Preparation of Thermoplastic Vulcanizates Based on Waste Crosslinked Polyethylene and Ground Tire Rubber Through Dynamic Vulcanization

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ABSTRACT: An environmental-friendly approach called high-shear mechanical milling was developed to de-crosslink ground tire rubber (GTR) and waste cross-linked polyethylene (XLPE). The realization of partial devulcanization of GTR and de-crosslinking of XLPE were confirmed by gel fraction measurements. Fourier transform infrared spectral studies revealed that a new peak at 1723.3 cm^{-1} corresponds to the carbonyl group (—C=O) absorption was appeared after milling. The rheological properties showed that the XLPE/GTR blends represent lower apparent viscosity after mechanical milling, which means that the milled blends are easy to process. Thermoplastic vulcanizates (TPVs) could be prepared with these partially de-crosslinked XLPE/GTR composite powders through dynamic vulcanization. The mechanical properties of the XLPE/GTR composites increased with increasing cycles of milling. The raw XLPE/GTR blends could not be processed to a continuous sheet. After 20 cycles of milling, the tensile strength and elongation at break of XLPE/GTR (50/50) composites increased to 6.0 MPa and 185.3%, respectively. The tensile strength and elongation at break of the composites have been further improved to 9.1 MPa and 201.2% after dynamic vulcanization, respectively. Re-processability study confirmed the good thermoplastic processability of the TPVs prepared. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2110–2120, 2011

Key words: rubber; polyethylene (PE); recycling; composites; mechanical properties

INTRODUCTION

The three-dimensional crosslinked structure of waste rubber makes it infusible, insoluble, and difficult to recycling. Numerous methods[1–10] have been proposed for recycling scrap rubber. One of the feasible ways for large-scale recycling waste rubber is to incorporate the waste rubber powder as a filler into thermoplastic matrices such as polyethylene.[11–15] Recently, there has been a growing interest in the application of dynamic vulcanization methods to produce thermoplastic vulcanizates (TPVs) based on scrap rubber and thermoplastic polyolefins.[16–26] It is well known that use of additional (fresh) elastomer and/or devulcanize the scrap rubber at least partially are the prerequisites of manufacturing scrap rubber-containing TPVs.[27]

Crosslinked polyethylene (XLPE) scraps which were derived from insulation materials such as elastic wires and cables, represent another type of environmental problem. Most of the industrial waste of crosslinked polyethylene is burned as fuel.[28] Material recycling of XLPE is difficult because of its low melt-fluidity and poor processability. The reuse or recycling of XLPE has also attracted many researchers' interests in recent years.[29,30]

The difficulty of recycling these two crosslinked polymer scraps brings a hypothesis: whether it is feasible to produce TPVs from them? By preparation of TPVs through dynamic vulcanization, the recycled products having excellent processing properties can therefore be used in high-quality products rather than being discarded to landfill, or used for low-grade purposes. What is more important is that the recycling of the TPVs based on these two crosslinked polymer scraps becomes easy.

There are two major problems associated with the preparation of TPVs derived from such two crosslinked polymer scraps. First, virgin thermoplastic polymers like polyolefin have linear polymer chains and can be processed into an arbitrary form. However, once the polyolefin is crosslinked, it is no longer processable due to the crosslinks and can not be

employed as the continuous phase of TPVs. On the other hand, the three-dimensional crosslinked structure of ground tire rubber (GTR) makes it impossible to be further re-vulcanized via dynamic vulcanization. Therefore, it is difficult to obtain well dispersed rubber phase in TPVs. To prepare TPVs from GTR and XLPE, it is quite necessary to develop a novel method being able to devulcanize of GTR and de-crosslinking of XLPE simultaneously.

The previous work[31–33] carried out in our laboratory demonstrated that scrap rubber vulcanizates could be partially devulcanized through high-shear mechanical milling with a pan-mill type mechanochemical reactor. The pan-mill equipment was designed in the authors' laboratory for solid state mechanochemical reactions of polymers, on the basis of a traditional Chinese stone-mill.[34,35] 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.[36–41]

In this work, the simultaneous devulcanization of GTR and de-crosslinking of XLPE scraps were investigated. A further aim of this study was to check the feasibility of producing TPVs from the de-crosslinked XLPE and GTR. Special attention was paid to the effects of mechanical de-crosslinking and dynamic vulcanization. The variation of gel fraction, morphology, and rheological behavior of XLPE/GTR blends during high-shear mechanical milling were investigated as well.

EXPERIMENTAL

Materials

The XLPE used in this study is widely applied in insulated cables, in which the molecular chains of low density polyethylene have been crosslinked by organic peroxide compounds, with a crosslinking degree (gel content) of $\sim$ 80%. As shown in Figure 1, the waste cable used in this study is a blend material composed of white XLPE pipe and a thin layer of black EVA. Such cables are composed of a central conductor surrounded by a polymeric insulating material, usually XLPE. Surrounding the insulation layer is a second metal layer consisting of grounding wires or foils. Separating the insulation from the metal conductors are layers of semiconductor, typically composed of ethylene copolymers (e.g., EVA, EEA) filled with carbon black. To develop an easily industrialized technique, no washing or cleaning, or processing was performed to remove foreign matter. It was cut into chips of about 1 cm^3 with a rotary blade chipping machine.

GTR was originated from ground tread layers of truck tires. The particle size of the GTR powder is in the range of 40–500 μm and the average particle size is 340 μm. Other vulcanizing ingredients such as zinc

Figure 1 Digital camera picture of the waste XLPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oxide, stearic acid, 2-mercaptobenzothiazole (MBT), tetramethyl thiuram disulfide (TMTD), sulfur and dicumyl peroxide (DCP) were obtained commercially.

