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Vegetable derived-oil facilitating carbon black migration from waste tire rubbers and its reinforcement effect

Pan Song [a], Chaoying Wan [b], Yanling Xie [a], Krzysztof Formela [c], Shifeng Wang [a,*]

[a] Department of Polymer Science and Engineering, Shanghai Key Lab. of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, China
[b] International Institute for Nanocomposites Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK
[c] Department of Polymer Technology, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland

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ABSTRACT

Three dimensional chemically cross-linked polymer networks present a great challenge for recycling and reutilization of waste tire rubber. In this work, the covalently cross-linked networks of ground tire rubber (GTR) were degraded heterogeneously under 150 °C due to the synergistic effects of the soybean oil and controlled oxidation. The degradation mechanism was discussed using Horikx theory and Fourier transformation infrared spectroscopy (FTIR). The results showed that the structural evolution of sol and gel parts, which indicated that the sols consisted of degraded GTR chains with low molecular weight, while the gels were mainly composed of bound rubber coated carbon black, which are separated from the cross-linked network of GTR in a high degradation degree. The degraded GTR compound demonstrated an excellent reinforcing effect on solution styrene-butadiene rubber (SSBR), due to the presence of core-shell structured carbon black. This work provide an efficient and economic approach to degrade GTR and transform it into useful products.

1. Introduction

With the rapid development of the automobile industry, the recycling of increasingly discarded tires has been a significant challenge for development of sustainable economy and environment. According to statistics, an average of about one billion tires end their service life and are abandoned, and more than 50% of the waste tires are directly discarded, landfilled or burned without any treatment (Thomas and Gupta, 2016) which result in a disastrous effect on the natural environment. Although the waste tire rubber has been recycled in different ways, a secondary pollution is produced during the recycling processes and the value of recycled products is lowered. Efficient disposal approaches of these waste tires known as the "black pollution" have been pursued worldwide, aiming to recycle waste tires in a more environmental-friendly and value-added way.

Grinding of waste tire into powder allows to obtain product called ground tire rubber (GTR), which is a common method and has been widely used as additives into rubbers (Formela and Haponiuk, 2014; Han and Han, 2002; Jacob et al., 2013) and thermoplastic elastomers (Magioli et al., 2010; Pan et al., 2017; Shu et al., 2009). Other example, the application of GTR also regards as modifier for asphalt (Navarro et al., 2010) or cement (Sukontasukkul, 2009) in construction industry. However, the cross-linked network structure of GTR strongly limits its dispersion in variable matrices, e.g. rubbers or asphalt. The poor interfacial interaction between the GTR particles and the rubber matrix also hinders its dispersion in the rubber. As a result, the mechanical properties of vulcanized rubber are often decreased with the addition of GTR (Karger-Kocsis et al., 2013). To solve the above issues, destroying the cross-linked structure of GTR is more feasible to prepare the high performance rubber compounds instead of direct usage. At present, the physical (Molanorouzi and Mohaved, 2016), chemical (De et al., 2015) and biological (Romine and Romine, 1998) reclaiming methods are mainly used to degrade it. The purpose of these methods is to break the cross-linked structure of GTR by degradation of the crosslinking bonds (mono-, bi- and polysulfide bonds) instead of the main chains of the GTR. In practice, the addition of the degraded GTR is often limited to less than 20 wt% to rubber matrices due to its poor dispersion (Grigoryeva et al., 2004). Therefore, thoroughly destroying the cross-linked network structure of GTR is needed in order to facilitate the dispersion of the reclaimed rubbers in the matrix.

In general, high temperature and pressure are employed to prepare the reclaimed rubber, and the addition of devulcanization aids is also helpful to facilitate devulcanization reaction during the recycling process. However, the high temperature and pressure

* Corresponding author.
E-mail address: shfwang@sjtu.edu.cn (S. Wang).

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not only raise the costs of production, but also cause the production of a large number of harmful gas during the recycling process resulting from the addition of devulcanization aids, such as desulfurization agent or softener (Gągol et al., 2015; Li et al., 2010). Currently, the coal tar and aromatic oil are mainly used as softeners to obtain a better performance of reclaimed rubber. Nevertheless, the addition of these softeners enhance the production of volatile polycyclic aromatic hydrocarbons (PAHs) which leads to a serious secondary pollution to the environment. Therefore, how to reduce the reclaiming temperature and the use of aromatic softeners to achieve environmental-friendly and non-polluted preparation of reclaimed rubber is an issue to be solved. As for recycling the GTR at a low temperature, research concerning the incorporation of $CuCl_2$ as a catalyst into the vulcanized polybutadiene rubber to degrade it by disulfide metathesis reaction (Xiang et al., 2015), and the cross metathesis reactions with the Grubbs' ruthenium catalyst were also studied to breakdown the rubber network (Lu and Guan, 2012; Smith et al., 2016; Wolf and Plenio, 2013). Although these methods can realize the aim of devulcanization at a low temperature, the high costs of catalysts and its poor distribution in the cross-linked network restricts its large scale application.

