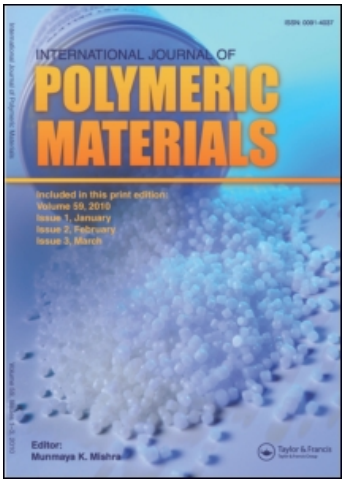

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Tannin-Treated Water for use in the Emulsion Polymerization of SBR. Effect of Ageing on Mechanical Properties

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The water used as the reaction medium in the emulsion polymerization of SBR was treated with a tannin-based derivative. The rubbers obtained were compounded and compared with a reference composition prepared with a rubber polymerized in water treated according to the conventional aluminum sulfate method. Mechanical properties, before and after ageing, were evaluated and were found to be of comparable magnitude, as long as no excess tannin is present in the emulsion reaction medium.

Keywords: ageing, emulsion SBR, mechanical properties, rubber compounding

INTRODUCTION

Unsaturated rubbers are always sensitive to thermo-oxidative degradation. The most remarkable example is natural rubber that degrades extensively if not protected conveniently. The ageing process can be

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slowed down by adding to the rubber composition antidegradant additives to combat the more common causes of degradation, that is, oxidation and ozone attacks [1]. For synthetic rubbers, particularly in the case of SBR produced by emulsion polymerization, a general procedure is to run the polymerization reaction in the presence of small amounts of an antioxidant to help prevent premature oxidation.

In emulsion polymerizations, the dispersing medium is usually water, in which various chemical components are dispersed. The most important property of an emulsion is its stability, which can be affected by a number of factors such as the presence of electrolytes, degree of stirring, temperature, and addition of organic solvents. The reaction is usually carried out in demineralized water, as the presence of extraneous ions can interfere with both the initiation process and the action of the emulsifier [2].

In a previous work [3] an alternative treatment for the water to be the emulsion medium in the SBR production was reported. It was found that the use of commercial tannin, a biodegradable material coming from vegetal source, provided water that, after being used in the SBR emulsion polymerization, gave rise to rubbers of characteristics comparable to those produced in water treated by the conventional aluminum sulfate method.

However, a careful evaluation must be carried out before modifying the conventional, well-established water treatment by adopting a new one, even when this replacement goes to meet environmental concerns and brings advantages coming from the use of naturally occurring materials. As SBR is the synthetic elastomer most used worldwide, any change in the properties of the water used as the reaction medium can introduce undesirable variations in the rubber produced.

This work evaluated the use of tannins in the treatment of the water used in the emulsion polymerization of styrene and butadiene to produce styrene-butadiene rubber. The compounded rubber was tested for mechanical properties before and after ageing.

EXPERIMENTAL

Water was submitted to different flocculation processes, the conventional one with aluminum sulfate and a new one with Tanfloc, a commercial tannin-based product, as described elsewhere [3]. Four water samples were used in the polymerizations. Reaction 1 (Reference) used water treated with aluminum sulfate, as in the conventional way. In reaction 2 (Tann0), the water was treated with tannin. After the treatment, the residual tannin in the water was found to be 0.036 mg/L. In reactions 3 (Tann1) and 4 (Tann3) the waters used were also treated

with tannin but, after the treatment, additional amounts (1 and 3 ppm, respectively) of tannin were introduced, to investigate the effect of higher contents of residual tannin on the properties. After coagulation of the latexes, the rubber samples produced in the different waters were compounded according to the following formulation (in phr): SBR (100.0); zinc oxide (3.0); sulfur (1.75); stearic acid (1.0), carbon black (50.0); N-tert-butyl-2-benzothiazol sulfenamide, TBBS (1.0). Mixing was carried out in a two-roll mill, according to ASTM D 3185, and the compounded mixes were submitted to rheometry analysis on a Monsanto oscillating disk rheometer, model 1005, according to ASTM D 2084. Mooney viscosity was measured before and after compounding.

After vulcanization, specimens were cut to be tested for hardness (ASTM D 2240), modulus, stress strength, and strain at break (ASTM D 412).

