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ORIGINAL CONTRIBUTION

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Polymeric positive-temperature-coefficient materials: dynamic curing effect

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Abstract The object of this work was to prepare high-density polyethylene (HDPE)/ethylene–propylene–diene terpolymer (EPDM)/conductive carbon black (CB) composites by dynamic curing and to characterize the positive-temperature-coefficient (PTC) performances of the composites. EPDM and dicumyl peroxide were preblended in a research mill. The roll-milled strands were blended with HDPE and CB in a Haake mixer. The sheet resistivity and morphology of the HDPE/EPDM/CB composites with or without the dynamic curing process were investigated. It was concluded that the dynamically cured blends exhibit better PTC performance than the simple blends without dynamic curing. The effects of shear intensity and dicumyl peroxide content during the dynamic curing process were discussed for the PTC characteristics of the HDPE/EPDM/CB composites.

Keywords Positive temperature coefficient · Dynamic curing · High-density polyethylene · Ethylene–propylene–diene terpolymer · Morphology

Introduction

Conductive polymer composites (CPCs) typically consist of a polymeric matrix into which a carbonaceous filler is incorporated. These multifunctional materials are routinely employed in various commercial applications owing to their good electrical conductivity, light weight, corrosion resistance and enhanced mechanical properties.

An interesting phenomenon exhibited by some CPCs is the positive-temperature-coefficient (PTC) effect. The main feature of PTC materials is that upon heating, the conductive system shows a sharp resistivity increase near the melting region of the semicrystalline polymer matrix. The PTC effect is sometimes followed by a negative-temperature-coefficient (NTC) effect, namely, a resistivity decrease. PTC materials can be used as self-regulating heaters, current limiters, overcurrent protectors, microswitches, sensors, and other devices [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12].

A comprehensive theory describing the PTC/NTC phenomenon is not available, although many researchers have tried to explain it. The most common explanation for the PTC effect is that as the melting temperature is approached, conductive pathways are broken because of the volume expansion of the polymer matrix. Above the melting temperature, carbon black (CB) particles cluster because of their tendency to agglomerate. This consequently results in the formation of new pathways, and thus a conductivity increase, giving rise to the NTC effect [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21].

A desired PTC performance, which includes low room-temperature resistivity, high PTC intensity, low NTC intensity and high reproducibility, together with a low conductive filler content, can be approached by employing immiscible polymer blends, instead of a single polymer system, thus expanding the possibility of tailoring the PTC performance using conductive blends [22, 23, 24]. The improvement in the reproducibility of the PTC effect can be attributed to the restricted dispersion and movement of the CB particles dispersed nonuniformly, preferably at the interfaces, within the immiscible polymer blends [23].

The morphology of immiscible blends was found to greatly affect PTC and NTC characteristics [25]. When the CB is entirely localized in the matrix, the PTC behavior is essentially the same as in a CB-filled single-polymer compound [26, 27, 28]. Another interesting possibility is the localization of CB particles solely at the interface of the immiscible polymer blend. Feng and Chan [29] reported that in a polypropylene/ultrahigh molecular weight polyethylene system, representing an immiscible blend of two semicrystalline polymers, a double-PTC effect is observed. Two sharp jumps in resistivity are observed at the melting temperatures of the two semicrystalline polymers owing to the large thermal expansion of the polymers at those temperatures. After the second PTC effect, a sharp NTC effect takes place, similar to that of a CB-filled single semicrystalline polymer.

Radiation cross-linking as a structural stabilizer has been used by several researchers [2, 19, 20]. When radiating a single-polymer/CB compound at room temperature, in most cases the PTC effect is increased [16, 19], although in some cases it is slightly decreased [2]. Furthermore, cross-linking results in diminishing and even elimination of the NTC effect, in relation to the level of the radiation dose [2]. Cross-linking of compounds may inhibit the rearrangement of the filler particles that would otherwise take place in the softened polymer [2, 21, 30], and so it imparts good electrical reproducibility in heating/cooling cycles [2, 20].

