

Effect of Modified Carbon Black on the Filler–Elastomer Interaction and Dynamic Mechanical Properties of SBR Vulcanizates

Jingjie Han, Xiliang Zhang, Weihong Guo, Chifei Wu

Polymer Alloy Laboratory, School of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Received 23 July 2005; accepted 14 September 2005

DOI 10.1002/app.23233

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new modified carbon black (GCB) was prepared by adding special RFL latex into N220. Dynamic properties were obtained over a wide range of temperatures and strains on vulcanizates filled with GCB and unmodified carbon black, respectively. The results show that the GCB can effectively decrease the $\tan \delta$ value at 60 and 90°C of SBR vulcanizates compared with that of the common unmodified carbon blacks, which responds to the fact that GCB is beneficial to lower rolling resistance and heat generation of the

vulcanizates in comparison to that of the unmodified carbon black. Among the factors responsible for this, filler networking and filler–elastomer interaction play a dominant role. The effects of filler loading on mechanical properties of vulcanizates were also investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3707–3712, 2006

Key words: modification; fillers; elastomers; mechanical properties

INTRODUCTION

Elastomers are widely used in a range of applications, particularly in automotive tires and vibration mounts, under several conditions of temperature, frequency, and deformation. But most of the usage of elastomers would be impossible without the reinforcing character of certain fillers, such as carbon black and high-structured silica. With an implicit reference to tire technology, reinforcement is usually defined as the “improvement in abrasion, tear, cutting and rupture resistance, in stiffness and hardness of vulcanized compounds through the incorporation of finely divided particles.”¹

Besides reinforcement effect, when added to polymer systems, fillers will cause a considerable change in dynamic properties, not only dynamic modulus, loss modulus, and storage modulus, but also their ratio, i.e., loss factor, which is related to the portion of the energy dissipated during dynamic deformation. In practice, the energy loss in rubber products during dynamic strain is of great importance. For example, it will affect the performance of automotive tires with regard to heat generation, rolling resistance, and skid resistance. It was reported that a high-performance tire should give a low $\tan \delta$ value at a temperature of about 60°C to reduce rolling resistance and a low \tan

δ value at a temperature of about 90°C to reduce heat build-up.^{2,3} With respect to the tire tread, its deformation can be cited as “approximately into a constant strain (bending) and constant stress (compression) condition; and since the geometric mean of the hysteresis under these two conditions is approximately proportional to $\tan \delta$, tire tread hysteresis is as a first approximation, proportional to $\tan \delta$.”⁴ Thus, the dynamic hysteresis was discussed via mainly $\tan \delta$, a dimensionless parameter that is a measurement of the ratio of energy lost to energy stored in a cyclic deformation.

In addition, rubbers filled with carbon black show a typical nonlinear viscoelastic behavior during dynamic deformation. At strains of about 1%, a significant decrease of storage modulus occurs from the zero strain value G_o' to a high amplitude plateau value G_∞' . This effect was described by Payne in the 1960s.^{5,6} He interpreted this behavior as the result of breakage and reforming of physical bonds between the filler aggregates. These bonds were assumed to build filler agglomerates of different size and an elastic filler network within the rubber matrix.

A general schematic illustration of reinforcement in filled vulcanizates is given in Figure 1 (also see Ref. ⁷). The modulus is composed of the following parts: the pure rubber network, the hydrodynamic effect, specific filler–matrix interactions, and in addition, a strain-dependent part caused by the filler network. Based on an agglomeration–deagglomeration mechanism between the aggregates within the filler network,

Correspondence to: X. Zhang (xlzh@ecust.edu.cn).

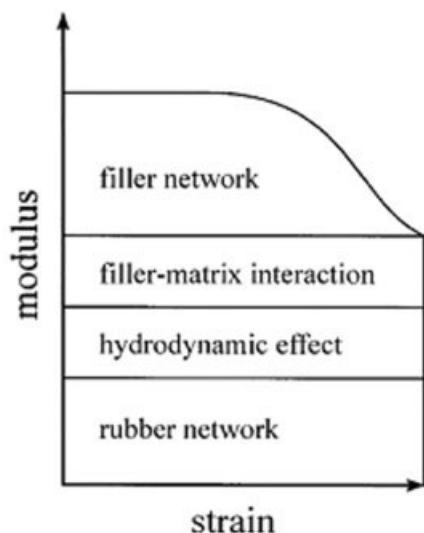


Figure 1 Modulus contributions as a function of strain (schematically).

some more molecular models were published to support the idea of filler network.^{8–11}

Our research work deals with the dynamic behavior of SBR vulcanizates filled with GCB and unmodified carbon black (Control). Also, the Payne effect of the vulcanizates was studied.

