

Effect of Carbon Black Type on Viscous Heating, Heat Build-up, and Relaxation Behaviour of SBR Compounds

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ABSTRACT

Generation of heat via viscous dissipation of uncured filled rubber compounds can lead to significant temperature increment, which its estimation is very important. In this work, viscous heating and stress relaxation of uncured carbon black and silica filled SBR compounds and heat build-up of the cured one were investigated by rubber process analyzer (RPA2000) instrument. These compounds were prepared in Haake internal mixer at 60°C, 10 min mixing time and a rotor speed of 40 rpm. The mixing was followed by using a two-roll mill with adding curing agents. A part of these compounds was used to prepare the cured samples for Goodrich flexometer, to determine the heat build-up of cured compounds. There was a similar trend in the data of both measurings. The results of this study showed that with increasing the particle size, i.e., decreasing the structure of carbon black, the amount of generated heat has been reduced. Fillers which cause higher viscous heating in the uncured compounds also impart higher heat build-up in the cured compounds. Results also demonstrated that compounds which contain larger particle size, i.e., lower structure carbon black have shorter relaxation time. In silica filled SBR, viscous heating, heat build-up, and stress relaxation have been increased, also.

Key Words:

heat build-up;
viscous heating;
stress relaxation;
rubber compound;
carbon black;
silica.

INTRODUCTION

Carbon black filled SBR compounds are widely used in truck tyres tread. These treads are massive and during cyclic deformation their temperature rise up. Tyre temperature has a marked effect on its performance characteristics such as durability,

wear resistance, handling and traction, as well as rolling resistance. Increase in tyre temperature is the principal cause of rubber thermal degradation.

It leads to fatigue cracking or permanent belt edge separation failure.

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Moreover, increase in temperature can also cause deterioration of wire-rubber adhesion and consequently belt separation. Elevated temperature also affects viscoelasticity and strength of rubber compound and cause air permeation more easily through the liners which latter accelerates oxidative degradation or pressure loss of tyre [1,2].

When an elastomer is subjected to repeated deformations with sufficient magnitude and frequency, it leads to generation of considerable heat (depending on the rate of heat removed) and significant rise in temperature. The vulcanizate temperature reaches steady state after running for a certain period of time when the balance between heat generation and heat dissipation becomes equal. The process is more severe in the thick rubber blocks and causes the interior part of the block becomes so hot that the rubber explodes consequently. It is an important mode of failure in thick rubber articles such as tyre treads and tank track pads [3-5].

The reinforcing fillers have the major effect in heat generation in rubber compounds. Carbon black as the most used filler in rubber industries is composed of fused aggregates. physical properties of reinforced rubber is directly related to the sizes and shapes of these primary aggregates [6].

Filler morphologies such as particle size, structure, and essentially surface characteristics have a drastic effect on the physical performance of the elastomeric material. The most important of these parameters however, are the surface characteristics and the chemical active sites which determine the interaction between filler and polymer chains [7]. The addition of carbon black to rubber not only enhances mechanical and physical properties, i.e., modulus, tear, tensile, and abrasion resistance but also degrades hysteretic properties, i.e., heat build-up and resilience. These changes depend on amount and type of carbon black [8].

The use of carbon black imparts higher hysteresis and heat build-up to the vulcanizate, as well as significantly increasing viscous heating during the mixing and processing of the compound. It is important to be able to measure and study accurately the different amount of viscous heating imparted by different carbon black to a rubber batch during mixing in order to predict the possible useful mixing time per batch [9].

Heat build-up is generally related to the energy loss under constant work input. Thus, the increase in tem-

perature during the measurement, ΔT , is related to $\tan \delta$. The factors that are influencing $\tan \delta$ can also be applied, to heat generation [10].