Mechanical de-crosslinking in solid state

The partial de-crosslinking of GTR and XLPE was carried out in the pan-mill type mechanochemical reactor at ambient temperature. References 33 and 35 provide details on high-shear mechanical milling equipment. 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}. Milling process of solid mass in the equipment was as follows, the materials are fed into the center of the pan from the inlet, driven by shear force, moving along a spiral route toward edge of the pan till it comes out from the outlet, thus one cycle of milling is finished. The discharged powder was collected for next cycle milling. The average retention time of the composite powders during milling is 25–40 s 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. Repeated operation continued for various cycles to produce XLPE/GTR compounding powder. The partially de-crosslinked samples were collected for measurement of gel fraction, rheological behaviors, and mechanical properties.

Preparation of TPVs through dynamic vulcanization

Blends were prepared in a Brabender Plasticorder PLE-330 by melt-mixing the components at

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 Table I. Then, the blends were left to cool down at ambient temperature prior to molding. Two-millimeter thick 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 a pressure of 10 MPa, subsequently cooling under pressure for 5 min.

Gel fraction measurements

Gel fractions of the partially de-crosslinked products and dynamically vulcanized samples were measured by Soxhlet extraction. The specimens (about 1 g) were accurately weighed (M_i) and closed in filter paper, and extracted by toluene for 24 h. The extracted samples were then placed in a vacuum chamber, dried at 60°C for 6 h, so that the solvent would vaporize and the dry, insoluble part was obtained. This yielded the weight of the dried sample, M. The gel fraction was determined as follows:

$$\text{Gel fraction } (\%) = M/M_i \times 100\%$$

Gel permeation chromatography (GPC) measurements

Gel permeation chromatography (GPC; Waters ALC/GPC 150c) was used to measure the molecular weight and their distributions of the sol part of raw and de-crosslinked XLPE/GTR blends. Toluene, used as the mobile phase (1 mL min^{-1}), was run at 80°C, and the system was calibrated with narrow-disperse polystyrene standards.

Fourier transform infrared (FTIR) analysis

To obtain information on structure changes of XLPE during high-shear mechanical milling, the soluble part of raw and partially de-crosslinked XLPE from Soxhlet extraction process was analyzed by Fourier transform infrared (FTIR) studies. After Soxhlet extraction, the soluble part of XLPE was placed in a vacuum chamber and dried at 60°C for 6 h so that the solvent would vaporize, and the dry part was obtained. The obtained samples were then hot-pressed at 180°C and 5 MPa for 1 min to prepare films. These films were used for the FTIR studies. The FTIR spectra were recorded on a Nicolet 560 spectrometer (USA). The spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} over 20 scans. The presented spectra were averages over four single measurements at different measurement

TABLE I
Compounding Formulations Used to Prepare TPVs with Various Vulcanization Systems

Ingredients	Amount used (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	–	Variable (0.25–1.0)

points on the coated foil to reduce statistic errors resulting from varying layer thickness.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded on an XPS-spectrometer (XSAM800, KRATOS, England) with a monochromatized Al Kα X-ray source (1486.6 eV photons). The X-ray spot size was 1000 and 300 μm for the acquisition of the survey and narrow scan regions, respectively. Binding energies were corrected to the carbon 1s peak located at 285.0 eV.

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.

Mechanical properties

The stress–strain properties of the samples were determined at room temperature in accordance with ASTM D412 using an Instron 5567 Universal Testing Machine at a crosshead speed of 100 mm min^{-1}. The data were averaged over at least five specimens.

Morphology observation

The morphological evolution of XLPE/GTR blends during high-shear mechanical milling was observed using a fluorescence microscope (Olympus IX-71, Japan). A sample of about 2-mm thick was illuminated using a blue light for excitation and viewed under the microscope with a magnification of 400× at room temperature. The wavelength of excitation is in the range 390–490 nm.

Thermal gravimetric analyzer (TGA) measurements

To measure thermal stability of XLPE/GTR composites, TGA2950 Thermal Gravimetric Analyzer (TGA) under nitrogen gas was used. The measurement was conducted at scanning rate of 10°C min^{-1} and temperature range of 40–600°C.

RESULTS AND DISCUSSION

Gel fraction reduction of XLPE/GTR blends during high-shear mechanical milling

The realization of partial de-crosslinking of GTR and XLPE was confirmed by gel fraction measurements. Figure 2 shows the effect of high-shear mechanical milling on the gel fraction of XLPE/GTR (50/50) blends. The gel fraction correlated to the crosslink density of the blends was decreased significantly after milling. To investigate whether both of the XLPE and GTR were partially de-crosslinked or only GTR component was devulcanized during high-shear mechanical milling, XLPE and GTR were separately milled eight cycles and the variation of their gel fractions after milling was measured. Table II indicates that both of the XLPE and GTR could be partially de-crosslinked through high-shear mechanical milling. In comparison with the chemical de-crosslinking technology, the mechanochemical method overcomes the expensive use and recovery of the expensive organic solvents.[42]

GPC measurements

To investigate the degradation of polymeric chains during high-shear mechanical milling, the molecular weights and molecular weight distributions of the sol part in raw and partially de-crosslinked XLPE/
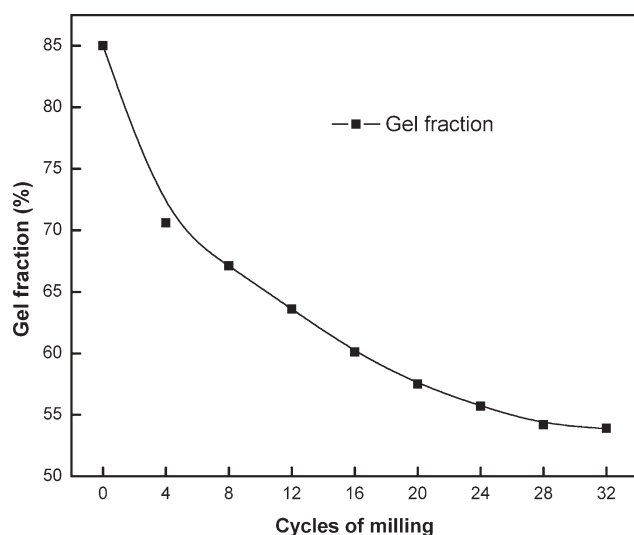
TABLE II
Gel Fraction of XLPE and GTR Before and After Separately Mechanical Milling