EXPERIMENTAL

Materials

The matrix material was emulsion-polymerized styrene–butadiene rubber containing 23 wt % styrene groups (SBR1502). The recipe and cure condition for preparation of the samples in this study are shown in Table I. Intermediate super abrasion furnace black (ISAF, grade N220) was supplied by Shanghai LISHI Chemical (China). The other agents used were commercial grade. GCB was prepared by the following steps: the first step is that 100 g of carbon black powder was pelletized with 8 g of the special RFL; then the pelletized carbon black was dried in an oven at 140°C for 3–4 h.

Processing and vulcanizate properties

Compounding was performed in an open two-roll mixing mill (O160) at a friction ratio 1.2. For determination of the bound rubber content, carbon black rubber masterbatches (without curatives) were kept at room temperature for 7 days for conditioning. After this period, the compound was cut into small pieces and about 0.2 g of the sample was immersed in 25 ml toluene in a stainless-steel wire cage. The solvent was renewed on the 4th day, and after 7 days, the samples were taken out of the solvent and vacuum-dried to a

constant weight. The bound rubber percentage was calculated by the following equation¹²:

$$\text{BR}\% = \frac{W_d - F}{R} \times 100 \quad (1)$$

where W_d is the weight of the dried gel; F , the weight of the filler in the gel (same as weight of the filler in the original sample); and R is the weight of the polymer in the original sample.

For measurement of the mechanical properties of filled vulcanizates, the compound was cured in a hydraulic press under a pressure at 140°C for optimum cure times determined by an MDR2000. Dumb-bell specimens were cut and tested according to ASTM D412. Tear strength was measured on unnotched 90°-angle testing specimens according to ASTM D624. The tests were performed with a universal testing machine at a crosshead speed of 500 mm/min. Hardness was measured using an indentation hardness tester according to ASTM D2240–75. The abrasion resistance index was evaluated by a cylinder abrader (Gotech Testing Machines, GT-7012-D) according to ASTM D5963–97a. The abrasion resistance index is calculated using eq. (2):

$$\text{ARI} = \frac{\Delta m \times d_t}{\Delta m_t \times d} \times 100 \quad (2)$$

where Δm is the mass loss of the standard rubber test piece; d , the density of standard rubber; Δm_t , the mass loss of the test rubber piece; and d_t is the density of the test rubber.

The swelling value Q was determined with the cured rubber specimen (10 mm × 10 mm × 2 mm) using toluene as the solvent, after the equilibrium swelling, the sample was taken out and the solvent was blotted from the surface of the sample and

TABLE I
Recipe and Cure Condition for Preparation of the Rubber Samples

Ingredient	Composition (phr) ^a
SBR1502	100
Zinc oxide	5.0
Stearic acid	3.0
Antioxidant (AO-20)	2.0
Carbon black	Variable
Sulfur	2.5
Accelerator CZ ^b	0.4
Accelerator DM ^c	1.0

Cure condition: 140°C for 20 min.

^a phr, parts per hundred parts rubber.

^b *N*-cyclohexyl-2-benzothiazole sulphenamide.

^c Dibenzothiazole disulfide.