Radiation cross-linking of CB-filled immiscible polymer blends results in effects on PTC/NTC phenomena similar to the cross-linking of a CB-filled single-polymer compound when the CB is localized in the same polymer phase, where the compound is cross-linked by irradiation. Thus, when irradiating at room temperature, the PTC intensity was reported to substantially increase, while the NTC effect diminished [23, 28, 31, 32].

On the other hand, dynamically cured thermoplastic elastomer blends have been widely used in plastics because of their advantages in processing [33, 34, 35, 36, 37]: even with the presence of cross-linked elastomers, thermoplastic nature can be obtained by dynamic curing. This prevents the formation of a three-dimensional infinite network in the elastomer phase. Therefore, it is expected that dynamic curing can be utilized to enhance the structural stabilization of the polymer/CB compounds, including an elastomer as one component, and thus also to improve the PTC behavior of the polymer/CB compounds, as regards radiation cross-linking.

The aim of this study was therefore to prepare high-density polyethylene(HDPE)/ethylene–propylene–diene terpolymer (EPDM)/CB composites by dynamic curing and to characterize the PTC performances of the composites. We wished to investigate how dynamic curing affects the PTC performance of the HDPD/EPDM/CB composites.

Experimental

The HDPE used in this study was HDPE 7600, from Hanwha Chemical Corporation, having a melt index of 7.5 g/10 min, a melting point of 136 °C and a density of 0.965 g/cm^3. CB, HIBLACK 40B2, from Korea CB Corporation, Korea, (having a surface area of 120 m^2/g, a particle diameter of 23 nm, a dibutyl phthalte absorption of 150 cm^3/100 g, and pH 8.0) was used as the filler. The elastomer selected for the study was EPDM, from Du Pont (USA), Nordel 1040 E, having a density of 0.90 g/cm^3. A peroxide, viz., dicumyl peroxide (DCP), obtained from Aldrich, was used as the curing agent. A flow chart on the production of HDPE–CB-based thermoplastic elastomers is shown in Fig. 1.

The EPDM and peroxide were preblended in a 3×7-in. research mill (Farrel) at a roll temperature of 100 °C for 10 min. The DCP contents ranged from 0 to 2.5 phr based on the amount of EPDM. The roll-milled strands were blended with HDPE and CB in a Haake mixer at 150 °C and at 10–70 rpm for approximately 15 min. The EPDM was dynamically cured under shear in the presence of HDPE and CB under different shear conditions. During the experimental runs, the shear intensity was controlled by adjusting the rotating speed of the mixer to 10, 30, 50 and 70 rpm. Hot-pressing at the same temperature under about 30 MPa followed, to form a plate with a thickness of 1 mm. Nickel foils were mounted onto the two sides of the plate during the hot-pressing. The resistivity of the composite along the dimension of its thickness as a function of temperature was measured at a heating rate of 2 °C/min using a computerized system comprising a computer, a multimeter and a programmable oven.

The morphology of the freeze-fractured and microtomed surfaces was analyzed using a scanning electron microscope (SEM). All the samples were gold-sputtered prior to observation.

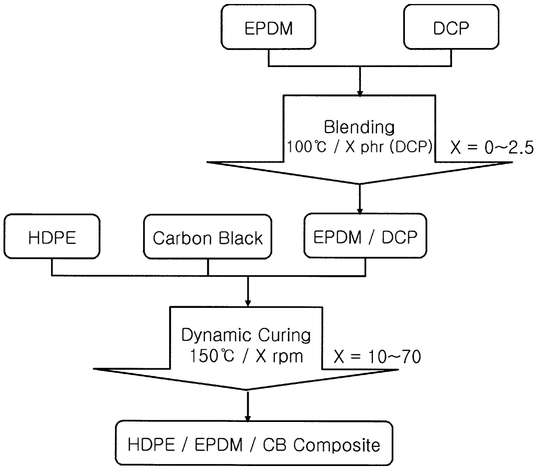


Fig. 1 Flow chart of the preparation of dynamically cured blends: ethylene–propylene–diene terpolymer (*EPDM*), dicumyl peroxide (*DCP*), high-density polyethylene (*HPDE*)