Samples	Without milling	After eight cycles of milling
XLPE	80.6 %	64.5 %
GTR	91.3 %	72.4 %

GTR blends were measured by GPC measurements. Figure 3 shows the intensity of the absorbance as a function of the mole mass obtained from the GPC measurements. There are three peaks in the GPC curves, including a main peak at higher mole mass ($\sim M_w = 8.7 \times 10^4$) corresponded to the polyethylene and tire rubber components, and the other two peaks at lower mole mass ($\sim M_w = 1.4 \times 10^4$ and 5.0×10^3, respectively) corresponded to the presence of low-molecular weight ingredients such as EVA. The molecular weight values and polydispersity index (PDI) of each peak calculated from these data are indicated in the figure, respectively.

To ascertain the peak assignation of the GPC curves, the black thin layer on the white XLPE pipe was removed. Then, the residual white XLPE was pan-milled for 20 cycles and investigated by GPC measurements. The results[43] showed that both of the samples before and after pan-milling exhibit a single peak in GPC curves. The molecular weight of XLPE was nearly kept invariable after milling ($M_w = 1.0 \times 10^5$ before milling, $M_w = 1.1 \times 10^5$ after 20 cycles of milling). Thus, the other two peaks at lower mole mass are originated from the black thin layer which composed of ethylene copolymers (e.g., EVA, EEA) filled with carbon black.
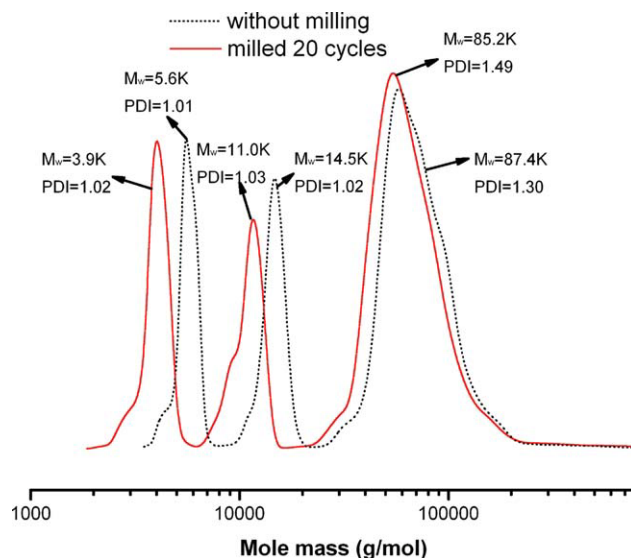

Figure 2 Effect of high-shear mechanical milling on the gel fraction of XLPE/GTR (50/50) blends.

Figure 3 GPC curves of the sol part in raw and de-crosslinked XLPE/GTR (50/50) blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
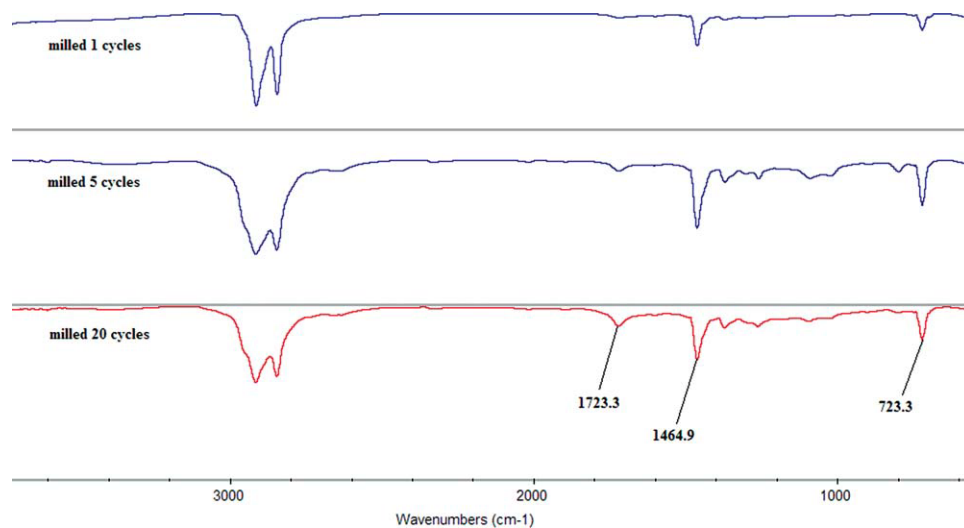
Figure 4 FTIR spectra of the soluble part of XLPE after 1, 5, and 20 cycles of milling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

After 20 cycles of milling, the weight-average molecular weight of the main peak was decreased from 8.7×10^4 to 8.5×10^4, the reduction is unconspicuous. The results indicated that the molecular weight reduction was mainly occurred at the lower mole mass peaks.

