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The Effects of Carbon Black-based Interactions on the Linear and Non-linear Viscoelasticity of Uncured and Cured SBR Compounds

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ABSTRACT

The role of carbon black (CB) in the viscoelastic behaviour of rubber compounds was investigated to better understand the reinforcing mechanism. The influence of CB nanoparticles on the strain-dependency and relaxation phenomena of several styrene butadiene rubber (SBR) compounds was evaluated using rubber-process-analyzer (RPA). Rheological results of uncured samples showed that reduced complex modulus with strain strongly depend on CB-rubber interactions. Filled master compounds showed greater modulus compared to raw SBR, which dropped rather abruptly; meaning more noticeable non-linear viscoelastic behaviour. The observed trend of damping factor recognized the linear viscoelastic behaviour for strain <15%, however, at higher strains a large positive deviation was noticed. In the strain region under 15%, CB-filled rubber showed more elastic behaviour than gum; more elastic as the CB loading increased while in the non-linear zone, the reverse trend was observed. Torsion relaxation modulus based on standard linear solid (SLS) model was plotted and found disputable changes regarding to varied factors. Both values of relaxed modulus and the relaxation slope increased as the functions of CB surface area and content, and also the relaxation time (τ) shifted to higher values. In addition, CB affected the cure characteristics and after cure relaxation. In the cured compounds, the slope of relaxed modulus was steeper at starting time (~0.01 s) and less steep at longer time than those of the master compound, reaching a considerable set at the end of relaxation which was dependent on CB level and size.

Key Words:

viscoelasticity;
stress relaxation;
carbon black-filled SBR;
rubber process analyzer;
carbon black-based interactions.

INTRODUCTION

Generally for formulation of the rubber compounds, carbon black (CB) is incorporated in rubber matrix as a reinforcement to modify the mechanical properties of finished product and to control the viscoelastic behaviour of the compound during process, before curing. The addition of CB into the elastomers is a significant commercial importance to improve the technical properties. In the presence of CB, the elastic modulus (G′) of rubber compound increases due to high modulus of CB as a filler and formation of CB-rubber strong interactions. Depending on formulation and compound mixing conditions, CB can be found in different dispersion states, from large agglomerates to small aggregates [1]. Concentration and

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type of CB affect dispersion of CB in the rubber matrix significantly. The status of CB agglomerates and resulting interactions can control the properties and viscoelastic parameters of the compound. The influence of CB on the viscoelasticity [2,3], processability [4] and extrudate swelling [5] of filled elastomers have been investigated. Normally, CB-filled rubber compounds have an ability to dissipate the main part of the mechanical energy applied during deformation by damping which depends on CB-CB and CB-rubber interactions. Damping factor can be studied performing the strain sweep test in dynamic mode. As a response to increasing strain, rubber compounds exhibit a non-linear viscoelastic behaviour named Payne effect [6], which is detected as a drop in elastic modulus versus strain related to the reinforcing effect of CB [7] or the changes in the conditions such as temperature [8]. In addition, tan δ (G''/G') increases when the strain rises, recognizing that the energy of dynamic deformation is dissipated.

At low strains, rubber compounds show linear viscoelastic (LVE) zone. In this zone, the complex modulus has a constant value (G^*_0), which is independent of the strain. Besides, at high strain values, the modulus reaches a minimum amount (G^*_∞). The G^*_∞ of a CB-filled rubber compound remains higher than that of the rubber gum or unfilled compound (G^*_g); because both CB-CB and CB-rubber interactions influence the modulus of compound. These effects are embodied in eqn (1).

$$G^*_\infty = G^*_g f(\Phi) f(I) \tag{1}$$

where Φ is the volume fraction of CB, f(Φ) and f(I) represent the effect of CB particles and CB-rubber interactions on the modulus. Guth and Gold have proposed an expression for f(Φ) assuming a perfect CB-rubber adhesion, as follows [9]:

$$f(\Phi) = 1 + 2.5\Phi_e + 14.1\Phi_e^2 \tag{2}$$

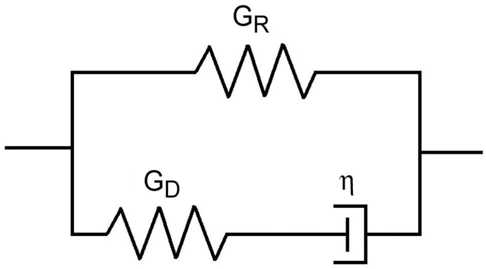
where Φ_e is the effective CB volume fraction.

Before vulcanization, the modulus of rubber compound depends strongly on chain structure, entanglements, CB-rubber and CB-CB interactions while after vulcanization the cross-link's properties (such as density and type of cross-link) are the other main controlling factors. It is well-known that the stress relaxation experiment is one of the important methods to study and compare the viscoelastic properties of compounds, before and after cure. When a fixed strain is applied to a rubber compound, the required stress for maintaining constant strain reduces with time. Before cure, this phenomenon is mainly due to the elastic memory of rubber chains based on two phenomena involving physical entanglements of chains and interaction between CB and rubber matrix. However, after cure the relaxed stress is directly affected by cross-link formation [10].

There are some rubber products like, seals or gaskets used in actual application condition which resembles with that of compression stress relaxation, although generally stress relaxation in torsion mode can be assumed to give a reliable data which are more related to agglomeration of CB and interaction between CB and rubber chains. To predict the stress relaxation in rubber compounds, constitutive models can be taken into consideration [11]. One of them is Zener or SLS model, which is a constitutive model containing a combination of Maxwell element and a spring parallel together, as shown in Scheme I. In this model, the stress-relaxation modulus (G(t)) can be estimated using eqn (3) [11]:

$$G(t) = G_R + G_D(\exp(-t/\tau)) \tag{3}$$

where G_R and G_D are the moduli of the springs and τ is the relaxation time of the model. At t = 0, when no relaxation has been permitted to take place, G is obtained as equal to G_R+G_D and it is represented as G_U; while at the end of test G(t) would be equal to G_R. In this model, τ is estimated from the time at which G(t) = $0.63G_U$ [12]. The stress relaxation phenomenon in rubber compounds has a viscoelastic



