Preparation and Properties of Carbon Black Filled EPDM/POE Thermaplastic Vulcanizates

Xiu Feng Lv, Bao Sheng Zhang, Gui Xue Qiu

College of Polymer Science and Engineering, Key Laboratory of Rubber-Plastics, Qingdao University of Science and Technology, Ministry of Education, Qingdao, 266042, People's Republic of China

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ABSTRACT: TPVs filled with different amounts (0–50 phr) of carbon black were prepared via melt mixing by dynamic vulcanization in Haake plasticorder at 150°C and 40rpm and then the properties of them were studied. Torque-time curves showed that the curing degree reached a biggest value at 10 phr and then decreased with the increase of filling content while the curing rate was always rising. Mechanical properties such as tensile strength, tear strength, modulus as well as hardness increased with the increment of carbon black content while the tension set at break was reduced dramatically. Two phase morphology was observed by SEM photographs and the effect of carbon black on curing extent was testified. To illuminate the effect of carbon black, curometer curves and carbon black dispersion pictures were also analyzed. Rubber processing analyzer (RPA) experiments proved that there was a progressive nonlinear behavior, which was more and more clearly expressed with the increment of carbon black content and could be explained via the Payne effect. But the TPVs containing highest carbon black exhibited the fastest drop of G' with increasing strain amplitude as obtained from the value of $G'_0 - G'_\infty$ The order of tanδ at different carbon black content was tanδ (10 phr) < tanδ (0 phr) < tanδ (30 phr) < tanδ (50 phr) at lower strain amplitude.

Key words: carbon black; EPDM/POE; TPV; cure; Payne effect

INTRODUCTION

In 1962, Gessler[1] first described dynamic vulcanization as a process of vulcanizing an elastomer during melt mixed with a molten thermoplastic resin, wherein the vulcanized elastomers were presented as finely dispersed particles in continuous thermoplastic matrices. And then the technology was developed by Fisher et al.[2] Thermoplastic dynamic vulcanizates (TPV) displayed the characteristics of both elastomers and thermoplastics. Therefore, they can be molded, shaped, and/or reprocessed at temperatures above the melting or softening of the thermoplastic resin. From the term of dynamic vulcanization was first referred, many researchers committed themselves to the investigation of the influences of process parameter, curative concentration on mechanical properties of EPDM/PP,[3] POE/PP.[4] Ahmad Mousa[5] studied the influence of dynamic vulcanization on the mechanical properties of EPDM/PP blend. Rajesh Babu[6] and his cooperator investigated the effects of mixing sequence on morphological, mechanical, and thermal properties of peroxide cured polypropylene(PP)/ethylene-octene copolymer (EOC) TPVs.

As TPVs have received much attention in polymer science and industry field during the last 30 years, some problems existing in TPVs such as high hardness, poor elasticity, big tension set at break, poor dispersion, and compatibility problems and so on gradually exposed. To solve the aforementioned problems, some researches about elastomer/thermoplastic elastomers TPVs have been done. Dhamodharan et al.[7] studied blends of Ethylene–propylene–diene rubber (EPDM) and thermoplastic polyurethanes (TPU) to understand the compatibility and morphology.

olyolefin elastomer(POE) is ethylene-octene or ethylene-butene copolymer synthesized by Dupont Dow chemical company via INSITE technology using constrained geometry catalyze technology(CGCT), and the brand is Engage. POE possesses special structure characteristics, such as the narrow molecular weight distribution, the regular short side-chains on macromoleculars, and long side chains, which provide excellent properties for it. The crystalline part of ethylene provides strength properties as the physical crosslink point, while the amorphous part of ethylene and the octene chains contribute to the elasticity of the copolymer. POEs offer exceptional performance and

Correspondence to: G. X. Qiu (qiuguixue@qust.edu.cn).

TABLE I
Composition of Carbon Black Filled EPDM/POE TPVs

Ingredients	EPDM	POE	Stearic acid	Zinc oxide	Sulfur	DM	TMTD	Carbon black
Content(phr)	40	60	X	5X	X	0.5X	X	variable(0-50)

Note: X is the sulfur concentration, which was 0.5 phr of EPDM rubber.

a unique balance of the properties when used alone or in blends and compounds. Additionally, it is compatible with most olefin materials. Compared with Polypropylene (PP), the difference such as low hardness, good processability is obvious. So, POE is a better polymer to prepare TPVs with good properties and so many people have paid attention to the study of this field. Babu[8,9] and coworkers have done much work on the research of properties of polypropylene-ethylene octene copolymer thermoplastic vulcanizates. Basuli et al.[10] studied the influence of Engage® copolymer type on the properties of Engage®/silicone rubber-based thermoplastic dynamic vulcanizates.

