MWRP is a WRP grafted by a long chain polymer through the application of desulfurization reaction (Figure 1). Desulfurizer with high molecular weight can destroy S–S or polysulfur bonds, contributing to long chain grafting on the WRP surface. Therefore, MWRP is worth investigating because this method has not been reported yet.

To achieve the objective of this study, the new desulfurizer with high molecular weight (named by polycardanol) can be synthesized from cardanol. The modified WRP (MWRP) will be prepared via the reaction between WRP and polycardnol. And the possibility of introducing MWRP into natural rubber (NR) to obtain excellent composites will be investigated.

EXPERIMENTAL

Materials

Cardanol was obtained from Shanghai Meidong Biomaterials Co., Ltd. Paraformaldehyde, p-toluenesulfonic acid (PTSA), phosphorus pentoxide (P_2O_5), phosphoric acid (H_3PO_4), cupric sulfate ($CuSO_4$), and toluene were purchased from Shanghai LingFeng Chemical Reagent Co., Ltd. WRP used in this study was provided by Suzhou Zhongjiao Renewable Resources Company. The average WRP particle size was 80 mesh. NR was purchased from Shandong Oriental Trading Co., Ltd. Other compounding ingredients, such as zinc oxide (ZnO), stearic acid, sulfur, accelerator tetramethyl thiuram disulfide (TMTD), and 2,2-dibenzothiazole disulfide (DM), were purchased commercially.

Preparation of Polycardanol

Polycardanol was synthesized in two steps.[29] The first step in synthesizing polycardanol was the synthesis of phenolic resin. Paraformaldehyde, cardanol, and PTSA were placed in a 500 ml three-necked round-bottomed flask with thermometer and condenser. The mixture was gradually heated to 80°C with stirring, and temperature was maintained at 80°C for a certain period. After the completion of the reaction, the reaction mixture yielded phenolic resin based on cardanol. The second step was the synthesis of polycardanol. Acidic monomer was charged into the phenolic resin with stirring for approximately 30 min.

The system temperature was maintained at 80°C. Finally, the reactant was washed with water, and the residual was dehydrated under reduced pressure to obtain polycardanol.

Preparation of MWRP

WRP was added to polycardanol with stirring for a certain time at ambient temperature. $CuSO_4$ aqueous solution was used to absorb the gas generated in the reaction. Figure 2 shows the schematic diagram. After the reaction, the excess polycardanol in WRP was extracted in a Soxhlet extractor using toluene (a solvent) for 24 h. Thereafter, the sample was dried to obtain MWRP, which was used as the experimental sample for the subsequent structure characterization and performance testing.

Preparation of Rubber Compounds

A two-roll mill was used to prepare the rubber compounds. Table I lists the basic formulation. Raw NR was masticated with various contents of WRP or MWRP (mass ratio between polycardanol and WRP was 0.05; MWRP was not extracted) and then mixed with the other additives. Mixing time was 10 min, and the roller temperature was maintained at approximately 50°C. The compounded rubber was kept overnight before undergoing vulcanization. Thereafter, vulcanization was conducted on a platen press at 150°C and under a pressure of 10 MPa for optimum curing time (t90). Dumbbell-shaped tensile specimens were obtained and used for mechanical testing.
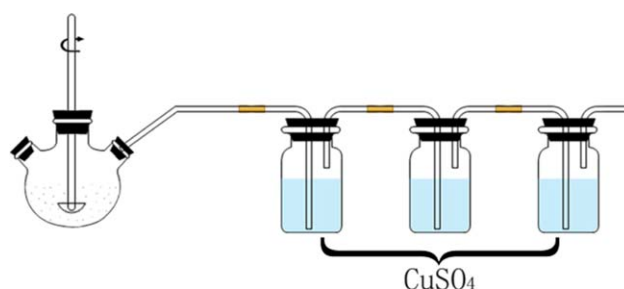

Figure 2. The schematic diagram of Preparation of MWRP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Table I. Formulation of NR Composites

Material	Weight/phr
NR	100
Zinc oxide	5
Stearic acid	2
Carbon Black N234	50
Accelerator DM	1.5
Accelerator TMTD	0.3
Antioxidant 4010NA	1
Sulfur	2.5
WRP or MWRP	Variable (0,50, 100, 150)

Measurements

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet 5700 spectrometer. The spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} over 20 scans.

^{31}P-NMR spectroscopy. The liquid state ^{31}P-NMR spectrum was recorded using a Bruker AVANCE 400 spectrometer at an operating frequency of 161 MHz. Deuterochloroform (CDCl$_3$) was used as the solvent of the polycardanol. The solid ^{31}P-NMR spectrum was recorded on a Bruker AVANCE 500 operating at 202 MHz. ^{31}P NMR experiments were conducted at room temperature. The chemical shifts (δ) were reported in parts per million (ppm) with respect to the resonance peak of 85% phosphoric acid (H$_3$PO$_4$) that was used as an external reference.

Gel Permeation Chromatography Measurement. The absolute molecular weight and the distribution of polycardanol were determined using gel permeation chromatography (GPC) (Waters515; Optilab rEX; ViscoStar) equipped with small angle laser light scattering (DAWN HELEOS). Tetrahydrofuran, which was used as a solvent, was operated at 30°C at a flow rate of 1 ml/min.