Results and discussion

The room temperature electrical conductivity data for the CB-filled EPDM/HDPE (20/50) composites with different blend methods as a function of CB loading levels ($\phi = 0$–0.25) is shown in Fig. 2. For the dynamically cured blend, the DCP contents is 1.0 phr throughout the text unless otherwise specified. The resistivity value of the simple blend (i.e. without DCP) undergoes a sharp transition over a CB volume fraction ($\phi = 0.03$–0.07) which is taken as the percolation concentration range.

As depicted in Fig. 2, the percolation threshold of the simple blend is at least a quarter of the dynamically cured blend's threshold. It should be noted that the dynamically cured blend exhibits double-percolation behavior, thus implying a different distribution of CB in the blends. Generally, the percolation threshold of the CPCs filled with CB is mainly affected by the viscosity of the matrix [38], the interfacial free energy between the CB and the matrix [39] and the dispersion of CB [40]. In fact, a large increase in the percolation threshold for CB-filled immiscible polymer blend composites is not common. In general, many experimental studies have shown that CB particles are always selectively located in one phase or at interfaces in immiscible polymer blends, resulting in a great reduction of the percolation threshold [41, 42, 43, 44, 45, 46].

Now, we return to discuss further the term "dynamic curing methods". The technology of dynamic curing is based on the principle of in situ vulcanization of conventional thermoset rubber polymers during mixing with thermoplastics [33, 34, 35, 36, 37]. Owing to the low EPDM viscosity during the early stage of dynamic curing, CB particles adhere to the external EPDM layer and penetrate it. These CB particles are surrounded by cross-linked EPDM domains when the dynamic curing process is finished. These CB particles cannot take part in the formation of conductive pathways, so the dynamically cured blends need more CBs to form a network of conductive pathways. This is why the percolation threshold for the dynamically cured blend increases significantly.

A typical plot of the logarithm of the resistivity of the 30 wt% CB-filled EPDM/HDPE(20/50) composites with different blend methods is shown in Fig. 3 as a function of temperature. When temperature increases to near the melting point of HDPE, a sharp jump in resistivity is observed in both blends. It is clearly seen, however, that the dynamically cured blend methods can significantly influence the PTC and NTC characteristics. In Fig. 3, the simple blend shows a jump in resistivity at about 130 °C, followed by an NTC effect, while the dynamically cured blend exhibits no NTC behavior as usually occurs in simple blends. Furthermore, the PTC intensity of the dynamically cured blend is higher than that of the simple blend. The reason for the difference in the PTC intensity lies in the fact that the PTC phenomenon is due to the deagglomeration or the breakage of the conducting network [47] and that the number of conductive pathways is smaller in the dynamically cured blend compared to that in the simple blend. When the number of conductive pathways is small, the resistivity of the composite is sensitive to even a small decrease in the number of conductive pathways. The degree of conductive network formation for the dynamically cured blend composites is much lower than that of the simple blend composites; thus, the movement of the polymer chains caused by thermal expansion due to the melting of the crystallites may introduce a major deformation of the conductive network structure and break up a large number of the conductive pathways. Therefore, dynamically cured blends show higher PTC intensity, but their room temperature resistivity is usually higher.

In the dynamically cured blends, the NTC characteristic is eliminated, suggesting a sufficiently strong cross-linked network which can stabilize the PTC activity of the material. These results are due to the fact that the CB conductive network becomes fixed in the

