The crosslink density of styrene butadiene rubber/nano copper oxide nanocomposites

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Abstract: Styrene butadiene rubber (SBR) is one of the most applicant rubbers in the world which could be used in the industrial usages and medical applications. In other some works, combination of styrene butadiene rubber with other rubbers could be used for composite and nanocomposites applications. In this paper, crosslink density of rubber based nanocomposites have been investigated by swelling test. Results showed that nano copper oxide nano copper oxide affect the crosslink density content of nanocomposites with presence of nano copper oxide. Moreover, extraction and swelling tests of nanocomposites has been carried out. The results showed that the nano copper oxide increased the amount of average molecular weight between two crosslinks.
[Maryam K Hafshejani, Ameneh Langari and Mehdi Khazaei. **The crosslink density of styrene butadiene rubber / nano copper oxide nanocomposites**. *Life Sci J* 2013;10(4):3666-3669]. (ISSN: 1097-8135). http://www.lifesciencesite.com. 494

Keywords: Nano copper oxide, Styrene butadiene rubber, crosslink density

1. Introduction

Styrene butadiene rubber (SBR) is one of the most applicant rubbers in the world which could be used in the industrial usages. The production of this synthetic was not actively pursued in the United States or elsewhere in the world until the supply of natural rubber had been curtailed by war activities in the Pacific during the late 1930s and early of the 1940s decay[1]. It should be noted that the Styrene butadiene rubber (SBR) is a general purpose synthetic rubber which has many applications. The high filler-loading capacity, good flex resistance, crack-initiation resistance, and abrasion resistance of SBR make it useful in several engineering and industrial applications [2-3]. Styrene butadiene rubber could be used as main matrix for nanocomposites applications. In the literatures, researchers investigated the influence of fillers and additives on the styrene butadiene rubber. In other some works, combination of styrene butadiene rubber with other rubbers could be used for composite and nanocomposites applications. Guo and et. al. worked on the SBR nanocomposites with nanotubes and with presence of methacrylic acid [4]. Gu and coworkers combined styrene butadiene rubber with natural rubber to form main matrix for nanocomposites preparation [5]. They used organo bentonite on the SBR/NR based nanocomposites and reported that the nano bentonite improved mechanical properties of rubbers. Melt mixing has been recognized for its flexibility and proper to use especially for industrial applications. For styrene butadiene rubber based nanocomposites, melt mixing could be one of the main routes for preparing the nanocomposites. Lai and coworkers prepared nanocomposites based styrene butadiene rubber by melt mixing [6]. They mixed their materials with batch mixer. For enhancing the properties, they used from clay nanoplatelets with this mixing method. Mohan and coworkers used banbury mixer for preparation styrene butadiene rubber and natural rubber compounds for assaying mechanical properties [7]. In this work, we use from two roll mills for mixing styrene butadiene rubber with nano iron oxide to prepare nanocomposites. Some researchers used nano particles or nano platelets for enhancing properties of SBR based nanocomposites. Some researchers used nano clay for enhancing SBR based nanocomposites properties [8-10]. In these papers, characterization of nanoclay/SBR nanocomposites especially mechanical properties has been investigated. Moreover, some other researchers investigated the nano particles like silica nano fillers and nano CaCO3 on the physical and mechanical properties of styrene butadiene rubber based nanocomposites [11-12]. But please note that the usage of nano copper oxide have less been investigated by previous researchers in the literature and very rare works have been dedicated to systematically investigation of the physical and mechanical properties of the SBR based nanocomposite materials. Hence, in this research paper the effect of nano copper oxide on the curing and swelling properties of styrene butadiene rubber nanocomposites have been investigated systematically

by the authors. The obtained test results are discussed in detail in the following parts of the present study.

2. Experiments

2.1.Materials

The SBR as main matrix of nanocomposites is SBR 1502 which purchased from Jilin Rubber Co. Ltd. China. Styrene content is 22.5% and Rubber Mooney viscosity ML(1+4)100°C.

Curing system was used Sulfur, Zinc Oxide, stearic acid as accelerator activator and MBT as accelerator. The curing system was kindly prepared by local company.

Nano iron oxide was supplied from nanophase Technologies Corporation with mean particle size of 30 nm and specific surface area 38 m2/g. The shape of nano iron oxide particles is spherical and their density and purity is 5.2 g/cm3 and 99% respectively. Industrial acetone and toluene solvent have been used for performing the extraction and swelling tests.

2.2. Sample preparation

For styrene butadiene rubber based nanocomposites, the melt mixing processing could be one of the main routes for preparing the nanocomposites. In preparation of rubber materials like styrene butadiene rubber, the first stage is mastication. Rubbers like styrene butadiene rubber have high viscosity which caused difficult conditions for sample compounding. For decrease the long of chains of polymer in rubber materials, the mastication process should be done for good preparation of samples.

Hence, in rubber compounding, first SBR was masticated by two roll mills. For this purpose, SBR was entered in to the two roll mills mixer over and aver. This process caused more shear stress on the SBR chains and resulted to decreasing of molecular weight of SBR compounds. Mastication stage was done for about 5 minutes.