Scheme I. Scheme of ″standard linear solid″ (SLS) model.

nature and can be affected by the variables such as CB level and type, for both cured and uncured compounds. However, the viscoelastic behaviour of CB-filled rubber compounds is complicated so the effects of different interactions existing in these compounds on the elastic and viscous responses have not been explicitly explained in the articles. Moreover, there is no specific report on viscoelasticity behaviours of uncured and cured states with variety of CB types and levels, by using the rheological tests. An applicable instrument especially designed for rheometric testing of rubber compounds is rubber process analyzer (RPA). By using RPA, cure properties and the viscoelastic responses of the gum, master and final compound can be detected [13,14]. In our previous work, RPA was used to investigate the mixing quality of rubber compounds comparing the torque of RPA and internal mixer [15]. In other research works, we evaluated the effects of curing system [16] and CB [17] on the cure characteristics of SBR compounds. Also, we have briefly studied some of viscoelastic properties of uncured compounds [17]. The novelty of this work is to investigate the important rheological properties of CB-filled SBR, before and after cure, with special emphasis to structural bonds between the CB and polymer chains to propose schematic details on the nature of these bonds. The elastic and viscous responses of compounds were analyzed by tracing the viscoelactic trends and considering CB-based interactions, which can be responsible for the rheological bahaviour. At first, the influence of CB on linear/non-linear transition in the viscoelasticity has been studied. In the next step, the viscoelasticity was compared for both uncured and cured states by paying attention to the results obtained from the stress relaxation measurements. In this regard, different compounds based on SBR were prepared containing three levels and two types of CB, and viscoelastic parameters were studied using RPA. The effect of the amount and type of CB on the strain dependency of complex modulus and damping factor was investigated. Also, torsion relaxation modulus of compounds before cure was analyzed considering SLS model and the regression curves. In addition, the cure characteristics and relaxation after cure were examined for filled compounds having different levels and CB particle sizes.

EXPERIMENTAL

Materials and Formulation

Two different grades of SBR (1502 and 1712), containing 22.5-24.5% styrene, were supplied by Bandar Imam Petrochemical Co. (Iran). SBR 1712 contained 25.5-28.5 wt% oil so the Mooney viscosities of 1712 and 1502 grades were 42-52 and 46-58, respectively. Compounds were formulated with variety of SBR types, CB particle sizes and loadings, as shown in Table 1. Ingredients including CB,

Table 1. Samples formulations.

Ingredients		Concentration (phr)	Supplier Co.
SBR	1502 1712	100	Bandar Imam Petrochemical Co., Iran
CB	N330[a] N550[b]	30, 50, 70	Pars Co., Iran
Aromatic oil		10.00	Behran Co., Iran
Zinc oxide		3.00	Rangineh Pars, Iran
Stearic acid		1.50	Unichema International
2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ)		1.00	Bayer, Germany
N-Tert-butyl-2-benzothiazolesulphenamide (TBBS)		1.25	Bayer, Germany
Sulphur		2.00	Rangineh Pars, Iran

(a) N330: High abrasion furnace (HAF), average particle size = 30 nm, specific area = 80 m^2/g; (b) N550: fast extruding furnace (FEF), average particle size = 50 nm, specific area = 50 m^2/g. (From ASTM D1765- Standard classification system for carbon blacks used in rubber products).

aromatic oil, ZnO, stearic acid, TMQ, TBBS and sulphur were provided by the companies listed in this table.

Mixing Procedure

Gum of SBR 1502 (or SBR 1712) with all ingredients (except curing system) were mixed uniformly for 15 min using a 200L Polymix two-roll mill (Schwabenthan Co., Germany) at room temperature with a rotor speed of 15 rpm. Then the mixture was placed under room condition for 24 h. Then, the curing agents (TBBS and sulphur) were added to the master on the two-roll mill to prepare the final compound. At the end, samples were made into sheets using the mill and kept at room temperature for 24 h before testing to relax the shear stresses due to mixing.

Analyses

RPA allows testing the strength of the CB network and the CB-rubber interactions in the green compound as well as in the vulcanizate, in a wide range of shear amplitudes. Figure 1 shows RPA cavity which is closed under pressure (4 MPa) during test to reduce wall slip and to give a perfect sample loading. The values of α and R of RPA cone are equal to 0.125 rad and 20.6 mm, respectively. The lower cone is moved with the rotational angular θ which induces the shear strain. In this instrument, a transducer at the upper cone measures the torque transmitted through the sample from the lower cone.

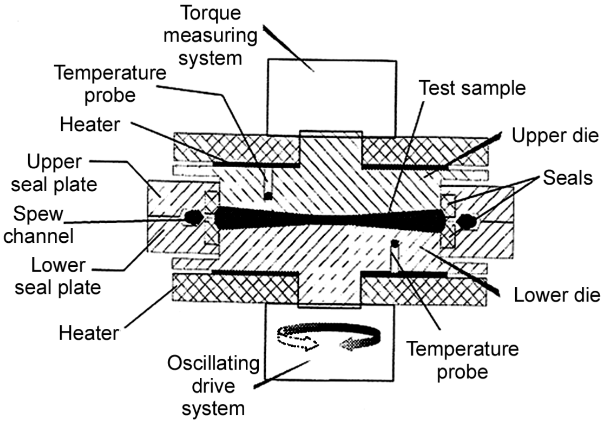


Figure 1. The cavity of rubber process analyzer (RPA).

Here, RPA2000 from Alpha Technologies Co. (UK) was used to investigate the viscoelastic properties of the gum, master and final compounds. Strain sweep, before cure and after cure relaxation tests were done using RPA under definite conditions according to Table 2. A disk shape sample (~5 cm^3) was placed into the gap between the plates. During the test, the lower plate was oscillated sinusoidally in the dynamic mode and twisted in the torsion mode.