FTIR analysis

After one cycle of milling, XLPE pellets were pulverized to produce powders. However, the XLPE powders changed to a soft and sticky material at ambient temperature after further cycles of milling. The results indicated that some structure changes occurred during milling. To obtain information on the structure changes and functional groups generation of XLPE during high-shear mechanical milling, the soluble part of XLPE from Soxhlet extraction process was analyzed by FTIR studies. Figure 4 compares the FTIR spectra of the sol fraction of XLPE after various cycles of milling. Compared with the XLPE after one cycle of milling, a new peak at 1723.3 cm^{-1} corresponds to the carbonyl group (—C=O) absorption was appeared after more cycles of mechanical milling. Solid state mechanochemical reactor equipment can exert fairly strong squeezing force in normal direction and shear force in both radial and tangential directions on milled materials, functioning like pairs of three-dimensional scissors. As confirmed by the gel fraction test, a combination of shearing, extension, and fracturing of polymer powder particles during high-shear mechanical milling induced chain scission and free radical formation. In this case, the macromolecular radicals which generated during milling react with oxygen in atmosphere and form carbonyl groups at the chain ends.

On the other hand, FTIR spectra of the sol fraction of GTR before and after high-shear mechanical milling was shown in our earlier studies.[33] The partial devulcanization of GTR and introduction of oxygen containing groups onto the GTR particles had also been observed. Thus, the increase in oxygen-containing polar functional groups on the surface of XLPE and GTR powders will lead to the compatibilization of the blends.

XPS analysis

XPS analysis was further used to detect the variation of chemical composition of the GTR surface after high-shear mechanical milling. Surface compositions determined from XPS analysis of GTR powders before and after 20 cycles of milling are summarized in Table III. The results indicated that the oxygen content of the surface of GTR powders increased after milling.

The C1s core spectrum of raw GTR powders [Fig. 5(a)] reveals the peaks at 284.2, 284.8, and 285.6 eV corresponding to conjugated C=C, C_xH_y, and C—S groups, respectively.[44] The C1s core spectrum of mechanical milled GTR powders is shown in Figure 5(b). Compared with Figure 5(a), a new peak

TABLE III
Relative Element Content of the GTR Powder Before and After High-Shear Mechanical Milling as Determined by XPS

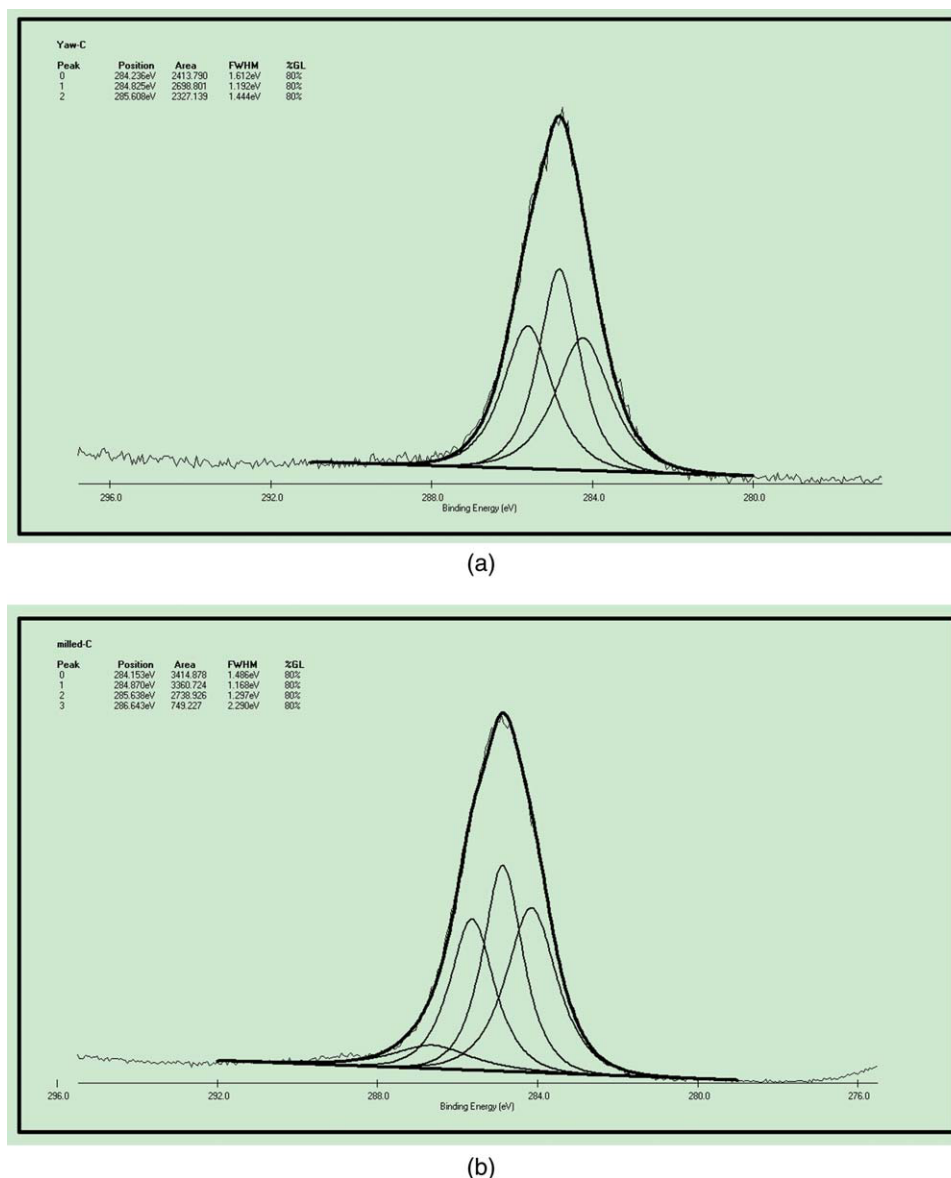| Element	Before milling	After milling
C (%)	90.9	86.4
O (%)	8.1	11.5
N (%)	0.6	1.6
S (%)	0.4	0.5

(a)

(b)

Figure 5 C1s core spectrum of GTR before (a) and after 20 cycles of milling (b), respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with binding energies at 286.6 eV appeared after milling, which can be assigned to the CO species. The introduction of the oxygen containing polar functional groups onto the GTR surfaces corresponds to the increase in surface energy.

