

Comparative Study of Silica-, Nanoclay- and Carbon Black-Filled EPDM Rubbers

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ABSTRACT: Silica-, nanoclay-, and carbon black (CB)-filled ethylene-propylene-diene terpolymer (EPDM) mixtures were prepared and subsequently vulcanized. Rheological properties and cure characteristics of the mixtures and mechanical properties of vulcanizates were measured. Rheological property measurements indicated the storage modulus, loss modulus, and complex dynamic viscosity of silica-filled EPDM mixtures were much higher than those of CB-filled EPDM mixtures while $\tan \delta$ values were lower. The optimum cure time of silica- and nanoclay-filled EPDM mixtures increased with filler loading, whereas the values for CB-filled mixtures slightly decreased with loading. The hardness, modulus, elongation at break, and tensile

strength of all the vulcanizates increased with increasing filler loading. The elongation at break of CB-filled EPDM vulcanizates increased insignificantly with CB loading. Among the three fillers, the increase of the tensile strength and elongation at break was most significant for silica-filled EPDM vulcanizates. Remarkably, for 30 phr silica-filled EPDM vulcanizates, a tensile strength and elongation at break of 23.5 MPa and 1045% was achieved, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 767–774, 2008

Key words: rubber; fillers; vulcanization; reinforcement; rheology

INTRODUCTION

Ethylene-propylene-diene terpolymer (EPDM) finds increasing application in automobile sectors due to its good aging properties and high filler-loading capacity.¹ Fillers are incorporated into EPDM rubber matrices mainly to achieve improvement of service properties and in many cases to reduce the material cost. The performance of a filler is governed by its characteristics.^{2–5} There are a number of widely used commercial fillers. Carbon black (CB), silica, and clay are the classical examples. Many investigations on EPDM blends have been carried out to study the effects of CB,^{2–17} silica,^{13,18–24} clay,^{25–27} and white rice husk ash (WRHA)^{28,29} on the electrical properties and the curing characteristics as well as the physical properties of the filled EPDM. These research efforts are briefly reviewed below.

The effects of mixing procedure, different CBs, and sequence of addition of plasticizer on the EPDM vulcanizate properties, including low-temperature properties, were considered.² Comparison of properties of the semireinforcing CB-filled sulfur-vulcanized EPDM and SBR was made.⁴ In addition, the

effects of various fillers (kaolin, quartz, PVC, talc, graphite, medium thermal CB, semireinforcing, and high-abrasion CB) on properties of the EPDM vulcanizates cured with tetramethylthiuram disulfide (TMTD) and sulfur/CBS before and after heat aging were studied.⁵ The compressive stress-strain properties, energy absorption characteristics and morphology of unfilled and conductive CB-filled oil-extended EPDM cellular vulcanizates were studied including the effects of filler, blowing agent loading, and strain rate.^{3,6} It was found that the average cell size, maximum cell size, cell density, and physical properties varied with variation of blowing agent and filler contents. The elastic nature of closed cells reduced the hysteresis loss compared with solid compounds. The stress-relaxation behavior was independent of blowing agent content. The cell morphology and rheological properties of gum and CB-filled EPDM compounds were studied as a function of the blowing and curing agent, extrusion temperature, and shear rate.¹⁵ Compared with the absence of curing agent, a significant reduction in stress and viscosity with the blowing agent in the presence of curing agent was observed. The rheological and cure behavior, gel content, crosslink density, and mechanical performance of the virgin unfilled and CB-filled EPDM was investigated and compared to ultrasonically devulcanized and revulcanized samples.^{7,8} Improvements in mechanical properties were observed in the unfilled revulcanizates, but the opposite was the case for the filled rubber. Blend vul-

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canizates containing the virgin, filled, and devulcanized EPDM provided improved physical properties over the blended vulcanizates of ground and virgin EPDM.⁷ The mechanical and dynamic properties and electrical conductivity of EPDM filled with untreated and nitric acid-treated conductive CB were studied.⁹ The effects of temperature and chemical and radiation crosslinking on the electrical conductivity of the composites were reported. A comparison of properties was also made with CB-filled EPDM and EVA-EPDM blends. An experimental and theoretical investigation of the mechanical properties of the CB-filled EPDM was carried out.¹⁰ Uniaxial experimental stress-strain curves were fitted to the Ogden strain energy function. The contour maps of the derivatives of the strain energy function with respect to strain invariants were obtained. EPDM compounds containing silica treated with silane of various aliphatic chain length coupling agents showed smaller agglomerate size, lower viscosity, and lower swell reduction compared to the untreated silica compound after equivalent mixing times.¹¹ Short-chain silane-treated silica compounds exhibited the smallest agglomerate size. The temperature-coefficient effects and electrical behavior of CB-filled semicrystalline and amorphous EPDM irradiated by γ -ray was reported.¹² The EPDM compound properties at various CB and silica loadings were studied to clarify the importance of volume fraction and a transition point at which abrupt changes in compound properties occur.¹³ By manipulating volume fraction in conjunction with colloidal properties of the fillers and using the theory of total volume and surface area, silica/CB-filled compounds were obtained with lower hysteresis than that of CB-filled compounds but matching the performance of silica-filled compounds. Physical and mechanical properties, aging behavior, and electrical conductivity of EPDM vulcanizates containing extra conducting CB were also investigated.¹⁴ CB loading caused a monotonic increase in density and hardness with tensile strength leveling off at CB filler loading >40 phr. Electrical conductivity indicated a percolation concentration in the range of 15–30 phr of CB loading. The shear viscosity, creep, and shear rate transient behavior of EPDM filled with 20% vol of calcium carbonate, CB, silica, and zinc oxide of similar particle size were studied.¹⁶ All of the compounds exhibited increased viscosity and yield stress with values being greatest in the compounds containing calcium carbonate and zinc oxide. CB-filled zinc sulfonated EPDM of high ethylene content containing both paraffinic oil and zinc stearate plasticizers indicated the lowest viscosity.¹⁷ It was shown that paraffinic oil acted as a plasticizer at ambient conditions, while zinc stearate acted as a plasticizer in the ionic domains at high temperatures.

