

A Study of Relationships Between State-of-Mix, Rheological Properties, Dynamic Properties, and Bound Rubber Content

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Received 16 August 1999; accepted 22 October 1999

ABSTRACT: The relationships between state-of-mix, rheologic properties, dynamic properties, and bound rubber content in N330 carbon black filled styrene butadiene rubber (SBR) were investigated. Shear viscosities measured from both Mooney viscometer and capillary rheometer decrease with increasing state-of-mix. By contrast, the stress relaxation determined from the Mooney relaxation viscometer (PR80) decreases with an increase in state-of-mix. In addition, glass transition temperature (T_g) is not strongly affected by a change in state-of-mix, whereas the magnitude of damping peak ($\tan \delta$) increases with state-of-mix. Bound rubber content appears to decrease as the state-of-mix increases. The concept of a change in an amount of immobilized rubber can be used to explain the results obtained. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1542–1548, 2000

Key words: state-of-mix; immobilized rubber; bound rubber content; rheological properties; dynamic properties

INTRODUCTION

It has been reported that the degree of filler dispersion in rubber compounds can be quantified in terms of state-of-mix. The greater the degree of dispersion, the greater the state-of-mix.^{1–5} Certainly, the state-of-mix has been found to affect rheological properties, mechanical and damping properties of rubber compounds.^{1–9}

The simplest technique utilized to measure the carbon black dispersion in rubber compounds is the optical microscopic technique.^{2–4,6,8,10} The use of a dark-field microscopy is also useful to

estimate the carbon black dispersion in rubber compounds. The poorer the dispersion, the smaller the light reflectance.^{9,11} However, this technique is mainly limited by its low magnification. The more complicated and expensive technique employed to determine the carbon black dispersion is the electron microscopic technique, in which the individual agglomerates or surface flaws can be observed. In addition to the microscopic techniques, a measurement of electrical conductivity can be utilized to quantify the degree of carbon black dispersion. The poorer the dispersion, the greater the electrical conductivity.^{6,10}

The present study aims to further the previous work⁴ of investigating an applicability of the concept proposed earlier: the change in state-of-mix caused by a release of immobilized rubber in rubber compounds. The main difference of the present study from the previous one is that the curing agents are added to complicate the system,

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Contract grant sponsors: The National Metal and Materials Technology Center and The Polymer Technology Research and Development Center.

Journal of Applied Polymer Science, Vol. 76, 1542–1548 (2000)
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compared to that without the curing agent. In addition, relationships between state-of-mix, rheological properties, dynamic properties, and bound rubber contents are drawn.

EXPERIMENTAL

Materials

The rubber formulation used in the present study is given below:

SBR 1502 (Japan Synthetic Rubber Co. Ltd., Japan)	100.0 phr
ZnO (Utids Enterprise Co. Ltd., Thailand)	5.0 phr
Stearic acid (Polychem Co. Ltd., Thailand)	2.0 phr
Carbon black N330 (Thai Carbon Product Co. Ltd., Thailand)	30.0 phr
CBS (Santocure, Flexsys)	1.5 phr
Sulphur (Chemmin Co. Ltd., Thailand)	2.5 phr

Mixing and Vulcanization

Mixing was carried out in a Banbury-type internal mixer with a fill factor of 0.5, circulating water of 40°C, and a rotor speed 40 rpm. The SBR was first masticated for 120 s, followed by the addition of stearic acid and zinc oxide. The mixing was continued further for 120 s and then the carbon black was charged and batches were produced with various mixing times of 90, 120, 180, 300, and 600 s. The sulphur and CBS were, subsequently, added and mixed for 120 s before discharge and, finally, sheeted on a cooled two-roll mill.

Curing time to be used for curing compounds was determined from the Monsanto Oscillating Disk Rheometer 100S at a test temperature of 155°C. Then, rubber compounds were compression-molded under a pressure of 15 MPa at 155°C by using a hot-platen hydraulic.