Rheological studies

The flow properties of the materials studied in the molten state were analyzed by rheometer. The variation of the capillary viscosity as a function of the shear rate for XLPE/GTR (50/50) blends with different cycles of mechanical milling is presented in Figure 6. The apparent viscosities of the composite powders decrease with increasing of shear rate, indicating pseudoplastic flow behavior. Furthermore, as the cycles of mechanical milling increases, the appa-

rent viscosity decreases. Such a decrease in viscosity is in accordance with the gel fraction test. The partial de-crosslinking of GTR and XLPE during high-shear mechanical milling may be responsible for the decrease in apparent viscosity.

Variation of the gel fraction of XLPE/GTR blends during melt-mixing and compression molding

To identify whether the vulcanization process occurred during melt-mixing in Brabender plasticorder or hot-press procedure, the gel fractions of the samples after being melt-mixed with vulcanizing agent (sulfur-accelerator system) and the samples after compression molding were investigated and compared with the samples before melt-mixing. The results are shown in Figure 7, it is clear that the gel
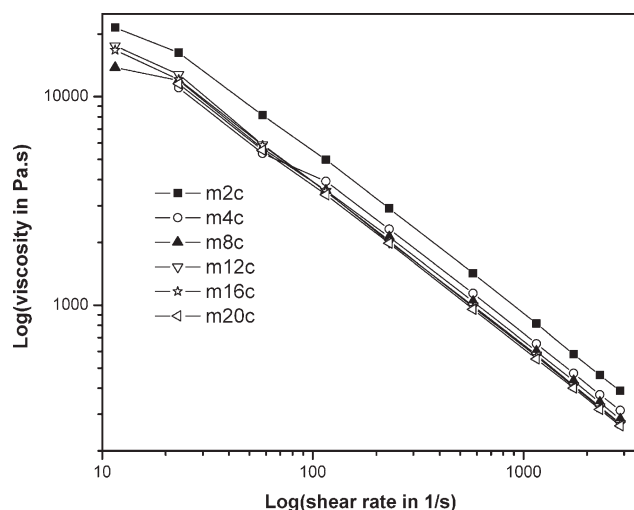
Figure 6 Variation of the capillary viscosity as a function of the shear rate for XLPE/GTR (50/50) blends with different cycles of milling.

fraction of the blends increased substantially after melt-mixing with vulcanizing agent in Brabender plasticorder, indicating that the vulcanization process mainly occurred during dynamic vulcanization, and further completed in hot-press procedure. It is worth noting that, despite the high gel fraction after melt-mixing, the XLPE/GTR blends are easily to be hot-pressed to a continuous sheet. The fine dispersion of crosslinked rubber particles into the plastic matrices may be responsible for the good melt-fluidity of XLPE/GTR blends.

Effect of different vulcanization system on the mechanical properties of the blends

One of the key properties of TPVs is their mechanical properties, which also yields the first information
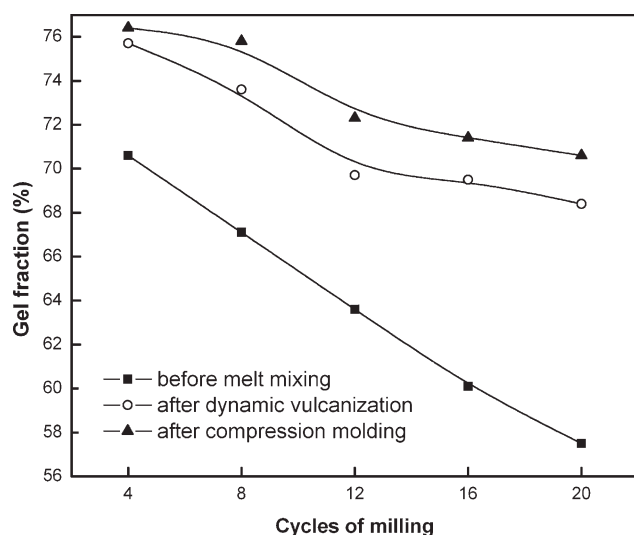

Figure 7 Variation of the gel fraction of XLPE/GTR (50/50) blends during melt-mixing and compression molding.

TABLE IV
Mechanical Properties of XLPE/GTR (50/50) Blends After Eight Cycles of Milling with and without Dynamic Vulcanization

Samples	Tensile strength (MPa)	Elongation at break (%)
Without vulcanization	5.7 ± 0.3	152.8 ± 7.2
DCP-cured system (with 0.25 phr DCP)	4.6 ± 0.5	82.3 ± 15.4
DCP-cured system (with 0.5 phr DCP)	3.7 ± 0.6	40.2 ± 26.7
DCP-cured system (with 0.75 phr DCP)	3.1 ± 0.8	19.6 ± 17.5
DCP-cured system (with 1.0 phr DCP)	3.3 ± 0.6	25.8 ± 19.2
Sulfur-cured system	8.1 ± 0.1	189.1 ± 4.3

on the compatibility of blends. Table IV shows the mechanical properties of the XLPE/GTR (50/50) composites after eight cycles of mechanical milling with and without dynamical vulcanization, respectively. Two different types of vulcanizing agent: sulfur and peroxide system have been investigated. Compared with the sulfur-cured system, the DCP-cured system showed deteriorated mechanical properties regardless of DCP content. DCP may cause crosslinking of polyethylene,[45,46] therefore it is not strange that the DCP-cured system had lower or no 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%.