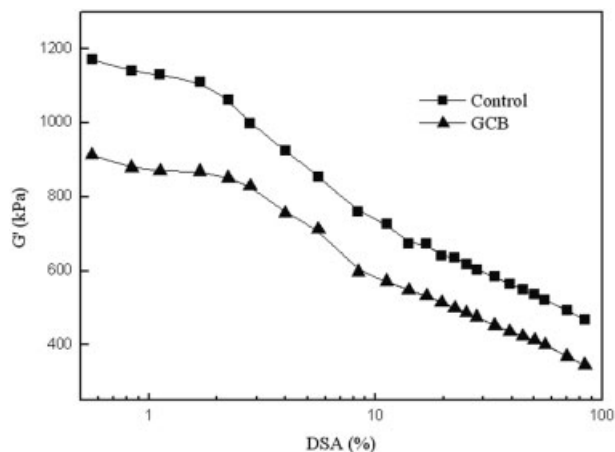


Figure 2 Strain dependence of G' at 60°C and 1.67 Hz for uncured SBR compound.

weighed immediately. The swelling value Q was estimated from eq. (3).

$$Q = \frac{m_1 - m_2}{m_2} \quad (3)$$

where m_1 is the swollen weight, and m_2 is the original weight of the specimen.

Dynamic mechanical properties were measured by a dynamic mechanical analyzer (UBM Rheogel E4000, Rheology) on sample specimens 3 mm in width, 2 mm in thickness, and about 20 mm in length. The temperature dependence of the dynamic tensile modulus was measured at a constant frequency of 1 Hz and a heating rate of $3^\circ\text{C}/\text{min}$. The dispersion of carbon black in vulcanized rubber was assessed by scanning electron microscope (SEM, JEOL, JSM-6360LV).

RESULTS AND DISCUSSION

Modification of carbon black

It is well known that carbon black possesses some molecular surface groups such as carboxylic acid, phenols, quinines, carboxylic lactones, and so on. This is why RFL was chosen as the modifier. The main chain of RFL has a good compatibility with the rubber matrix, whereas the pyridine function reacts with the acidic functional groups on carbon black surface, thus high-energy bonds are achieved between the polymer and the filler particles.

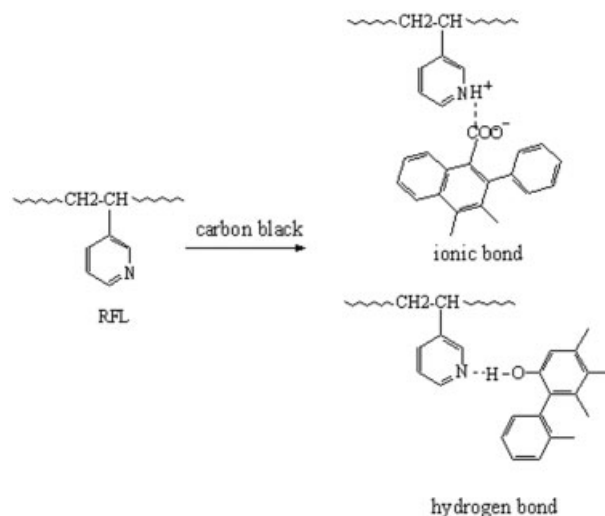
During the process of the heating of carbon black, the dangling pyridine function—by means of abstraction of one hydrogen atom—is capable of an ionic bond forming reaction with the carboxylic acids group present on the carbon black surface. Another possibility is that the formation of hydrogen bond between the

pyridine group and phenol functions present on the filler surface (Scheme 1).

Dynamic properties

Figure 2 shows a plot of storage modulus of the uncured compounds measured at 60°C and 1.67 Hz versus the double strain amplitude. Both figures show a reduction of G' with the increase of the double strain amplitude because of the breakdown of the filler network. It can be seen that the storage modulus of GCB-filled compound is lower than that of the control compound at the same strain amplitude after the same time of mixing. It is well known that hydrocarbon rubbers have low surface energy, while the surface energy of carbon black is much higher. It is difficult to disperse in rubber matrix during processing. This is because of RFL, which reduced the difference in surface energy between rubber and filler, and improved dispersion of GCB. So filler disagglomeration is accelerated as can be seen from SEM images (Fig. 3). Agglomerate breakdown releases immobilized rubber, and this causes a reduction in effective volume fraction of filler. Bound rubber measurements also showed that bound rubber decreases with the RFL-modified carbon black. Thus, the lower storage modulus is because of depressing filler networking.

