Mechanochemical Devulcanization of Ground Tire Rubber and its Application in Acoustic Absorbent Polyurethane Foamed Composites

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ABSTRACT: The use of recycled rubber in preparation of acoustic absorbent materials will help to combat the existing environmental problems of both waste disposal and noise pollution. The focus of this work is to investigate the influence of mechanochemical pretreatment of ground tire rubber (GTR) on the acoustic absorption properties of polyurethane (PU)/GTR foamed composites. GTR subjected to pan-milling could be mechanochemically devulcanized by breaking up the crosslinked structures through inducing fairly strong shearing and compressing forces. The significant increase in sol fraction of GTR confirmed the partial devulcanization during pan-milling. Moreover, thermal gravimetric analysis indicated that rubber content in the soluble part of GTR was also remarkably increased. The devulcanization increased flexible chains of the GTR particles, which could help to improve damping properties as well as acoustic absorption ability of the PU/GTR foamed composites. Dynamic mechanical analysis and acoustic absorption measurements well confirmed this hypothesis. The loss modulus and sound absorption coefficient of PU/GTR foamed composites were remarkably increased through the mechanochemical pretreatment of GTR. The mechanochemical pretreatment also enhanced foamability of the composites as revealed by cell morphology. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Noise pollution is becoming a more and more serious environmental issue that the human society faces in recent years due to its harmful effect on human health. As a result, extensive studies have been carried out to develop new materials with improved acoustic insulation or acoustic absorption properties. Among them, use of recycled rubber particles to prepare acoustic insulation and acoustic absorption materials is well recognized by market. It not only lowers materials costs but also in some cases improves acoustic performance of the composites. To name a few, Zhao et al.[1] investigated the acoustic insulation property of wood/ground tire rubber (GTR) composites prepared by using commercial urea-formaldehyde (UF) and polymeric methylene diphenyl diisocyanate (PMDI) as adhesives. The acoustic insulation property is improved with the increase of GTR content. Maderuelo-Sanz et al.[2] developed an acoustical underlay product made from GTR, cement mortar, and high viscosity polyurethane (PU) resin. It shows better performance than conventional layers in terms of their acoustical properties.

Sukontasukkul[3] used GTR to improve acoustic absorption property of pre-cast concrete panel. In a recent example, Benkreira et al.[4] presented a new processing route to transform tire shred residue into acoustic absorption and thermal insulation materials that could compete with commercial products. All these studies revealed that recycled rubber particles have potential applications in areas of acoustic insulation and acoustic absorption by virtue of its viscoelastic feature.

However, most of these works directly compounded recycled rubber particles with matrix materials without modification. It could lead to significant decline in material properties due to the inert surface of rubber powder. It is well known[5–7] that the three-dimensional crosslinked structure of the recycled rubber results in poor adhesion between rubber particles and matrix materials. In this study, we employed a self-designed pan-mill equipment to pretreat GTR for the enhancement of acoustic absorption property of PU/GTR foamed composites. Our previous investigations[8–10] on mechanochemical pretreatment of recycled rubbers by pan-milling suggested that the crosslinked
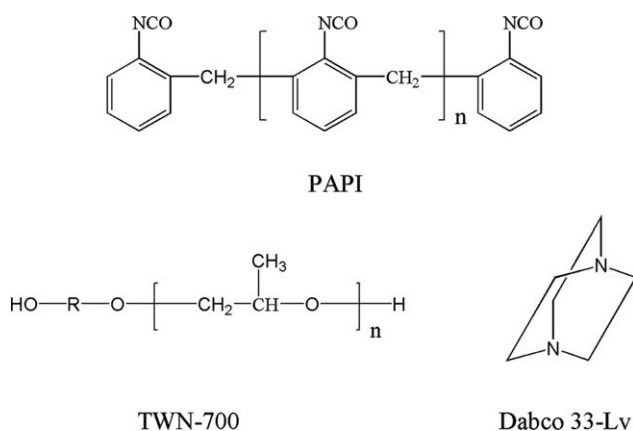
Figure 1. Chemical structures of the agents used in this study.

structure of rubbers can be effectively broken up to achieve partial devulcanization by exerting fairly strong shearing and compressing forces. Moreover, the breakage of crosslinked networks resulted in the introduce of oxygen containing polar functional groups onto the rubber surfaces.[11,12] These mechanochemically devulcanized rubbers are expected to obtain better interfacial interaction between rubber particles and polar matrix such as PU, leading to composites with enhanced performance.

The aim of this work is to prepare acoustic absorbent PU foamed composites using mechanochemically devulcanized GTR as reinforcement to enhance acoustic absorption property. The effects of mechanochemical devulcanization of GTR and GTR content on cell morphology, acoustic absorption, and damping properties of the composites will be discussed in detail.

