



Strain Dependency Behavior of SBR Compounds Filled with Different Nano Particles



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Submission: 📅 October 05, 2018; Published: 📅 October 10, 2018

Abstract

In this work, the nonlinearity responses of SBR 1500 compounds having black (N550) and clay (cloisite 10A) nano particles were studied. As expected, complex viscosity (η^*) of filled SBR 1500 was higher than unfilled SBR; higher loading, larger η^* . The strain dependency in complex viscosity was indicated as the critical strain, which was affected by nano particles type and content. In the presence of both black and nano clay, the nonlinearity zone of strain shifted to the lower strain especially at higher filler content. While black is more effective than nano clay on the nonlinearity phenomenon due to high loading and large black networks, which are highly sensitive to the applied strain. In addition, the elasticity response was investigated considering damping factor ($\tan \delta$). In the presence of nano clay, lower $\tan \delta$ was observed comparing with unfilled SBR, hence more elasticity. As the clay content increased, more elasticity was achieved because of more interactions between clay particles and rubber chains. However, black had two different effects on $\tan \delta$: at low strains, black caused more elasticity while the reverse trend was recognized at high strains.

Keywords: SBR compound; Nano filler; RPA; Viscoelastic property; Elasticity

Introduction

Many researchers have reported the enhancement of the properties by incorporation of nano fillers into the polymers. Using different types and concentrations of nano fillers, the obtained nanocomposites can exhibit enhanced properties relative to the virgin polymer such as better mechanical properties, lower permeability against the gases, higher heat deflection temperature or higher flame retardancy [1-4]. In addition, concentration and type of fillers affect significantly the viscoelastic behavior of the polymers [5,6]. Normally, filled rubber compounds have an ability to dissipate a main part of the mechanical energy applied during deformation by damping which depends on the formed interactions between rubber and filler. That can be studied performing rheological tests like strain sweep test in dynamic mode. Rubber processing analyzer (RPA) allows testing the strength of the filler networks and the filler-rubber interactions in the green compound as well as in the vulcanizate, in a wide range of shear amplitudes. Using this instrument, the viscoelastic responses of the gum, master and final compound can be detected [7,8]. As a response to increasing strain, rubber compounds show a non-linear viscoelastic behavior, which is detected as a drop in the elastic modulus versus strain [9]. In addition, $\tan \delta$ (G''/G') increases when the strain rises, recognizing that the energy of dynamic deformation is dissipated. Fillers can affect this strain dependent trend in rubber compounds. In this work, attempts have been made to the strain dependency and elasticity of different nano filled compounds. In this way, SBR

compounds having various amounts of clay (cloisite 10A) and black (N550) nano particles were prepared; and the effects of nano fillers type and content on the viscoelastic behavior were studied during the strain sweep tests.

Experimental

Table 1: Materials and formulations of samples.

Material	Content (phr)	Grade	Supplier
SBR	100	SBR-1500	Bandar Imam Petrochemical
Clay	3,6,9	Cloisite 10A	Southern Clay Products, USA
CB	30, 50, 70	N550	Pars Co., Iran
Aro. Oil	10	Behran	Behran

Table 1 depicts some information about the materials used in this study and the formulations of samples. Based on our previous work [10], mixing conditions were selected to ensure the best dispersion of the filler in the SBR matrix. RPA2000 from Alpha technologies Co. (UK) was used to investigate the viscoelastic properties of filled compounds and gum. Strain sweep tests were done using RPA at the temperature of 100 °C and the frequency of 1.68Hz, in the 0.1-100% strain domain. Wide-angle X-ray diffraction (XRD) measurements were done at room temperature on a D5000, Siemens, Germany.

Result and Discussion

Table 2: XRD result.

