Synthesis and characterization of in-situ precipitated silica filled rubber composite

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Introduction

In-situ precipitated silica can be used to replace carbon black partly in tires as well as in other rubber materials to increase strength, to reduce rolling resistance and heat build-up and hence to bring down the fuel consumption in tires. There have been numerous efforts to improve silica dispersion in conventional rubber/silica composites such as varying the chemistry and content of the coupling agents (Bokobza, 2006), improving the mixer rotor design (Miloskovska *et al*., 2012), ultrasound pre-treatment of the silica particles (Prasertsri *et al*., 2011), but dispersion still remains a serious issue for conventional rubber/silica composites.

The current research was carried out to enhance the properties of rubber such as tensile strength, swelling properties, hardness, water absorption properties and density using in situ precipitated silica. A relatively high cost method for reinforcing natural rubber (NR) using in-situ precipitated silica by swelling method has been reported previously (Murakami *et al*., 2000). The present work aims to prepare in-situ precipitated silica filled rubber composites with a better in-situ silica dispersion within rubber matrix than conventional silica composites using a low cost method (using solvent combination) of sol-gel technique.

Methodology

Sample was compounded according to the tire tread formulation (Murakami *et al*., 2000). The resulting sample was half cured and was cut in to five pieces (15 cm × 5 cm). Using a swelling test, the best solvent combination of Toluene:T-butylalcohol was found to be 70:30 volume ratio. Four half-cured samples were soaked for different times in a solution containing the best solvent and Tetraethylorthosilicate (TEOS). Next they were soaked in 10% aqueous .n-butylamine for two days and the samples were dried. Finally, the remaining half of the curing process was carried out and in-situ silica percentage in each sample was calculated. Using the same procedure, four more samples were prepared by gradually increasing the in situ silica percentage by weight. A sample without in-situ precipitated silica was used as the reference. Mechanical properties of the samples such as tensile strength, modulus, tensile strain at break and hardness were determined. Finally, samples were characterized for its density, swelling in toluene and water absorption.

Results and Discussion

Results of swelling analysis are graphically represented in Figure 01. In principle, the presence of inorganic filler should lead to a reduction of the swelling ratio with respect to the unfilled vulcanized rubber, since the filler does not absorb the solvents during the experiment. In the present case an opposite trend is observed. Results show that the swelling ratio is increased with increasing silica percentage thus decreasing the cross linking density of the rubber matrix (Kapgate *et al*., 2012). This clearly indicates an interfering effect of the sol–gel reaction of TEOS to silica on the vulcanization

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process of the rubber (Morselli *et al.*, 2013) and the extent of the cross linking of the natural rubber phase was limited.

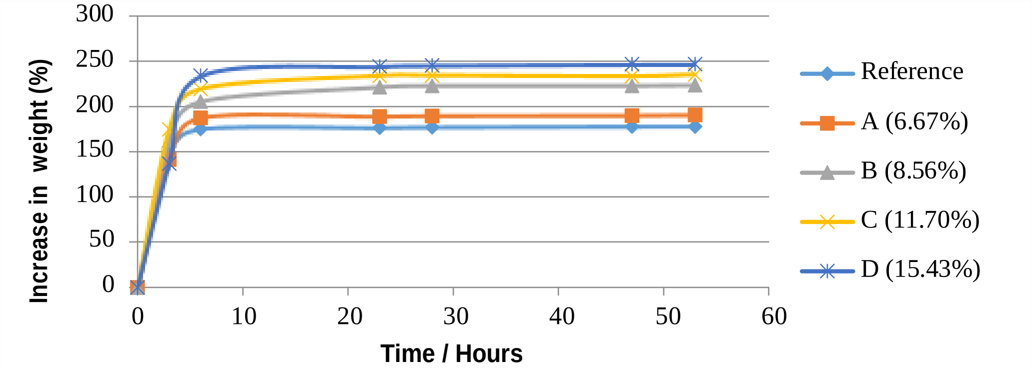

Figure 01: Variation of increase in weight percentage with time for in-situ silica composite samples with varying amount of in-situ silica filler percentage