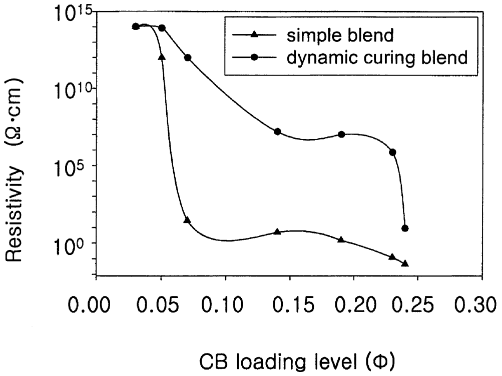


Fig. 2 Effect of the volume fraction, Φ, of carbon black (*CB*) on resistivity

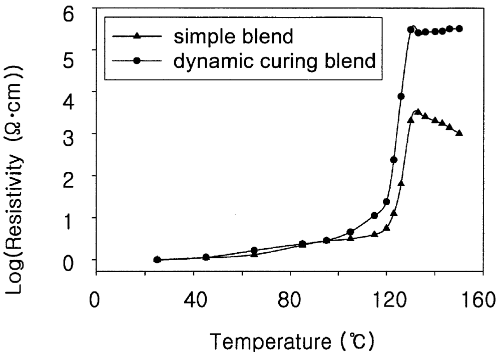


Fig. 3 Comparison of positive-temperature-coefficient (*PTC*) behavior of a simple blend and a dynamically cured blend

cross-linked EPDM/HDPE matrix and may even become chemically bound therein. The strong binding and/or attachment to the cross-linked EPDM/HDPE matrix reduces the freedom of movement of CB particles at all temperatures, especially in and above the polymer melting range. The strong binding and/or attachment of CB within the cross-linked EPDM domains not only makes the CB particles redistribute during the movement and expansion of the matrix at high temperatures, but also takes them back substantially to their original positions when the sample is cooled. Therefore, the NTC phenomenon is practically eliminated for the dynamically cured blends.

The morphological features of the fractured surfaces of the simple HDPE/EPDM/CB blend and the dynamically cured HDPE/EPDM/CB blend are presented in Fig. 4. For both blends, EPDM domains are distributed in the HDPE matrix. The white portions of the micrographs are the EPDM phase and dark portions represent the HDPE phase. Comparison of the SEM micrographs indicates the presence of large irregular domains for the simple blend, while for the dynamically cured blend the microdomains of EPDM have the shape of spherical or dumbbell-like microgel globules of about 0.1–0.5-μm size. It should be mentioned that the domain size of the EPDM phase is smaller as the shear intensity increases when the blend is prepared by dynamic curing methods [33]. Careful inspection of Fig. 4b reveals rough fractured surfaces, which indicate good adhesion of EPDM and HDPE. CB is attracted to the EPDM phase rather than to the HDPE, and it is able to penetrate the EPDM domains because of their low viscosity before the completion of the dynamic curing.

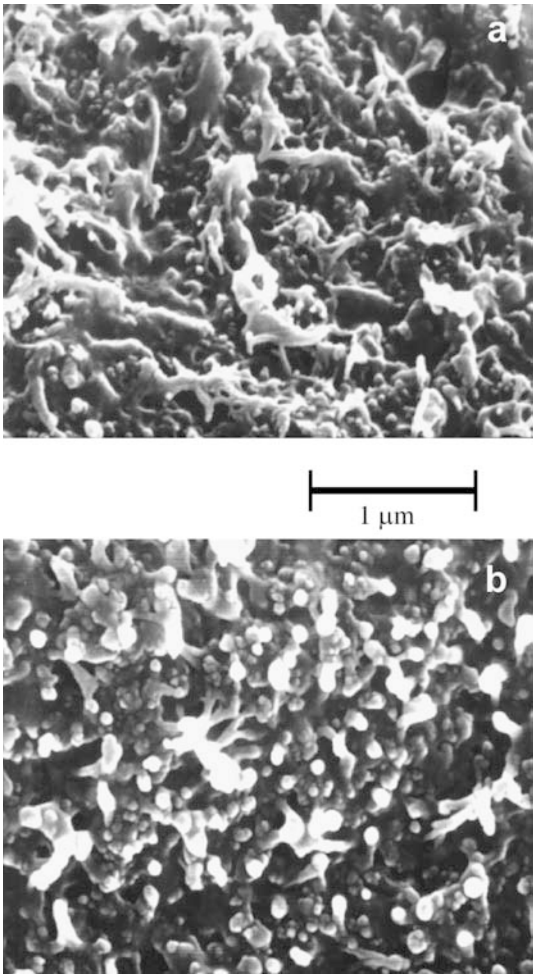


Fig. 4 Scanning electron microscope micrographs of **a** a simple blend and **b** a dynamically cured blend