In a rubber loaded with finely divided carbon black, polymer molecules are attached to the filler particles by physico-chemical bonds. Hence each filler particle may be bridged to others by many polymer chains, and it acts as a multiple cross-link as well as a rigid occupier of space (agglomeration of the particles may also complicate the picture) [11]. Most interpretations of elastic and viscoelastic properties of filled vulcanizates are based on the concept of two networks, one of cross-linked polymer and the other composed of carbon black particles that are joined by bridging polymer chains attached more or less firmly to the particles or perhaps adhere through direct particle contact. Those particles even without polymer can form structures with viscoelastic properties [12].

In this research, we studied viscous heating, heat build-up, and stress relaxation of different types of carbon black filled SBR compounds. A RPA2000 (Rubber process analyzer) instrument has been used to measure the heat build-up of cured compounds and viscous heating as well as stress relaxation of uncured master compounds [13]. A Goodrich flexometer was also used in determining the heat build-up. The data of both instruments was compared.

EXPERIMENTAL

Materials

SBR 1502, a product of National Iranian Petrochemical Co., was used as base polymer in this study. N220, N330, N339, N550, and N660 carbon blacks were obtained from Iran Tyre Co. Precipitated silica (Vulkasil S) was prepared from Bayer Company. Other additives were used as shown in Table (1). The specifications of used fillers in this study are given in Table (2).

All compounds contain equal part of black. One compound containing 50phr vulkasil S was also prepared for comparison.

Compound Preparation

The mixing was performed in two steps. First a master compound without curing agent and accelerator was prepared in Haake internal mixer at 60°C and rotor

Table 1. Compound recipe.

Final compound								
Master batch compound							Curing agents added on two-roll mill	
Material	SBR 1502	Black	ZnO	Naphtenic oil	Stearic acid	TMQ	Sulfur	TBBS accelerator
Content (phr)	100	50	5	10	1	1	1.5	1

Table 2. Specifications of carbon blacks and silica.

Carbon black	DBP Absorption (cm ³ / 100g)	Area (m ² /g)
N220	114	126
N339	123	89
N330	102	87
N550	115	42
N660	91	32
Silica (Vulkasil S)	-	175

speed of 40 rpm in accordance with Table 1. The mixing time in Haake internal mixer was lasted 10 min when the torque of the instrument became constant. The mixing was continued on two-roll mill by adding curing agent and accelerator. All compounds were prepared in accordance with ASTM D 3191. The final compound was stored for at least 24 h. A part of this compounds was used to prepare the cured samples of Goodrich flexometer.

Test Conditions

To operate the viscous heating test with RPA, about 6.5 g sample was placed in the chamber and after closing dies, it was allowed to preheat for 30 s to assure good flow in the sealed pressurized cavity. After the test was commenced according to Table 3, the temperature changes of the lower and upper dies are recorded. These test conditions also applied to rubber compounds in the cured state to measure the degree of heat build-

Table 3. RPA Setting to measure viscous heating.

Test duration (min)	5
Temperature (°C)	60
Frequency (cpm)	30
Strain, SSA ^a (%)	900

(a) single strain amplitude

up. Thus, the uncured samples were cured in situ at 180°C for 10 min. Then the temperature was reduced to 50°C for effective heat build-up measurements by RPA.

Table 4 shows the details of the RPA test configuration used to measure the heat build-up of cured samples. Heat build-up test also was done by a Goodrich flexometer on a cured sample according to ASTM D 623 as is shown in Table 5. The test consists of subjecting a cylindrical sample of rubber with a height of 25.4 mm and diameter of about 12.7 mm to rapidly oscillating compressive stresses under controlled conditions and the temperature rise, measuring. The applied load, its frequency, and the height of stroke were 108 N, 30 HZ and 5.7 mm, respectively. These uncured samples were also tested by the RPA stress relaxation with a 30 s preheat, %70 strain, and a 2 min stress relaxation time. The RPA conditions are given in Table 6.

RESULTS AND DISCUSSION

The rheological behaviour of uncured rubber is highly important from viewpoint of the manufacturer. At low shear rates the unfilled compounds undergoes Newtonian flow, while adding carbon black cause them to show not only highly non-Newtonian flow but also high viscosity. Figure 1 shows the viscous heating rate of SBR compounds with different carbon blacks and silica contents. As can be seen the most temperature increment is for silica and different carbon blacks have

Table 4. RPA Conditions for heat build-up.