After softening of SBR, nano iron oxide powders were gradually added to SBR paste. After that curing system was added to compound. Before adding of curing system to rubber paste, the components of curing system were mixed accurately.

After finishing the incorporation stage, the paste past for about 10 minutes thought the two roll mills for better distribution of nano copper oxide at styrene butadiene rubber matrix. The resultant sample was prepared for curing stage. The cure temperature is 145°C.

After completing the curing cycle of the nanocomposite compound, post curing reaction was done. The formulation of compounds is shown in table 1 based on one hundred parts of SBR.

2.3. Characterization

For investigation on the curing reaction the extraction and swelling tests were carried out. With swelling tests, we could estimate the Mc parameter. Mc is the average molecular weight of rubber chain between two crosslinks.

Moreover, we could calculate the crosslinking density of samples by swelling results. The extraction instruments are including condenser, siphon and flask. The samples were subject to acetone for 3 days for extracting parts of uncured rubber chains. In this research, the percent of extraction could be calculated from equation 1:

$$\%ext = \frac{m_2 - m_1}{m_1} \times 100 \qquad (1)$$

In equation 1, m2 and m1 are the weight before and after the test. Moreover the Mc values could be calculated by Flory-Rhener equation that shown in equation 2:

$$M_c = \frac{\rho_E V_s \left(\frac{V_E}{2} - V_E^{1/3} \right)}{Ln(1 - V_E) + V_E + \chi V_E^2} \qquad (2)$$

In equation 2, ρ_E is rubber density, Vs is solvent molar volume, V_E rubber mole fraction in swollen samples and χ is interaction parameter between SBR and toluene which considered 0.38.
More value of M_c shows the high molecular weight between two crosslinks and results in decreasing crosslinking density.

Table 1: Formulation of compounds based on phr of SBR.

Sample code	SBR	Nano-copper oxide	Sulfur	ZnO	Stearic acid	MBT
S	100	0	5	5	2	2
S-1CuO	100	1.5	5	5	2	2
S-2CuO	100	3	5	5	2	2
S-3CuO	100	4.5	5	5	2	2

3. Results and discussion

It is shown in the literature that nano particles of copper oxide influence of rubber curing reaction and increases the time of curing reaction.

The values of torque of curing reaction are also shown in table 1. It could be seen that nano copper oxide caused increase in maximum, minimum and difference of torques. The most torque difference has been occurred in S-1CuO samples with addition of 1.5 phr nano copper oxide.

In this sample, about 8% increase in torque difference was occurred compared to neat sample. It shows that nano copper oxide particles could interact with rubber chains and caused increase in torque difference.

Extraction tests results have been also showed in table 2. As it could be seen about 2 or 3 percent of extraction have been occurred. This low percent of extraction value shows that the curing reaction took place properly. Moreover, with addition of nano copper oxide, the percentage of extraction has not been increased.

Figure 1, shows the Mc values versus the nano copper oxide contents. It could be seen with addition of nano copper oxide, Mc values were increased compared to neat sample. It showed that presence of nano copper oxide caused increasing in average molecular weight between crosslinks.

Increase in Mc values is equivalent of decrease in crosslinking density. Addition of nano copper oxide to SBR samples caused to decrease in crosslinking density.

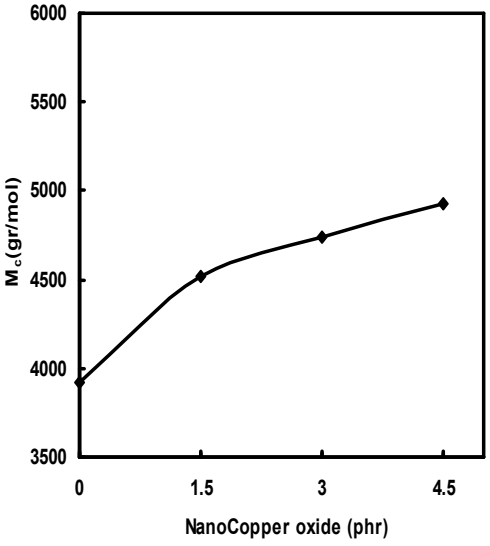

Fig. 1. M_c values versus nano copper oxide content for SBR/CuO nanocomposites.

4. Conclusions

The preparation of styrene butadiene rubber/nano copper oxide nanocomposites has been carried out by melt mixing. For this purpose, laboratory two roll mills were used and the samples were prepared properly. The results of rheometric rubber curing showed that with addition of nano copper oxide the scorch and times of 50% and 90% curing reaction have been increased. Moreover, rubber curing rheometric results showed that with addition of nano copper oxide the torque difference of samples have been increased. The most enhancements in torque difference of samples have been occurred in S-1CuO sample with 1.5 phr nano copper oxide. Moreover, extraction percent showed low content and indicated that the curing reaction done to some extent completely. The swelling results showed that with addition of nano copper oxide the Mc values have been increased. Increase in Mc indicates the reduction in crosslinking density with presence of nano copper oxide.

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Acknowledgement
Authors are thankful to Mr Eslami for their technical help on the manuscript.

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12/12/2013