By using two-stage vulcanization, the effect of a multifunctional rubber additive (bis diisopropyl thio-phosphoryl disulfide) and a silane-coupling agent (bis 3-triethoxy silyl propyl tetrasulphide) on the interaction between EPDM rubber and silica was enhanced.¹⁸ This was done by heating EPDM rubber along with additives up to the time just before the commencement of cure with subsequent addition of the filler to the preheated rubber to get the final mix. The effects of coupling agent [(triallyl cyanurate (TAC))] on peroxide vulcanization and mechanical properties of the precipitated silica-filled EPDM were studied.¹⁹ It was shown that silica improved mechanical properties and TAC decreased Mooney viscosity and scorch time while increasing the optimum curing time and rubber-filler interaction. Also, the addition of chloroprene rubber to EPDM affected the dispersion of silica in EPDM leading to an improvement of the network structure and physical properties of the vulcanizates.²⁰ Increasing the silica content in dynamically crosslinked 60/40 EPDM/PP blends led to the formation of large-size EPDM aggregates shelled by a layer of PP causing a reduction in damping behavior.²¹ Addition of a silane-coupling agent (Si69) to the silica-filled EPDM/PP blends caused higher rubbery-like tensile characteristics due to the strengthening of interfacial adhesion between the PP matrix and silica-filled EPDM phase. Incorporation of up to 20 phr of precipitated silica into a thermoplastic elastomer containing 100 phr maleated EPDM rubber, 10 phr zinc oxide, 1 phr stearic acid, and 30 phr zinc stearate, indicated an improvement in modulus, tensile strength, and tear resistance, a decrease in $\tan \delta$ at T_g , but an increase in $\tan \delta$ at the ionic transition.²² It was stated that, besides the dispersive-type forces between the backbone chains and the filler particles, the ionic domains in the thermoplastic elastomer interacted strongly with the polar sites on the filler surface. Large loading of precipitated silica into EPDM was shown to improve its adhesion to Nylon and brass.²³

A possibility of improvement of dispersion of nanoclay in EPDM by the addition of maleated EPDM (EPDM-g-MA) in combination with organoclay modified by maleic anhydride-grafted liquid vinyl polybutadiene (LVPB-g-MA) was shown.²⁴ In particular, use of LVPB-g-MA-modified organoclay increased the degree of dispersion, as measured by X-ray diffraction, giving increased thermal stability and modulus, and decreased swelling. Sulfur- and peroxide-cured EPDM/organic montmorillonite (OMMT) nanocomposites were prepared.²⁵ Sulfur-cured EPDM composites showed intercalation and exfoliation leading to better mechanical properties. But the peroxide-cured EPDM composites showed intercalated structure with properties being virtually unchanged by the addition of OMMT. Zinc-sulfo-

nated EPDM of high ethylene content with clay showed improvement in most of the physical properties.²⁶ Zinc stearate reduced the melt viscosity of the clay-filled zinc-sulfonated EPDM during high-temperature processing without adversely affecting the physical properties at ambient temperatures.

Mechanical properties, recyclability, and curing behavior of WRHA- and silica-filled EPDM/PP thermoplastic elastomers at loadings up to 50 phr were compared.^{27,28} The curing rate was increased with increasing WRHA loading, whereas the opposite trend was observed for silica-filled vulcanizates. Compared to the silica-filled vulcanizates, the effect of filler loading on the physical properties of WRHA-filled vulcanizates was not significant. It was concluded that WRHA could be used as a diluent filler for EPDM rubber, whereas silica can be used as a reinforcing filler. Study of the WRHA-filled PP/EPDM blends using different mixing sequences indicated similar tensile strength, tear strength, and hardness, except the blend prepared by mixing sequence of the PP followed by the addition of WRHA to molten EPDM.²⁹ The latter blend exhibited the highest tensile strength and the lowest elongation at break. The sequence, in which WRHA followed by addition of PP to molten EPDM rubber, gave the blend with the highest elongation at break and comparable tensile strength.