Because of the degradation effect of peroxide curing system on the continuous phase[6] and the relatively poor process property of Phenolic resin curing system,[11] the EPDM/POE TPVs were prepared by sulfur system via dynamic vulcanization technology. A kind of traditional filler for rubber–carbon black, which can improve the properties of the material and save the cost of production was also used as an effective reinforcing agent. And the effect of carbon black content on the curing characteristics, morphology, mechanical, and dynamic mechanical properties of dynamically vulcanized EPDM/POE elastomers were investigated systematically. The purpose of this work was to replace PP with POE to gain a novel material with low hardness and tension set at break and to study the effect of carbon black on the properties of EPDM/POE TPVs.

EXPERIMENTAL

Materials

The basic polymers used in this study were semicrystalline ethylene–propylene–diene terpolymer (EPDM) Nordel IP 4770P with an ethyldiene 2-norbonene(ENB) content of 4.9%, a Mooney viscosity (1 + 4) at 125°C of 70, an ethylene content of 70% and ethylene-Octene copolymer (POE) Engage 8150 with a density of 0.868 g/cm^3 and a MFI of 0.5 g/10min at 190°C, 2.16 kg. EPDM was obtained from Dupont company and POE was supplied by Dupont-DOW elastomer company. Sulfur system including Stearic acid(Hst), Dibenzothiazole Disulfide(DM), Zinc oxide (ZnO) and Tetramethyl Thiuram Disulfide(TMTD) was used as vulcanizer system. Table I listed the ingredients of the basic recipe in this study. Carbon black (N220) with a particle size of 30 nm and a BET surface area of 103 m^2/kg used in this investigation was supplied by Tianjin Carbon black company, respectively.

Formulation

The formulations shown in Table I were used in this study.

Sample preparation

Melt mixing and dynamic vulcanization were performed using a computerized PolyLab OS Haake plasticorder produced by Haake company, Germany. Mixing was carried out at a temperature of 150°C with a rotor speed of 40 rpm. The well blended EPDM and POE particles were initially charged into the mixing chamber of the Haake plasticorder to equilibrate, followed by fillers and vulcanization additives, then the curing agent (Sulfur) was added to the compound at last. Mixing process lasted one more minutes after the maximum torque was obtained, and then the compounds were removed from the chamber at hot condition and sheeted out in a two roll open mill at ambient temperature. After laid about 24 h, the sheets were cutted and pressed in an electric heated compression molding machine (Yantai rubber company, China) at 180°C for 5 min at 10 Mpa pressure after preheating 8 min. At last, the molded sheets were cooled down to room temperature under the same pressure and corresponding samples were prepared according to standards by pneumatic automatic slicing machine.

Characterization and testing

Mechanical properties

Tensile testing was carried out on a AI-7000S Universal Material Tester, produced by Taiwan Gaotie Company, at a crosshead speed of 500 mm min^{-1} according to ISO 37: 1994. Tear strength was determined according to ISO 34-1: 2004 test method using unnicked 90° angle test piece. Crosshead speed was maintained as the same as that of the tensile test. Hardness was measured using a LX-A Shore A

Sclerometer, manufactured by Shanghai Liuling Instruments, according to ISO 7619: 1986.

SEM analysis

Phase morphology of tensile fractured surface with different filling content was observed after the surfaces were coated with a thin layer of gold in a high vacuum evaporator by Scanning Electronic Microscope(SEM) model JSM-6700F manufactured by JEOL company, Japan.

Curometer curves

The cure characteristics of the TPVs were measured on a moving die Rheometer, Model GT-M-2000-A, Gotech, Taiwan.

Dispersion of carbon black

Photographs of samples with a width of 1 cm were taken on the equipment of EKT-2002MG provided by Ektron company.

Dynamic mechanical property

Dynamic mechanical property testing was performed on a Rubber processing analyzer RPA2000 by Alpha company, China' at the strain mode with a temperature of 160°C, and a frequency of 0.2 Hz.