State-of-Mix Determination

The state-of-mix was determined from the values of effective filler volume fraction (EFVF or ϕ_e) that can be quantified by using eq. (1), based on the release of immobilized rubber as the state-of-mix increases. Further details of the EFVF quantification were reported previously.²⁻⁵

$$\phi_e = (\alpha\phi_a) + \phi_t \quad (1)$$

where α is the volume fraction of immobilized rubber in an agglomerate (0.647 for N330, from the DBP absorption value),² ϕ_a is the volume fraction of agglomerates (equivalent to area fraction of agglomerates in thin section), and ϕ_t is the true volume fraction of carbon black (as calculated from the true density of carbon black, 1.8 g/cm³).²

Bound Rubber Measurement

The procedure for a measurement of bound rubber content used in the present study was based on that carried out by the other workers.¹² The small pieces of approximately 2 g of filled compounds were immersed in 25 mL toluene for 7 days at room temperature. The toluene was renewed after 3 days. After extraction, the rubber-black gel was dried in an oven at a temperature of 70°C until constant weight was obtained. The percentage bound rubber content was finally calculated from eq. (2) as:

$$R_B = \frac{W_{fg} - W[m_f/(m_f + m_p)]}{W[m_p/(m_f + m_p)]} \times 100 \quad (2)$$

where W_{fg} is the weight of carbon black-rubber gel, m_f is the weight of filler in the compound, m_p is the weight of polymer in the compound, and W is the weight of the test specimen.

Rheological Study

Rheological properties of the compounds were measured by using both a Mooney relaxation viscometer (Tech Pro) and a capillary rheometer (Rosand 612). The test temperature used for both cases was 100°C. For the Mooney viscometer, in addition to the Mooney viscosity (ML 1+4 at 100°C), the values of PR80, which is time for the torque to reduce 80% after rotors stops, can be determined.

For the capillary rheometer, the set shear rates were varied from 10 to 2000 s⁻¹. The die with 2 mm in diameter and 32 mm in length was utilized. The orifice die with a diameter of 2 mm was used for the two-die correction to correct shear stresses measured, whereas the Rabinowitsch correction was applied to the set shear rates to yield the corrected shear rates. The extrudate swell was determined from a ratio of extrudate to die diameters.

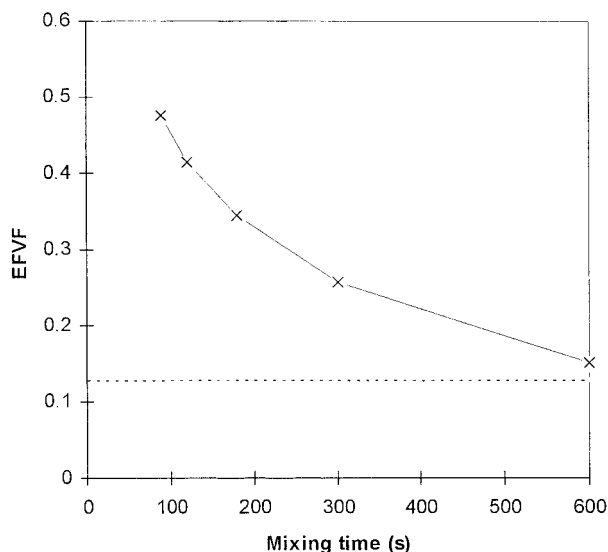


Figure 1 Effective filler volume fraction (EFVF) as a function of mixing time.

A Measurement of Dynamic Properties

Dynamic properties of rubber vulcanizates were measured on Polymer Laboratories DMTA Mk II in a bending mode at a frequency of 1 Hz. The sample length was 50 mm and peak-to-peak displacement was 64 μm . Measurements were carried out from -100 to 50°C at a heating rate of $5^\circ\text{C}/\text{min}$. Values of T_g determined from the damping peaks and of damping peak heights were recorded.

RESULTS AND DISCUSSION

Effect of Mixing Time on State-of-Mix

As mentioned, the degree of carbon black dispersion or state-of-mix can be determined from the

EFVF. Figure 1 shows that the EFVF of the compounds decreases with increasing mixing time, which can be explained by the release of immobilized rubber.²⁻⁴ Also, it can be seen that the EFVF of 600-s mix appears to approach the true volume fraction of carbon black (shown as dash line) as calculated from the density and weight of carbon black used in the compound, indicating that most of the agglomerates are disrupted into aggregates. In other words, mixing time of 600 s is sufficiently long for producing a well-mixed compound. Notably, the trend of the EFVF result obtained from the present study is similar to that obtained from the previous work,⁴ which means the presence of curing agents in the present study does not significantly affect the trend of relationship between state-of-mix and mixing time.