Effect of high-shear mechanical milling on the mechanical properties of the blends

The sample of raw XLPE/GTR blends was not obtained due to the fact that raw blends could not be plasticized. However, after high-shear mechanical milling, the partially de-crosslinked blends could be plasticized and thus be hot-pressed to a continuous sheets, indicating the characteristic of ease of processing. The effects of partial de-crosslinking on the tensile strength and elongation at break of the composites are shown in Figures 8 and 9, respectively. For the composites without dynamic vulcanization, the elongation at break of the composites increased with the increasing in cycles of mechanical milling (Fig. 9). After 32 cycles of mechanical milling, the elongation at break increased from 142.2 to 196.3%. The longer time of mechanical milling is considered to induce higher de-crosslinking degree of XLPE/GTR blends and thus can enhance melt-fluidity and processability of the blends. Moreover, comilling of XLPE and GTR gave rise to a better dispersion
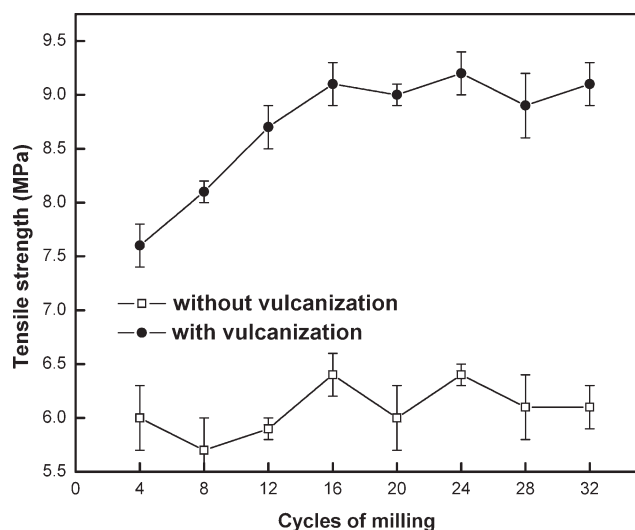
Figure 8 Effect of high-shear mechanical milling on the tensile strength of XLPE/GTR (50/50) composites.

Figure 9 Effect of high-shear mechanical milling on the elongation at break of XLPE/GTR (50/50) composites.

between both polymeric phases, and thus, a more homogeneous and continuous structure was obtained. After 16 cycles of milling, the fine dispersion and well processability were achieved. Therefore, further increase in milling cycles did not show significant influence on the tensile strength of composites. On the other hand, the effect of mechanical milling on the tensile strength of composites without dynamic vulcanization (Fig. 8) is unapparent. This could be due to the more soft and elastic characteristic of devulcanized GTR molecules than raw GTR.

Effect of dynamic vulcanization on the mechanical properties of the blends

As shown in Figures 8 and 9, the samples with sulfur-accelerator system vulcanized showed much better mechanical properties than that of samples without dynamical vulcanization. Both the re-vulcanization of the partially devulcanized GTR component *in situ* during melt-mixing and the ultimate fine dispersion of rubber particles in the partially de-crosslinked XLPE which forms the continuous phase may be responsible for the increase in
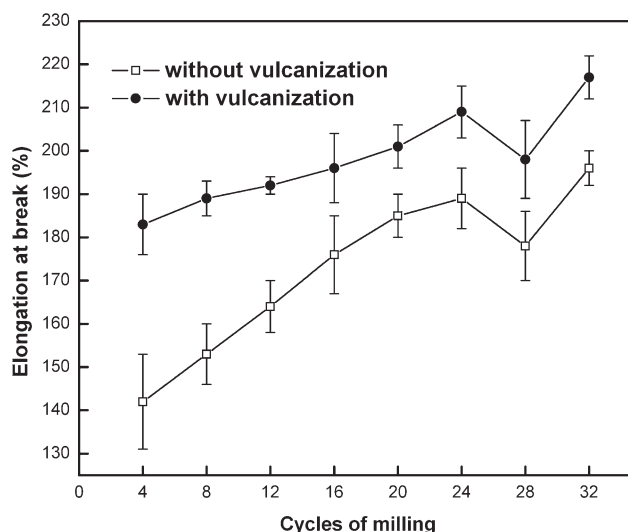
mechanical properties. Conventional melt-mixing was hardly to achieve fine dispersion and resulting in poor mechanical properties. The addition of a small quantity of a vulcanizing system during melt-mixing of rubber and plastic leads to the *in situ* vulcanization of the dispersed rubber particles as shown in Figure 10. The finely dispersed GTR domains were serve to dissipate stress energy and lead to the significant enhancement in mechanical properties.

Effect of processing temperature on the mechanical properties of the blends

The effect of processing temperature during melt-mixing on tensile strength and elongation at break of the XLPE/GTR blends (after eight cycles of milling) is shown in Figure 11. The tensile strength and elongation at break increased with increasing processing temperature up to 160°C, and then to reach a balance. At lower temperature, dynamic vulcanization was not achieved and resulted in poor mechanical properties.
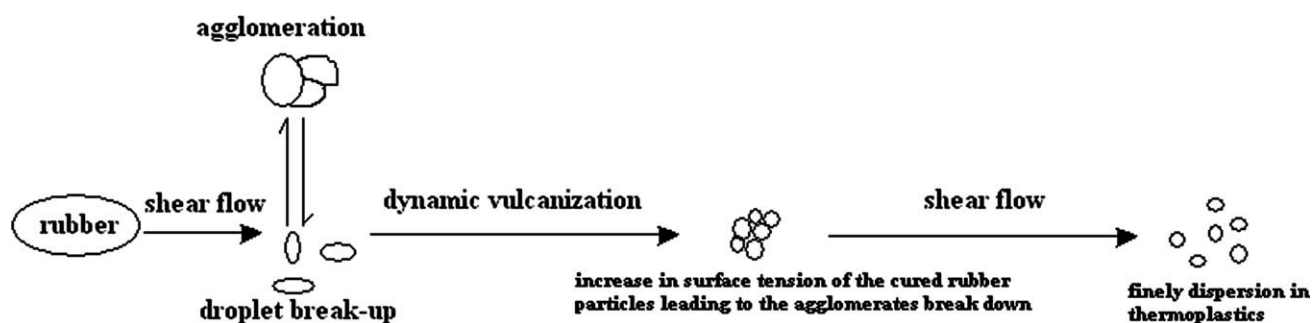