EXPERIMENTAL

Materials

GTR powder with the average particle size of 250 μm was generated from passenger car and light truck tires, purchased from Sichuan Tianlimin Rubber Co. (China). It composes of hydrocarbon, 59.9%; carbon black, 36.4%; ash, 3.7%; acetone extractable volatiles, 8.6%. Isocyanate used in this study was a polymethylene polyaryl isocyanate (PAPI, PM-200) with NCO content of 31% and was supplied by Yantai Wanhua Polyurethanes Co. (China). Polyol used in this study was polyether-

Table I. Compounding Formulations Used to Prepare PU/GTR Foamed Composites

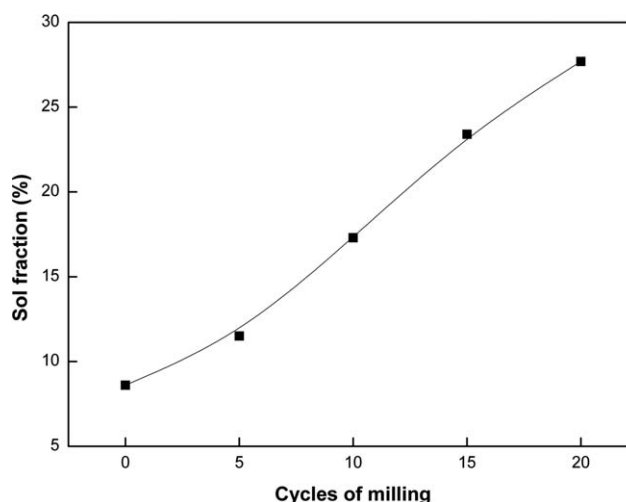| Ingredients	Amount (phr)	
	Untreated GTR-filled system	Devulcanized GTR-filled system
TMN-700	54.1	54.1
PAPI	44.7	44.7
H_2O	0.4	0.4
DABCO-33LV	0.3	0.3
Stabilizer (L-568)	0.5	0.5
Raw GTR	Variable (10–30)	–
Devulcanized GTR	–	Variable (10–30)

Figure 2. Effect of pan-milling on the sol fraction of GTR.

based, TMN-700 (OH value: 240) and supplied by Tianjin Company, China Petroleum & Chemical Corporation. The catalyst used was a tertiary amine (Dabco 33-LV) from Sigma-Aldrich Co. and the surfactant was a silicone glycol (L-568) from Momentive Specialty Chemicals. The chemical structures of the agents used in this study are shown in Figure 1.

Mechanochemical Devulcanization of GTR

The devulcanization of GTR was carried out in the pan-mill type mechanochemical reactor at ambient temperature. The details of the pan-mill equipment and operation procedure can be found in our previous publications.[10,11] The resulting material was blended with isocyanate and polyol to prepare PU/GTR foamed composites. To obtain fine GTR powders, high rotating speed and relatively low pressure were adopted during pan-milling.

Preparation of PU/GTR Foamed Composites

Before the synthesis of PU/GTR foamed composites, the polyol was dehydrated under vacuum at room temperature.
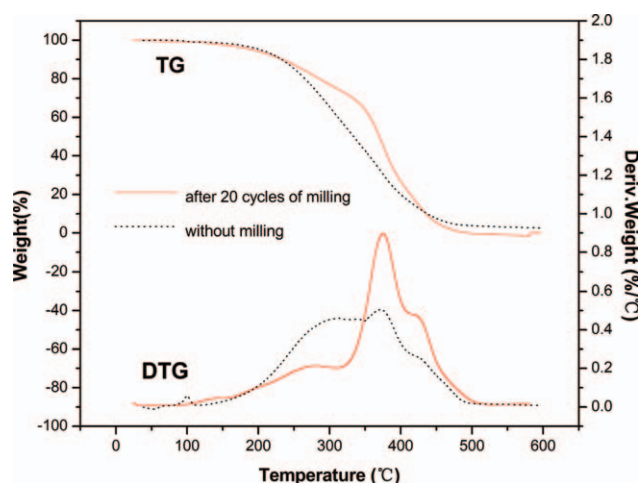

Figure 3. TGA Curves of the soluble component of GTR before and after 20 cycles of pan-milling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Content of Organic Non-polymeric Ingredients and Soluble Rubber Ingredients in the GTR Before and After Pan-Milling as Determined by TG Analysis

	Content of ingredients (%)	
Sample	Organic non-polymeric ingredients	Soluble rubber ingredients
Before milling	2.9	5.4
After 20 cycles of milling	6.2	21.4

For PU/GTR foamed composites, various content of GTR (up to 30 wt %) was first mixed with the polyol at 2000 rpm for 10 min using an overhead stirrer equipped with a dispersion disc. Subsequently, the surfactant, catalyst, and distilled water were added to the GTR/polyol mixture and mixed at 2000 rpm for 1 min. Finally, the isocyanate was added and stirred for 15 s before foaming in an open cylindrical mould. The foams were then transferred into an oven at 50°C overnight and demolded. The compound recipes are listed in Table I.

Sol Fraction Measurement
The sol fractions of GTR before and after pan-milling were measured by the Soxhlet extraction method using toluene as a solvent. The samples were reflux in toluene for 24 h and then dried in a vacuum oven at 60°C for 6 h. The weights of the samples before and after the treatment were recorded.