The effect of DCP concentration on the PTC characteristics of the samples at a constant mixer speed of 30 rpm for the HDPE/EPDM/CB (50/20/30) dynamically cured blends is shown in Fig. 5. Melt-mixing of these components occurred at 150 °C in a Haake mixer(around 15 min). It is seen that the PTC intensity increases with increasing DCP concentration to 1.0 phr and a transition zone (0.8–1.3 phr) corresponding to the loading of DCP is clearly indicated. Over a comparatively high DCP concentration range(1.3 phr and higher), the PTC intensity values tend to follow a leveling-off trend. A decreasing trend in the PTC intensity with the use of higher DCP concentrations (1.3 phr and higher) indicates the overdevelopment of a current pathway. It is clear that more restrictions of CB particles are brought about by the formation of chemical cross-links in EPDM with increasing DCP concentration for HDPE/EPDM/CB dynamically cured blends. Above 1.0 phr, NTC characteristics are eliminated, illustrating that the cross-linked network restoration force is sufficiently strong that it can effectively stabilize the PTC behavior of the material, as mentioned earlier.

The effect of DCP concentration on the morphology of the HDPE/EPDM/CB (50/20/30) dynamically cured blends is shown in Fig. 6. For the dynamically cured blends, when the DCP content is lower, the phase

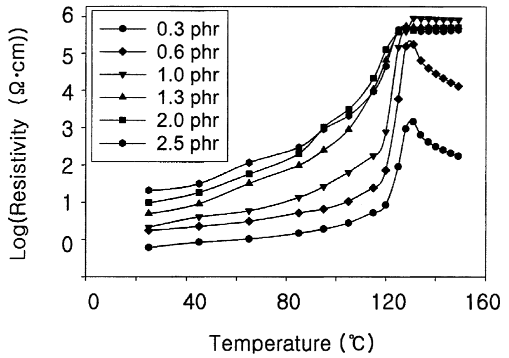
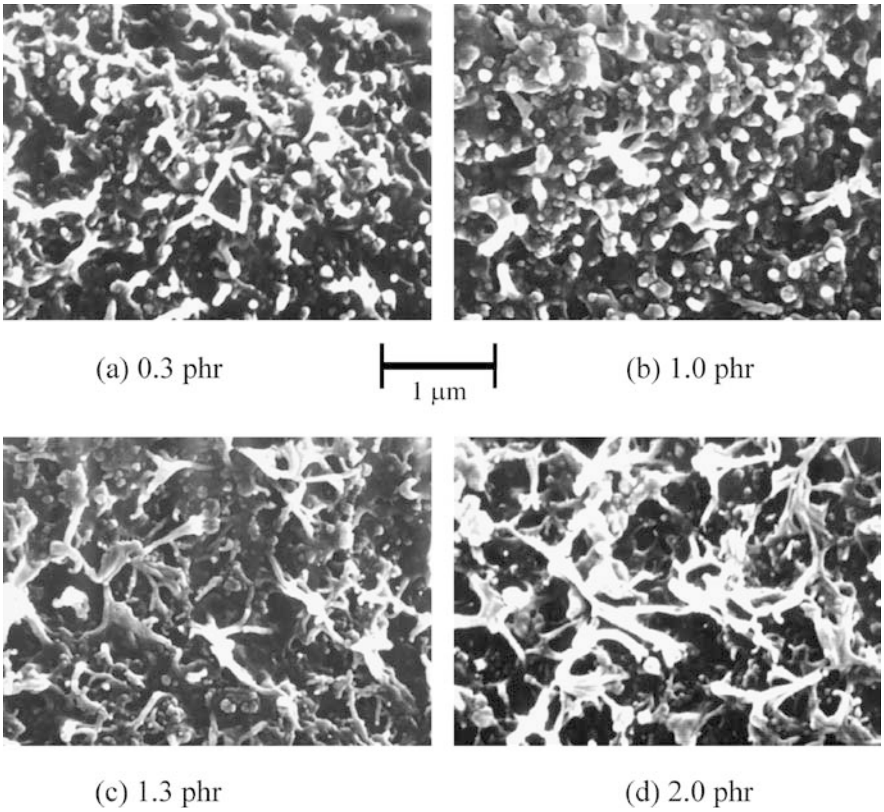


