Morphology, Rheology, and Mechanical Properties of Dynamically Cured EPDM/PP Blend: Effect of Curing Agent Dose Variation

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ABSTRACT: The structure development, rheological behavior, viscoelastic, and mechanical properties of dynamically cured blend based on the ethylene–propylene–diene terpolymer (EPDM) and polypropylene (PP) with a ratio of 60/40 by weight were studied. The variation of two-phase morphology was observed and compared as the level of curing agent was increased. Meanwhile, as the level of curing agent increased, viscosity as a function of shear stress always increased at a shear stress range of 2.2×10^4 to 3.4×10^5 Pa at the temperature of 200°C, yet viscosity of the blend approached each other at high shear stress. Dynamic mechanical spectra at different temperatures show that dynamic modulus (E') of the blend exhibits two drastic transitions corresponding to glass transition temperature (T_g) of EPDM and T_g of PP, respectively. In the blends T_gs of EPDM increase and T_gs of PP almost remain unchangeable with an increase in curing agent level. Tensile strength increased, yet elongation at break decreased as the level of curing agent is increased. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 357–362, 2004

Key words: polypropylene; ethylene–propylene–diene terpolymer; morphology; rheology property; dynamic mechanical property

INTRODUCTION

In the last two decades ethylene–propylene–diene terpolymer/polypropylene (EPDM/PP) thermoplastic elastomers (TPEs) have been intensively studied because of their theoretical and practical importance.[1,2] TPEs are materials with the processing behavior of thermoplastics but having an elastic property similar to the ordinary thermosets or cured rubbers.[3,4] Among different sorts of TPEs, those prepared by physical melt mixing of a polyolefin and an elastomer have gained significant attention due to the ease of tailoring the required properties and also the simple preparation method.[5]

Dynamically cured TPE blends were first presented by Fischer[6,7] and developed by Coran and Patel[8–10] and since then have been widely used in the rubber and plastic industries. The outstanding properties of these materials are mainly attributed to their specific microstructure, which consists of a continuous plastic matrix with tiny rubber particles dispersed throughout the matrix. This enables the blend to be melt-processed even though the particles are crosslinked. Both the mechanical and rheological properties of these materials are, therefore, critically dependent on their morphology.[11–13] Much work has been done that deals with the mechanical and rheological properties of dynamically cured TPEs.[2,12–15] Also, a few studies have been carried out, mainly to characterize the microstructure of dynamically cured TPEs based on different rubber–plastic blend systems.[2,11,16–19]

However, no literature has been published on the effect of curing agents, such as phenolic resin, on the morphology, rheology, and dynamic mechanical properties of this blend system. The objective of the present work was to study the effect of curing agent levels on the rheological and mechanical properties of dynamically crosslinked EPDM/PP blends. Meanwhile, the development of morphology in the blends is investigated as the level of curing agent is increased.

EXPERIMENTAL

Materials

PP:T300 (Shanghai Petroleum Chemical Co., Ltd., China), MFR = 2.5, (230°C, 2.16 Kg Load), homopolymer; EPDM:EP35 (Japan Synthetic Rubber Co. Japan), $ML_{1'+8'}$ (127°C) = 56; Phenolic resin:2402 (Jingmei Chemical Factory, Wuhan, China), C.P.; $SnCl_2 \cdot 2H_2O$ (Jiaozhui Chemical Factory, Henan, China), A.R.

In the present work, the following general recipe was used: EPDM 100, PP 66.67, Phenolic resin X, $SnCl_2 \cdot 2H_2O$ $X/5$, where X, the amount of phenolic resin, is varied.

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Processing and sample preparation

Dynamically cured binary blends of EPDM and PP were prepared in an open mill (SK-160B, Wuhan) at 180 ± 10°C for 10 min. Compositions of the blends relate to the 60/40 EPDM/PP ratio. The molten mass then was taken out from an open mill at 180 ± 10°C. After cooling, the mass was remelted and mixed for another 2 min in the open mill at 160 ± 10°C. Again the mass was removed from the open mill, cut, and compression-molded in a frame between plates under 10 MPa pressure at 210°C and then cooled to room temperature under pressure. Appropriate test specimens were cut from the molded sheet and used for testing after at least 24-h storage at room temperature.