The above-mentioned brief review indicates that no detailed work in open literature has been carried out to compare rheological and vulcanization behavior and mechanical performance of silica-, nanoclay-, and CB-filled EPDM rubber obtained using the same mixing procedures, equipment, and mixing conditions with silica and CB having the same surface area. Thus, in this study, the silica-, nanoclay-, and CB-filled EPDM mixtures were prepared using the same device, and their various behaviors were investigated. The effect of filler type and filler loading on dynamic properties and curing characteristics of the mixtures and mechanical properties of filled EPDM vulcanizates are studied and compared. Exceptionally high tensile strength and elongation at break were achieved for 30 phr silica-filled EPDM vulcanizate.

EXPERIMENTAL

Materials

EPDM with 5-ethylidene-2-norbornene (ENB) as a termonomer (pelletized, 70% ethylene content, 4.5% ENB unsaturation, and density 0.86 g cm^{-3}) under the trade name Keltan 5636A (DSM Elastomers Americas, Addis, LA) was used. Three different kinds of fillers were used. These included (1) an amorphous precipitated silica, Hi-Sil 132 with BET

surface area of $200 \text{ m}^2/\text{g}$ (PPG Industries, Barberton, OH); (2) an organoclay, Cloisite[®] 15A (Southern Clay Products, Gonzales, Texas); (3) CB, V1391 with a surface area of $202 \text{ m}^2/\text{g}$ (Cabot, Billerica, MA). The curing ingredients used were zinc oxide, stearic acid, sulfur, TMTD, and 2-mercaptobenzothiazole (MBT; Akrochem, Akron, OH).

Preparation of EPDM/filler mixtures

The precipitated silica, nanoclay, and CB were incorporated in EPDM at concentrations up to 30 phr using a Moriyama mixer (D₃-7.5, Kitau, Osaka, Japan) having a chamber capacity of 3 L. Compounding was performed at 150°C. The rotor speeds of the mixer were 50 and 75 rpm for front and rear rotor, respectively. After mixing, the mixtures were ground with a grinder (Nelmor, N. Uxbridge, MA) using a screen with 5-mm diameter holes.

The EPDM and prepared EPDM/filler mixtures were processed in a 1.5-in single screw coaxial extruder.³⁰ The temperature of the barrel was set at 100°C, the die gap was set at 2.0 mm, and the flow rate was 20 g/min.

Preparation of vulcanizates

The prepared samples were compounded with curatives on a two-roll mill (Dependable Rubber Machinery, Cleveland, OH) at room temperature. The nip of the rolls was kept at 2 mm at a speed of 40 rpm. One minute was required to soften the mixtures. After softening, zinc oxide, stearic acid, TMTD, MBT, and sulfur were added sequentially. The total mixing time was 20 min. The two-roll mill was cooled by cold water circulation during mixing. The cure recipe for the virgin vulcanizates was 5 phr zinc oxide, 1 phr stearic acid, 1.5 phr sulfur, 1 phr TMTD, and 0.5 phr MBT. This recipe was based on ASTM D 3568.

The sample was then molded into slabs (127 mm × 127 mm × 2 mm) at a temperature of 160°C and at a pressure of 13.8 MPa with an electrically heated compression-molding press (Carver, Wabash, IN). The cure time corresponded to the time required to achieve 90% of the maximum torque (t_{90}). Cure curves were obtained at a frequency of 100 cpm and a temperature of 160°C using an Advanced Polymer Analyzer (APA 2000, Alpha Technologies, Akron, OH). After curing, the vulcanized sheets were taken out from the mold and immediately cooled under tap water to restrict further curing.

Characterization

The rheological behaviors were investigated using an Advanced Polymer Analyzer (APA 2000, Alpha