RESULTS AND DISCUSSION

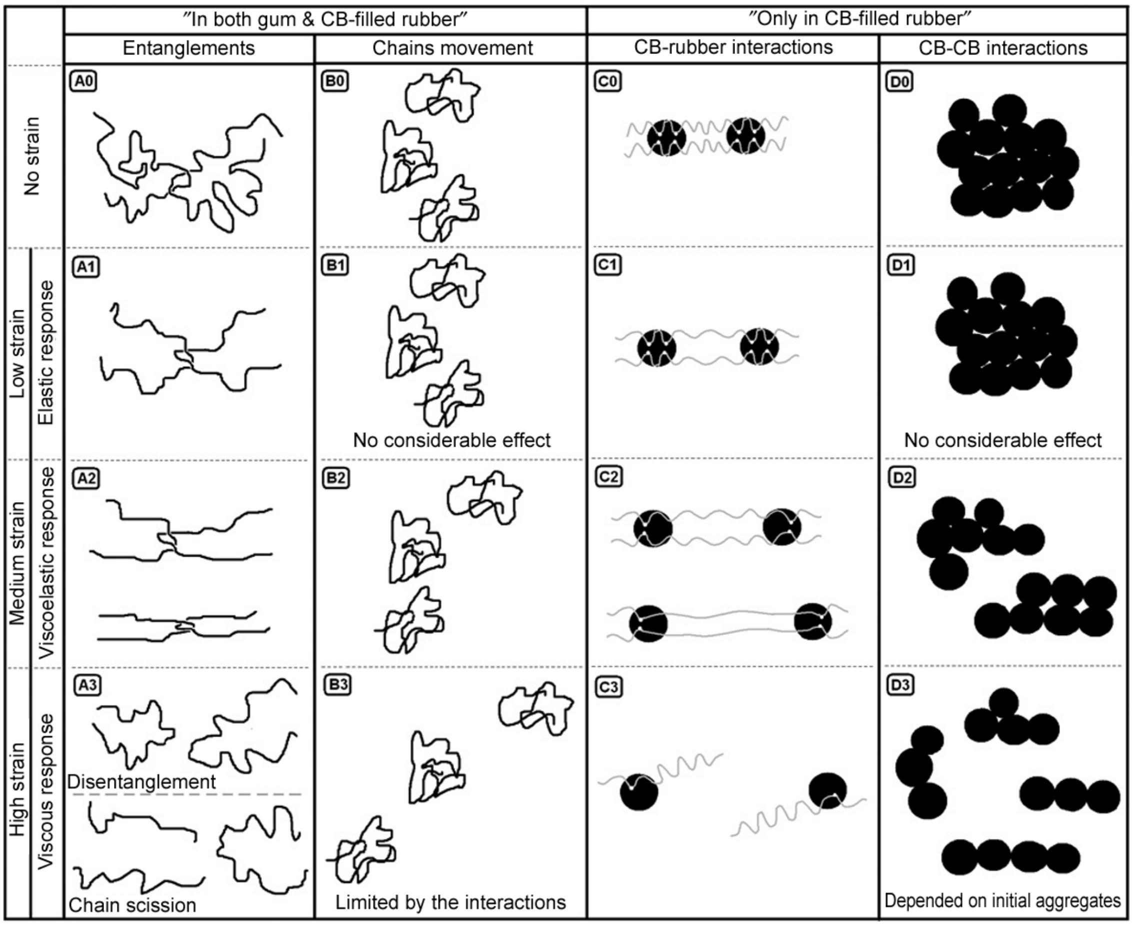
Strain Sweep Test

The variation in the viscoelastic properties versus strain for a rubber compound can be investigated by performing strain sweep test. To study in detail, the strain region can be divided to three steps: low, medium and high strains. Let us give a schematical view of various kinds of possible segmental motions at different strains for CB-filled and unfilled rubber

Table 2. Performed tests conditions.

Condition Test	Temperature (°C)		Strain (%)	Frequency (Hz)
Strain sweep	100		Range: 0.1-100	1.68
Relaxation before cure	50		14	Torsion mode
Relaxation after cure*	Cure	150	7	1.68
	Timed	50	7	1.68
	Relaxation	50	14	Torsion mode

*This test is performed at three stages: at first the rubber compound was cured at 150°C, then cooled to 50°C and timed for 4 min, and then relaxation test was done with the same conditions as the master compound.



Scheme II. Possible responses at various strain regions, for gum and CB-filled rubber.

in Scheme II. As illustrated, at zero strain there is not any deformation in SBR rubber gum as well as the compound. After applying a low strain, both the gum and compound lie in the elastic region which means that the reversible deformations take place: stretching of entanglements (A1) and bridged rubber chains between the CB particles (C1). Afterwards, with increasing the strain to a medium level, other variations occur in the sample and some viscoelastic responses are observed. In this region, the modulus is time dependent which is related to either reversible responses with time (stretching of entanglements and CB-rubber bonds: A2 and C2) or irreversible responses (chain movements and CB-CB breakdown: B2 and D2). All the motions comprising CB-CB breakdown, chain slippage and chain stretching happen simultaneously. As a consequence, the modulus drops gradually at medium strains, described as Payne effect. Later on, the last region of high strain, where only the irreversible viscous responses occur, involve disentanglement or chains scission (A3), chain slippage (B3), CB-rubber disturbing (C3) and CB-CB breakdown (D3). In this region, the resistance to deformation reaches its minimum level, and so does the modulus. In a word, both CB-rubber interactions (column A) and CB networks (column C) play the important roles in the viscoelastic behaviour of rubber compounds in the dynamic mode [18]. These two effective factors on the viscoelastic behaviour can overlap and may not be easily separated. They may be attributed to two incidents: breakdown of CB-CB interparticle bonds, stretching and finally the rupture of associations between CB and rubber chains.