The tensile behaviors were examined according to GB528–82 on an AG-2000A apparatus at a crosshead speed of 100 mm/min. The tests were carried out at 23 ± 2°C. All data were recorded and processed automatically.

Morphological characteristics

Samples were cryogenically cut with glass knives (V-LKB, Swiss) in liquid nitrogen and stained with OsO_4, which reacted with the double bonds of EPDM darkening it. The samples were examined using transmission electron microscopy (Model H-806, Japan).

Measurement of rheological property

Viscosity measurements were made using an Instron Capillary Rheometer (Instron, Model 3211, UK) at 200°C. The length and the diameter of the capillary were 0.1247 and 5.08 cm, respectively. The L/D ratio of the capillary was about 42, the diameter of the reservoir was 0.9525 cm, and the entry angle was 90°. The sample for testing was placed inside the barrel of the extrusion assembly and forced down to the capillary with the plunger attached to the moving crosshead. After a warming up period of 5 min, the melt was extruded through the capillary at preselected speeds of the crosshead, which varied from 0.06 to 20.0 cm/min. The melt height in the barrel before extrusion was kept the same in all the experiments and the machine was operated to give six different plunger speeds from lower to higher speed, with a single charge of the material. Forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate (γ_w) at wall by using the following equations involving the geometry of the capillary and the plunger:

$$\tau_w = \frac{F}{A_p(L_cD_c)}$$

$$\gamma_w = \left(\frac{3n + 1}{4n}\right) \times \frac{32Q}{\pi D_c^3}$$

where, F is the force applied at a particular shear rate, A_p is the cross-sectional area of the plunger, L_c is the length of the capillary, and D_c the diameter of the capillary. Q, the volume flow rate, was calculated from the velocity of crosshead and diameter of the plunger; n is the flow behavior index defined by $n = d(\log \tau_w)/d(\log \gamma_w)$ and was determined by regression analysis of the values of τ_w and obtained from the experimental data. γ_w is the apparent wall shear rate calculated as $32Q/\pi D_c^3$. The shear viscosity η was calculated from τ_w and γ_w.

Measurement of dynamic mechanical thermal analysis (DMTA)

All samples were compression-molded sheets (0.1-mm thickness, 3-mm width) prepared in a heated press at 200°C with a pressure of 15 MPa. The experiments were carried out by DMTA (Mk III, version 5.41, Rheometric Scientific Ltd.) at a rate of 10°C/min and a frequency of 5 Hz.

RESULTS AND DISCUSSION

Morphology

The phase morphology of dynamically cured EPDM/PP blend prepared with different amounts of phenolic resin as curing agent in an open mill is shown in Figure 1. It is interesting to note that, for dynamically cured EPDM/PP blend, the EPDM phase undergoes a series of changes from dispersed phase to continuous one, and again to dispersed phase, and PP always remains continuous phase with the increase in curing agent levels. But the size of EPDM particles in the blend with 2.0 phr curing agent is larger than those in the blend with 5.0 phr curing agent, and the numbers of EPDM particles in the former blend are more than those in the latter blend. Yin et al.[19] and Katbab et al.[20] reported that, at the ratio of 60/40, phase inversion occurs causing the two phases to coexist as a cocontinuous phase. As the EPDM phase is dynamically crosslinked during mixing, the viscosity of the EPDM phase becomes higher than that of the PP with increasing curing agent levels, which plays an important role in driving the morphology of the blends toward the formation of rubber particles dispersed throughout the continuous PP matrix. The formation of a dispersed morphology by the most viscous phase in the EPDM/BR blend system has been reported[21] and explained to be due to the tendency of the less viscous phase to encapsulate the most viscous phase to minimize the mixing energy. A previous paper[22]
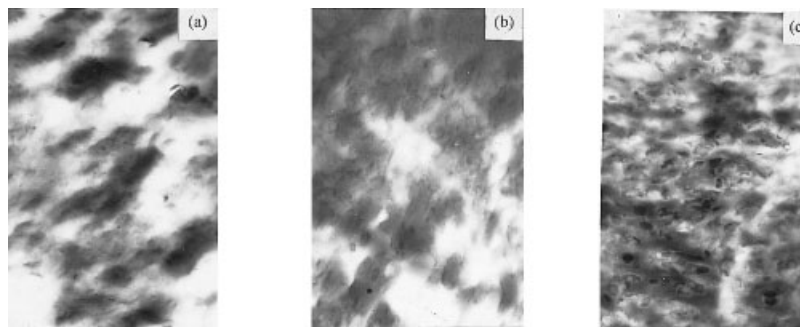
Figure 1 Micrograph (×6,000) of the dynamically cured 60/40 EPDM/PP blends with various amounts of phenolic resin in an open mill. The amounts of phenolic resin are (a) 2.0, (b) 3.5, and (c) 5.0 phr.