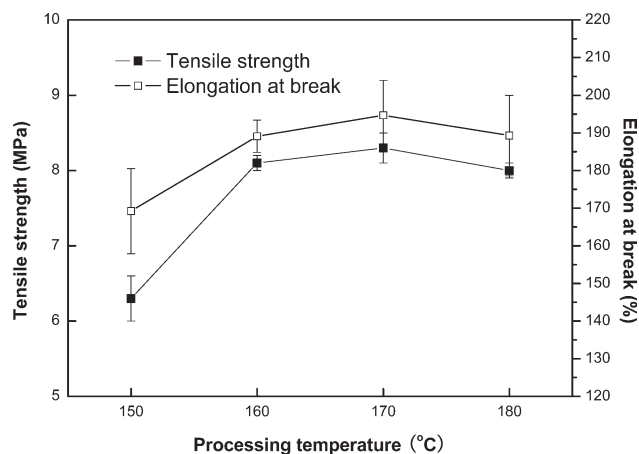**Figure 10** Schematic diagram of the model describing the mechanism of dynamic vulcanization.

Figure 11 Effect of processing temperature during melt-mixing on tensile strength and elongation at break of the XLPE/GTR blends.

Morphological observation by fluorescence microscopy

Fluorescence microscopy is the most valuable method for studying the phase morphology of polymer modified asphalt. It based on the principle that polymers absorb some of the aromatic organic matter of the asphalt matrix and display altered fluorescent characteristics when subjected to ultraviolet light.[47] In this study, the aromatic oil which is the plasticizing agents of tire rubber could be absorbed by XLPE matrix. Therefore, the XLPE rich phase appears light phase, whereas the GTR rich phase appears dark or black in the fluorescent images. In Figure 12(a), absence of aromatic organic matter in the neat XLPE makes it appear backdrop color (blue). As shown in Figure 12(b), GTR is poorly dispersed in the XLPE matrix for the melt-mixed XLPE/GTR (50/50) blends. In samples with same blend ratio made by high-shear mechanical milling (32 cycles of milling) followed by melt-mixing [Fig. 12(c)], the GTR agglomerates are sharply reduced in size to achieve excellent dispersion.

Mechanochemical methods based on cogrinding or milling of materials have been widely used to synthesis of novel molecular compounds[48,49] and obtain nano-powders.[50] Recently, mechanochemical methods have also been utilized in the field of polymer blending and compatibilizing, although the physical–chemical changes occurred in macromolecular backbone upon such processing remain largely unknown. Nano-scale blending and compatibilizing of immiscible polymers have been achieved by various solid state mechanochemical methods, such as CMA[51–55] and solid state shear pulverization (S³P).[56–58]

Pan-mill equipment can exert fairly strong squeezing force in normal direction and shear force in both radial and tangential directions on milled materials, functioning like pairs of three-dimensional scissors,
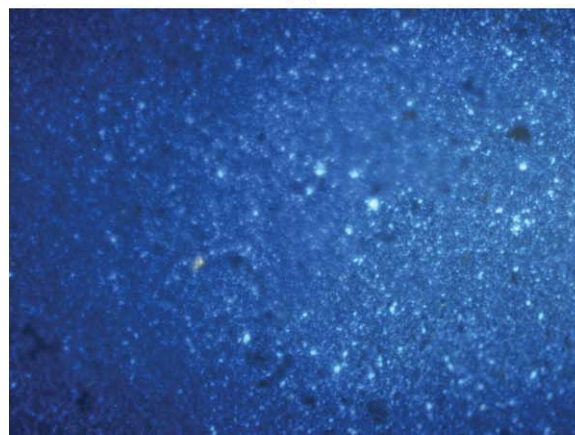
and exerts excellent pulverizing, mixing, and activation effects on the polymeric materials. A combination of shearing, extension and fracturing of polymer powder particles during high-shear mechanical milling may induce chain scission or hydrogen abstraction and, consequently, free-radical formation.
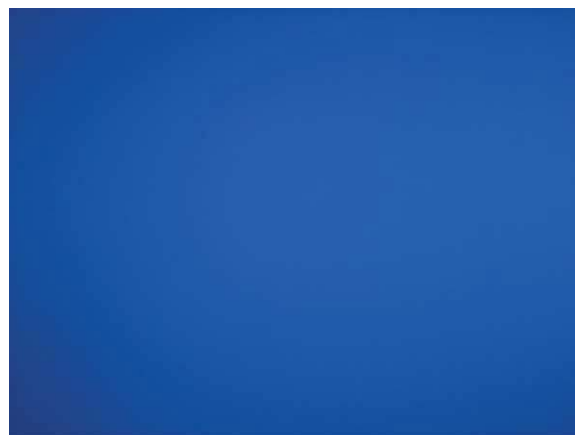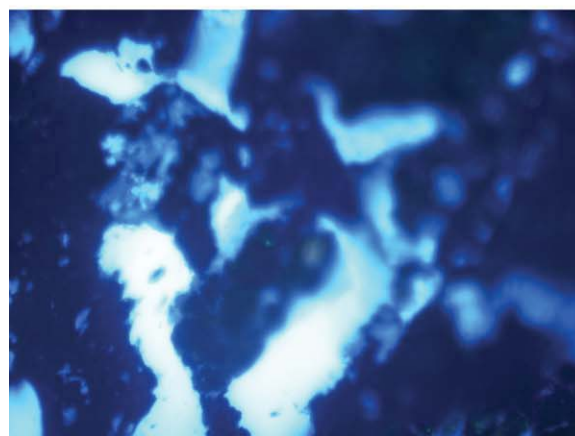
Figure 12 Fluorescent micrographs of neat XLPE (a), XLPE/GTR (50/50) blends prepared by melt-mixing (b) and high-shear mechanical milling (c), respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Such changes could be accompanied by chemical bond rupture (devulcanization of rubber crosslinks or degradation of rubber backbones) or interchain chemical reaction (possibly resulting in *in situ* compatibilization). Furthermore, repeated deformation of powder particles during high-shear mechanical milling may simply promote a physical reduction in the scale of mixing and ultimately resulting in nanoscale mixing.