Fig. 5 The effect of DCP concentration on the PTC behavior of the dynamically cured blends

Fig. 6a–d The effect of DCP concentration on the morphology of the dynamically cured blends


(a) 0.3 phr

(b) 1.0 phr

(c) 1.3 phr

(d) 2.0 phr

separation is not clearly observed. It is seen that the phase separation is more clearly observed at higher DCP concentrations (1.0 phr and higher) owing to the poor compatibility between the components for the HDPE/EPDM/CB dynamically cured blends. When the DCP concentration is 1.0 phr, the presence of spherical cross-linked EPDM domains of 0.1 μm in diameter is noticed, and these are very regularly distributed throughout the specimen. Over a comparatively high DCP concentration range (1.3 phr and higher), one can see the over-development of cross-linked EPDM domains. In this case, the stabilizing effect by cross-linking is dominant. The cross-linked EPDM domains become predominant when the DCP content is higher (especially at DCP content of 1.3 phr and above). These cross-linked EPDM domains maintain the CB particle-based conductive pathway. If these cross-linked EPDM domains are solid, current pathways are made firm and the PTC intensity values tend to follow a leveling-off trend.

The effect of shear intensity and composition (EPDM content) on the PTC intensity (namely, PTC factors obtained from the logarithm of the ratio of the peak resistivity to the resistivity at room temperature, hereinafter referred to as *P* or H_p, which is calculated according to the formula $H_p = \log(\rho_{max}/\rho_{RT})$, where ρ_{max} is the maximum resistance value and ρ_{RT} is the resistance value at room temperature) of the HDPE/EPDM/CB (30 wt% CB) dynamically cured blends is shown in Fig. 7. The PTC intensity is reduced with the increase of the EPDM content. The most common explanation for the PTC effect is that as the melting temperature of the polymer matrix is approached, the conductive pathways are broken because of the volume expansion of the polymer matrix. Therefore, the increasing of the cross-linked EPDM content makes the degree of the volume expansion of the polymer matrix smaller and the PTC intensity is reduced.

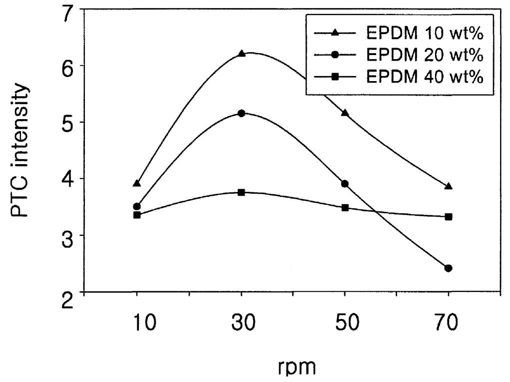


Fig. 7 The effect of shear intensity and composition on the PTC intensity of the dynamically cured blends

