Preparation and stress-strain behavior of *in-situ* epoxidized natural rubber/SiO₂ hybrid through a sol-gel method

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Abstract. In this paper, epoxidized natural rubber was reinforced by silica generated *in-situ* through the sol-gel method using tetraethoxysilane (TEOS) as precursor. The results showed that the ring opening reaction of epoxy group appeared in the *in-situ* reaction progress, where the hydrogen bond between Si–OH and C–OH was mainly formed to enhance the stress-strain behavior of ESH simultaneously. During the hot pressing progress, the compound was crosslinked via the chemical reaction of Si–OH and C–OH. The chemical bond between Si–OH and C–OH reinforced rubber-filler interaction, resulting further improved the stress-strain behavior. Besides, comparing with precipitated SiO₂ filled ENR, the dispersion of SiO₂ in ENR matrix was distinctly more uniform through the sol-gel method, along with the enhancement of mechanical properties. Herein, our findings open up a new way to prepare an environmentally friendly rubber composite with excellent dispersion and strong rubber-filler interaction without curing agent effectively.

Keywords: rubber, ENR/SiO₂ hybrid, sol-gel reaction, interaction

1. Introduction

Epoxidized natural rubber (ENR) is derived from the partial epoxidation of the natural rubber possessing some new properties such as good wet grip, oil resistance, excellent flexibility and low rolling resistance [1, 2]. The epoxy group of ENR is unstable that could be utilized for the modification of ENR or being a compatilizer [3, 4] in rubber composites. It is well known that SiO₂ is used widely in industry except for carbon black, usually as a reinforcement agent or a functionalized filler to impart specific properties for rubber compounds [5]. In our previous work, The ENR/SiO₂ hybrids prepared by an open-mill mixing method had been reported, and the interfacial interaction of ENR and SiO₂ was investigated. The results indicated that the ring-opening reaction of the epoxy groups of ENR chains occurs and the covalent bonds between C–OH of ENR and

Si–OH groups on the silica surfaces were formed, which can improve the dispersion of silica in the rubber matrix and enhance the interfacial combination between rubber and silica. However, the hybrid obtained a good strength only with a high content of SiO₂ [6], where the elongation at break of hybrid was limited regrettably. This might be attributed to the insufficient filler-rubber interactions. There are still improvements that need to be made in the elongation at break and processability.

Mark and Pan [7] firstly proposed a new approach for preparing silica-filled elastomers by generating the silica particles inside the crosslinked silicone rubber. The sol-gel process brings a good dispersion of the silica filling into the rubbery matrix. In general, the sol-gel reaction of tetraethoxysilane (TEOS) takes place easily and proceeds in the two steps, hydrolysis and condensation reactions, to produce SiO₂.

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To obtain a preferable interfacial interaction between polymer matrix and SiO_2 [8], *in-situ* synthesis method was widely used to reinforce polymers like natural rubber [9], NR latex [10], natural rubber grafted by methyl methacrylate [11] and SBR. The contact probability between hydroxyl of *in-situ* SiO_2 and rubber matrix was increased via an *in-situ* approach that is beneficial to the improvement of rubber-filler interaction.

There are several articles about *in-situ* SiO_2 reinforced ENR composites [12–14], which achieved high mechanical property improvements with the assistance of dicumyl peroxide (DCP) [13], benzoyl peroxide (BzO) [14] as the crosslinking agents. DCP crosslinked composites ENR exhibit higher tensile strength and modulus (almost 60 and 20% respectively) than those of the uncured composites, which showed better performance compared to BzO cross-linked system. Unfortunately, these low-molecular-weight assistants possess disadvantages of migration, volatility, and color contamination.

With the purpose of overcoming the drawbacks of crosslinking agent, we explored a novel preparation method of self-crosslinkable ENR filled with *in-situ* SiO_2 .

In this article, an *in-situ* ENR/ SiO_2 hybrid (ESH) was prepared through sol-gel method and self-crosslinked via the interaction of open-loop ENR and SiO_2 after hot-pressing process. Fourier Transform Infrared (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and contact angle measurement were used to characterize the structure changes of ESH. The morphology of ESH was also investigated. Additionally, mechanical properties of the hybrid were compared with that of precipitated

SiO_2 filled ENR compounds. The results indicated that the sol-gel method did a positive effect on the enhancement of ENR- SiO_2 interface interactions.