The observed responses and obtained modulus can be affected by different formulating factors especially filler-based interactions. Influence of CB type and content on the complex modulus (G^*)-strain

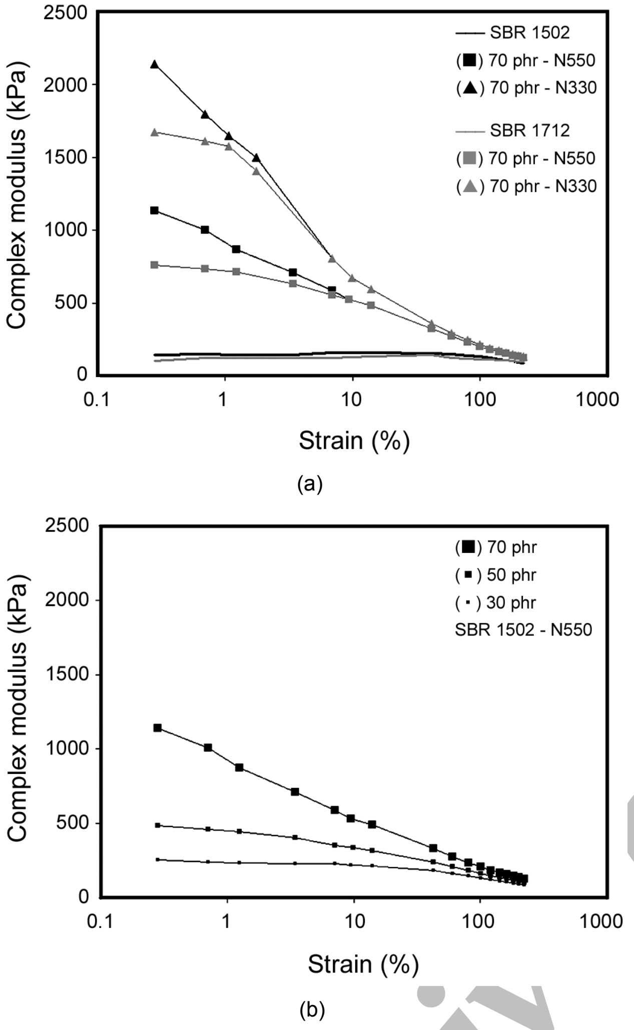


Figure 2. The complex modulus versus strain: (a) effect of CB and SBR type and (b) effect of CB loading.

curves for the master compounds based on SBR 1502 and 1712 as shown in Figures 2a and 2b. As can be seen in Figure 2a, the gums of SBR do not show any indication of non-linearity in the curve because the unfilled rubber is free of CB bonds and dependent only on the entanglements stretching and chain movements, the weaker links against force compared with CB associations. It is realized that at low strains, the main influential phenomena on the modulus of filled-SBR are the CB-rubber and CB-CB interactions. Master compounds containing CB have greater G^*_0 compared to gum itself, which falls rather abruptly; due to increasing CB-based interactions. Although the presence of CB data to higher G^*_0, both CB-CB breakdown and CB-rubber disturbance take place by increasing the strain, so the modulus decreases more rapidly, and finally all curves converge and reach to an approximately equal amount of G^*_∞. In other words, filled rubber shows more obvious non-linear viscoelastic behaviour, and subsequently higher G^*_0-G^*_∞.

Figure 2a also indicates higher modulus with lowering CB particle size (at 70 phr constant level). This phenomenon is maybe due to more interactions in N330 particles with greater surface area, especially at low and medium strains. Moreover, compounds based on SBR 1712 show more linearity at the strains under 10%; where above this point, SBR type does not have any considerable effect. As it is observed in this figure the extending oil in SBR 1712 plays a lubricating role and facilitates the moving of rubber chains, therefore the complex modulus of SBR 1712 is lower than SBR 1502. It is possibly because of trapped oil in the rubber chains of SBR 1712 which lowers the modulus and also leads to more chain slippage and less stretching in entanglements.

The effect of CB level on strain sweep results for type N550 is illustrated in Figure 2b. According to Scheme II, at higher CB content, the Payne-effect is more obvious due to greater possibility in CB-CB and CB-rubber interactions. As expected, samples with higher filler content have higher G^* while the curves are steeper. In these compounds, CB acts as a modulus increaser; at the same time, more active area is available for more interactions, so more CB-CB and CB-rubber bonds are exposed to deformation. Consequently, G^* drops more rapidly.

Figure 3 shows the variation of damping factor (tan δ) versus the strain, divided to two domains of linear (LVE) and non-linear (NLVE). For these compounds based on SBR 1502, the linear visco-elastic zone is found lower than strain of 15%, corresponding to the elastic and linear viscoelastic regions in Scheme II. The bulk elasticity of rubber compounds increases with increased carbon black loading. The result can be explained considering the dilution effect: the amount of the deformable rubber chains is diluted by the non-deforming rigid particles of CB, especially at high CB loadings [3]. As described earlier, the elastic responses are replaced with the viscoelastic and viscous responses as the strain increases. In LVE zone, lower tan δ or greater elasticity is observed with increasing Φ and

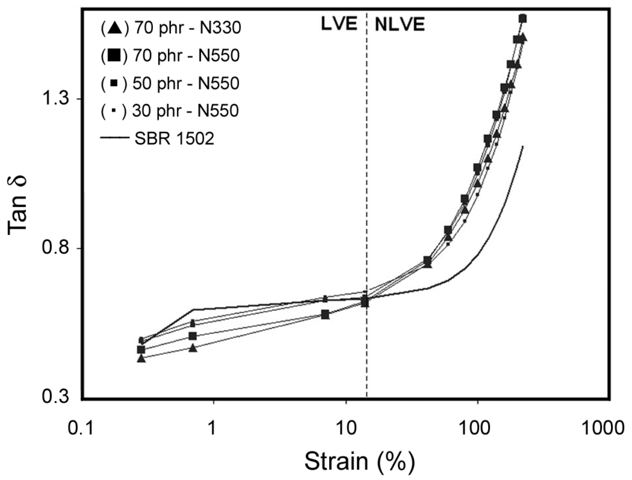


Figure 3. Tan δ versus strain: effects of CB particle size and loading.