Thermal Analysis of the Sol Component of GTR
To investigate the composition of the sol fraction of raw and devulcanized GTR after Soxhlet extraction, the TGA2950 Thermal Gravimetric Analyzer (TGA) under nitrogen gas was used. The measurement was conducted at a scanning rate of 10°C min^{-1} and a temperature range of 40–600°C.

XPS Analysis of GTR Before and After Pan-Milling
X-ray photoelectron spectra (XPS) 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.

Particle Size Analysis of GTR Before and After Pan-Milling
The average particle size and particle size distribution of GTR powder before and after pan-milling were measured by Masterizer 2000 Laser Particle Analyzer. The range of size analysis is 0.3–100 μm. An appropriate amount of each sample was dispersed in suspension medium (water/ethanol) with OP emulsi-

Table III. Relative Element Content of the GTR Powder Before and After Pan-Milling as Determined by XPS Analysis

| 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
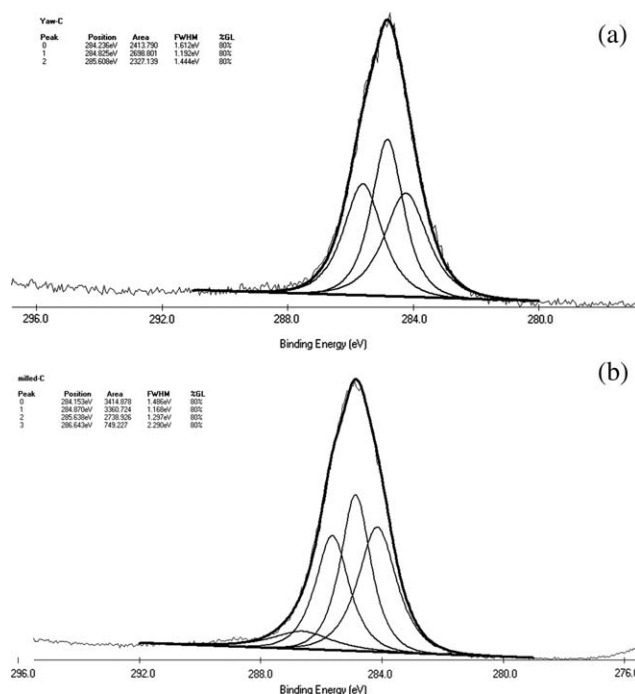
Figure 4. C1s core spectrum of GTR before (a) and after 20 cycles of milling (b), respectively.

fier (p-octyl polyethylene glycol phenyl ether) as dispersant agent, stirred at a pumping speed of 2400 rpm. More correct data were obtained by breaking up the flocculates ultrasonically. Then the particle size and particle size distribution were calculated from the light scattering pattern.