RESULTS AND DISCUSSION

Mixing torque

The effect of carbon black content on the mixing torque is shown in Figure 1. As we can see, the tendency of all torque-time curves is similar, but the high of the peak and the time that the peaks appear is different. With the increase of carbon black content, there are three low point which are labeled as a, b, and c (two in none carbon black curve) and one peak point marked as d in every curves. a, b, and c represents the filling time of carbon black, curing assistant agent and sulfur, respectively. While d represents the accomplishment of curing. In this article, we keep every filling time the same, and study the changing situation behind the c point. Obviously, curing time (the time difference between d and c) and curing degree (the torque difference between d and c) vary with the changing of carbon black content. For the reason of keepping the same capacity rate of Haake chamber, the gum content declines with the increase of carbon black content. So, the change tendency of torque cannot be distinguished from the torque-time curves directly. For convenience, the analytical data are shown in Table II.

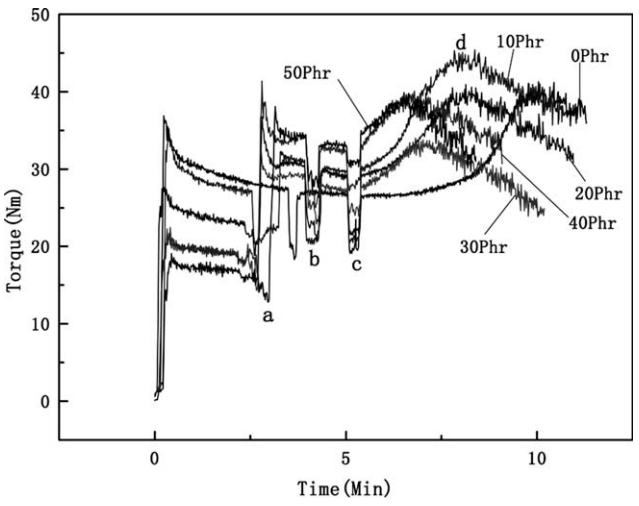

Figure 1 Mixing torque-timecurves of EPDM/POE TPVs with carbon black N220 at 0.5phr concentration of curing agent.

TABLE II
The Effect of Carbon Black Content on Curing Properties

	Carbon black content (phr)					
Curing properties	0	10	20	30	40	50
Curing degree (Nm)	13.26	13.99	10.29	5.49	5.52	4.28
Curing rate (min^{-1})	0.21	0.33	0.36	0.57	0.75	0.90

As we can see from Table II, the curing degree increases first and then decreases with the increase of carbon black content while the curing rate always increases in the studied range. The reason can be concluded as follows: Carbon black can accelerate the curing rate of sulfur system, but it can also affect the curing extent of EPDM because of the dilution effect and the dispersion problem of curing agent resulted by the increasing system viscosity. When the carbon black content reached 30 phr, the curing degree decreases dramatically because the carbon black effect on system viscosity surpasses that on curing extent.

Mechanical properties

Mechanical properties of materials or products are of the important criteria in the selection process for general purpose application. The mechanical properties of TPVs prepared with varied carbon black content are summarized in Figures 2, 3, and Tale III. We can see that the tensile strength, tear strength, and hardness are all improved with the increase of carbon black content. Using carbon black's excellent strengthening property to explain this phenomenon is reasonable. As for the hardness, the highest value

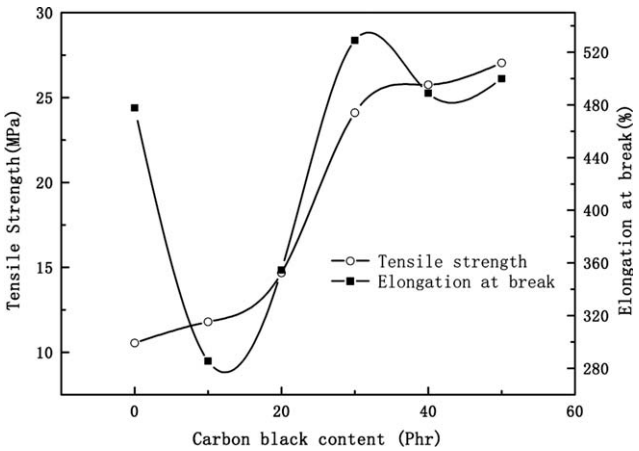

Figure 2 Effect of carbon black on tensile strength and elongation at break.

is 86 A which is lower than EPDM/PP TPVs. However, from Figure 2 we can know that the effect of carbon black content on elongation at break is intricate. This behavior can be explained by taking into consideration of the double effect of carbon black. When the filler content is less than 10phr, the increase of curing degree which is testified before played a leading role while the enforcement of carbon black is unconspicuous. The elongation at break reaches the highest at 30 phr after a soar and then decreases. This is expected that the interaction caused by surface adsorption and chemical reaction between polymer chains and carbon black dominates the property of TPVs. The decrease is attributed to the aggregation of carbon black.