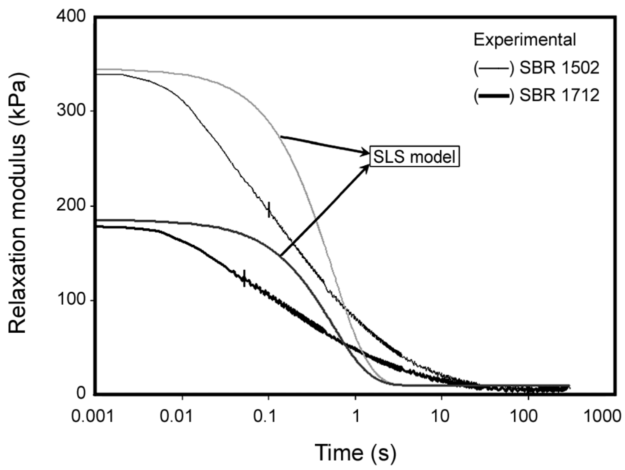


Figure 4. Relaxation modulus versus time, for SBR 1502 and SBR 1712 gums.

decreasing particle size of CB. As demonstrated above, the elastic behaviour of SBR gum is based only on the entanglements stretching whereas for filled compounds, it is related to both entanglements and CB-rubber stretching. So, in this zone (<15% strain), the CB-containing rubber has more elastic behaviour than gum (lower tan δ); more and more elastic as the CB loading increases.

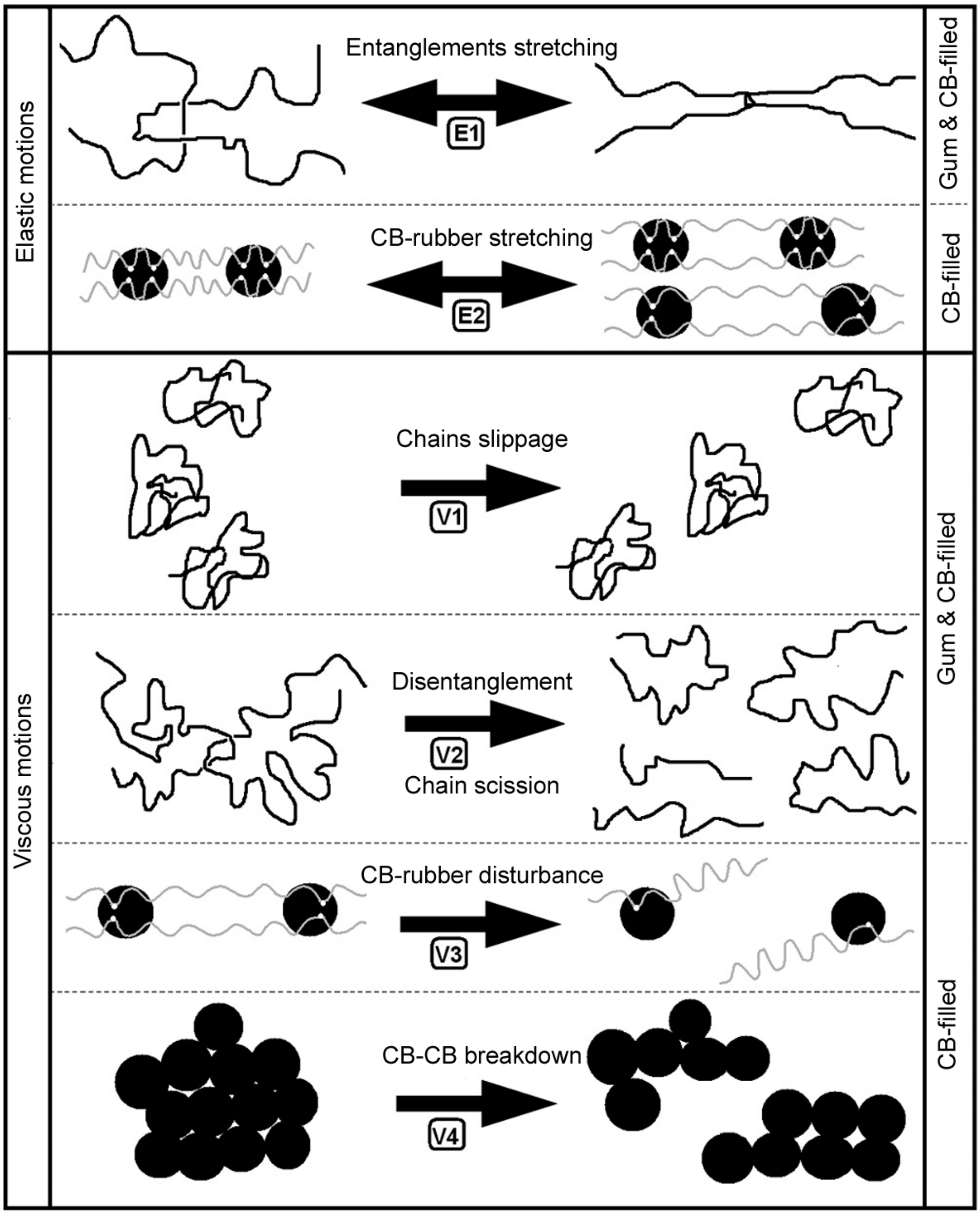
As can be seen in Figure 3, tan δ grows with strain at NLVE zone. The positive deviation in tan δ at high strains is due to more energy dissipation in the rubber compound through dissipating phenomena: CB bonds breakdown and rubber chains slippage or disentanglement (Scheme II). In unfilled compounds without any CB-CB and CB-rubber interactions, only the disentanglement (A3) and chains slippage (B3) can be considered as the source of damping while in CB-filled compounds, CB-rubber disturbance (C3) and CB-CB breakdown (D3) are additionally responsible. Therefore, in the presence of CB, non-linearity occurs sooner and the increment in damping is significantly greater than that of the SBR gum.