Re-processability studies

The re-processability of the dynamically vulcanized XLPE/GTR (50/50) composites was studied by re-mixing the sample in a Brabender plasticorder and re-molding 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 Figure 13. 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 reprocess, which indicates good thermoplastic processability of the blend.

Thermogravimetric analysis

Thermogravimetry was taken to evaluate the thermal stability of XLPE/GTR composites. Control of mechanical properties and the processing temperature would require this data. The DTG curves (Fig. 14) and the data show that there are clearly two areas of mass loss, giving two peaks on the DTG curves. As the milling cycles increased, more weight losses were found at the lower temperature than at the higher temperature. It has been attributed to the partial de-crosslinking of XLPE and GTR. A similar phenomenon was observed by Oh and Isayev[59] who
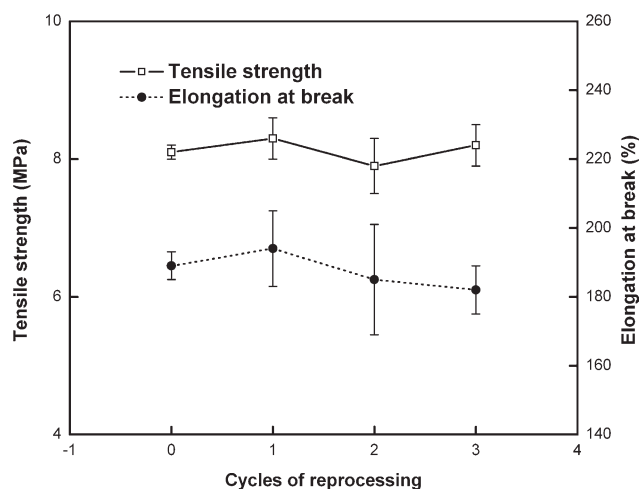
Figure 13 Effect of re-processing cycles on the tensile strength and elongation at break of XLPE/GTR (50/50) composites.
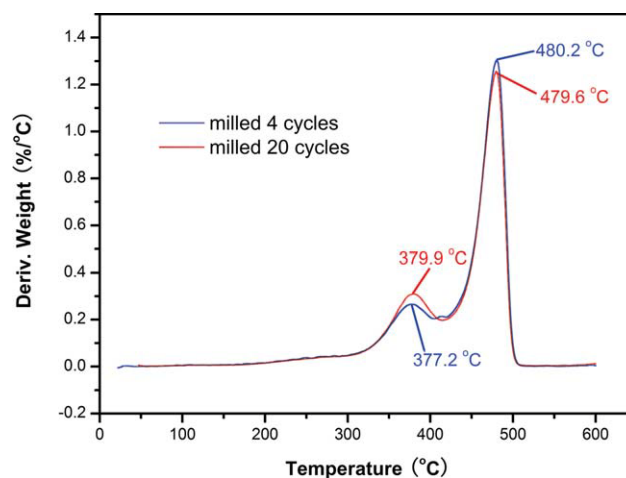
Figure 14 DTG curves of the XLPE/GTR blends after 4 and 20 cycles of milling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

used ultrasonic technology to devulcanize butadiene rubber vulcanizates. On the other hand, the DTG peak temperatures which can be used as a measure of processing temperature were nearly kept invariable after high-shear mechanical milling. The results illustrating that the high-shear mechanical milling was not alter the processing temperatures of XLPE/GTR blends.

CONCLUSIONS

The partial devulcanization of GTR and de-crosslinking of XLPE were realized through high-shear mechanical milling in solid state. The significant decrease in the gel fraction of XLPE/GTR blends during mechanical milling confirmed the partial de-crosslinking of GTR and XLPE. Fourier transform infrared spectral studies revealed that a new peak at 1723.3 cm^{-1} corresponds to the carbonyl group (—C=O) absorption was appeared after milling. The macromolecular radicals generated during milling reacted with oxygen in atmosphere and formed carbonyl or carbonyl groups at the chain ends. The apparent viscosity of the blends decreased with the increase of milling time, which further confirmed the partial de-crosslinking. The reduction in the molecular weight of the sol fraction of the partially de-crosslinked sample is unconspicuous. TPVs could be prepared from the partially de-crosslinked 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 dynamically vulcanized with the sulfur-accelerator system exhibited better mechanical properties than that of samples dynamically vulcanized with DCP system. The mechanical

properties of XLPE/GTR composites can be largely improved by mechanochemical de-crosslinking and dynamic vulcanization. Fluorescence micrograph of XLPE/GTR composites revealed that GTR agglomerates are sharply reduced in size to achieve excellent dispersion after high-shear mechanical milling. The blend vulcanizates maintained the re-processability, indicating the good thermoplastic processability of the blends. In comparison with the existing recycling methods, the recycling approach described in this article is cost-effective and easy for industrialization, showing a strong potential for future applications.

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