2. Experimental

2.1. Materials

Epoxidized natural rubber (ENR50, with 50 mol% of epoxy content) was kindly supplied by the Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agriculture Sciences (Zhanjiang, China). Precipitated SiO_2 (type 518) was provided by the Wanzai Huiming Chemical Limited Co. (Jiangxi, China). Tetraethoxysilane (TEOS), tetrahydrofuran (THF) and hydrochloric acid (HCl) were analytical reagents and used as received.

2.2 Preparation of ESH

Epoxidized natural rubber (ENR, 9 g) was dissolved in tetrahydrofuran (THF, 300 mL) at room temperature until homogeneous phase was obtained via the treatment of stirring for 30 min. Subsequently, tetraethyl orthosilicate (TEOS, 4.5 g) and deionized water (9 g) were added into the solvated rubber under stirring for 50 min to generate SiO_2 through sol-gel method. HCl was used to maintain the reaction pH at 1.5. The obtained *in-situ* SiO_2 filled ENR matrix was poured into a watch glass and dried for 24 h at room temperature. Then the product was dried in a vacuum oven (50°C) for 48 h until the sample weight became constant. The *in-situ* SiO_2 rubber compound were made into the sheets by flat vulcanizing machine at 60°C , 145°C for 20 min, which were called ESH-1, ESH-2, respectively. Figure 1 sketches the synthetic procedure. For preparing the reference sample ESH-3, precipitated SiO_2 (type 518) was directly added

Figure 1. Synthetic procedure of ESH

into dissolved ENR. The suspension was well blended and dried as per the *in-situ* SiO₂ rubber compound detailed above. And the ENR-SiO₂ compound was made into the sheets by flat vulcanizing machine at 145 °C for 20 min. The additive amount of precipitated SiO₂ was according to the residual weight of ESH-2 in the TGA test, which was 17% approximately.

2.3. Characterization

FTIR spectra of ESH were recorded with a Bruker Vector 70 FTIR spectrometer in the range of 4000 to 400 cm⁻¹. TGA was executed using a NETZSCH TG 209 F1 in the range of 35~700 °C under nitrogen at a heating rate of 20 °C/min. DSC was conducted with a NETZSCH DSC 204 F1 under nitrogen atmosphere. The temperature program involved 2 min isothermal hold at 50 °C followed by heating at 10 °C/min to 250 °C under nitrogen. The water contact angles (WCAs) were measured with a goniometer (KRÜSS DSA 100, Germany) using liquid droplets of 4 µL in volume. The morphology of the ESHs were obtained with a Zeiss Merlin SEM machine (Germany) at an acceleration voltage of 5 kV. The samples were immersed into liquid nitrogen to make brittle fracture sections. The fracture surface was sprayed with gold before testing. The stress-strain behaviors of ESH were carried out with a UCAN UT-2060 instrument according to ISO 37-2005 standard (dumbbell A shape), and five samples were selected for one parameter representation.

3. Results and discussion

Figure 2 shows the FTIR spectra of ENR, ESH-1, ESH-2, ESH-3 and SiO₂. The peaks at 876 and 1250 cm⁻¹ of ENR are attributed to the stretching and deformation vibration of epoxy group [15]. The peaks

Figure 2. FTIR spectra of ENR, ESH-1, ESH-2, ESH-3 and SiO₂

at 3409, 1080 cm⁻¹ of SiO₂ represents the stretching vibration of Si-OH and Si-O-Si. It can be seen that 876 and 1250 cm⁻¹ disappear in the spectrum of ESH-1, simultaneously a new peak at 3446 cm⁻¹ standing for the stretching vibration of hydroxyl appears which indicates the acid catalyzed ring opening reaction of the epoxy group that formed the alcohol hydroxyl. Besides, The ratio of -OH/ Si-O-Si stretching vibration is increased from SiO₂ to ESH-1 demonstrating the new hydroxyl was generated. Comparing with the spectrum of ESH-1, a new peak at 1713 cm⁻¹ shows up owing to the stretching vibration of -C=O in ESH-2, which was introduced by the oxidation of C-OH under hot-press treatment at 145 °C. Meanwhile, the increase of intensity and red shift of hydroxyl absorption peak from 3442 to 3411 cm⁻¹ imply the stronger hydrogen-bond interaction between -C=O/-OH than that of -OH/-OH.