Test duration (min)	5
Temperature (°C)	50*
Frequency (cpm)	1320
Strain (%)	20

(*) Cured at 180°C and 10 min.

Table 5. Goodrich flexometer conditions for heat build-up.

Test duration (min)	30
Force (N)	108
Chamber temperature (°C)	50
Cylindrical sample dimension (mm)	12.7×25.4 (L)
Frequency (cpm)	1500

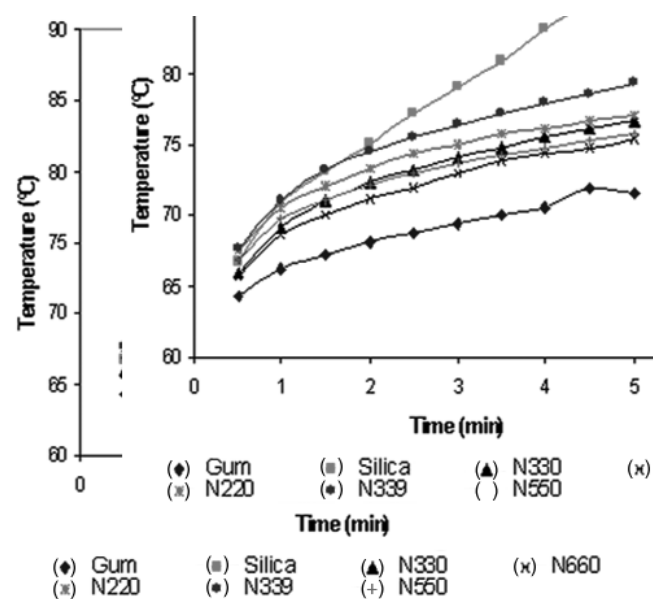
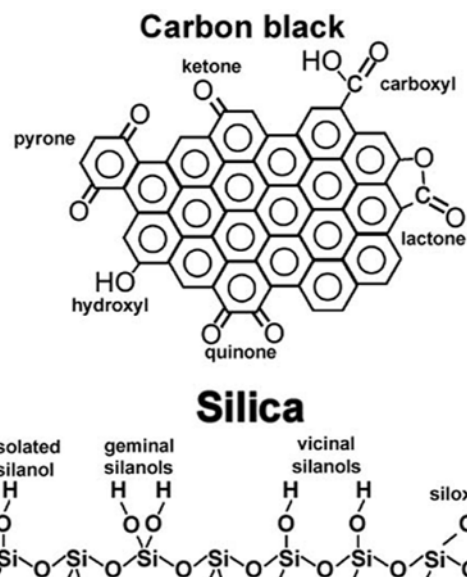
Table 6. RPA conditions in measuring stress relaxation.

Preheat time (s)	30
Relaxation time (s)	120
Chamber temperature ^a (°C)	60, 80
Strain (%)	70

(a) test was separately performed at two temperature.

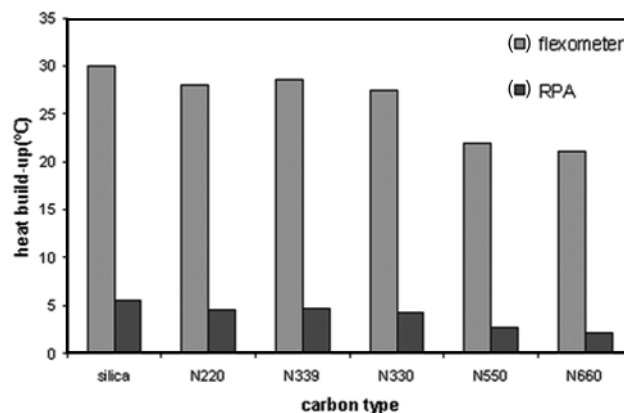
shown various behaviours. The temperature increment reduces in order of the highest structure carbon blacks to the lowest structure one. The unloaded SBR shows the lowest temperature increment. The smaller is the particle size, the more viscous heating has been generated.