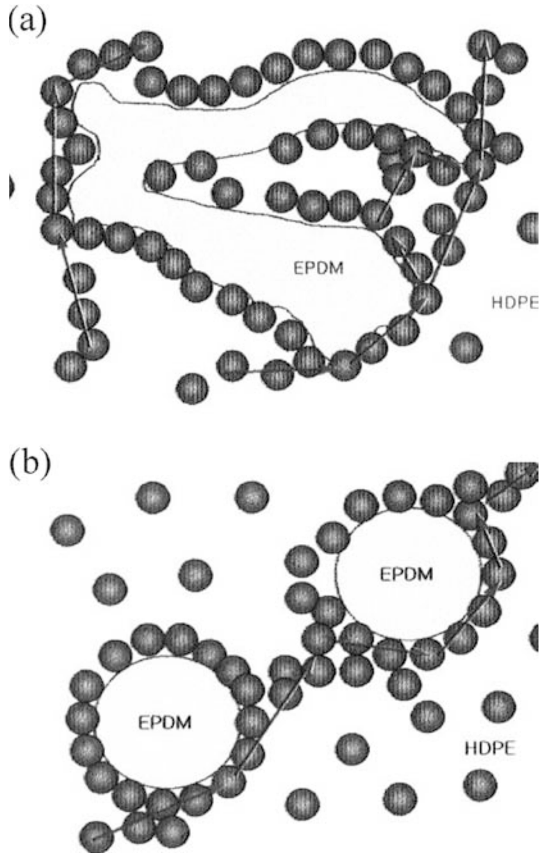


Fig. 8 Schematic illustration of various formations of conductive pathways in composites: **a** simple and dynamically overcured blends and **b** ideal dynamically cured blends

The PTC intensity is reduced with the increase of shear intensity, but very low shear intensity makes the uniform distribution of components in the blends difficult. It is seen that 30 rpm is the optimum condition. It should be mentioned that the domain size of the EPDM phase is smaller as the shear intensity increases when the blends are prepared by dynamic curing methods. When the domain size of the EPDM phase is smaller, the surface area of each particle of the EPDM phase becomes larger and then the number of conductive pathways is increased. Therefore, the PTC intensity will be reduced.

In summary, a schematic illustration of various formations of conductive pathways in composites is shown in Fig. 8. The shapes of the EPDM domains have a significant effect on the formation of conductive pathways. The EPDM domains play a leading role in the support of the CB particles which take part in the formation of conductive pathways. Figure 8a shows the formation of conductive pathways in simple blends and in dynamically "overcured" blends, where the dynamic curing process was done with comparatively high DCP concentrations (1.3 phr and higher) and overcuring of the EPDM phase might take place. Figure 8b shows the formation of conductive pathways in "ideal" dynamically cured blends, meaning that the blends were prepared under the dynamic curing condition with the appropriate DCP concentration (e.g. 1.0 phr) exhibiting desirable PTC behavior. In the case of simple blends and in dynamically overcured blends, the surface area of each particle of the EPDM phase becomes larger and the number of conductive pathways is increased, so the PTC intensity is smaller. In contrast, in ideal dynamically cured blends the surface area of each particle of the EPDM phase becomes smaller and the number of conductive pathways is decreased, so the PTC intensity is larger.

Meanwhile, different shapes of the EPDM domains with different surface area can be easily predicted by the well-known Taylor instability theory in polymer blend science [48, 49]. According to the theory, the breakup of discrete domain drops in a matrix is more favorable as the droplet size increases, the matrix viscosity is higher and the interfacial tension is smaller. The drop size is dependent mainly on the viscosity ratio, λ, of the domain drop to the matrix. According to Rumscheidt and Mason [50], for a low viscosity ratio ($\lambda > 0.2$), the deformed drop breaks through the center with the formation of two large drops and three satellite drops as the viscosity of the drop increases. For an even higher viscosity ratio ($\lambda < 2$), the drop extends into a long cylinder but eventually falls into many small drops. However, for $\lambda > 2$ the drop becomes deformed and is oriented along the flow without fracture. The melt viscosity of EPDM and HDPE measured by a capillary rheometer (Instron model 3211) at 180° C is the order of 130,000 and 55,000 P, respectively, at the shear rate of 3.5 1/s [51], where the viscosity ratio of the EPDM phase and the HDPE matrix is larger than 2. This may be why the simple blends prepared without DCP exhibit domain shapes of deformed spheres of a dumbbell shape.