Thermal Property. The thermal property of polycardanol was determined using TA instruments (DSC Q2000) at a heating rate of 10°C min^{-1} under flowing nitrogen (40 cm^3 min^{-1}). A sample mass of 10 mg in an aluminum pan was used. The temperature range was from 20°C to 300°C.

X-ray Photoelectron Spectroscopy. To evaluate the element composition, chemical state, and element relative content on the WRP surface modified by polycardanol, X-ray photoelectron spectroscopy (XPS) spectra were obtained using Thermo Scientific ESCALAB 250Xi. The binding energies were corrected based on the carbon 1 s peak at 285.0 eV.

Water Contact Angle Measurement. WRP samples were pressed into films using the platen press for 10 min at a press of 10 MPa. Contact angle of water was measured at room temperature (OCA20, Datephysics, Germany). The values of the contact angle were averaged over five different water drops.

Scanning Electron Microscopy. A scanning electron microscope (SEM, S-4800, Japan) was used to observe the surface morphologies of both WRP and MWRP, as well as the fractured surface
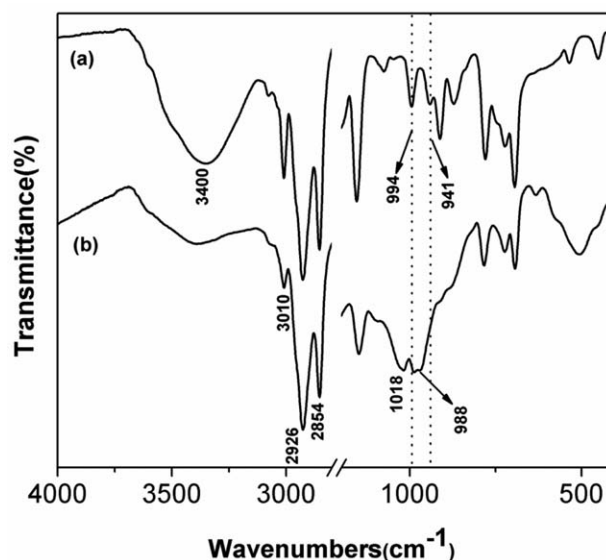
Figure 3. FTIR spectra of (a) cardanol and (b) polycardanol.

of the NR composites, which were broken in liquid nitrogen. All the surfaces of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging during the examination.

Energy Dispersive Spectroscopy. The element composition of both WRP and MWRP were analyzed using energy dispersive spectroscopy (EDS; JEOL JSM-6310LV, JEOL, Ltd., Japan).

Mechanical Properties. The mechanical properties of both WRP/NR and MWRP/NR were measured using an electronic tensile testing machine (CMT 2205, sans, China) at room temperature based on ASTM D 412. Dumbbell testing specimens were used at a crosshead speed of 500 mm min^{-1}. Mechanical data were averaged over three specimens.

RESULTS AND DISCUSSION

Characterization of Polycardanol

The FTIR spectra of both cardanol and polycardanol are shown in Figure 3. The peak at 3400 cm^{-1} is assigned to the stretching vibration of O—H. The peaks at 2854 and 2926 cm^{-1} are designated to the symmetrical stretching vibration of —CH$_2$ groups. In the infrared spectrum (a) the peaks at 941 and 994 cm^{-1} are of the conjugated double bonds of the side chain and disappear in the infrared spectrum (b) thereby confirming that the double bonds have reacted. The peak at 3010 cm^{-1} corresponds to C—H of the independent double bond of the side chain.[30] The bands at 988 and 1018 cm^{-1} are related to the P—O bond because of the reaction between phosphorus and phenolic resin. The FTIR spectrum confirms that phosphorus is successfully introduced into the polycardanol.

^{31}P-NMR spectroscopy is a valuable tool for characterizing phosphorus-containing compounds. The ^{31}P-NMR spectrum of polycardanol is presented in Figure 4. Compared with the non-phosphorous cardanol monomer, several new peaks are observed in the ^{31}P-NMR spectra. This result proves that a phosphorus-containing product is present. According to FTIR
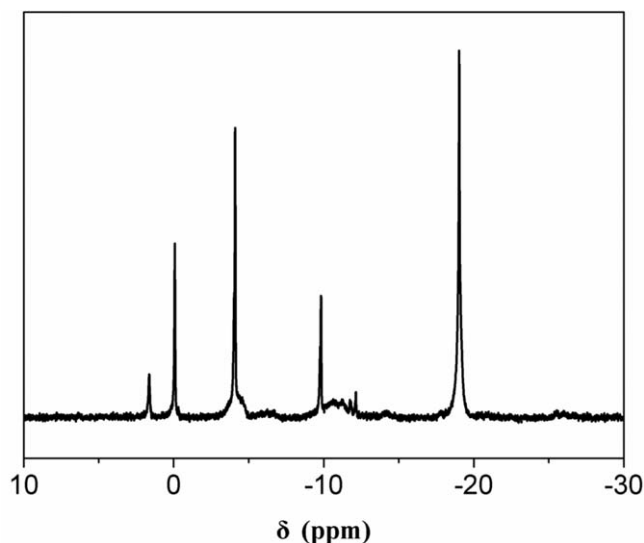
Figure 4. ^{31}P-NMR spectra of polycardanol.