Nano Amount (phr)	2 θ (°)	d(A)
3	1.3	67.7
6	2.1	42.2
9	2.8	31.1
Pure Nano Clay	4.59	19.2

Table 2 shows XRD results for various nano clay levels. The peak of organoclay at $2\theta=4.59^\circ$ corresponds to 1.952nm inter gallery distance. While in nanocomposites, diffraction peak shifts to the lower 2θ values, because of dispersion process; the peak of organoclay is weaker and the distance between layers is greater. Figure 1 shows the complex viscosity (η^*) of compounds versus the applied strain. As can be seen, samples containing nano fillers have higher viscosity than net SBR. In the presence of filler, the modulus increases and flowability declines so the viscosity increases. With increment in Black amount, η^* rises and the linear zone of the strain domain becomes shorter. By adding 70phr N550, the viscosity growth is 10times larger; and the curve state changes to fully nonlinear form. Higher nano clay content also made an increase in the viscosity, with less effect on the linear zone than Black does. It is interesting that 9phr of nano clay is more effective than 30phr of N550 on the viscosity value; having less disturbing effect on the linear zone.

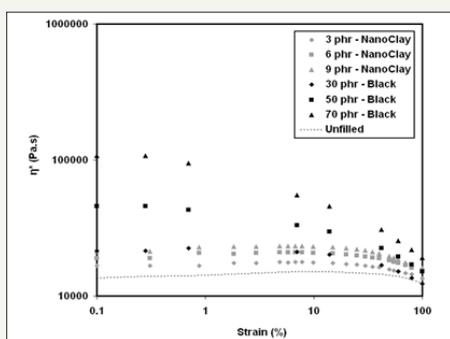


Figure 1: Complex viscosity versus strain for compounds with different nano filler loading.

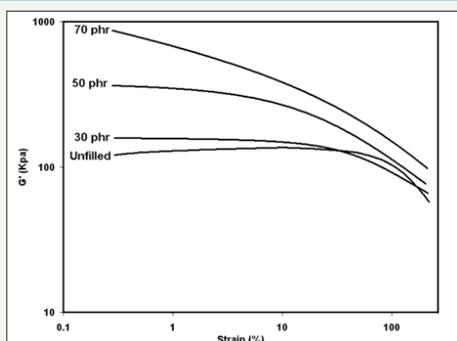


Figure 2: Elastic modulus versus strain for different CB content.

Figure 2 & 3 give the changes in elastic modulus (G') of compounds against the strain. As can be seen in this figure, firstly,

there is a region where the elastic modulus is independent of shear strain, which is named the linear viscoelastic region (LVER). In the lower strains, linear viscoelastic behavior is observed, while in the higher strains, the non-linear viscoelastic behavior is seen. We named the transition strain between linear and on-linear regions, as the critical strain which discussed later. According to Figure 2, as the CB amount increases in compounds, the linear viscoelastic region disappears and the elastic modulus increases. Reduction in the CB particle size has the same effect on the G' curves. Meanwhile, at higher CB loading, G' is more sensitive to the shear strain. The fall of the G' curve after the linear viscoelastic region (LVER) is due to the breakdown of the CB aggregates network, which is known as the Payne effect. The rise in G' with CB loading is for increasing in the effective filler volume fraction (Φ_e), that is the hydrodynamic effect. The trapped rubber chains in the CB network are immobilized and behave as the undeformable parts. The amount of the trapped chains is larger at the higher CB content, thus the G' increases. The figures also express that the strain dependence of G' is more pronounced with increasing the specific surface area especially at low strain amplitude. Because the amount of CB aggregates network is more at greater surface area. In all cases, linear viscoelastic behavior of compounds corresponds to an elastic modulus independent to deformation which can be observed at small amplitudes. Figure 3 gives the changes in elastic modulus (G') of compounds having various nanoclay content against the strain. At higher nano filler loading, G' is more sensitive to the shear strain. The fall of the G' curve after the linear viscoelastic region (LVER) is due to the breakdown of the filler-rubber networks, and the amount of formed networks is more at higher nano clay content. In all cases, linear viscoelastic behaviour of compounds corresponds to an elastic modulus independent to deformation which can be observed at small amplitudes.