Ageing was performed at 70°C for 70 h, in an air circulating oven.

RESULTS AND DISCUSSION

Figure 1 shows data of Mooney viscosity, weight average molecular weight, and polydispersion.

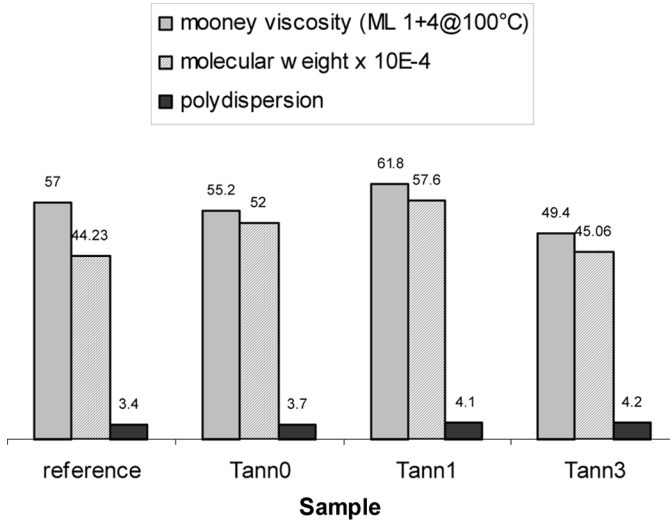

FIGURE 1 Results of mooney viscosity, weight average molecular weight, and polydispersion of SBR samples.

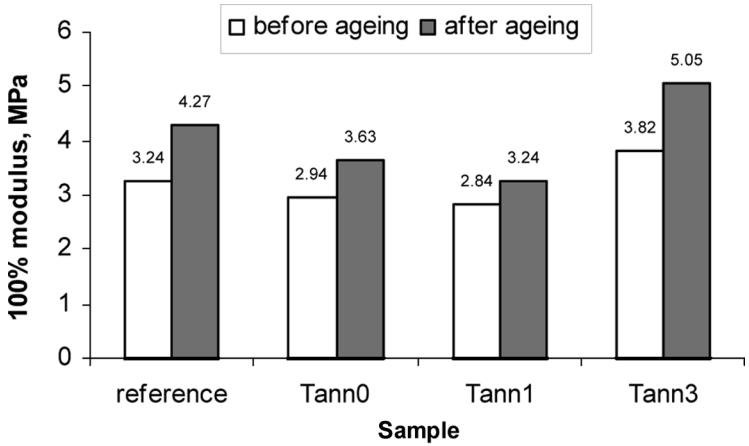

FIGURE 2 Ageing effect on 100% modulus of compounded SBR.

It can be seen that a small excess of tannin, as in sample Tann1, leads to a high value of viscosity. However, a further increment results in a significant decay of this property to a value inferior to that for the reference sample. The molecular weight follows the same tendency with a difference that, now, the result for sample Tann3 is slightly higher than that for the reference, which turned out to be the sample presenting the lowest molecular weight. However, the higher viscosity of this last sample, as compared with Tann3, can be credited to its low polydispersion. These differences tend to vanish upon compounding.

Values of 100%modulus, before and after ageing, are shown in Figure 2.

It can be seen that for samples Tann0 and Tann1 the values of modulus are lower than for the other two samples and the influence of ageing was not so significant. The sample produced in the presence of the largest excess of tannin, Tann3, presented the highest modulii, before and after ageing. It seems that somehow, the residual tannin favors crosslink formation. This is even more evident when the sample is kept under heating for longer periods of time, as during ageing. It is reported in the literature that, on ageing in the presence of oxygen, SBR tends to crosslink rather than exhibit chain scission as compared to natural rubber [1]. These results agree with data from hardness test, shown in Figure 3.

As expected, sample Tann3 showed the highest values of hardness, before and after ageing, corroborating the results of modulus. The other three samples gave comparable results.

Elongation at break can be seen in Figure 4.