and ^{31}P-NMR, we infer there are three reactions in the system: (1) the generation of phenolic resin; (2) the reaction between phenolic resin and acid monomers; (3) the addition of double bonds of side chain in cardanol. Therefore, the new peaks from left to right may be of phosphate monoester, phosphate diester, phosphotriester and phosphate polyester.[31]

The molecular weight and polydispersity index (PDI = Mw/Mn) of the polycardanol were measured using GPC equipped with a small angle laser light scattering. Figure 5 and Table II show the results. The molecular weight Mn of polycardanol is 1.07×10^4, which is 35 times higher than that of the cardanol monomer (Mn $\approx$ 300). This result indicates that polycardanol is different from cardanol. PDI (Mw/Mn) is also broad at up to 2.46. Figure 6 shows that the pH value of polycardanol is 2. Therefore, a new acid (i.e., polycardanol) that has high molecular weight was successfully prepared.

A typical differential scanning calorimetry (DSC) scan of polycardanol is presented in Figure 7. An exothermic peak was
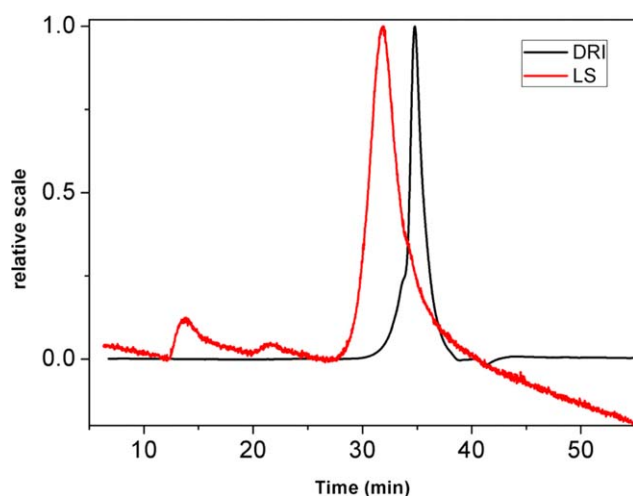

Figure 5. GPC data of polycardanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
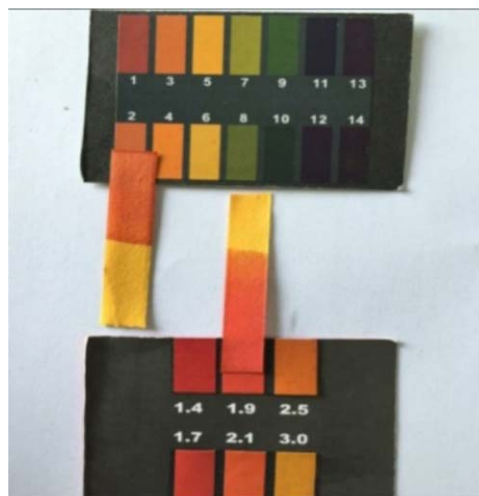

Figure 6. The pH of polycardanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observed, which is associated with self-crosslinked reaction. Self-crosslinking may be led by the residual double bonds of polycardanol.

Characterization of the Modified WRP

Based on the preceding discussion, polycardanol is characterized as an acid with high molecular weight. When polycardanol was added into WRP, a rotten egg odor reeked, and moistened lead acetate paper turned black (as shown in Figure 8). The gas is determined to be hydrogen sulfide gas. Therefore, the desulfurization reaction of WRP occurred. After the desulfurization, WRP is converted to MWRP.

MWRP Surface. The structures of both WRP and MWRP were characterized using FTIR (see Figure 9). For MWRP, the new peaks at 972 and 1125 cm^{-1} appear, thereby corresponding to the P—O stretching vibration. This result implies that polycardanol has been grafted on the WRP surface. Figure 10 also shows a new peak in the ^{31}P solid-state NMR spectrum of MWRP. If the sample is non-phosphorus, then the peak of phosphorus (the reference H_3PO_4) does not appear in the NMR spectroscopy. Therefore, the new peak in the ^{31}P solid-state NMR spectrum of MWRP is the phosphorus introduced on the MWRP surface. The ^{31}P solid-state NMR spectrum of WRP was used as the blank sample, and no peak was observed.

XPS analysis was also performed to detect the variation in the chemical composition of the WRP surface that was modified by polycardanol. Figure 11 shows the C1s core spectrum of the WRP and MWRP. For the WRP particles, the C1s signals are located at 284.2, 284.8, and 285.5 eV, corresponding to the bonding energy for C=C, CxHy/C—C, and C—S bonds, respectively.[7,32] Figure 11(b) shows that in the case of MWRP, the C1s signal can be fitted with four components. Except for the peak

Table II. GPC Data of Poly Cardanol

Material	Mn/10^4	Mw/10^4	Mz/10^4	Mw/Mn
poly cardanol	1.07	2.64	4.24	2.46

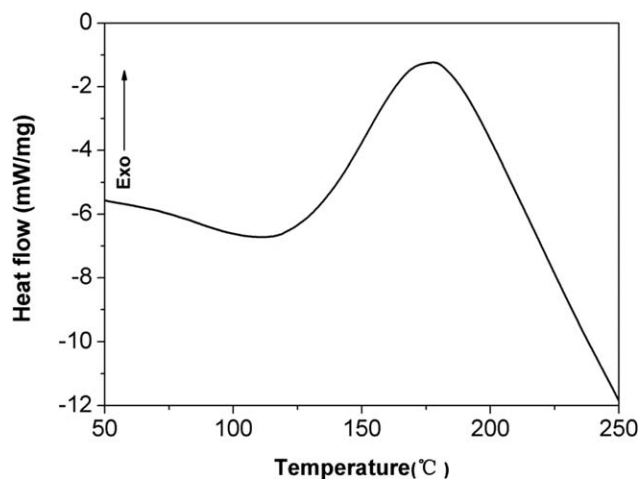**Figure 7.** DSC trace of polycardanol.

