Materials Science and Engineering B 181 (2014) 39–45

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Short communication

Styrene grafted natural rubber reinforced by *in situ* silica generated via sol–gel technique

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ARTICLE INFO

Article history:
Received 19 June 2013
Received in revised form
14 November 2013
Accepted 19 November 2013
Available online 2 December 2013

Keywords:
Graft copolymer
In situ silica
Sol–gel process
Nanocomposite materials

ABSTRACT

The filling of styrene graft natural rubber (ST-GNR) with *in situ* formed silica was performed using the sol–gel reaction *via* the latex solution method. The mechanical properties of ST-GNR/NR vulcanizate were improved when using the *in situ* formed silica to levels higher than those obtained with the commercial *ex situ* formed silica filled ST-GNR/NR vulcanizates at a comparable silica content of 12 parts by weight per hundred parts of rubber. Transmission electron microscopy analysis revealed that the *in situ* silica particles were small (~40 nm diameter) and well dispersed, while the commercial silica particles were larger (~60 nm diameter) and markedly agglomerated in the rubbery matrix. The mechanical properties of the composites prepared *via* both the solid rubber and latex solution methods were comparable.

1. Introduction

Natural rubber (NR) is the only agriculture product of all the types of rubber, and its use is widespread ranging from household to industrial products. Most industrial and engineering multiphase material products usually contain a rubber phase in order to improve their mechanical properties, especially their impact strength [1,2]. Additionally, thermoplastic elastomers are one type of product that consists of a rubber phase within the thermoplastic. The blend of NR and thermoplastics can not only lead to excellent elastic properties, but also to their superior processability. Unfortunately, it is difficult to simply blend NR and thermoplastics due to their low compatibility, which results in the poor mechanical properties of the obtained final products. The use of graft copolymers of vinyl monomers, *i.e.*, styrene (ST) or methyl methacrylate (MMA) onto NR is an interesting method to suppress this problem [1–6]. In most commercial processes the graft copolymer is synthesized *via* an emulsion polymerization using a redox-initiating system for grafting the monomer onto the NR [7–12].

Although the use of graft copolymerization can improve the compatibility of polymer blends, the strength of the resultant material is still one of the most important factors in many applications. Thus, the addition of a reinforcing filler has an indispensable role. In the rubber industry, silica is an alternative reinforcing filler used to improve some of the properties of NR, such as to impart a reduced heat buildup and a high tear strength, tensile strength and abrasion resistance [13]. The white colored silica filler is, therefore, often used in white or colored products. However, a problem with conventional silica reinforced rubber is that it is normally highly aggregated due to filler-to-filler interactions, resulting in a lower dispersion within the rubbery matrix and poor mechanical properties. One method to improve the reinforcement is to form the silica particles *in situ* inside the rubbery matrix *via* the sol–gel process using tetraethoxysilane (TEOS) and so obtain a fine dispersion [14–16]. Various matrixes have been used for silica filled rubber, such as styrene-butadiene rubber (SBR) [17], butadiene rubber (BR) [18], acrylonitrile-butadiene rubber (NBR) [19], polyimide (PI) [20], polyacrylate [21], NR [22–25], epoxidized NR [26] and grafted NR (GNR) [12]. Moreover, to generate the *in situ* silica by the sol–gel process, various techniques have been employed, such as the use of solid rubber [27–29], rubber latex [12,30] and rubber solution [31].

The *in situ* silica filling of MMA-GNR *via* the solid rubber and rubber latex methods has been reported [32], where the MMA-GNR/NR composite vulcanizates reinforced by *in situ* formed silica prepared by either method showed similar mechanical properties. In this study, ST was chosen to graft onto the NR because ST has been found to be the most suitable monomer to give a high level of grafting [3]. Moreover, the advantages of using ST-GNR are the high resistance to ozone, heat and weathering compared to NR [33]. In the previous work, the optimum condition for the sol–gel reaction

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http://dx.doi.org/10.1016/j.mseb.2013.11.018

Table 1
Conditions for the sol–gel reaction in ST-GNR using the latex solution method.

Condition number	Variables			
	TEOS content (phr)	Temperature (°C)	Additional time of TEOS	*In situ* silica content[a] (phr[b])
1	20	50	During graft copolymerization	6
2	20	60	During graft copolymerization	6
3	20	50	After graft copolymerization	5
4	40	50	After graft copolymerization	11
5	60	50	After graft copolymerization	16
6	80	50	After graft copolymerization	21

Recipe for the preparation of ST-GNR: 100 g NR latex, 200 g water, 3 g iso-propanol, 0.3 g potassium hydroxide, 0.9 g sodiumdodecyl sulphate, 60 g styrene monomer, 1.2 g tetraethylene pentamine (TEPA), 1.2 g cumene hydroperoxide (CHPO).