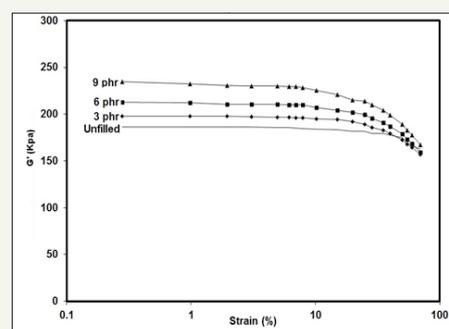


Figure 3: Elastic modulus (G') of compounds having various nanoclay content versus strain.

Viscoelastic behavior of compounds is depended on the inter-molecular bonds of rubber chains and filler particles. Figure 4 illustrates possible filler-rubber interactions for Black and nano clay schematically. Black particles can be found in the Black networks or dispersed Black-rubber bonds. Under the shear forces, breakdown of Black aggregates by applied strain is a viscous response while the stretching of Black-rubber bonds is an elastic response until abrupton at higher strains as a viscous deformation. As seen in Figure 4 nano clay (layered silica) can be dispersed in three different forms of flocculated, intercalated and

exfoliated. In the flocculated form, clay layers aggregates separately from the polymer phase, which happens at insufficient mixing conditions or very high concentration. By applying a suitable shear force, especially at higher temperature, the clay layers spaces far away from together; consequently, the intercalated and exfoliated

form are achieved. In our previous work [11], it was concluded that compounds containing 3, 6 and 9phr nano clay prepared at previously mentioned mixing conditions reach to the desirable intercalated or exfoliated morphology.

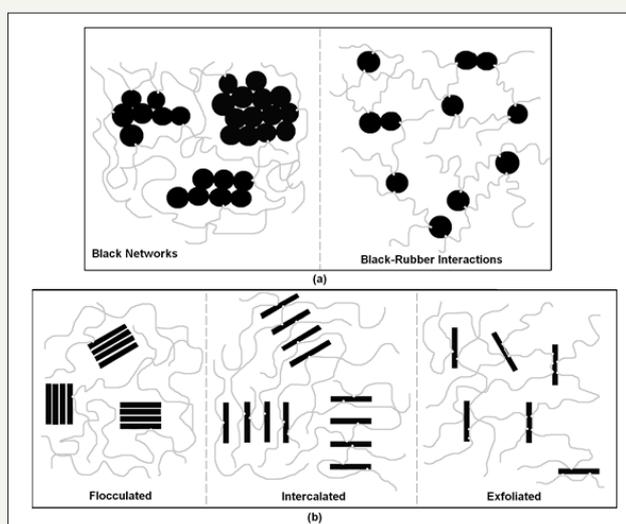


Figure 4: Possible filler-rubber interactions in black (a) and nano clay (b) filled compounds.

The filler-based interactions explained in Figure 4 are responsible for differences in viscoelastic behavior of filled and unfilled rubber. Zero shear rate viscosity (η^*0) is expressed in Figure 5. As discussed before, η^*0 is larger for SBR filled with nano particles increasing with filler amount. It is because of restrictive influence of filler on the flowability of rubber chains. Another parameter obtained from strain sweep test is the strain at which the modulus or viscosity curve is deviated from the linear state, here named as the critical strain. As shown in Figure 6, critical strain is affected meaningfully by the type and loading of nano fillers. With increasing the filler content, the nonlinear region starts from the lower strain. This observation is probably due to filler-based structures, which are sensitive to the applied strain undergoing the nonlinear irreversible breakdown. At higher Black loading, there are more networks to breakdown and the shifting in the critical strain is more obvious. While in nano clay filled compounds, considering to formation only intercalated or exfoliated structures, there is no filler agglomeration to break-down so the linear zone is broader than that of Black filled SBR. The curves of damping factor ($\tan \delta$) versus strain are plotted in Figure 7 for SBR compounds filled with various nano particles. As known, smaller $\tan \delta$ indicated stronger elastic manner so the elasticity of samples can be investigated giving notice to the variations of $\tan \delta$. In the presence of nano clay, lower $\tan \delta$ is observed in comparison with net SBR, hence more elasticity. It is resulted from the elastic stretching of clay-rubber bonds, which enhances the elasticity of the compound. However, Black has two different effects on $\tan \delta$. At lower strains, Black filled SBR exhibits more elastic behavior than SBR gum while at higher strains, reverse trend appears. The elastic stretching of Black-rubber bonds at lower strain make the elasticity to rise; and at higher strains, more