The variation of tensile strain at break of the samples is graphically represented in Figure 02. According to the Figure 02, maximum value for tensile strain at break is observed for the sample A (6.67%). Reason for this may be a result of a complex balance between the increasing content of rigid filler (introducing additional cross links) and the decreasing cross linking density of the rubber matrix. At lower silica percentages the silica filler aggregates into chair like structures producing a greater stiffening which gives additional cross links into the network by filler (Morselli *et al.*, 2013).

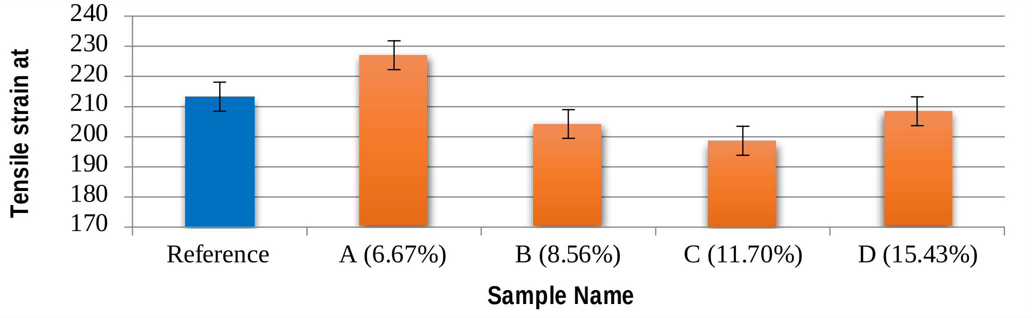

Figure 02: Variation of Tensile Strain at break with varying amount of silica filler percentage

At lower content of silica, the dispersion is better than at higher content of silica (Miloskovska *et al.*, 2012). Therefore tensile strain at break of sample A (6.67%) is higher compared to those of other samples. However, when silica percentage is increased, the silica tends to form agglomerates (Miloskovska *et al.*, 2012) and the interfering effect for vulcanization due to silica could not be balanced. Therefore, tensile strain at break of sample B (8.56%) and sample C (11.70%) are getting lower. At higher in-situ silica concentrations (more than 15% of in-situ silica) bridging gel structures between silica particles can be formed (Morselli *et al.*, 2013). It could provide a positive influence to increase tensile strain at break of sample D (15.43%) slightly higher than those of samples B (8.56%) and C (11.70%), though there are lot of agglomerates in sample D (15.43%).

As expected, the density is increasing with in-situ precipitated silica percentage. When filler is added to natural rubber matrix, mass per unit volume (density) is increasing.

Tensile strength, modulus, hardness properties of the samples are decreased with increasing in-situ silica percentage. This may be due to the interfering effect of silica on vulcanization.

Water absorption properties of rubber composites are increased with in-situ precipitated silica. One reason for the observed increase in water absorption could be due to the decrease in cross linking degree of the rubber matrix and the other reason could be due to the water absorption of silica (Bokobza, 2006).

Conclusions

According to the results, it seems that there is an interfering effect by in-situ generated silica on the vulcanization process. Silica particles generated before the full vulcanization of rubber may hinder the cross-linking reaction of the rubber compound by sulfur. Therefore in-situ generated silica reduce the cross linking density of the rubber matrix.

According to the results it is possible to conclude that in-situ generation of silica should do after the complete vulcanization of natural rubber or by simultaneous curing and filling with the presence of a suitable coupling agent (for example: (bis (3-triethoxysilylpropyl) tetrasulfide) for the enhancement of filler-matrix adhesion (Miloskovska *et al*., 2012). Thus the mechanical properties will be increased due to strong filler-filler interactions and filler-matrix interactions in the absence of possible interfering effect due to silica on vulcanization process.

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