Other properties such as tension set at break, 100% modulus and 200% modulus are shown in Table III. The former one reaches 75.0% at 30 phr of carbon black because of the big elongation at break. The latter two always increase except the value at 30 phr of carbon black which attributes to the dramatically decrease of the curing degree.

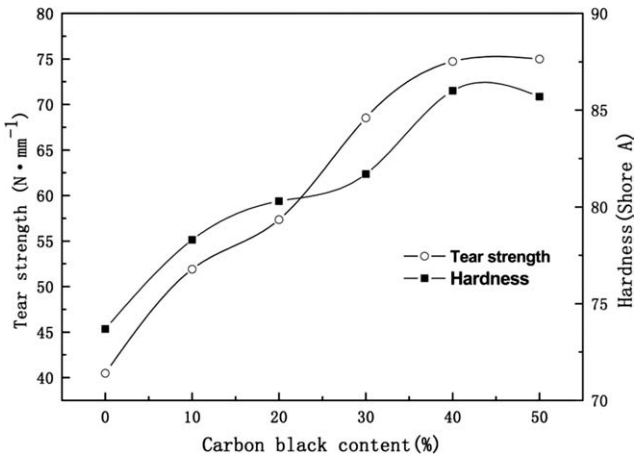

Figure 3 Effect of carbon black on tear strength and hardness.

TABLE III
Other Properties of TPVs with Different Carbon Black Content

	Carbon black content(phr)					
Properties	0	10	20	30	40	50
100% modulus (Mpa)	2.76	4.44	4.45	3.70	5.91	5.98
200% modulus (Mpa)	4.42	8.26	8.34	6.22	10.67	10.68
Tension set at break (%)	52.5	52.5	56.3	75.0	64.5	66.3

Morphology

The technical importance of thermoplastic vulcanizates is attributed mainly to the specific microstructure of these materials. TPVs consists of a continuous thermoplastic matrix with very tiny dispersed rubber particles which enabled the blend to be melt-processed similar to the ordinary thermoplastic materials even though the rubber particles are crosslinked.[12]

Morphology of immiscible polymer blends mainly determines the mechanical properties, especially for dynamic vulcanizates. When sulfur is used as curing agent in EPDM/POE TPVs, the final morphology is expected to be the interplay result of various factors. For example, (1) Viscosity ratio of the blend increases due to crosslinking in EPDM phase, which drives to form a dispersed phase morphology (crosslinked EPDM dispersed in POE matrix). (2) Higher degree of vulcanization in the EPDM phase favors finer dispersed phase morphology. And all these various processes take place simultaneously. SEM microphotographs of tensile failure surface of unfilled and filled TPVs are shown in Figure 4, two phase structure is observed. *a* and *c* is the microphotographs of pure TPV magnified to the multiple of 2000 and 5000, respectively. From image *a* we can see that there are some pellets and strips floating on or studded evenly in the matrix which is expected to be the cured EPDM particles. To evaluate the particle size and distribution of the dispersed domains, a statistic procedure is utilized and the results show that the average particle size accounted in this case is about 1 μm while the biggest is 3.5 μm and the smallest is 0.2 μm. From the smooth surface of floating dispersed particles we can imagine that the failure takes place at the interfacial surface, the reason is that crosslink decreases the interaction of EPDM and POE and the chain entanglements are lowered. As carbon black is filled, the special structure of it made the formation of bound-rubber and production both of chemical interaction and physical adsorption. All these factors enhance the interface interaction between EPDM and POE because of the media role carbon black plays. So the increasing of mechanical properties can be explained reasonably.