energy is dissipated due to the viscous breakdown of Black based interactions, which increases the elasticity.

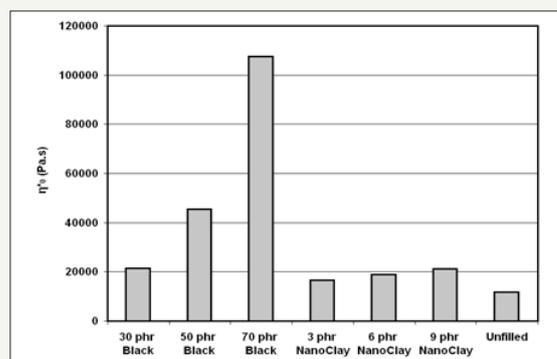


Figure 5: Zero shear rate viscosity (η^*0) of SBR nano-compounds.

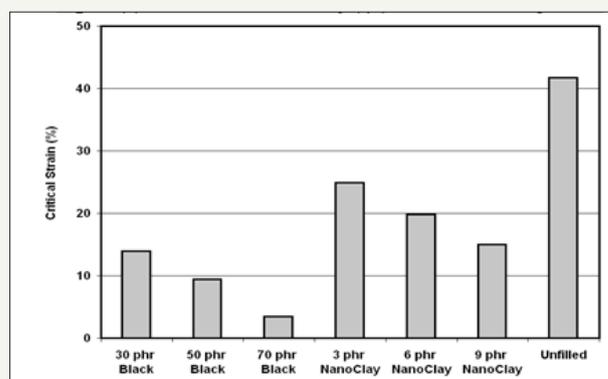


Figure 6: Critical strain of SBR nano-compounds.

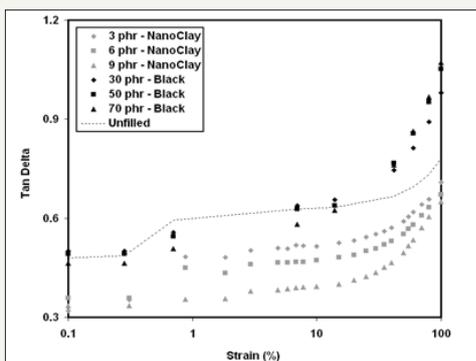


Figure 7: $\tan \delta$ versus strain for compounds with different nano filler loading.

Conclusion

In this work, SBR compounds having various amounts of clay (closite 10A) and black (N550) nano particles were prepared; the effects of nano fillers type and content on the viscoelastic behavior were studied performing the strain sweep tests and the following conclusions were achieved:

A. Complex viscosity of filled SBR was higher than unfilled; higher loading, larger viscosity.

B. The amount of 9phr of nano clay had more increasing effect on the viscosity values than that 30phr of Black did.

C. In the presence of both nano fillers, the critical strain reduced especially in the case of Black.

D. With increasing the filler concentration, the nonlinear region starts from the lower strains.

E. Compounds containing nano clay had more elastic nature than gum.

Black had two different effects on the elastic behavior: at low strains, it caused more elasticity while the reverse trend was recognized at high strains.

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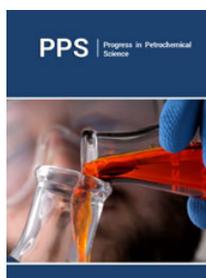
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