Figure 9. FTIR spectra of (a) WRP and (b) MWRP.

positions at 284.2, 284.8, and 285.5 eV, a new peak with binding energy at 286.6 eV appears; such peak is attributed to the C–O species.

Table III shows the surface composition determined by the XPS analysis of both WRP and MWRP. Table III also shows that after grafting modification by desulfurization, the sulfur content is lowered by 0.47% (from 0.71% to 0.27%), oxygen content increases by 13% (from 8.44% to 21.61%), and phosphorus content is up to 5.25%. XPS also presents evidence of the introduction of phosphorus on the WRP surface. EDS analysis (Figure 12) shows that the new peak in MWRP corresponding to the phosphorus appears compared with the WRP spectrogram. The aforementioned results provide a consistent conclusion that MWRP can be prepared via the reaction between WRP and polycardanol.

Wettability of WRP And MWRP. The measurement of water contact angle was used to evaluate the wettability of both WRP and MWRP. When drops of water were dripped onto the WRP surface, the outmost surface layers could interact with the water. Hydrophobic surface with low free energy has a large contact angle; hydrophilic surface with high energy allows the drop to spread to produce a small contact angle. Figure 13 shows that the water contact angle of WRP is 123.7°, whereas that of
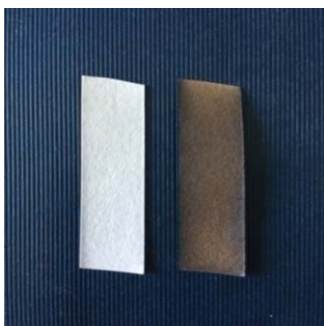

Figure 8. The lead acetate test paper of before and after contact with gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
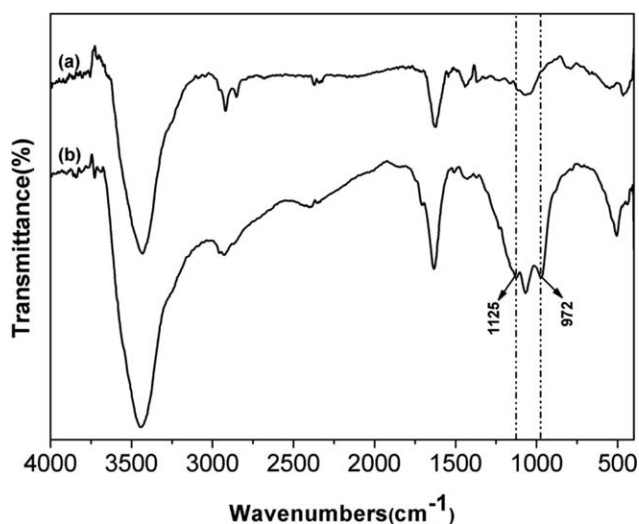
MWRP is down to 91.5°. These results imply that MWRP is significantly more hydrophilic than WRP.

SEM Observation. The SEM photographs of WRP and MWRP are shown in Figure 14. As displayed in the SEM micrographs, the MWRP surface is different from that of WRP; the former becomes smooth and has few pores, which is similar to the reference.[28] This difference can be ascribed to the grafting of polycardanol on the surface of the rubber particles.

NR Composites

The property of WRP re-vulcanizates is not good because of the inert surface and cross-linked structures. WRP grafted by long-chain polymer with active groups (i.e., MWRP) may enhance the interfacial adhesion with a matrix; thus, the properties of the NR composites filled by MWRP are worth studying.