Influences of State-of-Mix on Rheological Properties

From Figure 2, it can obviously be seen that the Mooney viscosity (ML 1+4) decreases with increasing state-of-mix (i.e., with decreasing EFVF), which supports the explanation of the release of immobilized rubber with increasing state-of-mix, as mentioned previously.^{2,4}

Figure 3 shows the true shear viscosities at high-shear rates determined from the capillary rheometer of the compounds with various mixing times. It is evident from Figure 3 that the shear viscosities of each mixing time are not significantly different, which means that the use of flow curve for determining state-of-mix is not practical for the system studied. However, the zero-shear viscosity determined from the flow curve [i.e., $\log(\text{shear stress})$ against $\log(\text{shear rate})$] appears to be useful for determining state-of-mix, as

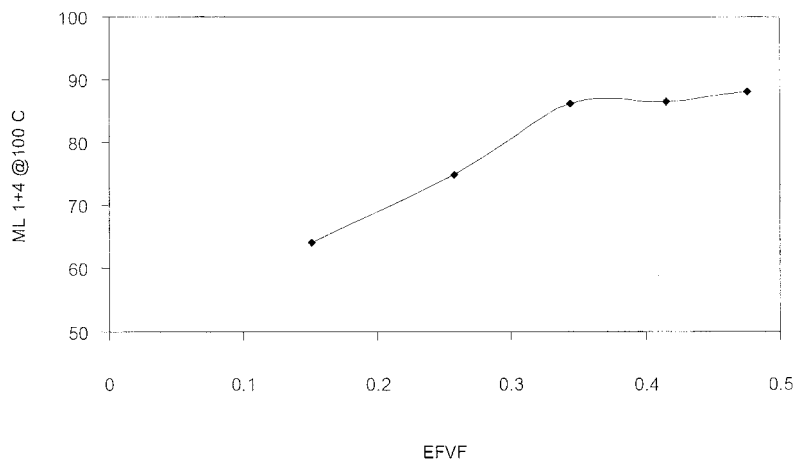


Figure 2 An influence of state-of-mix on Mooney viscosity.

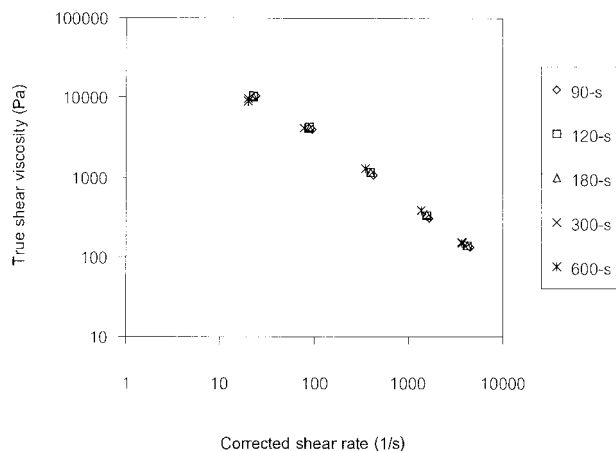


Figure 3 Flow curves of rubber compounds with various mixing times.

shown in Figure 4. The higher the state-of-mix, the lower the zero shear viscosity. The plot of Mooney viscosity against zero shear viscosity shown in Figure 5 gives a good relationship, particularly if the Mooney viscosity (ML1+4 at 100°C) is > 70.

Apart from the zero-shear and Mooney viscosities, the magnitude of extrudate swell can be used as an indicator for the state-of-mix.⁴ It can clearly be seen from Figure 6 that extrudate swell increases with increasing state-of-mix, which is attributed to an increase in an amount of free rubber caused by a release of immobilized rubber.

From the results of extrudate swell as a function of state-of-mix, it can be seen that the trend of the extrudate swell is controlled strongly by the state-of-mix. It is clear that the result trends obtained from the present study, where the curing agents is added to the compounds, and those ob-

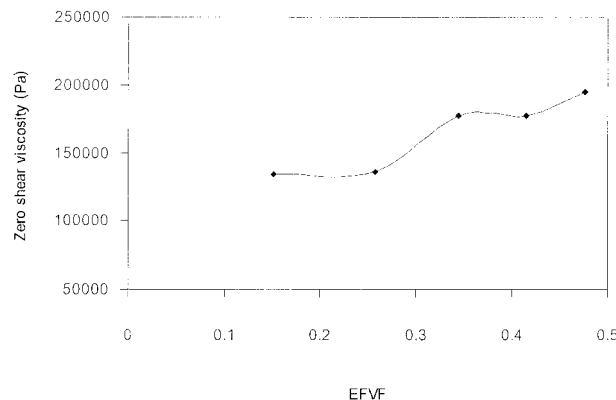


Figure 4 Relationship of zero shear viscosity against state-of-mix.