Torsion Stress Relaxation Test

Another applicable rheological test to evaluate the viscoelastic nature of the rubber compounds is the stress relaxation [19-21]. Sample is set at a constant torsion in the cavity of RPA, and the reduced modulus with time is plotted. Figure 4 demonstrates the experimental relaxed modulus for gums along with the estimated relaxed modulus considering SLS model. As it is known, G_U is the intrinsic property of rubber gum which depends on the restricted polymer chains as entanglements and moveability of chains under applied torsion deformation. As seen in Figure 4, G_U of SBR 1712 is lower than that of SBR 1502. The extended oil in 1712 grade acts as a lubricant for rubber chains and reduces the moving resistance, so in SBR 1712 the rubbery chains can slip over each other more easily, meaning less modulus. Finally, modulus reaches a plateau for both gums. Relaxation over the long time allows the free chains to flow, so at that point the main part of the initial applied stress would not allow strain changes and therefore the chains are relaxed and the final modulus is indeed very low (G_R).

Figure 4 also denotes that the inflection point of SBR 1712 is at shorter time which means lower relaxation time of SBR 1712 in comparison with SBR 1502. The total relaxation time is obtained from the relaxation times of all molecules existing in the gum sample. Therefore, SBR 1712 which has low molecular weight oil with low relaxation time shows a shorter inflection point than that of SBR 1502.

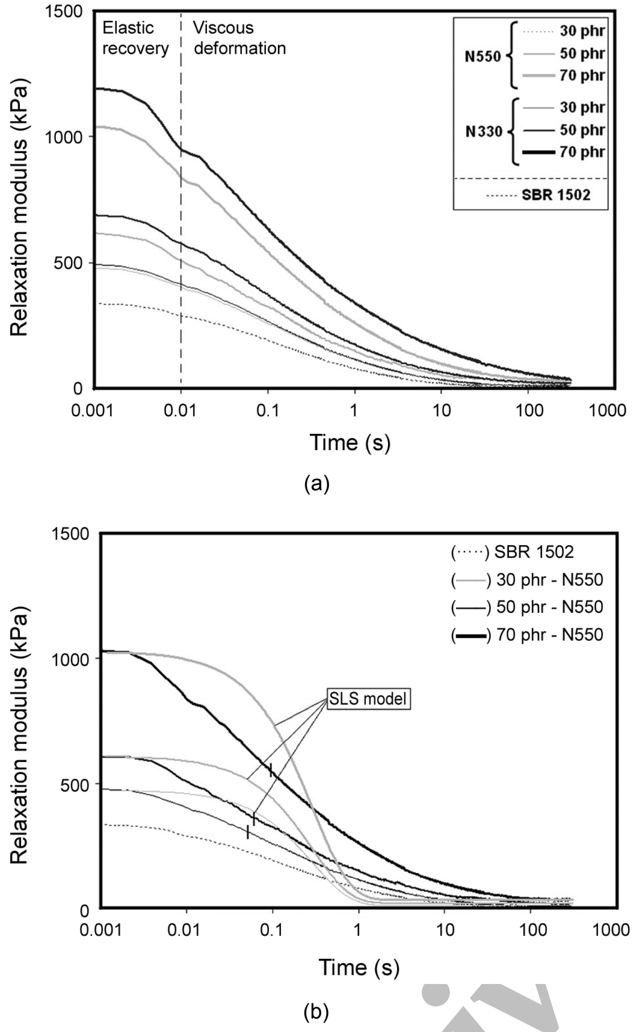
In CB-filled rubber, the stress relaxation behaviour is more complicated than gum. Scheme III is proposed to clarify the complexity of responses in a CB-containing compound. The relaxation mechanism includes several kinds of molecular motions involving both elastic and viscous



Scheme III. Possible elastic and viscous motions in stress relaxation for gum and CB-filled rubber.

components. The elastic part of deformation is the reversible stretching of entanglements (E1) and CB-rubber bridges (E2). Recovery of the elastic motions occurs initially at the start of the test, causing a rapid drop in the modulus [11]. Thereafter, mostly the viscous motions take place. As the time passes chain slippage (V1), disentanglements (V2), disturbed CB-rubber (V3) and CB-CB breakdown (V4) happen, which govern the flow of the system. Occurrence of the irreversible viscous motions in this period of time reduces the necessary stress for certain strain or in other words, modulus gradually falls down to very low amounts depending on the final configuration.

Figure 5a displays the relaxation modulus for uncured compounds with various CB levels of N330 and N550. Filled compounds containing higher CB content or finer particle have higher G_U which falls more rapidly with time. This relaxation trend can be



(a)

(b)

Figure 5. The relaxation modulus versus time: (a) for uncured compounds with various CB levels of N330 and N550 and (b) SLS model for various CB levels.

explained by Scheme III. In comparison with gum, CB-filled rubber exhibits further molecular motions in both elastic and viscous components, including elastic CB-rubber stretching (E2) and viscous breakdown of CB-based interactions (V3 and V4). One can conclude that in the presence of CB, the quantity of these responses is larger, and so do both elastic and viscous motions. Thus, slope of the curve in the relaxation modulus at short and long times is dramatic for CB-having SBR. Decreasing the particle size of CB affects the relaxation modulus in the same manner. Compounds filled by finer CB have higher modulus with rapid reduction, due to higher probability of existence of the CB interactions, while the difference between the slopes of curves is not very considerable.

The obtained relaxation curve from SLS model is presented in Figure 5b for different levels of N550. With increasing CB content, inflection point shifts to the longer time which means increasing the relaxation time (τ). As known, τ comes from the ratio of viscous to the elastic component [11] and its rising means more viscous and less elastic responses of the compound. At higher CB concentration, more CB-CB and CB-rubber bonds exist in the sample, so more bonds should be broken, which require longer times.

As mentioned before in SLS model, the total of two springs′ moduli is equal to G_U or the observed modulus at the beginning of the relaxation test which is attributed to the structure and stiffness of the compound. As seen in relaxation curves with increased CB content and surface, G_U increases which expresses the stronger springs or more elastic responses at the relaxation start in these samples while their higher G_D (time dependent drop in relaxation modulus) denotes greater possibility of viscous motions. From G_R and G_D, it can be concluded that both elastic and viscous motions are more considerable at the presence of more and finer CB. This is in agreement with what was discussed above for Figure 5a.

