

MECHANOCHEMICAL RECYCLING AND PROCESSING OF WASTE CROSSLINKED POLYMERS: WASTE TIRE RUBBER AND WASTE XLPE FROM CABLE SCRAPS

Canhui Lu*, Xinxing Zhang, Mei Liang

*State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute,
Sichuan University, Chengdu 610065, China
E-mail: canhuilu@scu.edu.cn*

Abstract: The accumulation and disposal of polymer wastes including waste plastics, waste rubber, waste synthetic fibers and waste composites is a worldwide concern. Until now, there are many technical barriers in recycling polymer wastes with crosslinked structure, such as vulcanized rubber, crosslinked polyolefine and other thermoset materials. In this study, a mechanochemical approach was used to conduct the devulcanization of waste tire rubbers (WTR) and de-crosslinking of waste crosslinked polyethylene (XLPE) from cable scraps, for turning WTR and waste XLPE to re-formable materials. The stress-induced mechanochemical devulcanization of waste tire rubber and decrosslinking of XLPE at ambient temperature can be achieved through self-designed solid-state mechanochemical reactor. Several high-valued composites, such as natural rubber/WTR, nitrile rubber/WTR, HDPE/XLPE, thermoplastic vulcanizates (TPVs) from partly de-crosslinked XLPE scrap and partly devulcanized WTR, with improved mechanical properties were obtained through mechanochemical processing. The objective of the present research is to develop a feasible technique for reusing unsegregated waste crosslinked polymer materials.

1. Introduction

The accumulation and disposal of polymer wastes including waste plastics, waste rubber, waste synthetic fibers and waste composites is a worldwide concern. Until now, there are many technical barriers in recycling polymer wastes with crosslinked structure, such as vulcanized rubber, crosslinked polyolefine and other thermoset materials. The reuse or recycling of waste crosslinked polymer has become an important topic and attracted many researchers' interests in recent years. Nowadays, most waste crosslinked polymeric materials have been subjected to incineration or landfilling, and only a small percentage of them have gone into a variety of reuse/recycle options. However, incineration and landfilling produce severe environmental problems such as air pollution and soil contamination. The reuse of crosslinked polymer scraps not only protects the environment but also saves limited petroleum resource from which the raw material is originated.

The previous work carried out in our laboratory demonstrated that scrap rubber vulcanizates could be partially devulcanized through solid state mechanochemical milling with a pan-mill type mechanochemical reactor, designed on the basis of a traditional Chinese stone-mill. Because of its unique structure, the pan-mill equipment acts as pairs of three-dimensional scissors during milling, exerting very strong shear forces on milled materials, and showing multi-function such as pulverizing, dispersion, mixing as well as activation.

In this study, a mechanochemical approach was used to conduct the devulcanization of ground tire rubbers (GTR) and de-crosslinking of waste crosslinked polyethylene (XLPE) from cable scraps, for turning GTR and waste XLPE to re-formable materials. Thermoplastic vulcanizates (TPVs) from partly de-crosslinked XLPE scrap and partly devulcanized GTR, with improved mechanical properties were obtained through mechanochemical processing. The objective of the present research is to develop a feasible technique for reusing unsegregated waste crosslinked polymer materials.

2. Experimental

2.1 Materials

The crosslinked polyethylene used in this study is widely applied in insulated electric wires and cables, in which the molecule chains of low density polyethylene have been crosslinked by organic peroxide compounds, with a crosslinking degree (gel content) of approximately 80%. The raw XLPE were cut into chips of about 1 cm³ with a rotary blade chipping machine.

Ground tire rubber, with an average particle size of 340 μm, was originated from ground tread layers of truck tires. Other vulcanizing ingredients such as zinc oxide, stearic acid, 2-mercaptobenzothiazole (MBT), tetramethyl thiuram disulfide (TMTD), sulfur and dicumyl peroxide (DCP) were obtained commercially.

2.2 Mechanochemical treatment of crosslinked polymer scraps

The partial degradation of XLPE and GTR was carried out in the pan-mill type mechanochemical reactor at ambient temperature. XLPE/GTR mixture was fed into the mechanochemical reactor through the hopper in the center of the milling pan at a rotating speed of 30 rev min⁻¹. The average retention time of the composite powders during milling is 25~40 seconds per cycle, and the heat generated during milling was removed by water circulation. A chain transmission system and a screw pressure system are set to regulate the rotation speed of moving pan and imposed load respectively, which can strictly control two major dynamic parameters during milling, velocity and force. Milling process of solid mass in the equipment was as follows, the materials are fed to the center of the pan from the inlet, driven by shear force, moving along a spiral route towards edge of the pan till come out from

the outlet, thus one cycle of milling is finished. The decomposed samples were collected for the measurements of gel fraction, rheological behaviors and mechanical properties.