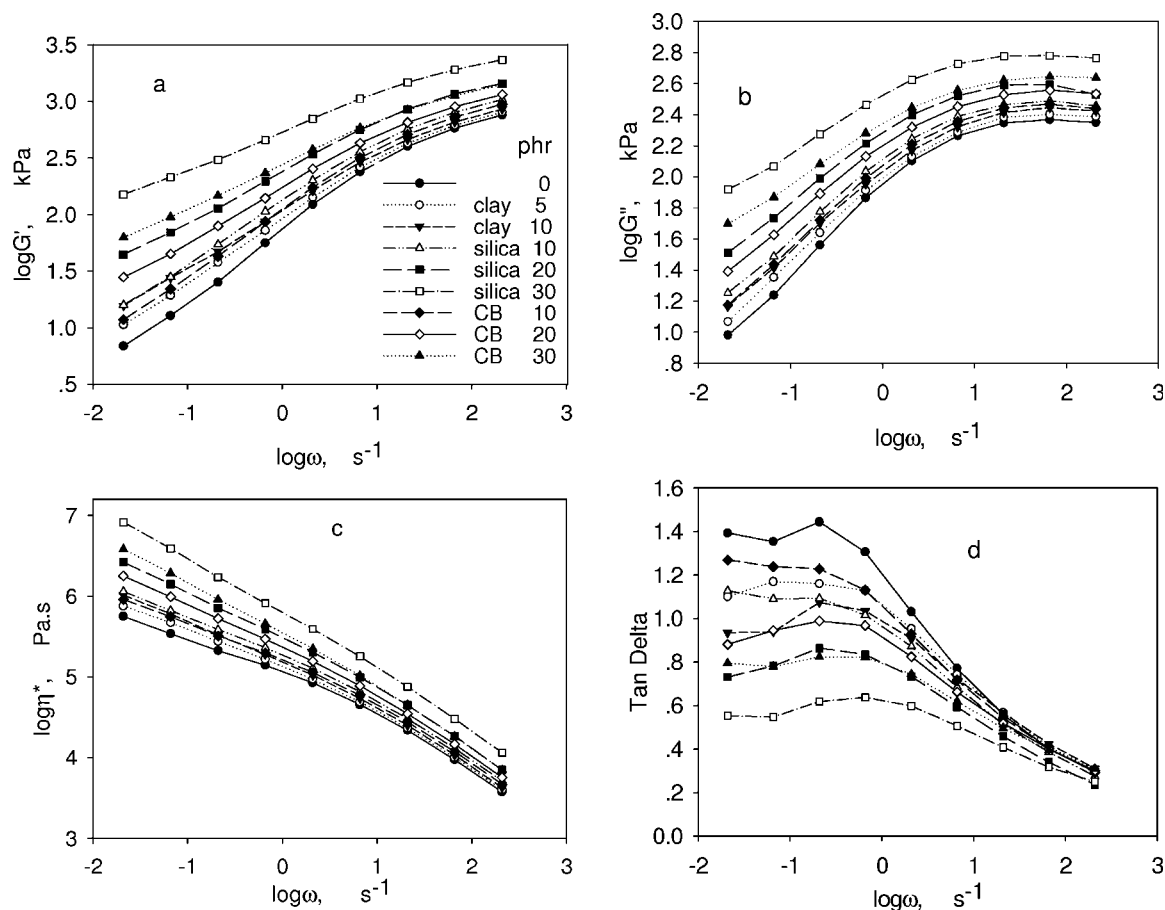


Figure 1 The storage (a) and loss (b) moduli, complex dynamic viscosity (c), and $\tan \delta$ (d) as a function of a frequency for EPDM and EPDM/filler mixtures at 100°C.

Technologies) at a temperature of 100°C and a frequency range of 0.2–2000 cpm at a strain amplitude of 7.1%. A biconical rotor with an angle of 7° and a diameter of 63.5 mm was used. Obviously, the large angle of the biconical rotor in APA 2000 does not provide a strictly uniform strain rate field. Nevertheless, the data generated is suitable for a comparative analysis of rheological behavior of different compounds. Also, it should be noted that APA 2000 is widely used as an instrument for the rheological characterization of compounds in rubber industry.

An Instron tensile tester (Model 5567, Instron, Canton, MA) was used for the mechanical property measurements. Stress–strain tests were performed at room temperature at a crosshead speed of 500 mm/min (ASTM D 412). At least 10 samples were used for tensile property measurements. The average values of these data are reported. The relative error in modulus, tensile strength, and elongation at break was 2.5, 8.8, and 14.4%, respectively.

The hardness shore test was carried out using the international rubber hardness tester according to ASTM 2240.

RESULTS AND DISCUSSION

Rheological properties

Figure 1 is a comparison of the storage (a) and loss (b) moduli, complex dynamic viscosity (c) and $\tan \delta$ (d) of EPDM and various filled EPDM mixtures versus frequency at 100°C and at a strain amplitude of 0.07. It is clearly seen that the storage and loss moduli and complex dynamic viscosity of the silica-, nanoclay-, and CB-filled EPDM mixtures are higher than those of the unfilled EPDM over the frequency measurement range. These properties continuously increased with increased filler loading with different fillers showing their different level. In general, the storage and loss moduli and complex dynamic viscosity of the silica-filled EPDM rubber shows much higher values than that of the CB-filled EPDM. Evidently, filler–filler and filler–polymer interactions are significantly higher in case of the silica-filled EPDM rubber. However, there was no significant variation in the storage modulus between 10 phr silica- and nanoclay-filled EPDM mixtures at low-frequency values, indicating that the filler–filler network was not formed at this low concentration. At the same time,