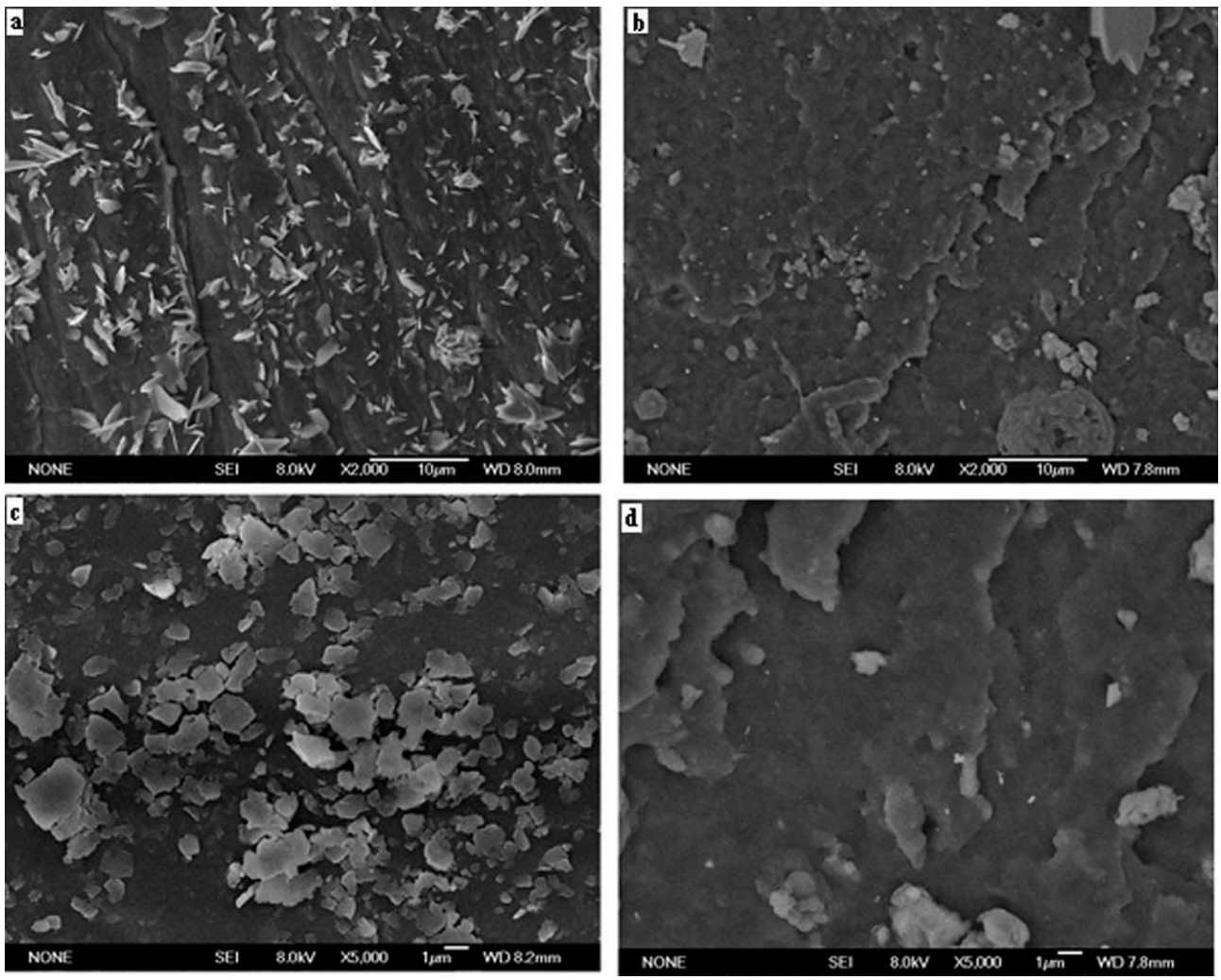

Figure 4 SEM microphotographs of tensile failure surface of EPDM/POE dynamic vulcanizates with carbon black (blending temperature: 150°C), (a) filler content: 0 phr (×2000); (b) N220 content: 50 phr(×2000); (c) filler content: 0 phr (×5000); (d) N220 content: 50 phr (×5000).

Just for the existence of above-mentioned factors, curing extent of TPVs declines and this is confirmed by curometer curves (Fig. 5). As a result, only few curing particles are found in Figure 4(b,d), relatively, but the fracture surface is coarse and some better mechanical properties are derived.

Curometer curves

From curometer curves, a minimum torque (ML), a maximum torque (MH), the optimum cure time (t_{90}) and other parameters can be obtained which are used to determine the process parameter of traditional rubbers. This method is also useful for TPVs. In this investigation, $\triangle$H(MH-ML) of part of prepared TPVs is calculated from the data tested on moving die Rheometer to characterize the curing extent of TPVs prepared via Haake plasticometer. From Figure 5, it can be calculated that the $\triangle$H of TPVs with 0, 10, 30, 50 phr carbon black is 0.4, 0.6, 1.6, and 1.8, respectively. So we can conclude that the second vulcanization extent increase with the increase of carbon black content, that is to say, there are some sulfur that do not be fully reacted in Haake plasticorder.