WRP/NR And MWRP/NR Properties. Figures 15 and 16 depict the tensile strength and elongation at break of WRP/NR and MWRP/NR vulcanizates, respectively. The tensile strength and elongation at break of the NR vulcanizates definitely decreased with the increase of WRP or MWRP loading; these results are consistent with the references.[33–35] In the same rubber particle content, the tensile strength and elongation at break of the MWRP/NR vulcanizates are significantly higher than those of the WRP/NR vulcanizates. Compared with the virgin NR vulcanizates without rubber particles, the tensile strength of the MWRP/NR composites, particularly with the MWRP content of 50 phr, decreased by 13.3%; the elongation at break increased by 6.7%. The change in the mechanical properties of MWRP/NR may be associated with the improvement of interfacial adhesion between MWRP and the NR matrix. Figure 17 shows the SEM photographs of the cryogenically fractured surface of the NR vulcanizates filled with 50 phr WRP or MWRP. Figure 17 (a1, a2) shows a clear gap and several cracks on the section, thereby indicating that the adhesion of WRP to the NR matrix is poor. Figure 17 (b1, b2) shows the homogeneous and single-phase structure; no void and crack were observed between MWRP and the NR matrix. The MWRP/NR vulcanizates have significantly better compatibility than that of WRP/NR.
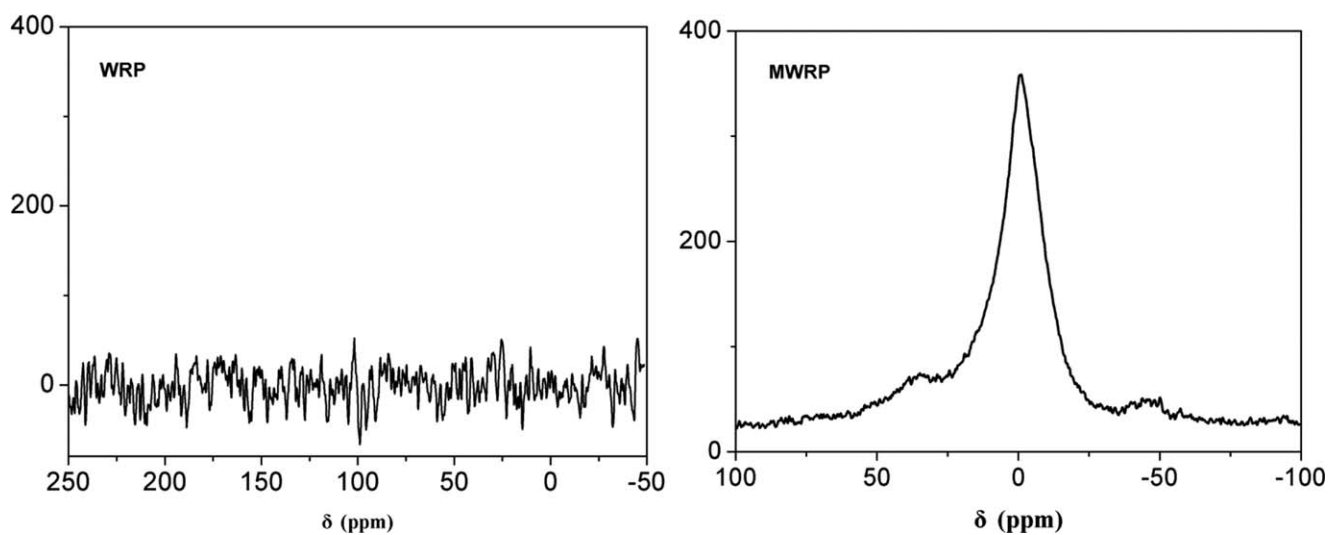
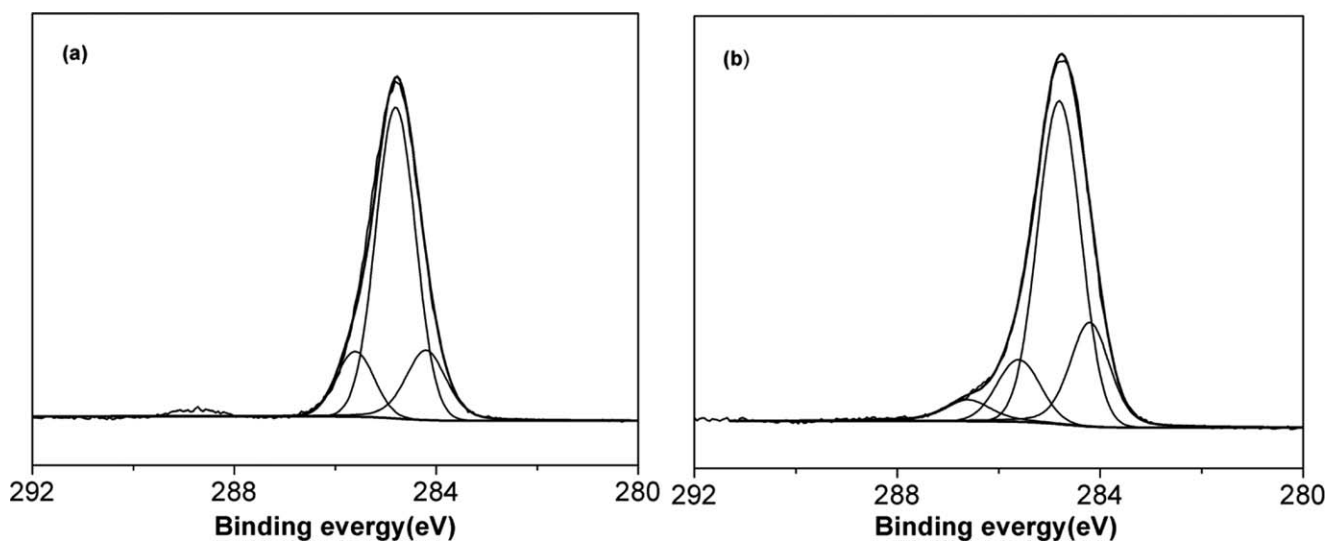**Figure 10.** ^{31}P solid-state NMR spectra of WRP and MWRP.