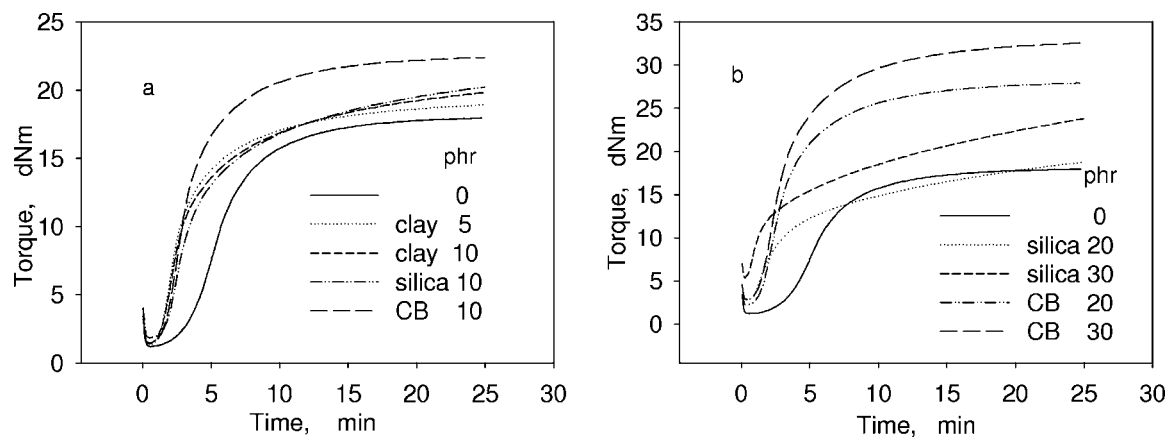


Figure 2 Cure curves of EPDM and various EPDM/filler mixtures.

the storage modulus of the 10 phr silica-filled EPDM mixture was slightly higher than that of the 10 phr nanoclay-filled EPDM mixture in the high-frequency region, evidently indicating better filler-polymer interactions in case of the silica-filled EPDM rubber. The storage modulus for the 10 phr nanoclay-filled EPDM mixture was slightly higher than that of the 10 phr CB-filled mixture in the low-frequency region. However, the storage modulus showed an opposite trend at high frequency. Similar observation can be seen on the loss modulus and complex viscosity behaviors.

The dependences of $\tan \delta$ on frequency for EPDM and various EPDM/filler mixtures shown in Figure 1(d) indicates that $\tan \delta$ decreases with frequency but its frequency dependence decreased with increased filler loading. The reduction of $\tan \delta$ with frequency was due to the fact that EPDM and EPDM/filler mixtures were in the transition region from the fluid state to the rubbery state within the frequency measurement range.³¹ The $\tan \delta$ of the various EPDM/filler mixtures decreased with increased filler loading. Because of the strong polarity of the silica filler and the presence of silanol groups,³² the samples at 10, 20, and 30 phr silica-filled EPDM mixtures showed lower $\tan \delta$ values than the CB-filled samples at the same filler loading.

This indicates that the silica-filled EPDM mixtures are more elastic than the CB-filled ones. In addition, $\tan \delta$ of the 10 phr silica-filled EPDM mixture was higher than that of the 10 phr nanoclay-filled one in the low frequency region, whereas the $\tan \delta$ of the 10 phr silica-filled EPDM mixture was lower than that of the 10 phr nanoclay-filled one at high-frequency values. This indicated that the 10 phr silica-filled EPDM mixture was less elastic than the 10 phr nanoclay-filled sample in the low frequency region. At the same time, the 10 phr silica-filled EPDM mixture was more elastic than the nanoclay-filled sample. It is also seen that the effect of various fillers on $\tan \delta$ diminishes in the high-frequency region.

Cure characteristics

Figure 2 shows the curing curves of the silica-, nanoclay-, and CB-filled EPDM mixtures at different loadings. It is seen that the curing behaviors of silica-, nanoclay-, and CB-filled EPDM mixtures are significantly different, indicating strong effects of filler loading and filler type. Table I lists various parameters characterizing curing behavior including the minimum torque (M_L), maximum torque (M_H), scorch time (t_{S1}), and optimum cure time (t_{90}). It can be seen from the results that the optimum cure time

TABLE I
Curing Characteristics of EPDM and Silica-, Nanoclay-, and CB-Filled EPDM Mixtures

Filler type	Loading of filler (phr)	M_L (dNm)	M_H (dNm)	t_{S1} (min)	t_{90} (min)
Nanoclay	0	1.19	18.0	2.74	11.22
	5	1.25	18.9	1.28	10.30
	10	1.40	19.8	1.34	13.40
Silica	10	1.83	20.2	1.72	14.72
	20	2.79	19.1	1.05	17.53
	30	5.36	23.8	0.65	18.69
CB	10	1.46	22.4	1.53	9.32
	20	2.18	27.9	1.27	9.50
	30	2.82	32.6	1.15	9.94