TGA and DTGA curves of ENR, ESH-1, ESH-2 and ESH-3 are depicted in Figure 3a, respectively and

Figure 3. a) TGA and b) DSC curves of ENR, ESH-1 and ESH-2

Figure 4. The contact angle of a) ESH-1, b) ESH-2 and c) ESH-3

the DSC plots are shown in Figure 3b. It was observed that the initial degradation temperature of ESH-1 and ESH-2 both shift to a lower value comparing with ENR, which means a decrease of thermal stability for hybrid that is in line with our previous work. Simultaneously, there is an obvious difference between ESH-1 and ESH-2 obtained from the DTG curves in the range of 120~200 °C. A rapid decline arises around 170 °C for ESH-1 while a similar phenomenon shows up around 120 °C for ESH-2. The former is related to the volatilization of water generated from the chemical reaction between Si–OH and C–OH, where an endothermal effect had been detected at 172 °C peak by DSC in Figure 3b. The latter reflects the volatilization of absorbed water, which was absorbed on the sample's surface by the generated polar –C=O group that formed a strong hydrogen-bond interaction with hydroxyl of H₂O. This could also be proved through an exothermic effect that presents among 130~160 °C by DSC in Figure 3b caused by the destruction of hydrogen-bond interaction. The endothermal peak of ESH-1 around 192 °C by DSC might be caused by the oxidation of C–OH to –C=O, which could be confirmed in FTIR spectra. There are no endothermal peaks arise in ESH-2 curve indicating

the chemical reaction between Si–OH/C–OH and oxidation of C–OH had been finished in the hot press process. Actually, the hot press temperature (145 °C) is different from the DSC result that is due to the impact of pressure. TGA and DSC curves of ESH-3 show no much differences with ENR.

To illustrate the hydrophilic character of ESH, the contact angle measurement was employed and the result is described in Figure 4. As it can be seen the contact angle of ESH-1, ESH-2 are 100.7, 73.9°, respectively. That means a better hydrophilicity for ESH-2 comparing with ESH-1. Thus, a stronger interaction between ESH-2 and water is confirmed caused by the effect of polar –C=O group. The consequence sustains the deduction of the volatilization of absorbed water for ESH-2 in TGA curve. The contact angle of ESH-3 is a little bigger than that of ESH-1, which means their surface features are similar.

To investigate the morphology of the hybrids, SEM measurements were employed to view the morphology of cryofracture surfaces in Figure 5. In the SEM images of ESH-1 and ESH-2, SiO₂ particles were scattered uniformly throughout the hybrid. On the contrary, large aggregates and agglomerates can be seen in the ENR matrix for ESH-3. The better dispersion

Figure 5. SEM images of a) ESH-1, b) ESH-2, c) ESH-3.

Figure 6. The stress-strain curves of ESH-1, ESH-2, ESH-3 and its interaction diagrams

of *in-situ* SiO₂ in ENR matrix by the sol-gel method of ESH-2 would be expected to result in the superior mechanical properties than ESH-3, which is addressed in the next section.

Figure 6 illustrates the stress-strain behaviors of ESH-1, ESH-2 and ESH-3. Comparing with the curve of ESH-3, the modulus and strength of ESH-1 are improved significantly, which indicates a stronger hydrogen-bond interaction exists in ESH-1 than in the case of the traditional mechanical mixing method. This is because the excellent dispersion of SiO₂ in ENR matrix via *in-situ* reaction way leading to a stronger rubber-filler hydrogen-bond interaction, supporting by the morphology of the hybrids. The schematic can be seen in Figure 7. After the hot press treatment in 145 °C, ESH-2 gains a higher modulus or strength than ESH-1, as well as a good elongation at break. According to our previous works, this depends on the chemical bond between CH₃-C-OH and Si-OH generated during the hot press process at 145 °C for 20 min. Thus, SiO₂ served as both self-vulcanizing agent and reinforcing agent in ESH matrix.

4. Conclusions

In summary, *in-situ* epoxidized natural rubber/SiO₂ hybrid was prepared though the sol-gel method where SiO₂ acted as self-vulcanizing agent and reinforcing agent without any curing additives. The results showed that the ring opening reaction of epoxy group happened during the *in-situ* reaction process, where hydrogen-bond interaction among –OH was formed to enhance mechanical properties of ESH. Besides, the chemical bond between Si–OH and C–OH and –C=O groups were generated during the hot press process, which reinforces rubber-filler interaction and promotes the mechanical properties of ESH significantly. The sol-gel method gained a more uniformly dispersion of SiO₂ in ENR matrix by comparing precipitated SiO₂ filled ENR. Therefore, the *in-situ* method provides a new opportunity to prepare the environmental friendly rubber composite effectively with excellent dispersion and strong rubber-filler interaction without curing agent effectively.