Dispersion of carbon black

Carbon black dispersion is one of the most significant factors that determine the quality of TPVs, and effects of the type and content on carbon black dispersion are much different from each other. Figure 6 exhibits the photographs of TPVs with different carbon black content, and the white points represent carbon black particles, aggregates or agglomerates whose dimension exceeds 5 μm. With the carbon black content increase, the average value of dispersion degree (ASTM) and the average particle size increase. In our experiment, the dispersion properties deteriorate a little in the latter two pictures.

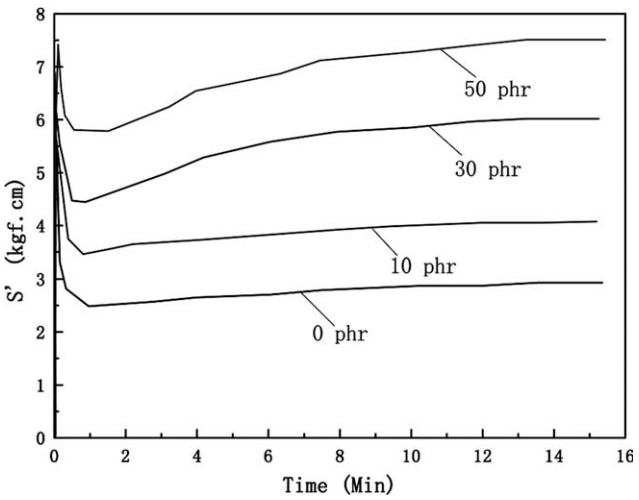

Figure 5 Curometer curves of TPVs.

Dynamic mechanical properties

RPA is one of the suitable testing tools that can provide proper understanding of melt elasticity and process ability of filled TPVs in terms of the dynamic functions like dynamic modulus of elasticity and viscosity over wide range of strain amplitude. Especially the nonlinear viscoelastic systems in which a dependence of the dynamic mechanical properties upon dynamic strain amplitude plays an important role. The theory of Payne effect in which three network structures of rubber-rubber, rubber-filler and filler-filler networks are presumed is used extensively to explain the reinforcement action of filler. It basically interprets the sigmoidal decline from a "zero-amplitude" value of the storage modulus, G_0' to a high amplitude plateau G_∞' as a result