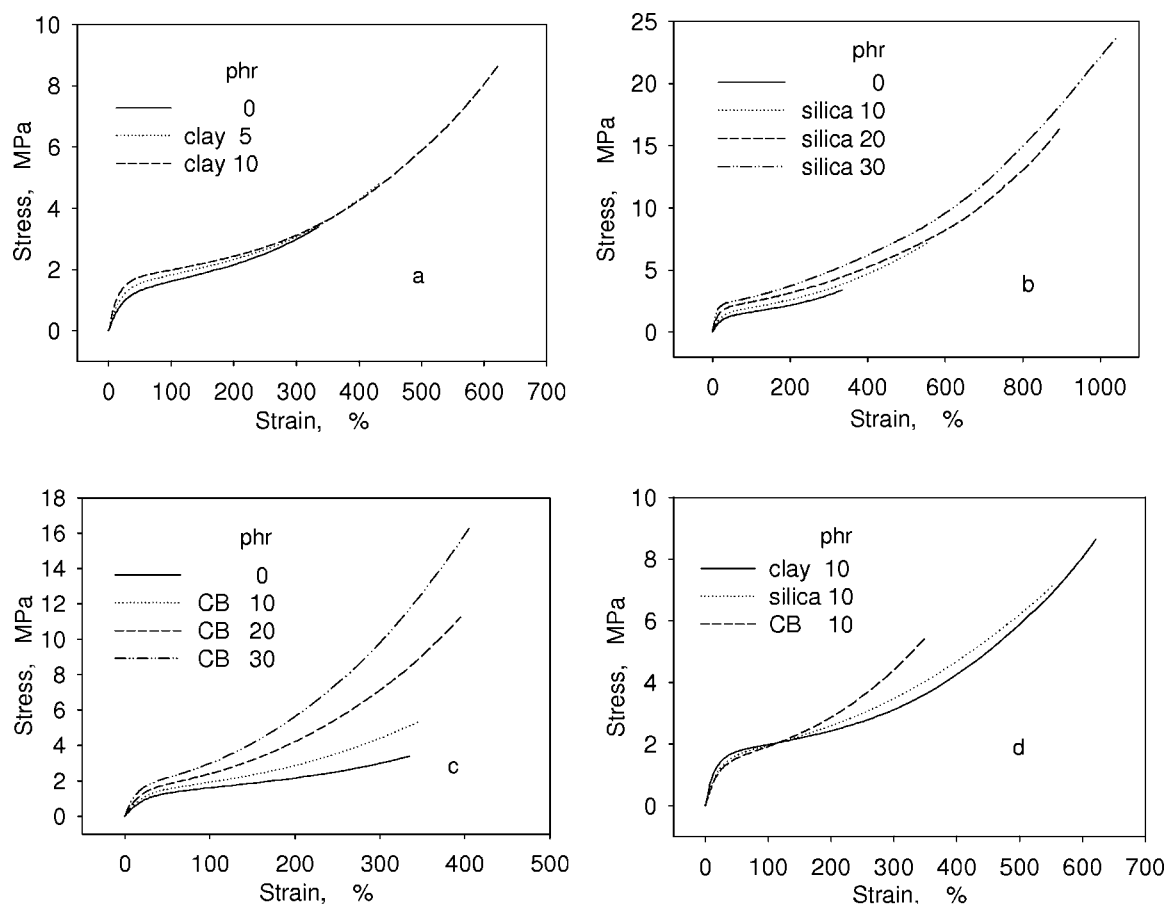


Figure 3 The stress–strain curves for EPDM vulcanizates and various filled EPDM vulcanizates.

of silica- and nanoclay-filled EPDM mixtures gradually increases as filler loading increases. The curing behaviors of the silica-filled EPDM mixtures are consistent with results reported earlier.²⁸ This can be explained by the fact that silica and nanoclay interacts with accelerators such as MBT and activators such as ZnO during compounding, leading to cure retardation.^{28,33,34} Therefore, as silica and nanoclay loading increases, this interference becomes more significant such that the vulcanization process is retarded. However, the optimum cure time of CB-filled mixtures slightly decreases with CB loading, suggesting that the incorporation of CB enhances the cure rate. This is due to CB surface reactivity, which speeds up the curing process. The minimum and maximum torques of vulcanization increased with increasing silica, nanoclay, and CB loading. Filler particles dispersed in EPDM matrix restrict the mobility of the EPDM macromolecular chains. Consequently, the torque increases with the filler loading. At the same time, the maximum torque of CB-filled mixtures was significantly higher than those of silica- and nanoclay-filled ones. The minimum torque of filled EPDM mixtures, however, exhibits a different trend being highest for silica-filled mixtures. It should be noted that the minimum torque is

related to the viscous behavior of rubber. Thus, a comparison of behavior of the minimum torque can be made with that of the complex viscosity data discussed earlier. The higher minimum torque for silica-filled mixtures is a result of the higher complex viscosity of their compounds. Clearly, this observation is in agreement with the complex viscosity behavior discussed earlier. The scorch time of all mixtures decreased with increasing filler loading. It can be seen that the scorch time of silica-filled mixtures decreased at a higher rate than that of CB-filled ones.

Mechanical properties

The stress–strain curves of silica-, nanoclay-, and CB-filled EPDM vulcanizates are shown in Figure 3. Clearly, the tensile strength, modulus, and elongation at break of the silica-, nanoclay-, and CB-filled vulcanizates increased with filler loading. These properties of the silica- and CB-filled EPDM vulcanizates agree with the results reported earlier for the silica-²⁸ and CB-filled³⁵ vulcanizates. All the filled vulcanizates show the strain hardening effect as indicated by the upturn in the stress–strain curves.