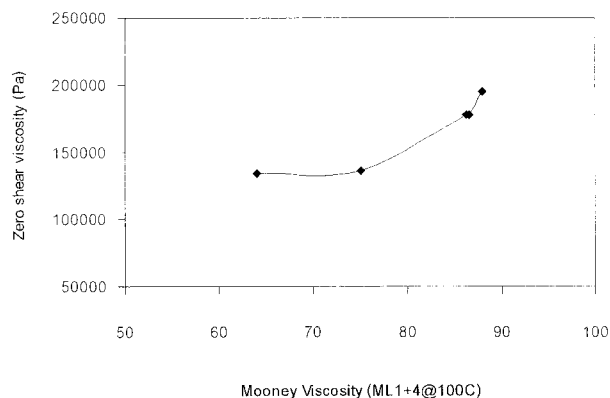


Figure 5 Plot of Mooney viscosity against zero shear viscosity.

tained from the previous study,⁴ where no curing agents is added, appear to be similar. Consequently, the use of state-of-mix to control extrudate swell is applicable to carbon black-filled SBR compounds with and without curing agents.

Where the stress relaxation of the compounds is concerned, one can generally expect that the greater the extrudate swell, the longer the relaxation time.¹³⁻¹⁵ Unexpectedly, the results of relaxation of the filled compounds determined from the Mooney relaxation viscometer shown in Figure 7 are not the way expected. It can be seen that the values of time for the torque to decrease 80% after rotor stops (PR80) decreases with increasing state-of-mix (i.e., with increasing extrudate swell, as illustrated in Fig. 6), indicating the shorter relaxation time for the greater state-of-mix. To investigate this peculiar result further, the relaxation of the unfilled compounds is carried out, as shown in Figure 8. It is evident that the slopes of

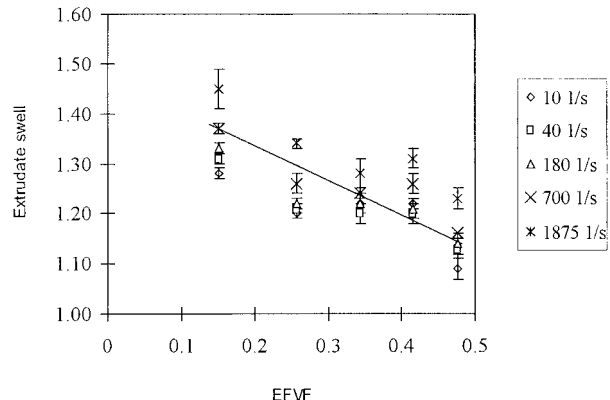


Figure 6 Influences of state-of-mix on extrudate swell (L/D = 16).

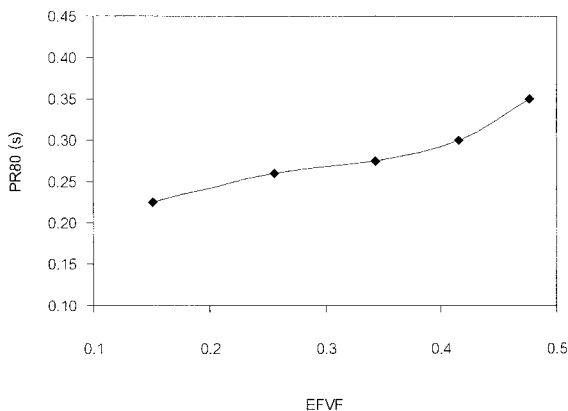


Figure 7 Relationship of PR80 against state-of-mix of filled compounds.

relaxation results of both filled and unfilled compounds are approximately similar, which means the increase in Mooney relaxation's PR80 of filled compounds with increasing EFVF is caused by a rubber phase, not by the state-of-mix.