2.3 Preparation of TPEs through dynamic vulcanization

Blends were prepared in a Brabender Plasticorder PLE-330 by melt-mixing the components at a temperature of 160 °C and a rotor speed of 80 rev min⁻¹ for 10 min. The dynamically vulcanized blends were prepared from the formulations shown in Tab.1. Then, the blends were left to cool down at ambient temperature prior to molding. Samples of the blends were compression molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 180 °C for 5 min, followed by compression for 8 min at the same temperature and subsequently cooling under pressure for 5 min.

Tab. 1 Compounding formulations used to prepare the TPEs with various vulcanization systems

| Ingredients | Amount (phr) | |
|-------------------------|---------------|-----------------|
| | Sulfur system | Peroxide system |
| XLPE/GTR (50/50) blends | 100 | 100 |
| ZnO | 2.5 | — |
| Stearic acid | 1 | — |
| MBT | 0.375 | — |
| TMTD | 0.75 | — |
| Sulfur | 1.5 | — |
| DCP | — | 0.5 |

2.4 Gel fraction measurements

Gel fractions of the decomposed and dynamically vulcanized samples were measured by Soxhlet extraction. The samples were reflux in toluene for 24 hours and then dried in a vacuum oven at 60 °C for 6 hours. The weights of samples were recorded before and after the treatments.

2.5 Rheological measurements

The rheological measurements were done in a Gottfert capillary rheometer (Rheograph 2002) at different plunger speeds. The plunger speed was varied from 0.06 to 20 cm min⁻¹. The melt was extruded through the capillary at predetermined plunger speeds after a warm-up period of 4 min. The measurements were done at a temperature of 180 °C.

2.6 Mechanical properties

The stress-strain properties of the samples were determined in accordance with ASTM D412 using an Instron 5567 Universal Testing Machine at a crosshead speed of 100 mm/min.

3. Results and discussion

3.1 Gel fraction reduction of XLPE/GTR blends during mechanochemical milling

The realization of partial degradation of XLPE and GTR was confirmed by gel fraction measurements. Fig.1 shows the effect of mechanochemical milling on the gel fraction of XLPE/GTR (50/50) blends. The gel fraction which correlated to the crosslink density of the blends was decreased significantly after solid state mechanochemical milling. In order to investigate whether both of the XLPE and GTR were partially decomposed or only GTR component was devulcanized during mechanochemical milling, XLPE and GTR were separately milled 8 cycles and the variation of their gel fractions after milling was measured. Tab.2 indicates that both of the XLPE and GTR could be partially de-crosslinked through mechanochemical milling.

Tab. 2 Gel fraction of XLPE and GTR before and after separately mechanochemical milling

| Samples | Without milling | After 8 cycles of milling |
|---------|-----------------|---------------------------|
| XLPE | 80.6% | 64.5% |
| GTR | 91.3% | 72.4% |

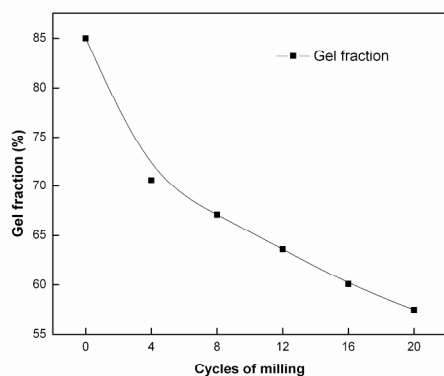


Fig. 1 The effect of mechanochemical milling on the gel fraction of XLPE/GTR (50/50) blends

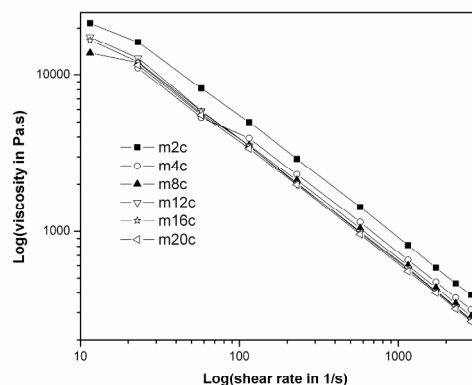


Fig. 2 The variation of the capillary viscosity as a function of the shear rate for XLPE/GTR (50/50) blends with different cycles of milling