Through regression at the start of the relaxation, in the range of 0.5-1 s, the relation between modulus (G) and time (t) can be determined as G(t) = A-Bt; an example is given in Figure 6 for different loadings of N550. In this equation, constant "A" implies the initial intrinsic modulus of sample whereas the value of "B" shows the reduction in the modulus with time. The time growing term of "Bt" is deducted continuously from "A", expressing the drop in the relaxation modulus. Obtained coefficients of all master compounds are listed in Table 3. With increasing CB loading and surface area, both "A" and "B" increase. It is because of more CB content and higher interactions in these samples which influence the elastic and viscous reflexes. In other words, "A" is related directly to G_U which is greater for higher level and surface area of CB, and so "A" is greater as well. In addition, "B" represents the time dependency and the rate of falling in relaxed modulus. However, the ratio of "A/B" is a better mark of τ; bigger "A/B", longer τ. As seen, increasing trend of "A/B" obeys the observed variation of τ: "A/B" increases with CB

Table 3. Estimated coefficients of the linear equation for the relaxation test, before cure.

SBR 1502 Compounds		A	B	A/B	R-squared (%)
CB type	CB content (phr)				
N330	30	198.3	70.2	2.82	97.0
	50	266.6	82.6	3.23	98.2
	70	477.4	131.8	3.62	98.4
N550	30	182.8	68.4	2.67	97.7
	50	221.5	72.7	3.05	98.3
	70	394.2	116.9	3.37	98.1

content and surface, similar to what described for the relaxation time.

Relaxation Test After Curing

The properties after vulcanization are concerns for investigation in the field of rubber viscoelasticity, as well as the uncured properties. The effect of CB on the cure behaviour of SBR has been fully discussed in our previous work [17]. Figures 7a and 7b illustrate the cure-timed-relaxed curves for compounds with different CB loadings and particle size, respectively. At first, curing was accomplished at high temperature of 150°C and then, the sample cooled down to 50°C; after which, the stress relaxation test was performed. The pertinent cure properties are given in these figures. As can be seen, the rate of cure (K) rises as the CB loading increases. Also both the scorch ($t_{10\%}$) and cure ($t_{90\%}$) times come to be shorter for higher CB level and finer particle size, which have been explained in detail earlier [17]. One noticeable point in these figures is the increment in the modulus in "timed" subtest. It is attributed to more rigidity and less flowability caused by 100°C drop in temperature.

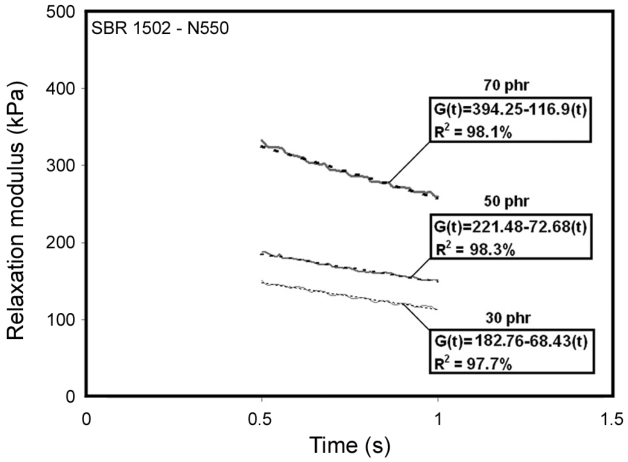
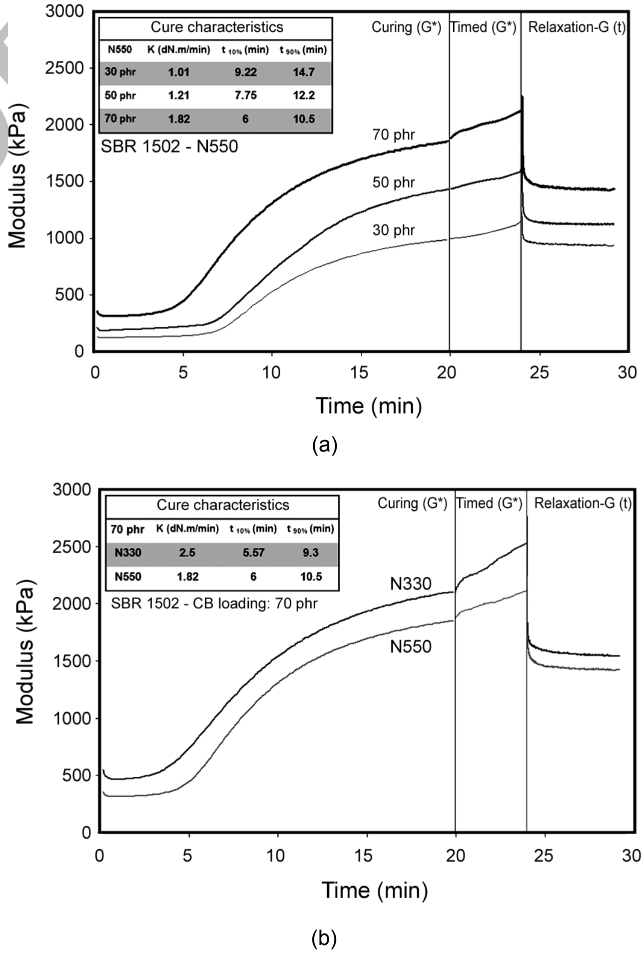


Figure 6. Linear regression at 0.5-1 s of relaxation curves.