Cell Morphology Observation
Scanning electron microscopy (SEM) was used to observe the cellular morphology of foamed samples. The samples were frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact. Subsequent gold coating provided necessary conductive surface for the electron
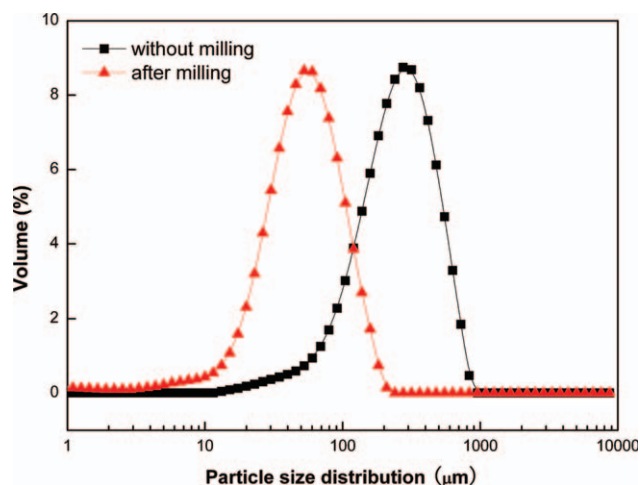
Figure 5. Effect of pan-milling on the particle size distribution of GTR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
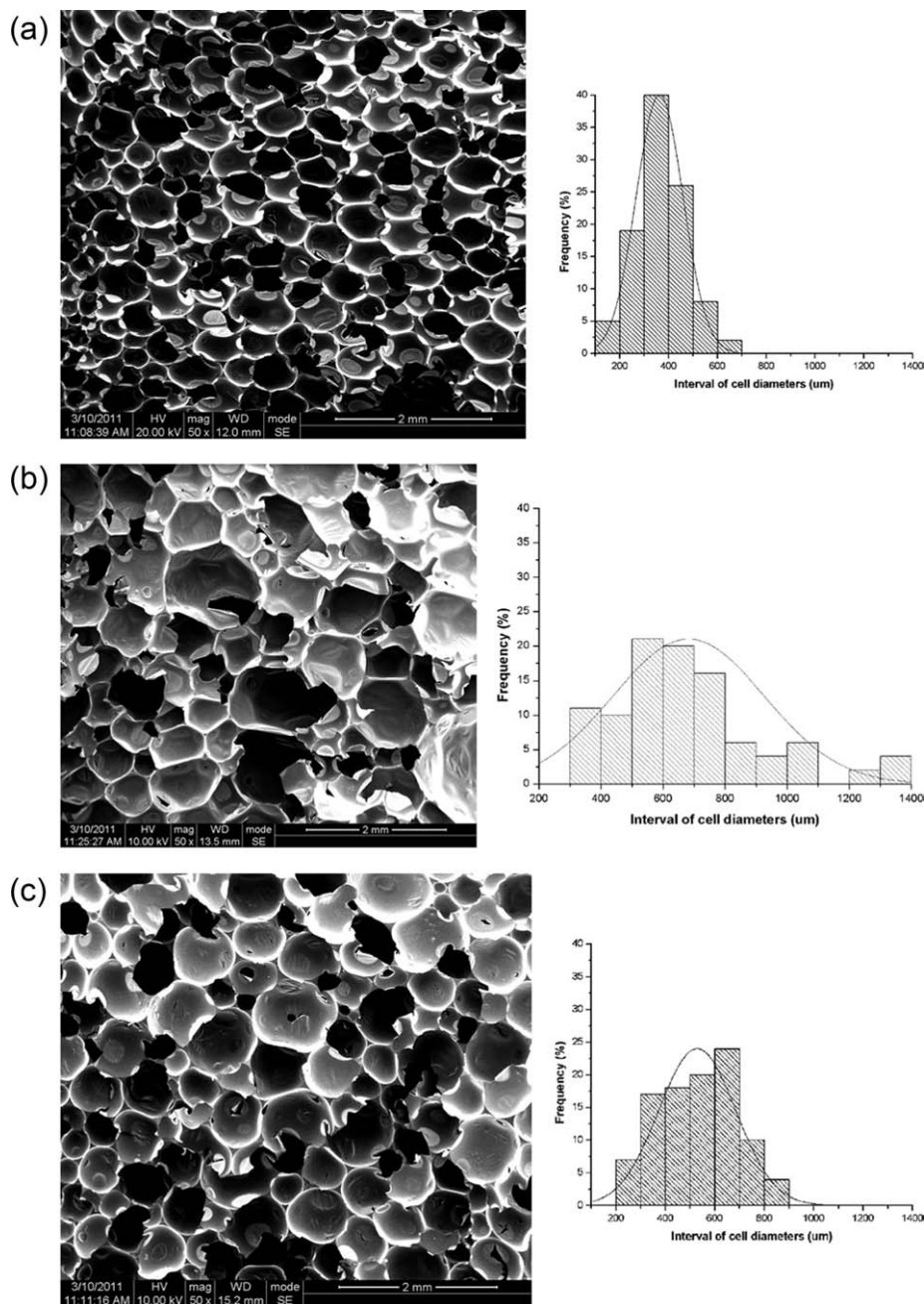
Figure 6. SEM images of the pristine PU foams (a) and PU/GTR foamed composites: (b) 10% untreated GTR; (c) 10% devulcanized GTR; (d) 30% untreated GTR; (e) 30% devulcanized GTR.

microscope. The morphology study was performed on JEOL JSM-5600 scanning electron microscope (Japan). The cell size of foamed samples was determined from the micrographs showing 80–100 bubbles as the average diameter for all the bubbles in the micrographs.

Acoustic Absorption Measurement

Small scale acoustic test was performed according to ISO 10534-2[13] using a BSWA Technology Company (China) acoustic test system which comprises of an impedance tube, two microphones and a digital frequency analyzer. The acoustic absorp-

tion coefficient (α) was defined as the ratio of the acoustic energy absorbed by the foam ($I_{incident} - I_{reflected}$) to the acoustic energy incident ($I_{reflected}$) on the surface and is depended on frequency. The absorption coefficient was calculated as the average value of five cylindrical foam pieces, 30 mm in diameter and 10-mm thick, over the frequency range from 500 to 2500 Hz.