The effect of filler loading and filler type on the tensile strength, elongation at break, modulus at

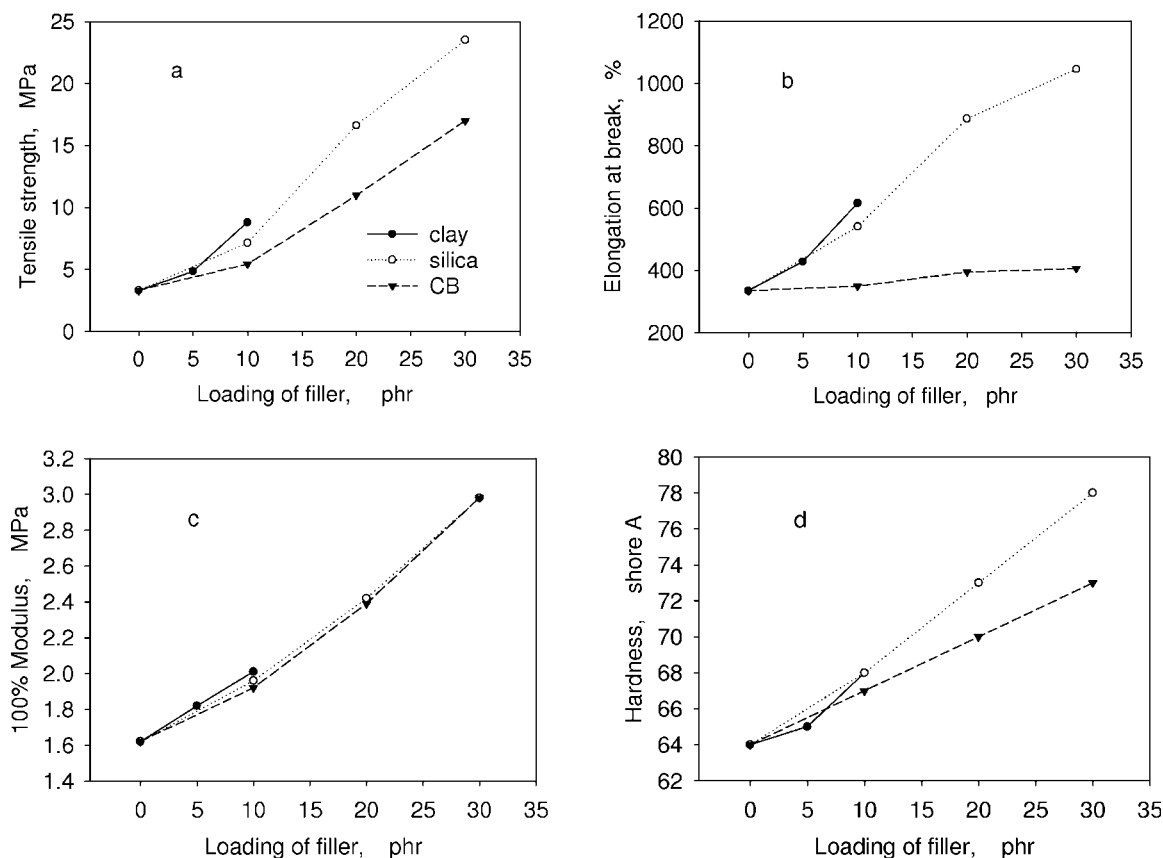


Figure 4 The tensile strength (a), elongation at break (b), modulus (c), and hardness (d) as a function of filler loading for EPDM-filled vulcanizates.

100% elongation, and hardness of the silica-, nanoclay-, and CB-filled EPDM vulcanizates are shown in Figure 4. The tensile strength and elongation at break of vulcanizates are significantly increased with filler loading, with 30 phr silica-filled EPDM vulcanizates showing highest values. Remarkably, the tensile strength and elongation at break of the 30 phr silica-filled EPDM vulcanizates was 23.5 MPa and 1045%, respectively. Among various fillers at 10 phr loading, the tensile strength and elongation at break of the nanoclay-filled EPDM vulcanizates was highest. Clearly, the rate of increase of the hardness, modulus, elongation at break, and tensile strength with loading is highest for silica- and nanoclay-filled vulcanizates. An increase in the elongation at break of CB-filled EPDM vulcanizates with loading was insignificant. The effect of different fillers on the modulus at 100% elongation was about same.

CONCLUSIONS

The storage modulus, loss modulus, and complex dynamic viscosity of the silica-, nanoclay-, and CB-filled mixtures increased with increased filler loading. The values for silica-filled EPDM mixtures were

much higher than those of the CB-filled ones. The $\tan \delta$ for the filled EPDM mixtures decreased with increase of filler loading. At the same filler loading, $\tan \delta$ values for the silica-filled EPDM mixtures were lower than that of CB-filled samples. The optimum cure time of silica- and nanoclay-filled EPDM mixtures increases with filler loading, whereas the optimum cure time of CB-filled mixtures slightly decreases as CB loading increases. The maximum torque and the minimum torque of the silica-, nanoclay-, and CB-filled mixtures increased with filler loading. The scorch time of silica-filled mixtures with loading decreased at a higher rate than that of CB-filled mixtures. The hardness, modulus, elongation at break, and tensile strength of all the vulcanizates increased with increasing filler loading. However, an increase in the elongation at break of CB-filled EPDM vulcanizates with loading was insignificant. The increase in tensile strength, elongation at break, and hardness of silica-filled EPDM vulcanizates was significantly higher than that of CB-filled ones with increasing filler loading. In particular, at 30 phr silica loading, the tensile strength values as high as 23.5 MPa and the elongation at break value as high as 1045% were obtained. Difference in dependencies of the modulus at 100% elongation of

the EPDM vulcanizates with filler loading was insignificant among various fillers.