Based on recycling the GTR by using the supercritical carbon dioxide, the achievement of better devulcanization effect mainly arises from the supercritical carbon dioxide with low viscosity and high thermal conductivity, which contribute to the swelling of the GTR cross-linked network and the diffusion of devulcanization aids (Jiang et al., 2013; Kojima et al., 2004). It is found that a good swelling effect is an important factor to degrade the GTR, the fully swollen cross-linked network can weaken the interaction between the molecular chains of GTR and inhibit the occurrence of recombination reaction between broken chains, which is beneficial to realize the devulcanization at a lower temperature. Vegetable oil as a natural softener is extracted from oleaginous plants or trees and has the advantages of environmental-friendly, biodegradable and low toxicity (Bocqué et al., 2016). It mainly composes of triglycerides, according to its molecular structure as shown in Fig. 1, the molecular chain of vegetable oil contains a long carbon chain with double bonds, indicating chain flexibility compared with aromatic oil. It is relatively easy to penetrate and swell the cross-linked network of GTR and weaken the interaction between the molecular chains of GTR, and thus potentially leads to a better devulcanization effect. Besides, using vegetable oil as a softeners can reduce the production of PAHs. The effects of naphthenic oil, wood tar, shea butter oil and recycled cooking oil on the properties of reclaimed rubber was compared and found that shea butter oil as softener resulted in a better devulcanization effect compared with other plasticizers (Xu et al., 2014). This indicates the potential of using vegetable oil as a softener during the reclaiming of rubbers.

As the bio-oil easily swell the cross-linked network of GTR and reduce the interaction between the GTR chains, a high devulcanization degree can be achieved in a mild recycling condition. The lower recycling temperature reduces not only the energy consumption but also the volatilization of harmful degradation products (Gągol et al., 2015). Because soybean oil has the advantages of large output and low cost compared with other vegetable oil, it has been extensively studied as a plasticizer in the rubber compound (Li et al., 2015, 2016a; Petrović et al., 2013). In this study, soybean oil was chosen as a green plasticizer during the low temperature reclaiming process. In order to achieve a better devulcanization effect, it is necessary to add high content soybean oil to fully swell GTR. The GTR was swollen by soybean oil with different ratios and reclaimed at 150 °C. The reclaiming mechanism was analyzed by Horikx theory and Fourier transform infrared spectroscopy (FTIR). The components and morphology of the sol and gel fraction in the reclaimed rubber were studied. The prepared rubber was further blended with solution styrene-butadiene rubber (SSBR), and its reinforcement effect was investigated.

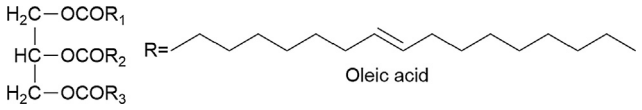

Fig. 1. The chemical structure of the vegetable oil.

2. Experimental

2.1. Materials

GTR (24 meshes) was supplied by the Jiangsu Baoli International Investment Co., Ltd (Jiangyin, China). It was composed of 5.8 wt% soluble material, 42.2 wt% natural rubber (NR), 12.9 wt% styrene-butadiene rubber (SBR), 32.1 wt% carbon black and 7.0 wt% inorganic filler. The soybean oil was provided by the Shanghai Liangyou Oil Industry Co., Ltd. SSBR with bonded styrene content of 23.5–26.5% was obtained from the Sinopec Shanghai Gaoqiao Company. The rubber additives, such as sulfur, accelerator, stearic acid and zinc oxide, are commercial grades.

2.2. Preparation

2.2.1. Preparation of the RGTR

GTR and soybean oil were mixed with different ratios according to Table 1. The mixed samples were degraded in a hot-air (XMTD-8222, Jinghong Laboratory Instrument, Shanghai) at 150 °C for 4 h. The reclaimed GTR was labeled as the RGTR, the content of the soybean oil of 20 parts per hundreds of rubber (phr) in the RGTR was labeled as $RGTR_{20}$.

2.2.2. Preparation of the SSBR/RGTR blends

RGTR was firstly extracted by acetone to remove the soybean oil. The RGTR with different devulcanization degree (different plasticizers content) after extraction was blended with SSBR in a batch lab mixer (HAAKE Polylab OS, Thermo Electron Gmbh, Germany) at 70 °C for 10 min with a rotor speed of 60 rpm. These blends were cured at a temperature of 150 °C using a temperature-controlled hydraulic press (LP-S-50, Labtech, Thailand) and the curing times were tested by a rubber processing analyzer (RPA 2000, Alpha technologies, USA). The SSBR blended with the untreated GTR and the pure SSBR were used as control samples. The specific formulation was shown in Table 2 and the curing time was shown in the Table 3.

2.3. Measurements

2.3.1. Sol fraction

RGTRs with a certain weight were wrapped by filter paper and placed into the Soxhlet extractor to remove the sol parts. The samples were extracted by toluene for 72 h and the low molecular weight compounds, such as broken chains of GTR, vegetable oil and soluble materials in the GTR, can be removed during the

Table 1
The different ratios between GTR and soybean oil.

Samples	$RGTR_{20}$	$RGTR_{60}$	$RGTR_{100}$	$RGTR_{150}$
GTR	100	100	100	100
Soybean oil	20	60	60	150