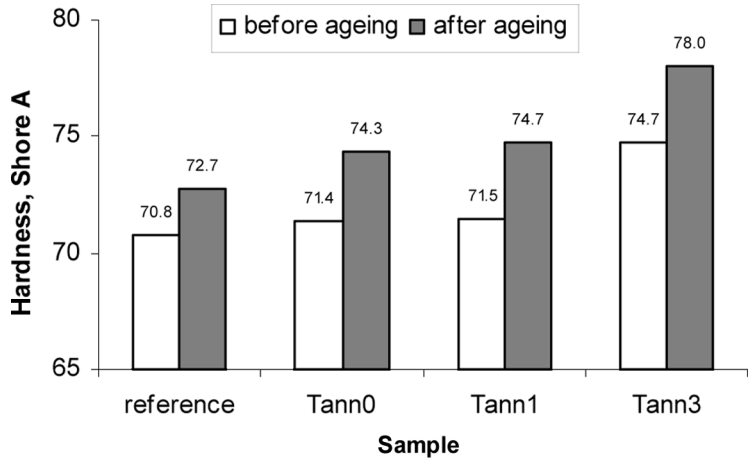

FIGURE 3 Influence of ageing on hardness of compounded SBR.

As shown in Figure 4, samples Tann0, Tann1, and the reference presented the same value of elongation before ageing, whereas for Tann3 the deformation ability was a little smaller. On ageing, Tann0 and Tann1 showed better retention of this property, as compared with the reference sample but Tann3 underwent a little more significant negative effect. This is in good agreement with the results of modulus and hardness.

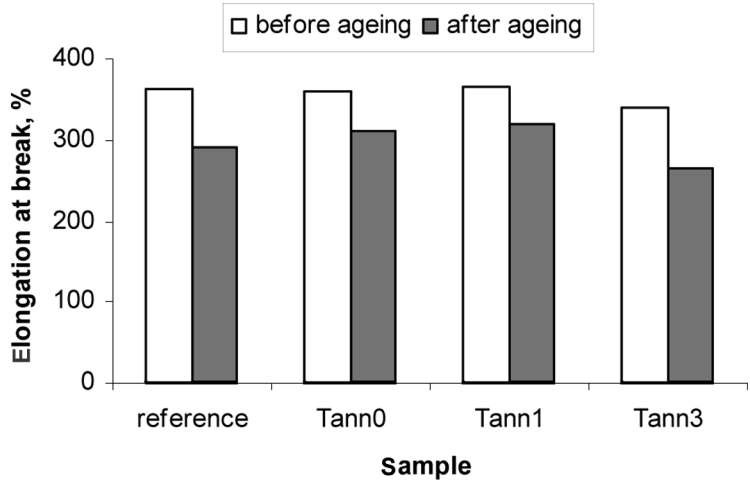

FIGURE 4 Effect of ageing on elongation at break of SBR compounds.

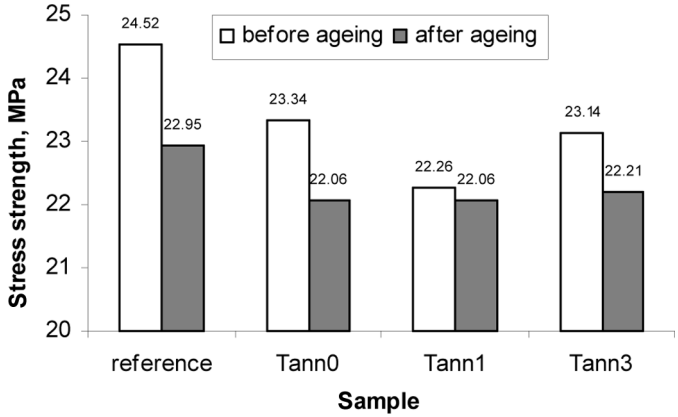

FIGURE 5 Effect of ageing on stress strength of SBR compounds.

Figure 5 presents data of stress strength. It can be seen that the results given by the samples prepared with the tannin-treated water were only slightly lower than the value for the reference sample. Nevertheless, the compositions prepared with those samples allowed better property retention.

CONCLUSION

The results of mechanical properties indicate that the tannin treatment of the water used as the reaction medium in the emulsion polymerization of SBR can be considered as an alternative environmentally more acceptable than the conventional aluminum sulfate method. After compounding the samples obtained in water treated both ways, in the presence or not of residual tannin, it was found that data of mechanical properties were comparable, except in the case of the highest amount of residual tannin.

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