Damping Property Measurement

The damping property measurement was carried out on a dynamic mechanical thermal analyzer (DMA, TA Q800) of Polymer Laboratory (USA). The samples were cut from the
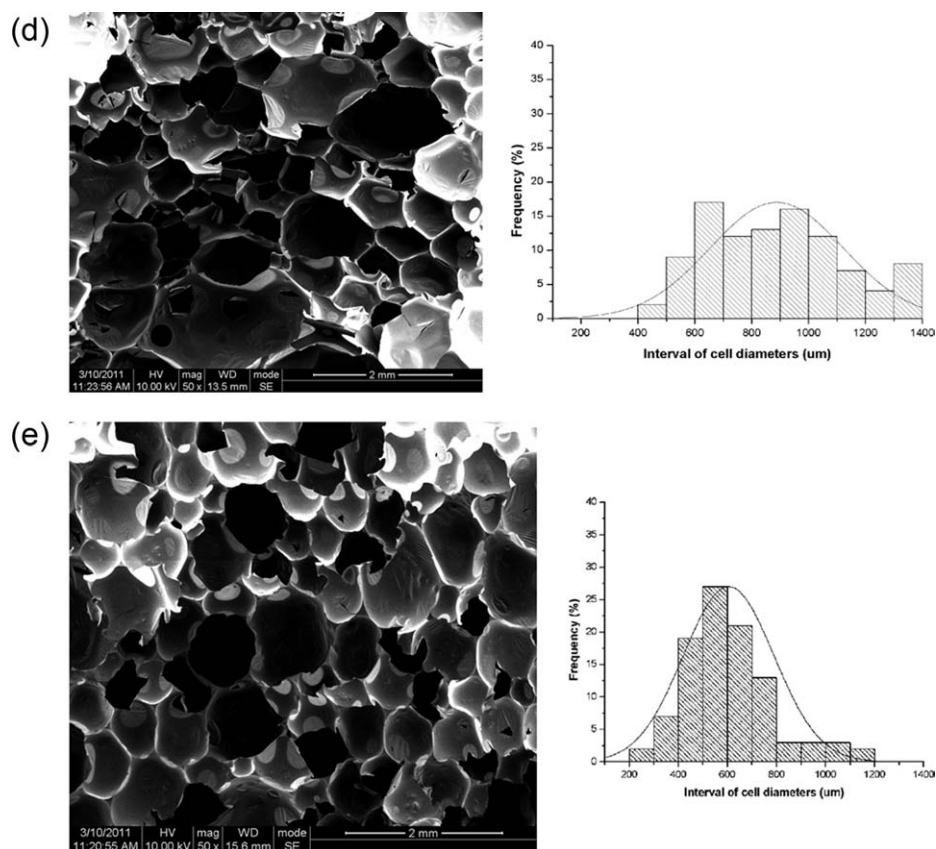
Figure 6. Continued.

RESULTS AND DISCUSSION

Sol Fraction Variation of GTR During Pan-Milling

The fraction of soluble matter (sol component) presented in the sample evaluated via Soxhlet extraction can indicate the efficiency of the devulcanization process. In general, the higher the sol fraction is, the more efficient the devulcanization process is. Figure 2 shows the effect of pan-milling on the sol fraction of GTR. It is apparent that the sol fraction correlated to the crosslink density increased significantly from its original 8.6 to 27.7% after 20 cycles of milling. The results indicate that the crosslinked structure of GTR was broken during pan-milling, which made the soluble fractions of the sample increase.

### TGA Analysis of Sol Component of GTR Before and After Pan-Milling

To further confirm the achievement of mechanochemical devulcanization of GTR after pan-milling, the soluble component of GTR derived from Soxhlet extraction process was investigated by TGA analysis. Figure 3 compares TG/DTG curves of the sol component of GTR before and after 20 cycles of milling. Both of the samples show a mass loss in the temperature range

between 100 and 300°C. The mass loss in this temperature range is due to the evaporation or decomposition of extender oil and other organic non-polymeric additives present in the rubber compound.[14] For the tire rubber, the extender oil is typically a mixture of hydrocarbons such as aromatic oil which serves to soften the rubber and improve processability. Another two stages of mass loss between 300 and 500°C on the TG curve correspond to the decomposition of rubber components. The low-temperature (approximately 375°C) and high-temperature (approximately 420°C) decompositions occurred due to the decomposition of natural rubber and styrene–butadiene rubber and/or polybutadiene rubber, respectively.[15]

The content of organic non-polymeric ingredients and soluble rubber ingredients in the GTR before and after mechanochemical treatment could be calculated from TG curves according to ISO 9224-1.[16] The results are presented in Table II. As expected, the content of soluble rubber components in the GTR increased significantly from its original 5.4 to 21.4% after 20 cycles of milling. The produce of soluble rubber components during pan-milling effectively confirmed the realization of stress-induced mechanochemical devulcanization of GTR.