Our previous work reported that the melt viscosity of the dynamically cured EPDM and HDPE blends with similar blend ratios as for this work, which was measured by a capillary rheometer at 180° C, increased from the order of 63,000 P for the simple blends to the order of 158,000 and 199,000 P for the dynamically cured blends with 1.0 and 1.33 phr DCP, respectively, at the shear rate of 3.5 1/s [51]. The result suggests that for the dynamically cured blends, the viscosity ratio of the cross-linked EPDM and HDPE in the blends tends to increase with increasing DCP concentrations owing to an increasing degree of cross-linking of the EPDM phase. Accordingly, deformed spheres of a dumbbell shape are preferred as the shapes of the domains in dynamically overcured blends (where $\lambda \gg 2$ is expected), while broken-up small particles of the globular EPDM phase are preferred as the shapes of the domains in ideal dynamically cured blends (where $\lambda \leq 2$ is expected), as in

Fig. 8. For the ideal dynamically cured blends, the inhibition effect of EPDM particle growth at high cross-linking density under shear force, the so-called stabilization effect, also plays a significant role in the formation of small particles of the globular EPDM phase domain [35, 52]. It is interesting to note that the stabilization effect works simultaneously and competitively together with the Taylor instability phenomena in the formation of domain shapes for the ideal dynamically cured blends, even for a viscosity ratio higher than 2. Note that there is no such stabilization effect in simple blends and thus only Taylor instability should be taken into consideration for the formation of deformed spheres of a dumbbell shape, as in Fig. 8a.

The dynamically cured blend has a finer dispersion, while the dynamically cured blend under high shear intensity (30 rpm and higher) shows distinct and small domains of EPDM, so the conductive pathways increase in number. The PTC intensity values showed a leveling-off trend. Before concluding, it should also be mentioned that the peroxide radicals from DCP can move only in the EPDM domain, so such a cage effect may also be the cause of the different conductive pathways in Fig.8 depending on the DCP concentrations. Further work on the subject will be in the future.

Conclusions

Owing to the low EPDM viscosity, CB particles adhere to the external EPDM layer and penetrate it during dynamic curing. These unusual morphologies result in the increased percolation thresholds of the dynamically cured HDPE/EPDM/CB blends compared to those of the simple HDPE/EPDM/CB blends. It is clear that the dynamic curing methods can significantly influence the PTC and NTC effects. The PTC intensity of the dynamically cured blends is higher than that of the simple blends and the NTC effect is eliminated. The SEM micrographs of the fractured surfaces of the dynamically cured HDPE/EPDM/CB blends show the presence of spherical domains of 0.1 μm in diameter regularly distributed throughout the specimen. The domain size of the EPDM phase was smaller as the shear intensity increased when the blend was prepared by dynamic curing methods. The PTC intensity increased with increasing DCP concentrations to 1.0 phr and a transition zone (0.8–1.3 phr) corresponding to the loading of DCP was clearly indicated. Over a comparatively high DCP concentration range(1.3 phr and higher), the PTC intensity values tended to follow a leveling-off trend. A decreasing trend in the PTC intensity for higher DCP concentrations (1.3 phr and higher) indicates the overdevelopment of a current pathway. The phase separation was more clearly observed at higher DCP concentrations owing to the poor compatibility between the components of the HDPE/EPDM/CB dynamically cured blends. Over a comparatively high DCP concentration range(1.3 phr and higher), the overdevelopment of cross-linked EPDM domains was observed and the stabilizing effect by cross-linking was dominant. Therefore, current pathways were made firm and the PTC intensity values tended to follow a leveling-off trend.

The PTC intensity was reduced with the increase of EPDM content. It was found that 30 rpm is the optimum condition. At a certain volume fraction of filler, the conductive pathway was formed in an insulating network structure. The dynamically cured blend showed a finer dispersion, while the dynamically cured blend under high shear intensity (30 rpm and higher) showed distinct and small domains of EPDM, so the conductive pathways increased in number. Thus, the PTC intensity values showed a leveling-off trend. Therefore, it is concluded that the dynamically cured blends exhibit better PTC performance than the simple blends.

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