But the result is on the contrary for the SBR vulcanizates shown in Figure 4. As can be seen, the plot of GCB is above the plot of Control, though, with strain amplitude increasing, the modulus decreases for the filled rubber showing a typical nonlinear behavior, which is generally termed the "Payne Effect."^{13,14} As is well known that the modulus of filled vulcanizates is attributed to the following parts: the pure rubber network, the hydrodynamic effect, specific filler–elastomer interactions, and in addition, a



Scheme 1

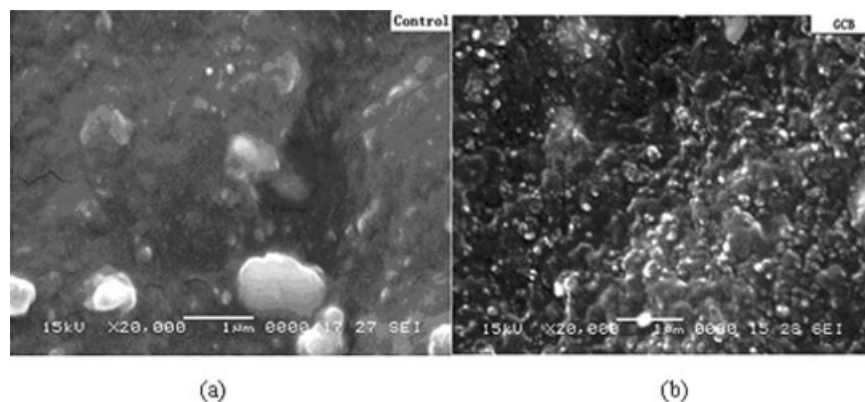


Figure 3 SEM photograph of fracture surface of SBR vulcanizates filled with 45 phr filler: (a) control compound, (b) GCB filled SBR vulcanizate.

strain-dependent part caused by the filler network. It has been widely accepted that the Payne effect is mainly, if not only, related to the filler network formed in the polymer matrix. This suggests that the Payne effect can serve as a measure of filler networking that originates from filler–filler interaction. From Figure 4, it can be seen that there is a stronger filler–filler interaction in control compound than that in compound filled GCB. As is well known, the rubber trapped or caged in the filler network would be at least partially “dead,” losing its identity as an elastomer and behaving as filler in terms of stress–strain properties. Therefore, the effective volume of the GCB would decrease, hence the decreased modulus that is the part of the hydrodynamic effect. So it is obvious that the increased modulus of vulcanizate filled with GCB is mainly contributed to the stronger specific filler–elastomer interactions. That is, GCB shows a stronger

filler–elastomer interaction and a weaker filler–filler interaction than Control.

Figure 5 shows the comparison of dynamic mechanical spectrum of vulcanizates employing unmodified carbon black (Control) and GCB, respectively. It can be found that the $\tan \delta$ of the vulcanized SBR filled GCB at about 0°C is bigger than that of Control, which indicates that GCB has higher wet skid resistance in SBR than that of Control. It has been well established that there is a good correlation between rolling resistance of tread and dynamic loss factor, $\tan \delta$, over the temperature range of 50 to 80°C . The dynamic loss factor, $\tan \delta$, at 60°C is reduced by 19.4%, from 0.129 to 0.104, which indicates that it has lower rolling resistance, and the $\tan \delta$ at 90°C is decreased by 26.5%, from 0.134 to 0.098, which shows that it has lower heat generation in fatigue process.

It is widely accepted that for given polymer and cure systems, filler networking, or microdispersion in the polymer matrix, is the main parameter governing

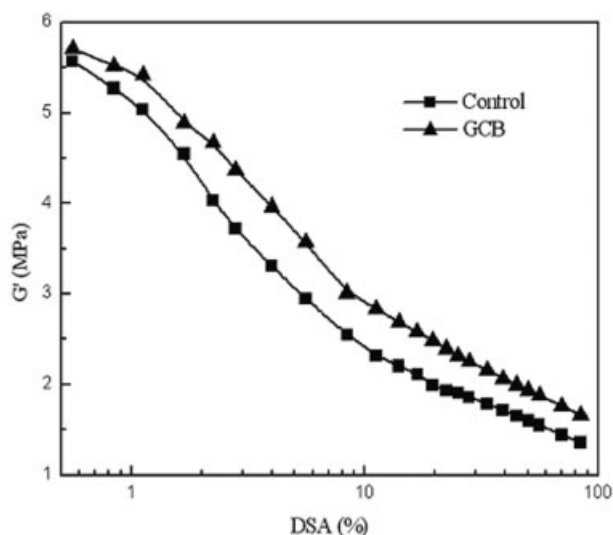


Figure 4 Strain dependence of G' at 60°C and 1.67 Hz for SBR vulcanizates.