XPS Analysis of GTR Before and After Pan-Milling

XPS analysis was used to detect the variation of chemical composition of the GTR surface after pan-milling. Surface
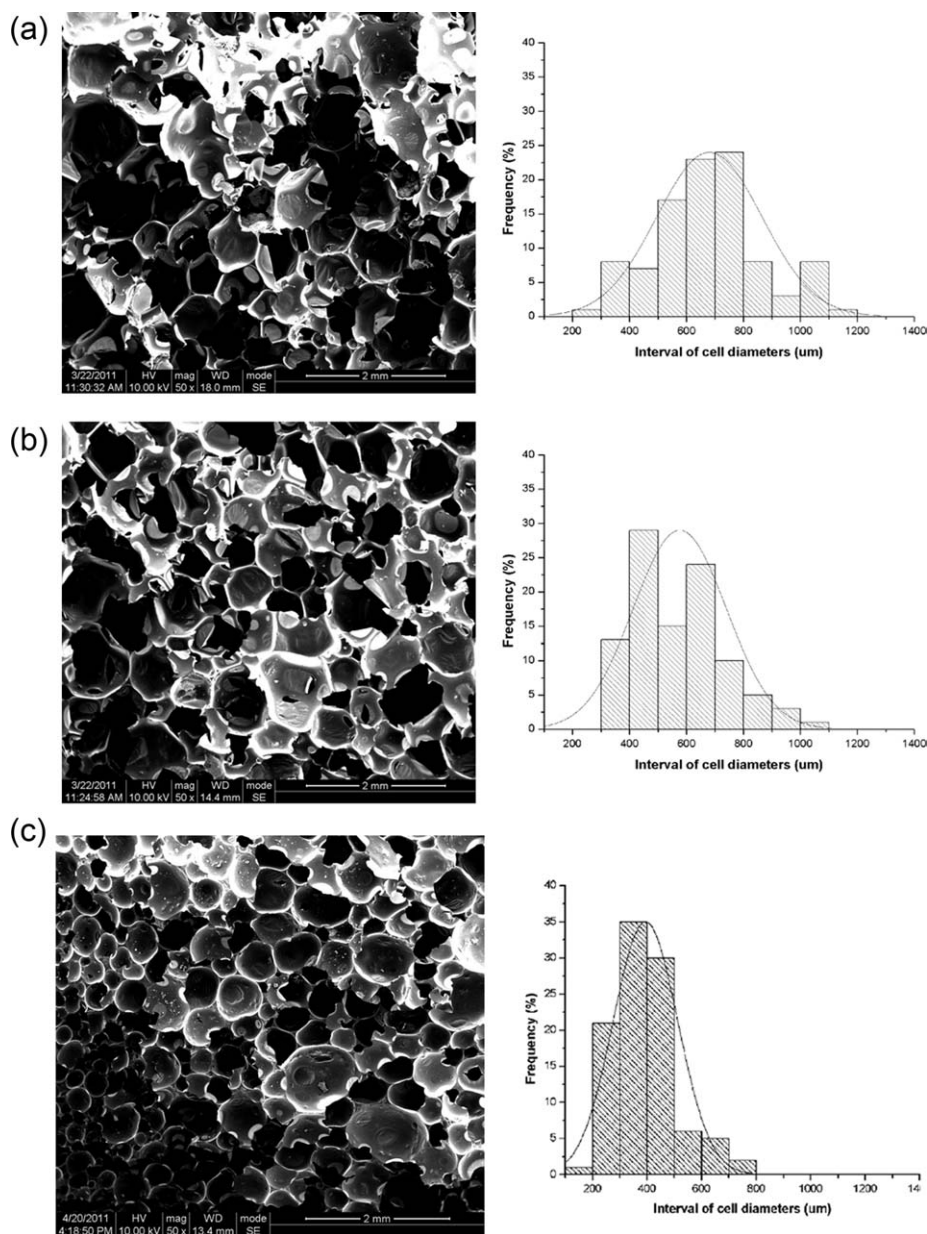
Figure 7. Effect of GTR particle size on the cell morphology of PU foams with the GTR content of 20 wt %: (a) with the particle size of 40 mesh; (b) with the particle size of 100 mesh; (c) with the particle size of 140 mesh.

compositions determined from XPS analysis of GTR powders before and after 20 cycles of milling are summarized in Table III. The results indicate that the oxygen content of the surface of GTR powders increased after milling. The C1s core spectrum of raw GTR powders [Figure 4(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.[17] The C1s core spectrum of mechanochemical milled GTR powders is shown in Figure 4(b). Compared with Figure 4(a), a new peak with binding energies at 286.6 eV appears after milling, which is assigned to the C=O species.

The pan-mill equipment can exert fairly strong squeezing force in normal direction and shear force in both radial and tangen-tial directions on milled materials, functioning like pairs of three-dimensional scissors.[18,19] A combination of shearing, extension and fracturing of GTR particles during milling induced crosslink scission and free radical formation. These free radicals can react with oxygen in air and form peroxide bond on the surface of GTR. The introduction of oxygen containing polar functional groups onto the GTR surfaces after pan-milling would benefit its interfacial adhesion with the polar PU matrix.