Adding carbon black to raw rubbers causes viscosity of resulted compound to increase for several reason such as the hydrodynamic effect of carbon black loading, the structure of carbon blacks which is associated with

**Figure 1.** Viscous heating of gum, SBR, and SBR filled with different types of carbon black and silica at 5 min, strain of 900%, frequency of 30 cpm, and 60°C.**Figure 2.** Comparison of silica and carbon black from bonded groups point of view.

anisometry of the filler aggregates, the occlusion of rubber within the aggregates, and adsorption of rubber molecules on the filler surface which is treated as shell of immobilized rubber or as bound rubber. The later case seems sensible, once a segment is anchored on the filler surface, because movement of whole molecules in the flow field is restricted [10].

In the case of silica, which are poorly compatible with hydrocarbon rubbers, it can be proved that agglomeration between aggregates occurs by means of direct contact through hydrogen bonding (Figure 2). As for carbon black which well wetted by rubber, the filler

**Figure 3.** Heat build-up for SBR cured compound having different types of carbon black measured by Goodrich flexometer and RPA according to the conditions mentioned in tables 4 and 5.

network might be formed by the joint shell mechanism [10, 14, 15,16].

Figure 3 shows RPA and Goodrich flexometer measured heat build-up of different SBR cured compounds. The condition of testing in both method is almost similar but the type of deformation mode is shear in RPA and compression in Goodrich flexometer. A similar trend can be seen in both measuring. In other words, selected RPA heat build-up data correlated to the heat build-up imparted by the Goodrich flexometer. Because of more bulkiness of samples in Goodrich flexometer, the value of generated heat for the same carbon black in two instruments is completely different. Variations in compounds' thermal conductivity will have a much greater effect on the Goodrich flexometer heat build-up measurements than they have on the RPA measurements.

Heat build-up is determined not only by the hysteresis of the sample, but also by the heat exchange with the environment. The temperature of the sample at equilibrium could therefore be affected by the thermal conductivity of the filled vulcanizates. Silica filler imparts significantly poorer thermal conductivity than carbon black in cured compound. It is related to a filler-filler interaction dominates in silica filled compound. It can also be seen that with increasing the particle size, as well as, decreasing the structure of carbon black, the amount of generated heat is reduced. In other words, fillers which imparted high viscous heating to the uncured SBR compound, also impart high heat build-up to the cured compound. Finer particles (large surface area) of carbon black forms a higher density aggregate network than larger particles of carbon black. The

fomer generates more heat when it is destroyed through the application of high strain. It is worth mentioned that with the formation of cross-links through vulcanization, the elastic modulus increases greatly compared to the loss modulus, Therefore the amount of heat generated in vulcanizate is considerably less than that in the corresponding uncured stocks [9].

Stress Relaxation

Stress relaxation testing provides a measure of viscoelastic response of the material over a period of time without destroying the structure of the sample. In this test, both the instantaneous and time dependent response to an applied deformation are measured [17]. Stress relaxation subtest can be performed by the RPA2000.

Tables 7 and 8 show the stress relaxation results of gum, silica, and carbon black filled SBR at 60°C and 80°C, respectively. the stress relaxation is measured by the torque transducer which is attached to the upper die. The highest torque recorded resulting from the deformational pulse which is correlated to compound viscosity in the initial portion of the stress relaxation curve. Every stress relaxation curve is divided into three zones [18] in which, a log-log regression is performed over the data and the slope of the line through the zone boundaries is determined.

In Table 7 time to percent drop columns shows how much time is needed to achieve a given percent drop in the peak torque [13]. As can be seen in this table, the gum peak torque (unfilled) SBR is the lowest one, while filled compounds show higher peak torque which its value is depend on carbon black particle size and

Table 7. Stress relaxation results of SBR gum and filled with 50 phr carbon black and silica at 60°C.