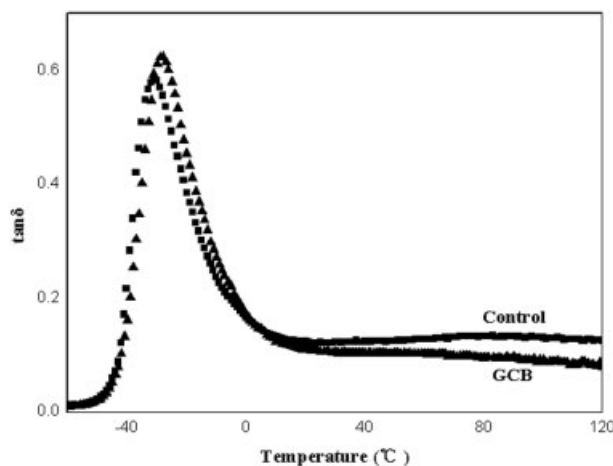


Figure 5 Temperature dependence of $\tan \delta$ for carbon black filled SBR compounds.

TABLE II
Effect of GCB on Vulcanizate Properties and Bound Rubber Content

	Tensile strength (MPa)	Elongation (%)	300% Modulus (MPa)	Hardness, Shore A	Abrasion resistance index	Bound rubber content (%)	Swelling value (Q)
Control ^a	25.1	649.4	10.9	60	115	18.3	3.19
GCB ^b	27.6	616.6	12.1	62	127	10.6	2.51

^a Control compound is filled with 45 phr commercial black.

^b GCB compound is filled with 45 phr GCB.

the dynamic hysteresis of filled rubber.¹⁵ From the results shown in Figure 5, it is obvious that the filler networking effects on dynamic hysteresis at different temperature regions are different.

At sufficiently low temperature (below T_g), it can be seen that both of the $\tan \delta$ values are very low. It is because that the viscosity of the rubber is so high and the free volume in the polymer is so small that the movement of the polymer segments can hardly take place in the time scale involved in the normal dynamic experiment. The fillers have no evident effect on energy dissipation. This results in low energy dissipation and low hysteresis of both GCB and Control. With the increase in temperature the movement of polymer segments increases. When the temperature reaches the transition zone, the viscosity of the polymer decreases very rapidly and the molecule adjustments take place more easily so that the polymer *per se* would be responsible for the high portion of energy dissipation. From Figure 5 it can be seen that at temperatures above the $\tan \delta$ peak in the transition zone, the presence of GCB gives a higher hysteresis for a given energy input. This can be interpreted in terms of an increase in polymer fraction that can be deduced from the reduction of bound rubber content of GCB filled rubber compound (Table II). In this transition zone (about $T_g \sim 0^\circ\text{C}$), the main portion of the composite

for energy dissipation is not filler but polymer matrix, which is mainly due to the movement of segments.

However, at temperatures above 0°C , the viscosity is so low in the polymeric solid that the molecule adjustment is quick enough to be able to follow the dynamic strain. In this rubbery state of the polymer, the filler–filler interaction and the breakdown and reformation of the filler network is the main cause of energy dissipation during dynamic strain.¹⁶ It can be seen from Figure 5 that GCB filled vulcanizate gives a lower $\tan \delta$ value than control vulcanizate, and it is because that after coated by RFL, GCB performs a so weak filler–filler interaction that low energy dissipation due to breakdown and reformation of the network is achieved. Practically, a good balance of $\tan \delta$ at different temperatures with regard to GCB filled tire tread performance, namely, higher hysteresis at low temperature and lower hysteresis at high temperature, is anticipated.