even reported that dispersion of EPDM particles has a great relationship to mixing equipment. Dynamical cure must be accompanied by continuous shear agitation during the process, otherwise, EPDM particles will coalesce and form continuous phase. Dynamically cured blend is prepared in an open mill, which cannot exert vigorous and continuous force on the blends, so that EPDM particles don't disperse easily. Under the same condition of mixing equipment and ratio of rubber to plastic, dispersion of EPDM in the blend mainly depends on both viscosity difference between EPDM and PP and interaction between EPDM particles. The former favors formation of dispersed EPDM and the latter does not. As a small amount of curing agent is added (e.g., less than 3.5 phr), both viscosity difference between EPDM and PP and interaction between EPDM particles are increased. Yet, it may be that the effect of shear force on morphology of the blends is dominant; vigorous shear results in dispersion of EPDM particles in the blend. As the amount of curing agent is more than 3.5 phr, interaction between EPDM particles is dominant, so EPDM particles aggregate easily and form continuous phase. As a large amount of curing agent is added (e.g., more than 3.5 phr), viscosity difference between both EPDM and PP plays a critical role, which can be attributed to the immobilization of the EPDM particles by enough crosslinking and therefore breaking down to small size under the applied shear field. Under such conditions, size of the EPDM particles decrease and they get dispersed easily.

Rheological property

The rheological property of the 60/40 EPDM/PP blend cured with various amounts of curing agent (60/40 mass ratio of rubber/plastic) is presented in Figure 2. It can be seen that viscosity of the blends is highly shear-sensitive with significant drops at higher shear stress, which demonstrated that the melt blends were pseudoplastic and had distinct non-Newtonian

properties. At high shear stress, the viscosity difference between the blends prepared with different amounts of curing agent is reduced. It is clear that more molecular restrictions are brought about by the formation of chemical crosslinking in EPDM with increasing phenolic resin concentration for 60/40 EPDM/PP blend. As shown in Figure 2, the melt viscosity of the blends increases with increasing curing agent concentration, with the exception of uncured EPDM/PP blend, and viscosities of the blends based on different curing agent levels as the function of the shear stress are almost equal, especially at comparatively high shear stress. The viscosities of the blends of lower curing agent levels are shifted to lower than those of highly crosslinked blends at low shear stress, but by increasing the shear stress, the curve for highly crosslinked blends decreases quickly. It is also seen that the blends with curing agent have higher viscosity than the blends with no curing agent included over the range of shear stresses examined. At higher shear stress, viscosities of EPDM/PP blend approach each other, which may be explained as follows: when two components having different rheological characteristic
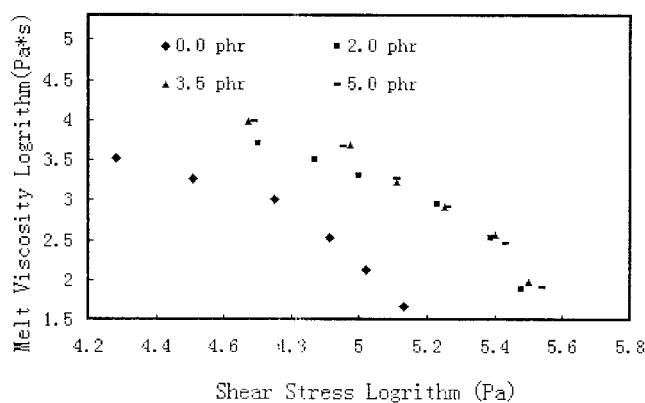