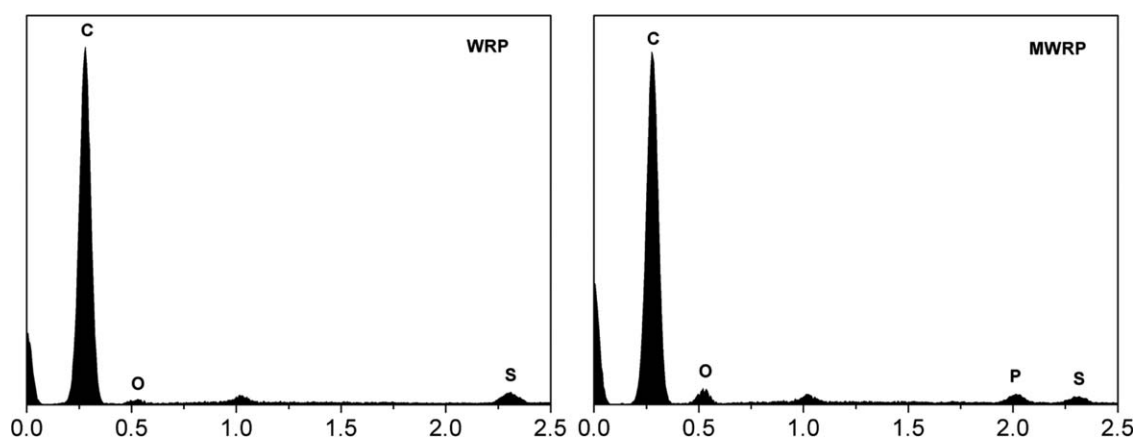**Figure 11.** C1s core spectrum of WRP (a) and MWRP (b), respectively.

Figure 12. EDS patterns of WRP and MWRP.

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Table III. Relative Element Content of the WRP and MWRP as Determined by XPS

Element	WRP	MWRP
C%	90.85	72.87
O%	8.44	21.61
S%	0.71	0.27
P%	0.00	5.25

Therefore, the interface zone between MWRP and NR could withstand considerable strain.

MWRP/NR Properties after Heat Treatment. Polycardanol can be self-crosslinked at high temperature; therefore, studying the influence of heat treatment on the properties of MWRP/NR is necessary. The samples were placed in an oven for 24 h at 100°C.

Figures 18 and 19 depict the mechanical performance of MWRP/NR vulcanizates before and after heat treatment, respectively. After heat treatment, the tensile strength and elongation at break of the virgin NR vulcanizate are reduced, which is attributed to the poor heat resistance of NR because of the existence of C=C. At high MWRP content, the tensile strength of MWRP/NR composites after heat treatment is higher than that of the untreated vulcanizates; by contrast, the opposite is true at the low MWRP content. When the low MWRP content is introduced into NR, the latter is a continuous phase and contributes to the mechanical property. With the increase in the MWRP content, the NR role is gradually replaced by MWRP; the latter can then influence the mechanical property of the entire system. During the heat treatment, the self-crosslinked reaction of polycardanol on the MWRP surface occurs, which is conducive to the increase of the crosslinking density of the interphase. This result benefits the performance enhancement of the entire system. However, excess MWRP can also negatively affect the mechanical property due to the gap between MWRPs. Therefore, a maximum tensile strength is observed at the MWRP content of 50 phr after heat treatment.

CONCLUSIONS

Polycardanol was successfully synthesized in the present study. MWRP grafted by long chain was successfully prepared through desulfurization reaction between polycardanol and WRP. MWRP was used as filler to obtain composites. We obtained the following conclusions:

a. Polycardanol is an acid with high molecular weight, and can be self-crosslinked at high temperature, which can be used as a desulfurizer.
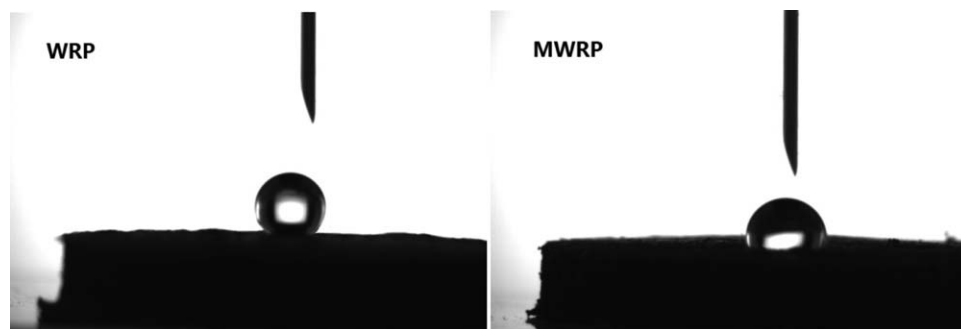