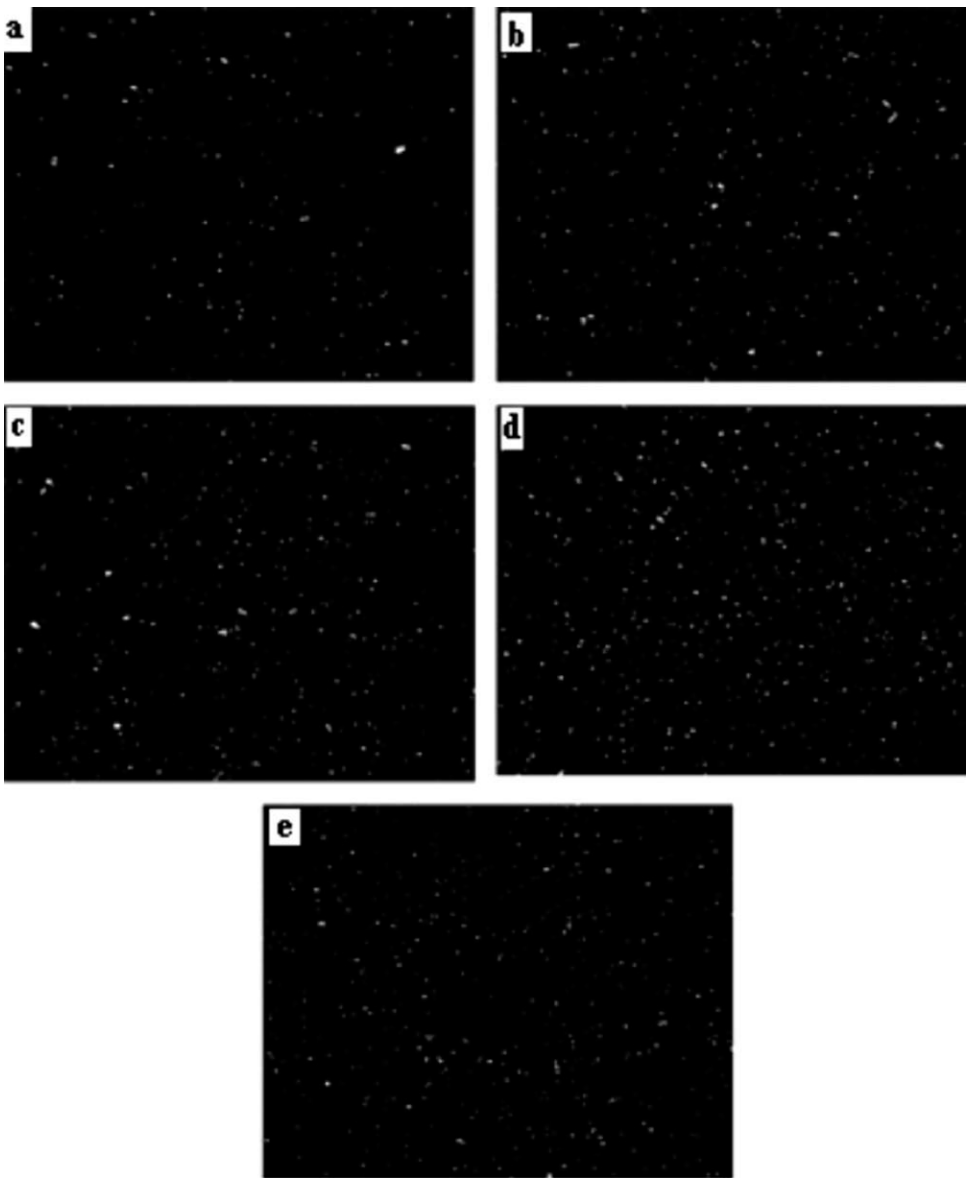

Figure 6 The photographs of carbon black dispersion in EPDM/POE dynamic vulcanizates filled with (a) 10, (b)20, (c)30, (d)40, (e)50 phr of N220.