3.2 Rheological studies

The flow properties of the materials studied in the molten state were analyzed by rheology. The variation of the capillary viscosity as a function of the shear rate for XLPE/GTR (50/50) blends with different cycles of mechanochemical milling is presented in Fig. 2. The apparent viscosities of the mechanochemically treated mixtures decrease with increasing of shear rate, indicating pseudoplastic flow behavior. Furthermore, as the cycles of

mechanochemical milling increases, the apparent viscosity decreases. Such a decrease in viscosity is in accordance with the gel fraction test. The partial de-crosslinking or devulcanization of XLPE and GTR during mechanochemical milling may responsible for the decrease in apparent viscosity.

3.3 Effect of different curing system on the mechanical properties of the blends

One of the key properties of thermoplastic vulcanizates is their mechanical properties, which also yields the first information on the compatibility of blends. Tab.3 shows the mechanical properties of the XLPE/GTR (50/50) composites after 8 cycles of mechanochemical milling with and without dynamically vulcanizing, respectively. Two different types of curing agent: sulfur and peroxide system have been investigated. Compared with the sulfur-cured system, the DCP-cured system showed deteriorated mechanical properties. DCP may cause crosslinking of polyethylene, therefore it is not strange that the DCP-cured system lead to poor processability. On the contrast, the mechanical performance of the sulfur-cured system was significantly improved. The tensile strength increased by about 42% from 5.7 to 8.1 MPa. Meanwhile, the elongation at break rose by about 24% from 152.8% to 189.1%.

Tab.3 Mechanical properties of the XLPE/GTR (50/50) blends after 8 cycles of mechanochemical milling with and without dynamic vulcanization

| Samples | Tensile strength (MPa) | Elongation at break (%) |
|-----------------------|------------------------|-------------------------|
| Without vulcanization | 5.7 | 152.8 |
| DCP-cured system | 3.7 | 40.2 |
| Sulfur-cured system | 8.1 | 189.1 |

3.4 Effect of mechanochemical treatment on the mechanical properties of the blends

The sample of raw XLPE/GTR blends could not be obtained due to the fact that raw blends could not be plasticized and thermoformed. However, the partially de-crosslinked blends could be plasticized and thus be hot-pressed to a continuous sheets, indicating the characteristic of thermoforming. The effects of mechanochemical de-crosslinking on the tensile strength and elongation at break of the composites are shown in Fig.3 and Fig.4, respectively. The results showed that the tensile strength and elongation at break of the composites increase with the cycles of mechanochemical milling. After 20 cycles of mechanochemical milling, the composites reached the maximum tensile strength (9.1 MPa) and elongation at break (201.2%). The longer time of mechanochemical milling treatment is considered to induce higher degradation degree of XLPE/GTR blends and thus improved the

compatibility of the XLPE/GTR blends due to improved molecule entanglement. Moreover, mechanochemical co-milling of XLPE and GTR gave rise to a better dispersion between both polymeric phases, and thus, a more homogeneous and continuous structure was obtained.

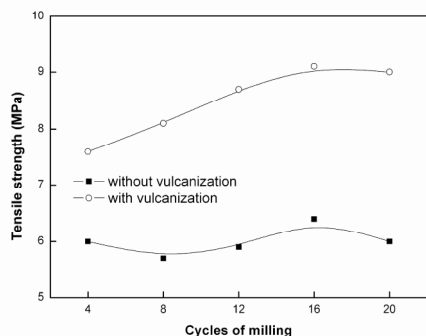


Fig. 3 The effect of mechanochemical degradation on the tensile strength of XLPE/GTR (50/50) composites

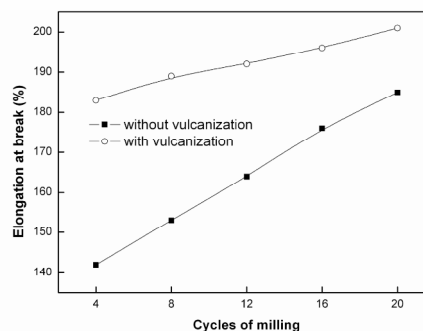


Fig. 4 The effect of mechanochemical degradation on the elongation at break of XLPE/GTR (50/50) composites

3.5 Morphological studies

Fig. 5 (a) and (b) show the cryogenically fractured surface of the XLPE/GTR (50/50) composites after 8 cycles of milling without and with dynamic vulcanization, respectively. As can be seen, the interfacial adhesion between XLPE and GTR was considerably improved through dynamic vulcanization. The improved interfacial adhesion was ascribed to the ultimately fine dispersion of rubber particles in the partially decomposed polyethylene phase after dynamic vulcanization.