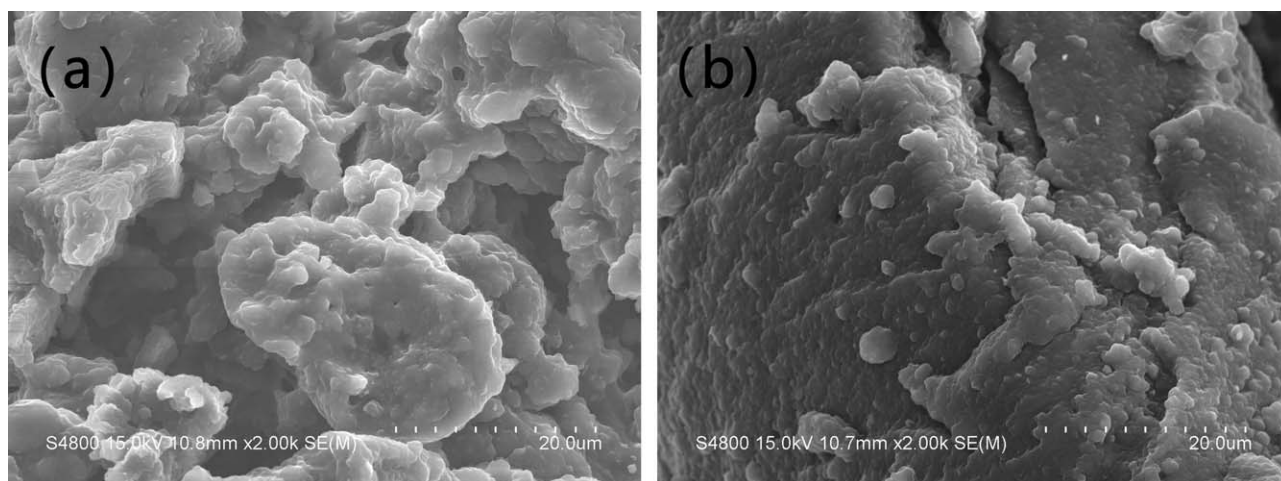**Figure 13.** Water contact angle measurement of WRP and MWRP.

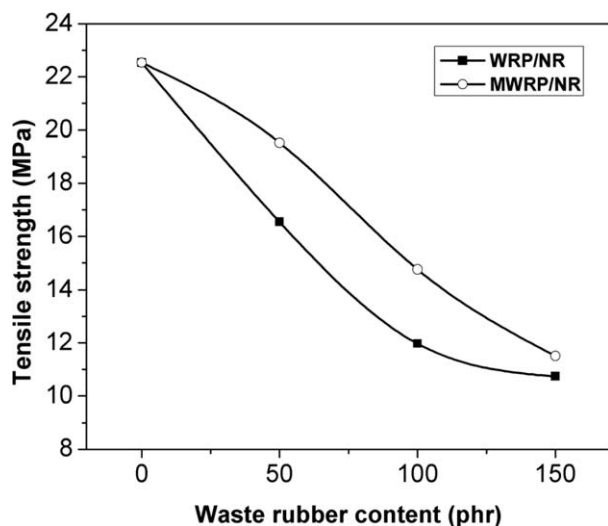**Figure 14.** SEM photographs of the WRP and MWRP (a—WRP, b—MWRP).

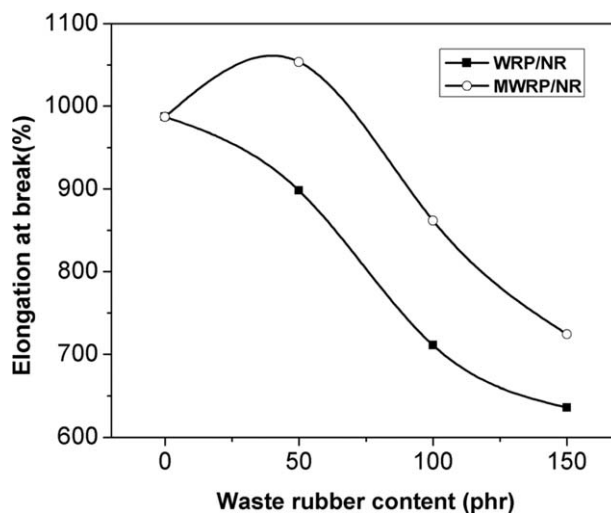**Figure 15.** The tensile strength of WRP/NR and MWRP/NR.

Figure 16. The elongation at break of WRP/NR and MWRP/NR.

b. MWRP is more hydrophilic than WRP because of the grafted long chain, which was created by the reaction between polycardanol and WRP.