(a)

(b)

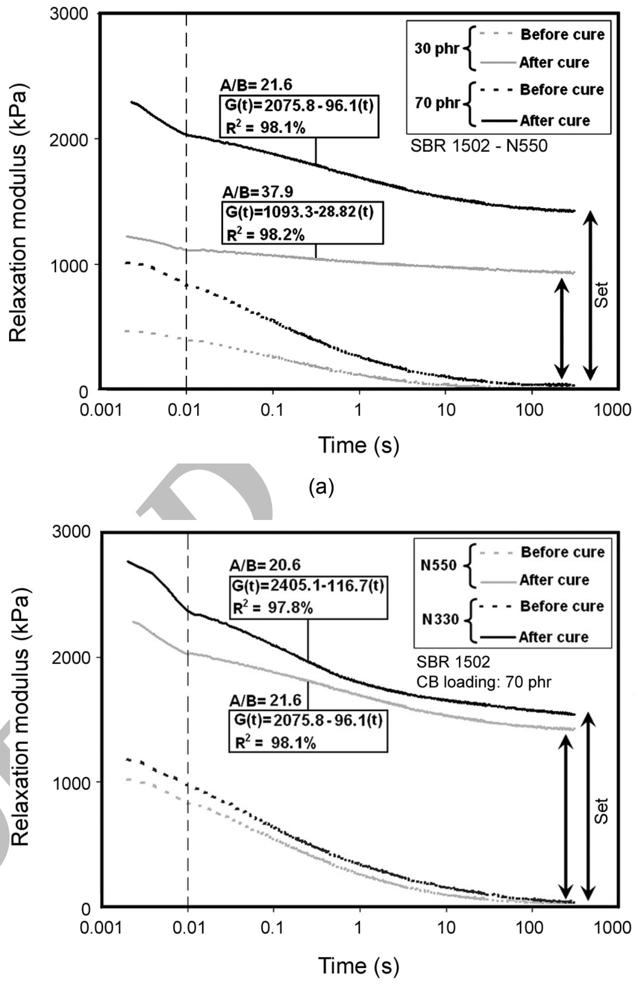
Figure 7. Cure-timed-relaxed curves: (a) effect of CB loading and (b) effect of CB type.

In all stages of cure-timed-relaxed, filled rubbers having more and finer CB exhibit the greater modulus. After looking at the relaxation modulus, one can conclude that the drop in the relaxation modulus after cure is more obvious for higher concentration and surface area of CB, as well as seen for the relaxation modulus of uncured compounds.

Figures 8a and 8b show before and after cure relaxations for compounds with various CB loadings and particle size, respectively. Curing procedure makes the relaxation phenomenon to be meaningfully different: in each compound, the slope of reduction in the modulus at lower time increases while the drop in the modulus at longer time decreases, comparing with that of the master. As described earlier, the first falling in modulus is mainly related to the recovery of elastic responses whereas at longer times, generally the viscous motions are responsible. The cross-links formed in the vulcanized samples have two important effects. On the one hand, these links can act as the desirable junctions for rubbery chains to perform the elastic responses, facilitating the recovery of motions. On the other hand, the mobility of molecules is restricted by the network, and thus the viscous component is weaker. In a word, the elasticity increases after cure, so the modulus decreases rather rapidly at shorter times, and even more slowly at longer times.

The regression of relaxed modulus after cure is depicted in Figures 8a and 8b. "A" which indicates the initial intrinsic modulus is significantly higher in vulcanized compounds comparing with unvulcanized ones, due to formation of cross-links. In addition, compared to unvulcanized samples, the value of "B" which expresses the time dependency of the relaxation modulus is considerably reduced after curing. The greater "A/B" obtained in the cured compounds denotes slow falling in the relaxed modulus and really long τ caused by the curing process, as a result of restricting effect of cross-links on the viscous motions. This effect is more obvious at 30 phr CB where a higher "A/B" is observed, because of more predominant restriction effect at lower CB content.

As mentioned before, during the stress relaxation, the modulus decreases, reaching a final value (G_R). The greater G_R implies higher elasticity of the polymer, or closer to a real solid elastic model [11]. As observed, there is an impressive set (higher G_R) at the end of relaxation curves of the vulcanized compounds. Before cure, rubber compounds have a viscous manner at long times and flowable chains, so they do not show any significant set at the end of the test (very low G_R). However, the cured rubber has more elastic nature and a part of viscous motions in the uncured state do not happen anymore due to restrictive operation of cross-links. On the other hand, the amount of G_U-G_R, equal to G_D, represents the time dependency in SLS model (Scheme I). In stress relaxation experiment, the viscous deformation of dashpot lets the nearby spring to recoil, so G_D is relaxed as time passes. Since cross-links confine the freely movement of dashpot, lower drops in G are



(a)

(b)

Figure 8. Comparison between before and after cure relaxation curves: (a) effect of CB loading and (b) effect of CB type.

observed in the cured component; resulting in a greater set or G_R at the end. Furthermore, the value of set is higher for the compounds containing more CB content and finer CB particle size, regarding to Figures 8a and 8b, respectively. The clear relaxation set at the presence of higher CB can be attributed to those of lost viscous motions which are related to CB interactions trapped in the cross-links and cannot be broken down. The volume of this type of confining is larger for higher level and surface area of CB; therefore, the higher G_R is obtained. This behaviour can also be considered as a result of greater cross-link density associated with the better thermal conductivity and hydrodynamic effect of CB.

CONCLUSION

This paper dealt with some key issues related to the viscoelasticity of filled rubber compounds. The rheological behaviour of SBR compounds containing various contents of CB N330 and CB N550 were investigated performing strain sweep and stress relaxation tests using rubber process analyzer (RPA). The following conclusions were achieved and explained considering proposed schemes of segmental motions.

- Filled rubber has greater G^*_0 than SBR gum, which falls rather abruptly; meaning more obvious non-linear viscoelastic behaviour, and thus higher G^*_0-G^*_∞.

- The trend of tan δ versus the strain was divided into two main domains of LVE and NLVE. For SBR 1502 based compounds, LVE was found lower than 15% strain.

- In LVE zone, lower tan δ was observed with increases in loading and surface area of CB, while in NLVE zone the reverse trend is detected.

- Filled compounds containing higher CB or finer CB show higher initial relaxation modulus which drop more rapidly as time passes. In these samples, τ shifts to the higher times.

- In the cured compounds, the slope of the modulus in the short time zone is steeper, while the drop in the modulus at the longer times less steep, comparing with that of the uncured.

- An obvious set at the end of the relaxation curves of the vulcanized compounds appeared; higher for the compounds with more CB content and finer CB, meaning more elastic nature after cure.

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