Particle Size Reduction of GTR During Pan-Milling

The effect of pan-milling on particle size distribution of GTR is shown in Figure 5. The results indicate that the particle size of GTR decreases sharply from its original ∼ 250 to ∼ 60 μm after 20 cycles of milling. During pan-milling, the GTR powders were
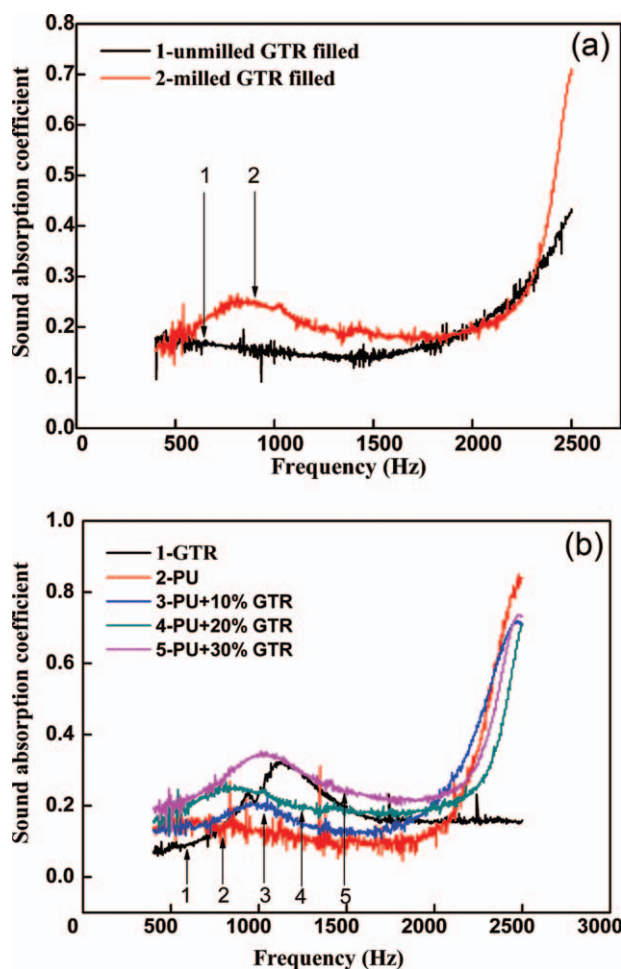
Figure 8. The sound absorption coefficient of PU/GTR foamed composites: (a) Effect of mechanochemical pretreatment of GTR (with the GTR content of 20 wt %); (b) Effect of devulcanized GTR content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

repeatedly flattened and fractured. With continuous deformation, the particles are fractured by a fatigue failure mechanism and/or by the fragmentation of fragile flakes. However, the fine particles have a strong tendency to aggregate, which can be promoted by the decrosslinking of GTR. To obtain fine GTR powders, high rotating speed and relatively low pressure were adopted during pan-milling. The simultaneous reduction of particle size and large increment of specific surface area of pan-milled GTR would benefit its dispersion in PU matrix.

### Cell Morphology of PU/GTR Foamed Composites

PU/GTR foamed composites were successfully produced with loading fractions up to 30 wt %. Figure 6 compares SEM images of the foamed composites derived from GTR before and after mechanochemical pretreatment. Figure 6(b,d) shows that untreated GTR particles have the propensity to disrupt foam formation, producing a less regular structure with a larger cell size. Some larger cells (>1000 μm) and structure defects are observed in Figure 6(b,d). Similar phenomenon has been reported by Sims and Angus[20]. Their results indicated that the

addition of ground flexible polyester PU powders without pretreatment drastically affected the foamability of PU foams. They ascribed it to the aggregate of filler particles. In comparison, the structure of the foams containing mechanochemically pretreated GTR particles, as shown in Figure 6(c,e), is more uniform and well-defined. Better dispersion and foamability of mechanochemically devulcanized GTR particles are expected since the partial decrosslinking and surface activation were achieved after pan-milling.

The effect of GTR particle size on the cell morphology of PU foams is shown in Figure 7 (with 20 wt % of GTR). It is apparent that the smaller the particle size is, the more uniform the cell morphology of the PU/GTR foamed composites is. As shown in Figure 5, the particle size of GTR decreases sharply after pan-milling. It suggests that the mechanochemically pretreated GTR is a suitable low cost filler for PU foams and has potential for large scale industrial applications.

Acoustic Properties of PU/GTR Foamed Composites

For the development of acoustic absorbent materials, lightweight and low-cost materials that absorb sound waves in wide frequency regions are strongly desired. It is found that the
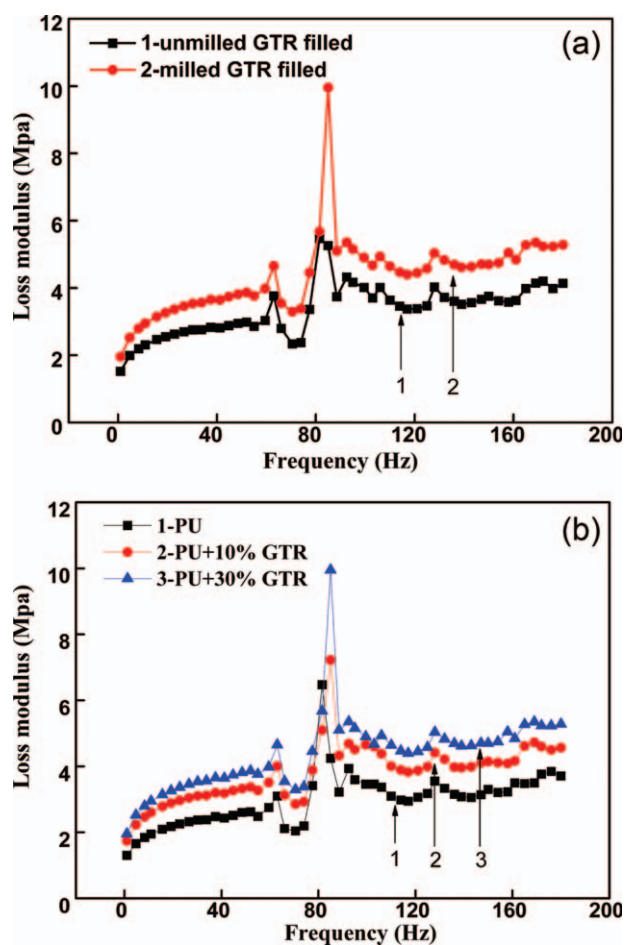
Figure 9. The loss modulus of PU/GTR blends: (a) Effect of mechanochemical pretreatment of GTR (with the GTR content of 20 wt %); (b) Effect of devulcanized GTR content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recycled rubber has a higher sound absorption coefficient than conventional porous acoustic absorbent materials in the middle-frequency region.[21] Therefore, the investigation of acoustic absorbent abilities in this study was focused on the middle-frequency region, that is, at the ranges of 500–1500 Hz.