c. MWRP/NR composites possess better mechanical properties than WRP/NR composites because of the good interfacial adhesion between MWRP and the NR matrix. After post-
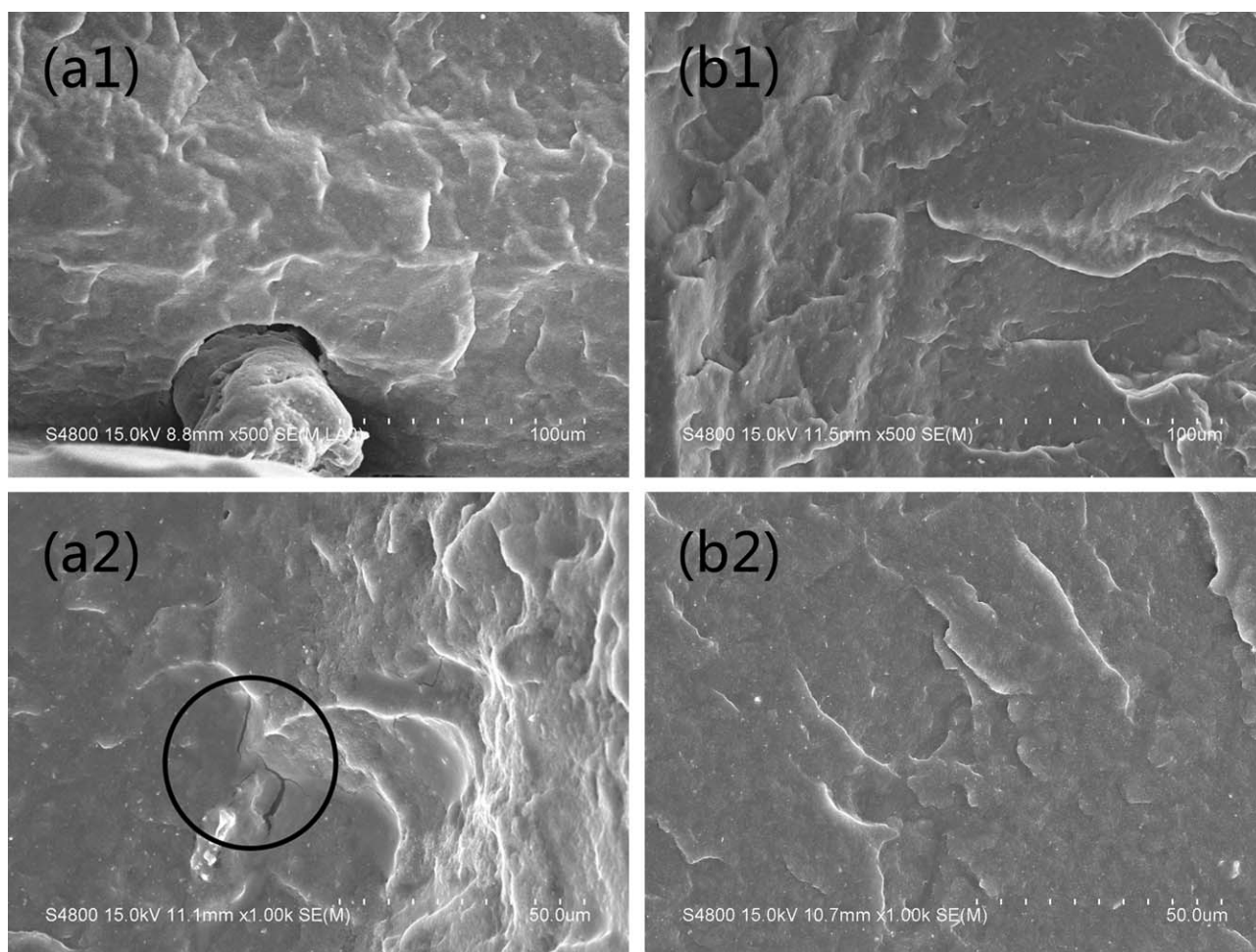

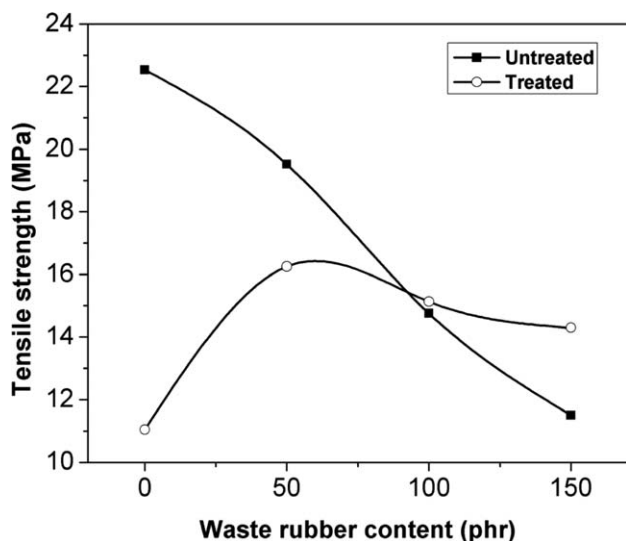**Figure 17.** SEM photographs of the WRP and MWRP (a—WRP, b—MWRP).

Figure 18. The tensile strength of MWRP/NR before and after heat treatment.
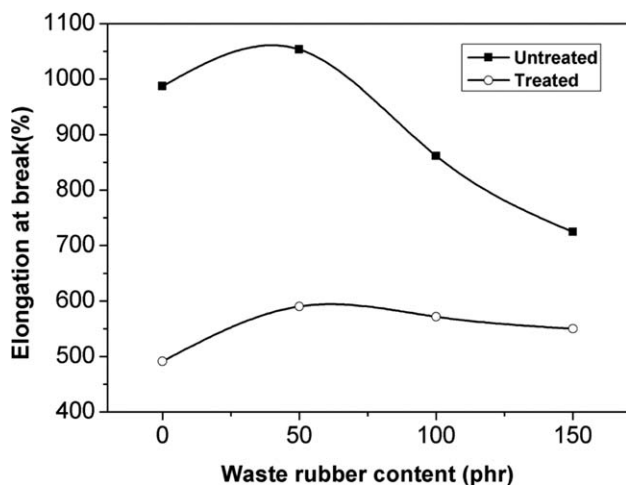

Figure 19. The elongation at break of MWRP/NR before and after heat treatment.

treatment for 24 h at 100°C, the mechanical property of MWRP/NR composites is improved, resulting in the self-crosslink of polycardanol at high temperature. The appropriate content of MWRP is a good modifier and antioxidant for NR.

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