Relationship Between State-of-Mix and Dynamic Properties

Figure 9 shows the damping properties of the filled compounds as a function of temperature. It is clear that the glass transition temperatures of each compound are approximately similar. By contrast, from Figure 10, the damping peak height tends to increase with increasing state-of-mix, which can be explained by the release of the immobilized rubber, as mentioned earlier. The increase in the amount of free rubber phase leads to a larger molecular mobility and thus in $\tan \delta_{\max}$.¹⁶ Consequently, it can be seen that the damping properties are controlled strongly by the state-of-mix. In other words, the damping peak ($\tan \delta_{\max}$) measurement can be utilized as a measure of state-of-mix in rubber vulcanizates.

Effect of State-of-Mix on Bound Rubber Content

The result of bound rubber content measured from the immersion in toluene for 7 days, as shown in Figure 11, indicates an unexpected decrease in bound rubber content with increasing state-of-mix, particularly at the low state-of-mix (i.e., high EFVF). The possible explanation is based on the previous work^{2,4} that states that the immobilized rubber is a rubber having an interaction with carbon black and, therefore, can be either occluded rubber, bound rubber, or both. A

bound rubber content result is believed to be a measure of bound rubber in well-mixed compounds (due to an absence of agglomerate) but of both bound and occluded rubber in poorly mixed compounds. As a consequence, at low state-of-mix, the occluded and bound rubber are both determined as the bound rubber content, resulting in a large amount of bound rubber content. As the state-of-mix increases, the agglomerates are disrupted and the immobilized rubber in those agglomerates (or the so-called occluded rubber) is released to be a free rubber, leading to a decrease in occluded rubber and thus bound rubber content. The explanation is supported by the plot of EFVF against mixing time, as shown in Figure 1, that the reduction in immobilized rubber is greater at the beginning of the mixing process (i.e., high EFVF).

CONCLUSIONS

The carbon black filled styrene butadiene rubber compounds were investigated by using the relationships between state-of-mix, rheological properties, dynamic properties, and bound rubber content. The following conclusions can be drawn.

The measure of EFVF can be used to determine the state-of-mix in carbon black filled compounds with and without curing agents.

The concept based on the release of immobilized rubber, as the state-of-mix increases, is applicable to the system with curing agents (i.e., the

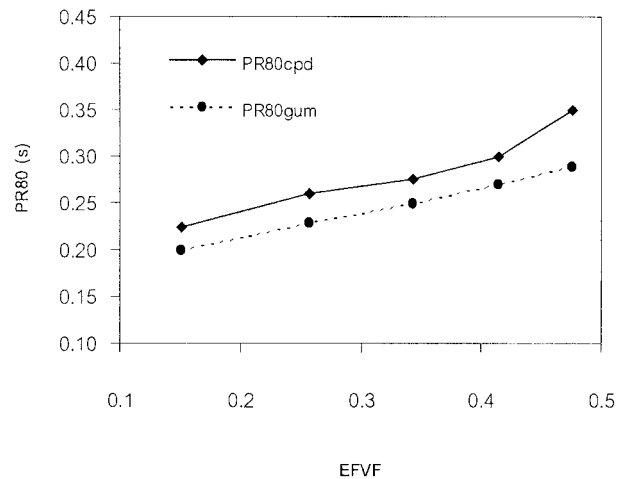


Figure 8 Comparison of PR80 in filled and unfilled compounds.