To sum up, for a given rubber system, filler networking which is dominated by the filler–elastomer interaction and filler–filler interaction is the critical factor in the determination of the hysteresis of filled vulcanizates. It plays a great role in determining the dynamic properties of the filled rubber, hysteresis in particular.

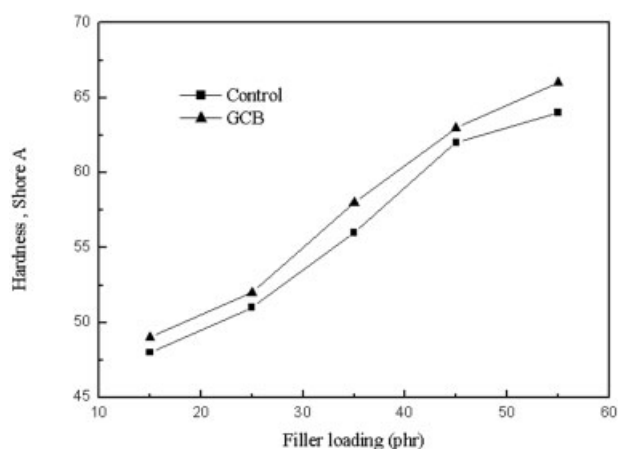


Figure 6 Variation of hardness with filler loading for SBR vulcanizates.

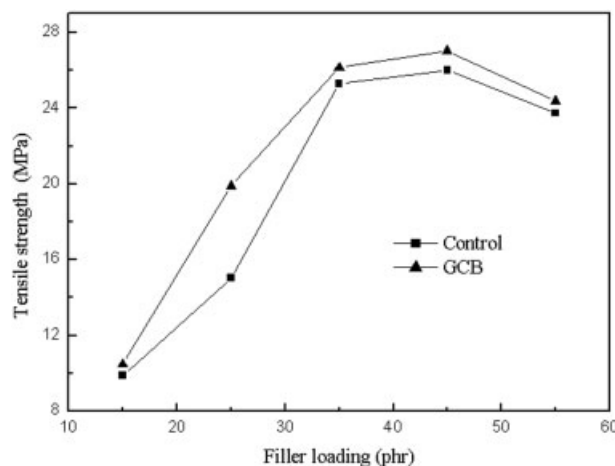


Figure 7 Variation of tensile strength with filler loading for SBR vulcanizates.

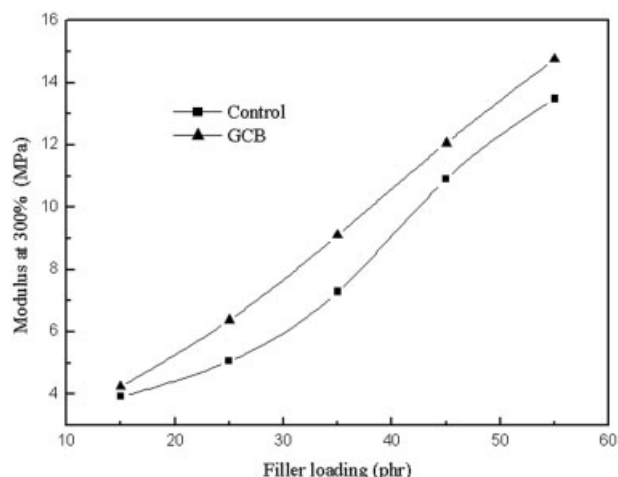


Figure 8 Variation of modulus at 300% with filler loading for SBR vulcanizates.

Mechanical properties

The mechanical properties of vulcanized SBR employing 45 phr Control and 45 phr GCB, respectively, are shown in Table II. The results show that GCB improved both 100 and 300% moduli to a large extent. The modulus is a function of the filler loading, surface area, and structure of carbon black. At higher strain, the value also depends on the filler–elastomer interaction.¹⁷ In this study, with the same loading level of carbon black in both the formulations, the increase of the modulus in the GCB formulation should be attributed to the increase of filler–elastomer interaction. These observations are in tune with the fact that the high extension modulus is a function of rubber crosslink density, which is corroborated by the observations in the swelling value Q (Table II).