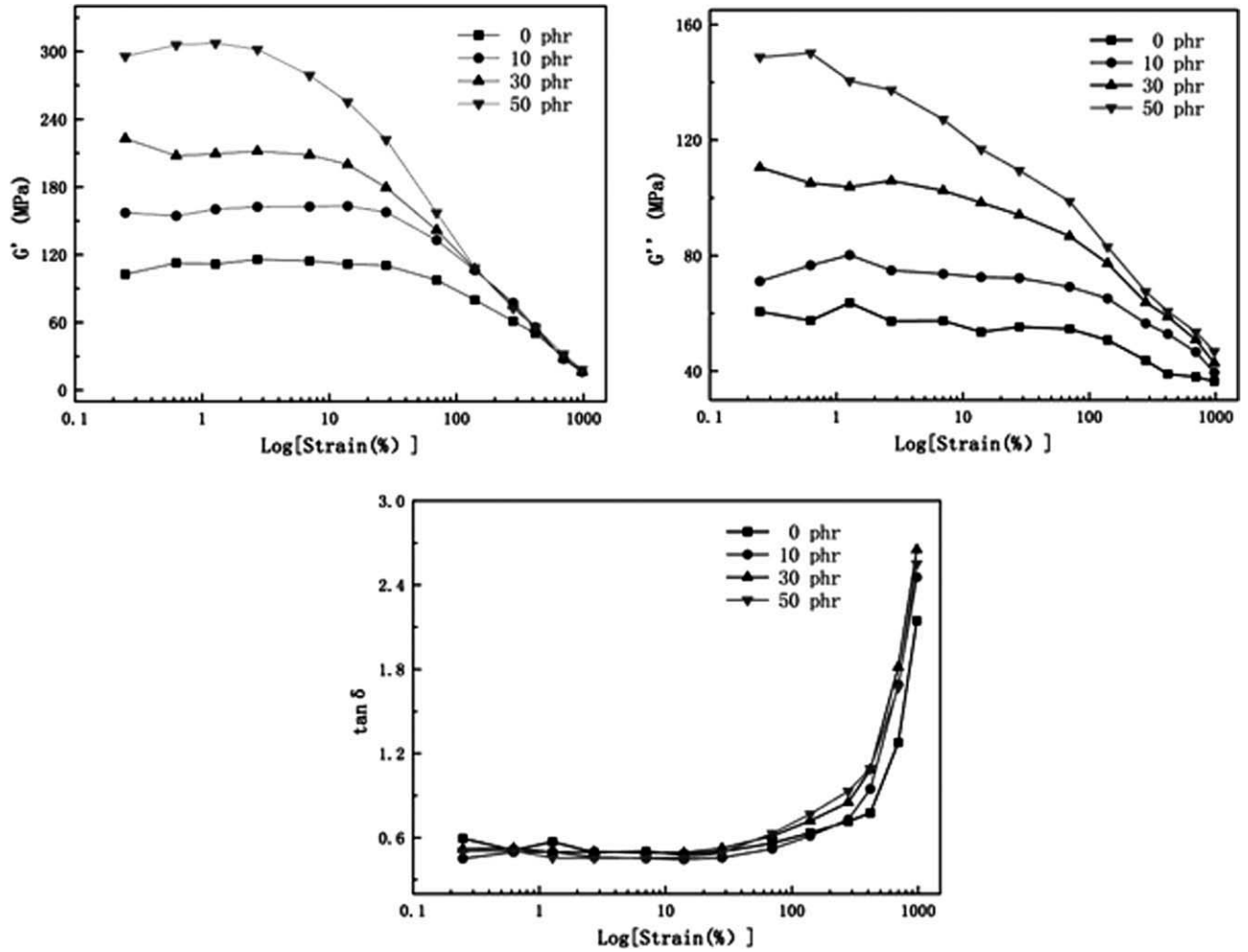

Figure 7 Effect of carbon black content on (a) G', (b) G'', (c) tanδ of EPDM/POE TPVs.

of breakage and reforming of physical bonds between filler aggregates (secondary structure) that is assumed to build an energetically elastic filler network within the soft rubber matrix. At large strains, this filler network break down and the modulus is then determined only by polymer–polymer network, elastically effective filler-polymer interactions and hydrodynamic filler effects. However in this investigation at a high temperature of 160°C, the secondary structure is represented by combination of cross-linked EPDM particles and carbon black aggregates.[13]

Figure 7 presents strain amplitude dependence of G', G'' and tanδ of EPDM/POE TPVs filled with different loading of carbon black. From figures a and b we can see that there are a clearly fall in the non-filled curve which indicates the existence of a progressive nonlinear behavior and all the curves of filled TPV superpose that of unfilled one at low strain amplitude, and the higher, the more filling content. But the TPVs containing highest carbon black exhibit the fastest drop of G' with increasing strain amplitude as obtained from the value of $G_0' - G_\infty'$. This phenomenon illuminates that, as aforementioned, the cured EPDM particles exist in the continuous phase just as a kind of rigid filler, the breakdown and formation of the interaction between domains and matrix results in the decrease in G' at high strain amplitude. Filling of carbon black enhances this effect in filled TPV although the curing extent decreases a little. So the step becomes more and more conspicuous with the increase of carbon black content. Figure 7(c) shows the tanδ dependence on strain amplitude. When the strain amplitude is below than 300%, the order of tanδ at different carbon black content is tanδ (10 phr) <tanδ (0 phr) <tanδ (30 phr) <tanδ (50 phr), this is expected that the increased curing degree and filling of carbon black at 10 phr reduces the plastic deformation and then decreases the tanδ.

CONCLUSIONS

The properties of EPDM/POE TPVs filled with carbon black have been studied using various methods. Results showed that the effect of carbon black

content on the torque-time curves was complex. The curing degree reached a biggest value at 10 phr and then decreased with the increase of filling content while the curing rate was always rising. Some mechanical properties such as tensile strength, tear strength, modulus as well as hardness increased with the increment of carbon black content while the tension set at break was reduced effectively and the highest value was 75% at the filling content of 30 phr. Two phase morphology was observed from SEM photographs and testified the effect of carbon black on curing extent and explained the enhancement of mechanical properties. The curometer curves showed that the sulfur in carbon black filled TPVs was not fully reacted in Haake plasticorder and the trend became more and more obvious with the increase of carbon black content. RPA experiments showed that there was a progressive nonlinear behavior which was more and more clearly with the increment of carbon black content and can be explained via Payne effect. But the TPVs containing highest carbon black exhibited the fastest drop of G' with increasing strain amplitude as obtained from the value of $G_0' - G_\infty'$. The order of tanδ at different carbon black content was tanδ (10 phr) $<$ tanδ (0 phr) $<$ tanδ (30 phr) $<$ tanδ (50 phr) at lower strain amplitude.

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