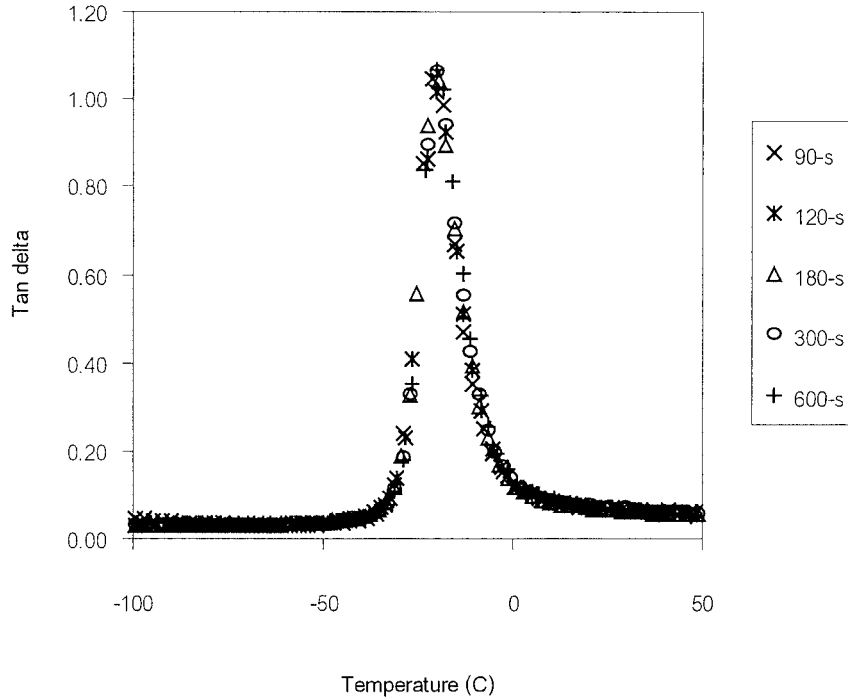


Figure 9 Damping properties of rubber compounds with different mixing times.

present system studied) and without curing agents (the previous system studied⁴).

Both zero-shear and Mooney viscosity can be used as a practical indicator for determining the state-of-mix. The lower the viscosity, the greater the state-of-mix.

As state-of-mix increases, the PR80 measured from the Mooney relaxation viscometer decreases. This result contradicts that of the extrudate swell.

A change in state-of-mix does not affect significantly the glass transition temperature of the compounds studied. By contrast, the increase in state-of-mix gives an obvious increase in damping

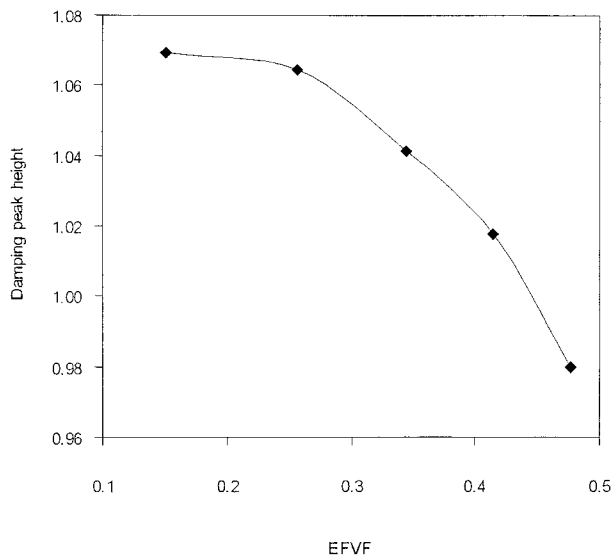


Figure 10 Relationship between state-of-mix and damping peak height.

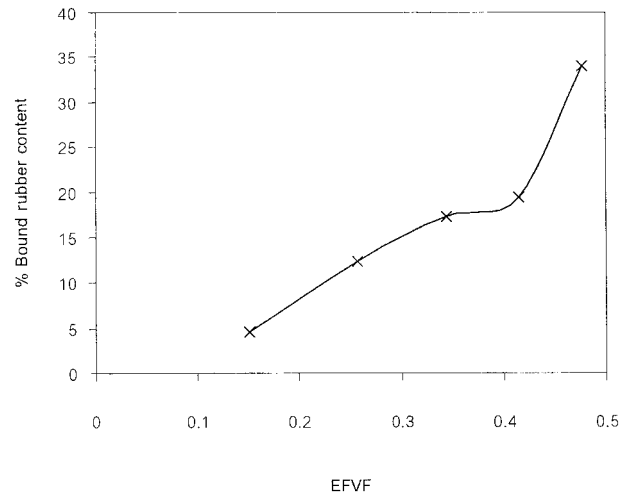


Figure 11 Relationship between state-of-mix and bound rubber.

peak height ($\tan \delta_{\max}$) of the compounds studied attributed to an increase in the amount of free rubber.

Bound rubber content appears to decrease with increasing state-of-mix, which is probably due to the decrease in immobilized rubber that resided in the carbon black agglomerates.

The financial support from the National Metal and Materials Technology Center (MTEC) and from the Polymer Technology Research and Development Center, Institute of Science and Technology for Research and Development, are gratefully acknowledged.

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