Compound	Peak torque (dNM)	Time to 50% drop (s)	Time to 63% drop (s)	Time to 80% drop (s)
Gum	30.97	0.1	0.233	0.84
N220	77.92	0.083	0.223	1.11
N339	86.03	0.087	0.232	1.19
N330	78.57	0.082	0.216	1.05
N550	84.6	0.081	0.209	1.00
N660	69.14	0.081	0.206	0.9
Silica	133.38	0.092	0.330	2.79

Table 8. Stress relaxation results of SBR gum and filled with 50 phr carbon black and silica at 80°C.

Compound	Peak torque (dNM)	Time to 50% (sec)	Time to 63% (s)	Time to 80% (s)
Gum	24.70	0.072	0.165	0.59
N220	58.76	0.065	0.167	0.82
N339	67.42	0.065	0.166	0.86
N330	60.28	0.063	0.157	0.75
N550	66.75	0.061	0.154	0.73
N660	54.33	0.063	0.151	0.69
Silica	107.2	0.081	0.284	2.71

structure. The silica filled sample showed much greater peak torque than carbon black filled samples. This is related to filler network structure formed between the silica aggregates compared to carbon black aggregates. Therefore the destruction of the interaggregate bonding needs the greater range of strain amplitudes.

Three time zones, i.e., time to reach 50%, 63%, and 80% relaxation have been selected to compare behaviour of gum, carbon black and silica filled SBR compounds. The third column in Table 7 shows the time need to reach 50% relaxation. Compounds which are containing larger particle size or lower structure carbon blacks show shorter relaxation time. In the case of silica filled SBR, it seems that strength of filler aggregates (filler networking) is high enough that it can resist against chain movements and then prolongs the relaxation time. The interesting point in this column is for gum with a relaxation time of 0.1 s which is higher than all the filled compounds.

Time to reach 63% relaxation has been shown in forth column in Table 7. As can be seen, the large difference between gum and carbon black filled compounds has been diminished as the structure of carbon black was increased. While silica filled SBR has still kept its distance with other filled compounds. In this column, carbon blacks with larger particle size have shown shorter time to reach 63% relaxation.

The fifth column in Table 7 shows time to reach 80% of peak torque. The difference among these values for carbon black filled SBRs are the same as second column, but the gum compound has taken a much lower value in comparison with carbon black filled SBRs. This behaviour clearly shows that although gum

compounds can keep their resistance to chain movements against a given stress (strain) during the first period of stress imposing, but lose their strength with time. Mechanisms for viscoelastic relaxation in filled vulcanizates may include configurational changes of segments of polymer molecules (like in unfilled vulcanizates), i.e., detachment and reattachment of polymer molecules on particles, and adjustment of direct contacts between particles [12].

The silica filled SBR compound has kept its strength against chain movements and gives a 80% relaxation time much more than carbon black filled compounds which can be attributed to greater silica agglomerate structure. The same behaviour can be seen for the compounds in 80°C (Table 8) except that peak torque and three mentioned time to percent relaxation has reduced. Raising the temperature would weaken interaggregate interaction and diminish the modulus levels of the compound. Consequently reduced filler agglomeration would be expected, therefore the relaxation process for the filled and unfilled SBR compounds at 80°C take place easier and in shorter time than those at 60°C.

CONCLUSION

Viscous heating, stress relaxation, and heat build-up of uncured and cured carbon black and silica filled SBR compounds were studied. The results of this study showed that by increasing the particle size or decreasing the structure of carbon black, the amount of generated heat is reduced. Fillers which cause high viscous

heating to uncured compounds also impart high heat build-up to the cured compounds. Results also demonstrated that compounds which are containing larger particle size, i.e., lower structure carbon black have shorter relaxation time. For silica filled SBR it seems that the filler networking caused it resist against chain movements therefore viscous heating, heat build-up, and stress relaxation increased.

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