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References

1. Guriya, K. C.; Tripathy, D. K. *Plastics, Rubber Compos Process Appl* 1995, 23, 193.
2. Sosnowski, J.; Zmuda, W. A. *Elastomery* 2007, 11, 26.
3. Mahapatra, S. P.; Tripathy, D. K. *Cell Polym* 2005, 24, 209.
4. Yurovska, I.; Gaudet, G.; Novakoski, D.; Dickinson, R. Paper 14 presented at 167th ACS Rubber Division Meeting; San Antonio, TX, 2005.
5. Wazzan, A. A. *Intern J Polym Mater* 2005, 54, 783.
6. Mahapatra, S. P.; Tripathy, D. K. *Cell Polym* 2004, 23, 127.
7. Yun, J.; Isayev, A. I. *J Appl Polym Sci* 2004, 92, 132.
8. Yun, J.; Yashin, V. V.; Isayev, A. I. *J Appl Polym Sci* 2004, 91, 1646.
9. Das, N. C.; Chaki, T. K.; Khastgir, D. *J Appl Polym Sci* 2003, 90, 2073.
10. Kakavas, P. A. *Polym Eng Sci* 2001, 41, 1589.
11. Kim, K. J.; White, J. L. *Compos Interf* 2002, 9, 541.
12. He, X.; Wang, L.; Chen, X. J. *J Appl Polym Sci* 2001, 80, 1571.
13. Patel, A. C. *J Elast Plast* 2000, 32, 211.
14. Ghosh, P.; Chakrabarti, A. *Eur Polym J* 2000, 36, 1043.
15. Guriya, K. Ch.; Bhattachariya, A. K.; Tripathy, D. K. *Polymer* 1997, 39, 109.
16. Li, L. L.; White, J. L. *Rubber Chem Technol* 1996, 69, 628.
17. Kurian, T.; Bhattacharya, A. K.; De, P. P.; Tripathy, D. K.; De, S. K.; Peiffer, D. G. *Plast Rubber Compos Proces Appl* 1995, 24, 285.
18. Das, A.; De, D.; Naskar, N.; Debnath, S. C. *J Appl Polym Sci* 2006, 99, 1132.
19. Abtahi, M.; Bakhshandeh, G. R.; Darestani F. T. *Polym Plast Technol Eng* 2006, 45, 183.
20. Das, A.; Debnath, S. C.; De, D.; Basu, D. K. *J Appl Polym Sci* 2004, 93, 196.
21. Bazgir, S.; Katbab, A. A.; Nazockdast, H. J. *Appl Polym Sci* 2004, 92, 2000.
22. Datta, S.; Bhattacharya, A. K.; De, S. K.; Kontos, E. G.; Wefer, J. M. *Polymer* 1996, 37, 2581.
23. Hewitt, N. L.; Wagner, M. P. *Adhes Age* 1974, 17, 35.
24. Kang, D. H.; Kim, D.; Yoon, S. H.; Kim, D.; Barry, C.; Mead, J. *Macromol Mater Eng* 2007, 292, 329.
25. Zheng, H.; Zhang, Y.; Peng, Z. L.; Zhang, Y. X. *Polym Polym Compos* 2004, 12, 197.
26. Kurian, T.; De, P. P.; Tripathy, D. K.; De, S. K.; Peiffer, D. G. *J Appl Polym Sci* 1996, 62, 1729.
27. Siriwardena, S.; Ismail, H.; Ishiaku, U. S. *Plast Rubber Compos Process Appl* 2002, 31, 167.
28. Siriwardena, S.; Ismail, H.; Ishiaku, U. S. *Polym Intern* 2001, 50, 707.
29. Siriwardena, S.; Ismail, H.; Ishiaku, U. S. *Polym Test* 2001, 20, 105.
30. Isayev, A. I.; Chen, J.; Tukachinsky, A. *Rubber Chem Technol* 1995, 68, 267.
31. Feng, W.; Isayev, A. I. *J Polym Sci Part B: Polym Phys* 2005, 43, 334.
32. Havet, G.; Isayev, A. I. *Rheol Acta* 2003, 42, 47.
33. Wagner, M. P. *Rubber Chem Technol* 1976, 49, 704.
34. Bachmann, J. H.; Sellers, J. W.; Wagner, M. P.; Wolf, R. F. *Rubber Chem Technol* 1959, 32, 1286.
35. Chul, H. L.; Sang, W. K. *J Appl Polym Sci* 2000, 78, 2540.