All tensile properties are improved except elongation at break. In addition, it is observed that GCB leads to a higher resistance to abrasion. Carbon black has been reported to play an important role in abrasion resistance. In a recent review, Medalia¹⁸ clearly described the effects of carbon black on the abrasion and the tread wear. There was an early report that the treatment of carbon black played a prominent role toward the abrasion resistance.¹⁹ It has come to an agreement that abrasion resistance of filled compounds is mainly determined by morphology of carbon black and polymer–filler interaction. Because of the similar morphology of the two kinds of carbon black, the higher filler–elastomer interaction of vulcanizate employing GCB contributes to the higher abrasion resistance. In addition, better carbon black dispersion (as shown in Fig. 3) may be another reason of the improvement of abrasion resistance.

The mechanical properties of vulcanized SBR employing different loading level of carbon black were also investigated.

The effect of filler loadings on the hardness of SBR compound vulcanizates is shown in Figure 6. The hardness increases with increasing filler loading. And also GCB shows higher value of hardness because of higher crosslink density. Figure 7 shows the effect of filler loading on the tensile strength of SBR vulcanizates. The tensile strength of SBR vulcanizates has a maximum value at about 45 phr filler loading. And also the modulus at 300% of SBR vulcanizates increases with filler loading increasing (Fig. 8).

CONCLUSIONS

It can be concluded from the study on dynamic properties that carbon black modified with RFL could effectively enhance the filler–elastomer interaction and weaken the filler–filler interaction. Practically, it is observed that there would be a good balance of loss factor at different temperature with regard to tire tread performance, namely, higher hysteresis at low temperature and low hysteresis at high temperature. And SBR vulcanizates filled with GCB show improved mechanical properties due to the better dispersion of filler.

References

1. Medalia, A. I.; Kraus, G. In *Science and Technology of Rubber*, 2nd ed.; Mark, J. E., Erman, B., Eirich, F. R., Eds.; Academic Press: San Diego, 1994; Chapter 8.
2. Nordsiek, K. H. *Kautsch Gummi Kunstst* 1985, 38, 178.
3. Wolff, S.; Wang, M.-J. In *Carbon Black, Science and Technology*, 2nd ed.; Donnet, J. B., Bansal, R. C., Wang, M.-J., Eds.; Marcel Dekker: New York, 1993; Chapter 9.
4. Medalia, A. I. *Rubber Chem Technol* 1991, 64, 481.
5. Payne, A. R. In *Reinforcement of Elastomers*; Kraus, G., Ed.; Interscience: New York, 1965; Chapter 3.
6. Payne, A. R. *Rubber J* 1964, 146, 36.
7. Donnet, J. B.; Bansal, R. C.; Wang, M.-J. *Carbon Black*; Marcel Dekker: New York, 1993.
8. Kraus, G. *J Appl Polym Sci Appl Polym Symp* 1984, 39, 75.
9. Lin, C.-R.; Lee, Y.-D. *Macromol Theory Simul* 1996, 5, 1075.
10. Huber, G.; Vilgis, T. A.; Heinrich, G. *J Phys: Condens Matter* 1996, 8, L409.
11. Wu, C.-F.; Otani, Y.; Namiki, N.; Emi, H.; Nitta, K.-H.; Kubota, S. *J Appl Polym Sci* 2001, 82, 1788.
12. Brennan, J. J.; Jermy, T. E.; Boonstra, B. B. *J Appl Polym Sci* 1964, 8, 2689.
13. Payne, A. R. *J Polym Sci* 1962, 6, 57.
14. Payne, A. R.; Whittaker, R. E. *Rubber Chem Technol* 1971, 44, 1207.
15. Wang, M.-J.; Lu, S. X.; Mahmud, K. *J Polym Sci Part B: Polym Phys* 2000, 38, 1240.
16. Wang, M.-J.; Patterson, W. J.; Brown, T. A.; Money Penny, H. G. *Rubber Plast News* 1998, 9, 12.
17. Wolff, S.; Wang, M.-J.; Tan, E. H. *Kautsch Gummi Kunstst* 1994, 47, 873.
18. Medalia, A. I. *Kautsch Gummi Kunstst* 1994, 47, 364.
19. Sweitzer, C. W.; Burgess, K. A.; Lyon, F. *Rubber World* 1961, 143, 73.