Figure 7. Hydrogen bond interaction between ENR and SiO₂ in sol-gel reaction process

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References

- [1] Hamzah R., Bakar M. A., Dahham O. S., Zulkepli N. N., Dahham S. S.: A structural study of epoxidized natural rubber (ENR-50) ring opening under mild acidic condition. *Journal of Applied Polymer Science*, **133**, 44123/1–44123/13 (2016).
<https://doi.org/10.1002/app.44123>
- [2] Soheilmooghaddam M., Wahit M. U., Akos N. I.: Regenerated cellulose/epoxidized natural rubber blend film. *Materials Letters*, **111**, 221–224 (2013).
<https://doi.org/10.1016/j.matlet.2013.08.109>
- [3] Xu T., Jia Z., Luo Y., Jia D., Zheng P.: Interfacial interaction between the epoxidized natural rubber and silica in natural rubber/silica composites. *Applied Surface Science*, **328**, 306–313 (2015).
<https://doi.org/10.1016/j.apsusc.2014.12.029>
- [4] Xu T., Jia Z., Li J., Luo Y., Jia D., Peng Z.: Study on the dispersion of carbon black/silica in SBR/BR composites and its properties by adding epoxidized natural rubber as a compatilizer. *Polymer Composites*, in press (2016).
<https://doi.org/10.1002/pc.23946>
- [5] Manoharan P., Naskar K.: Exploring a highly dispersible silica–elastomer composite for tire applications. *Journal of Applied Polymer Science*, **133**, 43531/1–43531/10 (2016).
<https://doi.org/10.1002/app.43531>
- [6] Xu T., Jia Z., Wang S., Chen Y., Luo Y., Jia D., Peng Z.: Self-crosslinkable epoxidized natural rubber-silica hybrids. *Journal of Applied Polymer Science*, **134**, 44605/1–44605/10 (2017).
<https://doi.org/10.1002/app.44605>
- [7] Mark J. E., Pan S.-J.: Reinforcement of polydimethylsiloxane networks by *in-situ* precipitation of silica: A new method for preparation of filled elastomers. *Macromolecular Rapid Communications*, **3**, 681–685 (1982).
<https://doi.org/10.1002/marc.1982.030031006>
- [8] Ikeda Y., Kameda Y.: Preparation of ‘green’ composites by the sol-gel process: *In situ* silica filled natural rubber. *Journal of Sol-Gel Science and Technology*, **31**, 137–142 (2004).
<https://doi.org/10.1023/B:JSST.0000047975.48812.1b>
- [9] Poompradub S., Thirakulrati M., Prasassarakich P.: *In situ* generated silica in natural rubber latex via the sol-gel technique and properties of the silica rubber composites. *Materials Chemistry and Physics*, **144**, 122–131 (2014).
<https://doi.org/10.1016/j.matchemphys.2013.12.030>
- [10] Miloskovska E., Nies E., Hristova-Bogaerds D., van Duin M., de With G.: Influence of reaction parameters on the structure of *in situ* rubber/silica compounds synthesized *via* sol-gel reaction. *Journal of Polymer Science Part B Polymer Physics*, **52**, 967–978 (2014).
<https://doi.org/10.1002/polb.23516>
- [11] Watcharakul N., Poompradub S., Prasassarakich P.: *In situ* silica reinforcement of methyl methacrylate grafted natural rubber by sol-gel process. *Journal of Sol-Gel Science and Technology*, **58**, 407–418 (2011).
<https://doi.org/10.1007/s10971-011-2407-x>
- [12] Hashim A. S., Kohjiya S., Ikeda Y.: Moisture cure and *in-situ* silica reinforcement of epoxidized natural rubber. *Polymer International*, **38**, 111–117 (1995).
<https://doi.org/10.1002/pi.1995.210380202>
- [13] Bandyopadhyay A., Sarkar M. D., Bhowmick A. K.: Epoxidized natural rubber/silica nanoscale organic-inorganic hybrid composites prepared by sol-gel technique. *Rubber Chemistry and Technology*, **77**, 830–846 (2004).
<https://doi.org/10.5254/1.3547854>
- [14] Bandyopadhyay A., Sarkar M. D., Bhowmick A. K.: Epoxidised natural rubber/silica hybrid nanocomposites by sol-gel technique: Effect of reactants on the structure and the properties. *Journal of Materials Science*, **40**, 53–62 (2005).
<https://doi.org/10.1007/s10853-005-5687-0>
- [15] Xu H., Liu J., Fang L., Wu C.: *In situ* grafting onto silica surface with epoxidized natural rubber *via* solid state method. *Journal of Macromolecular Science Part B, Physics*, **46**, 693–703 (2007).
<https://doi.org/10.1080/00222340701388854>