The sound absorption coefficient of PU/GTR foamed composites (the GTR content is 20 wt %) with and without pretreatment of GTR as a function of frequency are given in Figure 8(a). Apparently, the mechanochemically pretreated sample seems to have superior sound absorption properties to that of untreated sample, especially at the frequency near 1000 Hz. The results indicate that the GTR particles without pretreatment are difficult to impart excellent sound absorption properties to PU foamed matrix. It could be ascribed to the poor adhesion between untreated GTR and PU matrix. As a result, the untreated GTR particles were not included in the foamed structures of the composites. The mechanochemical pretreatment of GTR is effective to enhance acoustic absorption properties of the foamed composites. As shown in Figure 8(b), the sound absorption coefficient of PU/GTR foamed composites increases with the increase of devulcanized GTR content. With the addition of 30 wt % devulcanized GTR, the sound absorption coefficient of PU foams at the frequency near 1000 Hz increased significantly from its original 0.15 to 0.35, enhanced by 133.3%. The sound absorption value of the PU/GTR foamed composites prepared in this study is similar to that of crumb rubber concrete panel as reported by Sukontasukkul[3]. The improvement of sound absorption coefficient could be attributed to the increase in viscoelastic properties of GTR. When GTR particles are subjected to the alternating stresses from vibration and sound wave, their forms would become highly elastically deformed due to the movement of rubber molecular chains, which is characterized by the remarkable lag of deformation behind the stress change. The movement of lagged deformation works by overcoming great resistance, converting into heat energy and dissipating into the environment.[1] The mechanochemical devulcanization of GTR faciliated the movement of rubber molecular chains. As a result, the increase in the lagged deformation and enhancement in the dissipation of heat energy was achieved. Finally, more sound energy was consumed. To authenticate this assumption, it is necessary to investigate the damping properties of the PU/GTR blends.

Damping Properties of PU/GTR Blends without Foaming

The presence of the bubbles within foamed materials is known to have a strong influence on loss modulus in DMA experiments. Therefore, samples of PU/GTR blends without foaming were prepared for the DMA measurements. The loss modulus of PU/GTR blends (the GTR content is 20 wt %) with and without pretreatment of GTR as a function of frequency is shown in Figure 9(a). As expected, the mechanochemical devulcanization of GTR significantly improved the loss modulus of the blends due to the facilitated molecular mobility. Figure 9(b) shows the effect of devulcanized GTR content on the loss modulus of the blends. With the addition of devulcanized GTR into PU matrix, the loss modulus of the blends improved over the entire frequency range. It was attributed to the increased flexible chains of the mechanochemically milled GTR particles. In general, the more the soft molecular chains dispersed in the matix, the more energy consumed through internal friction. The results

indicate that the mechanochemically pretreated GTR powder could help to improve the damping properties of the PU/GTR blends. The observed experiment results effectively support the hypothesis mentioned above. The improvement in loss modulus of the PU/GTR blends leads to the enhancement in acoustic absorption properties.

CONCLUSIONS

This work provides a facile and environmentally friendly mechanochemical approach to pretreat GTR for the enhancement of acoustic absorption properties of PU foams. Soxhlet extraction measurements and TGA analysis confirmed the achievement of stress-induced partial devulcanization of GTR through pan-milling. The incorporation of mechanochemically devulcanized GTR into PU foams imparts excellent acoustic absorption properties in the middle-frequency region to the foamed composites. However, the untreated GTR-filled PU composites did not show the enhancement effect. It could be ascribed to the improvement of damping properties of PU/GTR blends after mechanochemical pretreatment as confirmed by DMA studies. Compared with untreated GTR, the foamed composites containing mechanochemically pretreated GTR particles also exhibited remarkably enhanced foamability, showing more uniform and well-defined cell morphology.

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