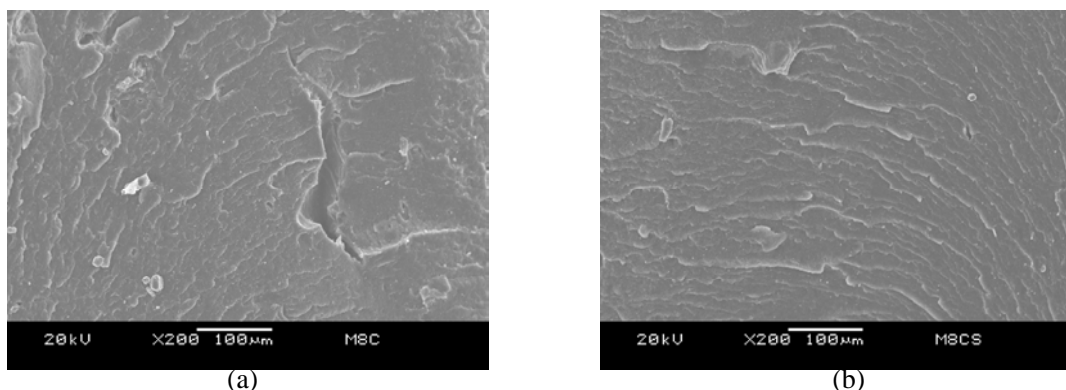


Fig. 5 SEM fractographs of XLPE/GTR (50/50) composites after 8 cycles of milling (a) without and (b) with dynamic vulcanization

3.6 Reprocessability studies

The reprocessability of the dynamically vulcanized XLPE/GTR (50/50) composites was studied by remixing the sample in a Brabender plasticorder and remolding the material. The process was repeated for three times and the changes in tensile strength and elongation at break of the blend vulcanizates are shown in Fig.6. It is clearly observed from the figure that

the tensile strength and elongation at break are kept almost the same even after three cycles of reprocesses, which indicates a thermoplastic nature of the blend.

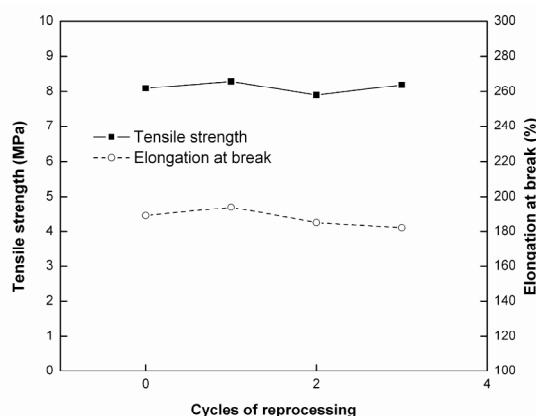


Fig. 6 The effects of reprocessing cycles on the tensile strength and elongation at break of XLPE/GTR (50/50) composites

4. Conclusions

The mechanochemical recycling of XLPE and GTR was realized using our self-designed solid state mechanochemical reactor. The significant decrease in the gel fraction of XLPE/GTR blends during mechanochemical milling confirmed the partial degradation of these polymer scraps. The apparent viscosity of the blends decreased with increasing the mechanochemical milling time, which confirmed the partial mechanochemical degradation. TPVs could be prepared from the partially decomposed XLPE/GTR blends through dynamic vulcanization. However, the blends of raw XLPE and GTR could not be plasticized due to their crosslinking structures. The composites obtained by dynamic vulcanization with the sulfur-accelerator system exhibit better mechanical properties than that of samples dynamically vulcanized with DCP. The mechanical properties of XLPE/GTR composites can be largely improved by mechanochemical treatment and dynamic vulcanization. The blend vulcanizates maintain the reprocessability, indicating the thermoplastic elastomeric nature of the blend. In comparison with the existing recycling methods, the recycling approach described in this paper is cost-effective and easily to industrialization.

Acknowledgments

The authors would like to thank National High Technology Research and Development Program (863 Program, 2008AA06Z343) for financial support.

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