[a] Measured by TGA after 5 days of sol–gel reaction.

[b] Parts per one hundred rubber by weight.

in the solid state of ST-GNR has been reported [34], although the mechanical properties of NR composite material have never been studied. In this study, the modification of ST-GNR using the *in situ* sol–gel reaction of TEOS in ST-GNR was performed by the latex solution method. The effects of the reaction time, reaction temperature, TEOS content and addition time of TEOS were investigated to find the more optimal conditions (defined as a high but well dispersed *in situ* formed silica content). A comparison of the mechanical properties between each *in situ* silica modified ST-GNR (both the latex solution and solid rubber methods) and the commercial filled ST-GNR was investigated. Finally, the morphology of the *in situ* silica filled ST-GNR was characterized.

2. Experimental

2.1. Materials

The high-ammonia NR latex containing a dry rubber content of 60% was supplied by the Thai Rubber Latex Co., Ltd. (Thailand). ST monomer was supplied by the Siam Chemical Industry and purified in order to eliminate inhibitor before using. TEOS, used as a precursor of silica, was purchased from Fluka. Sodium dodecyl sulfate (SDS) as an emulsifier, isopropanol as a stabilizer, potassium hydroxide (KOH) and sodium hydroxide (NaOH) were purchased from Ajax Finchem. Cumene hydroperoxide (CHPO) and tetraethylene pentamine (TEPA) as a redox initiator were purchased from Merck. Light petroleum ether (PE) and methyl ethyl ketone (MEK) were purchased from Lab Scan Analytical Sciences. *n*-Hexylamine was purchased from Sigma–Aldrich. Active zinc oxide (ZnO), stearic acid, mercaptobenzothiazole disulfide (MBTS), polyethylene glycol (PEG 3000) and sulfur were used as curing agents and were purchased from PI Industry Ltd. Commercial silica (Hisil-255) with a specific surface area of *ca.* 200 m^2/g was obtained from PPG-Siam Silica Co., Ltd., and was dried at 120 °C for 2 h before use.

2.2. Modified ST-GNR using TEOS via the sol–gel process in NR latex and solid rubber

In this study, the addition time of TEOS into the sol–gel reaction was varied as follows: the TEOS was added during or after the graft copolymerization [32]. In the case of adding TEOS during the graft copolymerization, the TEOS was added with the ST monomer and so the graft copolymerization and sol–gel reaction proceeded simultaneously at 50–60 °C in the presence of the CHPO: TEPA (1:1 molar ratio) initiator (conditions 1 and 2 in Table 1). In the case of adding TEOS after the graft copolymerization, the ST-GNR latex was prepared by graft copolymerization at 50 °C for 8 h, also using 1 phr of CHPO: TEPA (1:1 molar ratio) as the initiator, but the TEOS was then added into the GNR latex and the sol–gel reaction was carried out at 50 °C (conditions 3–6 in Table 1). In both cases, during the sol–gel reaction, the solution was sampled every day until the reaction reached equilibrium and the ST-GNR latex was coagulated using ethanol. The conditions for the sol–gel reaction of TEOS in ST-GNR are summarized in Table 1. The procedure for the synthesis of the modified ST-GNR by TEOS *via* the sol–gel process in solid rubber was performed as previously reported [34]. ST-GNR sheets of *ca.* 1 mm thick were prepared using a two-roll mill. The rubber sheets (70 mm × 70 mm × 1 mm) were immersed in TEOS in a glass container at 40 °C for 1 h and at room temperature for 16 h. The swollen sheets were then immersed in an aqueous solution of *n*-hexylamine at 40 °C in order to conduct the sol–gel reaction. Finally, the rubber sheets were dried under vacuum at 40 °C to a constant weight.

2.3. Sulfur based vulcanization of modified ST-GNR

The formulations of rubber compounding are shown in Table 2. Then, the rubber blend was mixed with active ZnO, stearic acid, MBTS, PEG and sulfur, respectively. The cure time (t_{90}) for the

Table 2
Formulations for the rubber compounding, in parts by weight per hundred parts (phr).

	NR	GNR/NR	GNR-Si-12/NR	GNR-In-12-L/NR	GNR-In-12-S/NR	GNR-In-24-S/NR
NR	100	50	50	50	50	50
ST-GNR	–	50	50	–	–	–
Silica filled ST-GNR	–	–	–	62	62	74
Commercial silica	–	–	12	–	–	–
Active zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
MBTS[a]	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	3	3	3	3	3	3
PEG[b]	–	–	0.40	0.40	0.40	0.83
Curing time at 150 °C (min)	7.20	5.14	7.05	6.65	6.81	10.99

[a] Mercaptobenzothiazole disulfide.

[b] Polyethylene glycol.