Figure 2 Viscosity–shear stress plot showing the effect of the amount of phenolic resin in 60/40 EPDM/PP blends at 200°C.
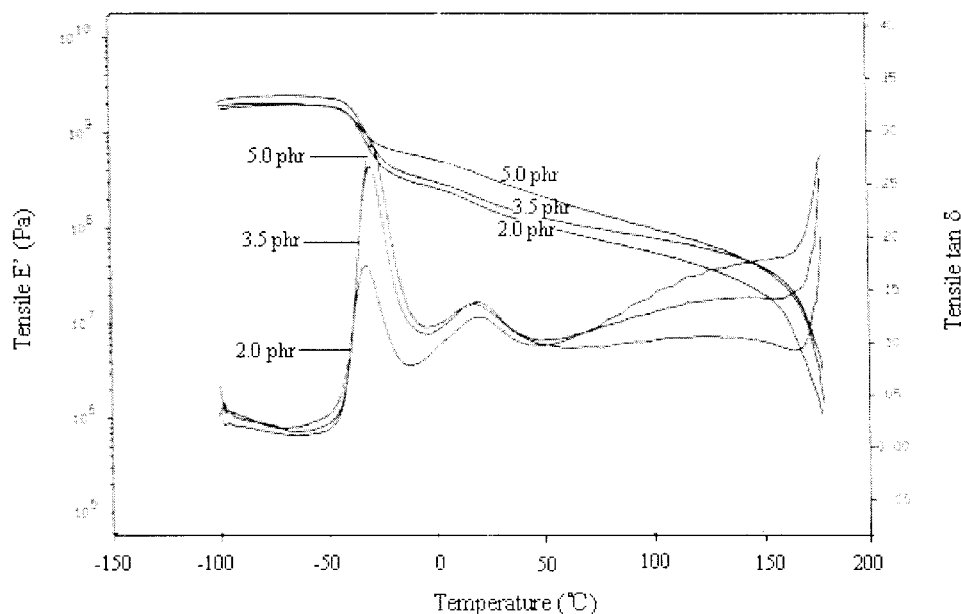
Figure 3 Dynamic mechanical properties of 60/40 EPDM/PP blends as a function of temperature.

flow through capillary, the components tend to rearrange into a sheath-core configuration, with the component of low viscosity (i.e., PP) forming the sheath.[23] This sheath will act as a lubricant between the extrudate and the capillary wall. Such a trend is highly plausible at higher shear stress than at lower shear stress, which will result in the more rapid reduction in melt viscosity at higher shear stress. On the other hand, rapid reduction of melt viscosity of the blends may have much to do with the morphology change in the blends. As seen in Figure 1, EPDM phase in the blends undergoes a series of changes with increasing curing agent levels. Meanwhile, the size of EPDM particles decreases and the number of EPDM particles increase as the amount of curing agent is increased. The combined effect of the abovementioned factors resulted in the conclusion that, at high shear stress, viscosities of 60/40 EPDM/PP blend approach each other as curing agent levels increase.

Dynamic mechanical properties

The dynamic mechanical spectra of the mass ratio of 60/40 EPDM/PP blends are depicted in Figure 3. It can be seen that the blends showed two apparent peaks (i.e., the blends presenting two T_g values), the high temperature corresponds to the T_g of PP and the lower one to the T_g of EPDM. The results show that, as curing agent levels are increased, the T_g peak of EPDM shifts slightly toward a higher temperature and varies from -33.4 to -27.4°C and the tanδ of the peaks broaden, which is ascribed to an increase of crosslinking degree of EPDM with the increase in the curing

agent levels. Crosslinking restricts the chain mobility and causes an increase in the apparent T_g as the curing agent level is increased. The T_g ($\approx$ 20°C) of PP, however, remains almost unchanged; the T_g peak height of the two components becomes closer and gradually approachs each other as the amount of the curing agent is increased.

Upon careful observation of Figure 3, it is found that the dynamic modulus (E') of the blends is increased slightly with increasing curing agent levels, which can mainly be attributed to such factors[24] as crosslinking density, crystallinity degree, and interfacial adhesion between EPDM and PP. On the one hand, as the amount of curing agent is increased, crosslinking density of EPDM is increased and miscibility between EPDM and PP is improved,[22] which favors the increase of dynamic modulus of the blends. On the other hand, the higher degree of crosslinking prevents the alignment of chains in crystal lattice, hindering crystallization and leading to the decrease of the degree of crystallinity of PP,[22] which didn't favor an increase of dynamic modulus of the blends. The combined effect of the abovementioned factors made the dynamic modulus of the cured blends increase slightly. From Figure 3, it can be seen that, with the increase in curing agent levels, the effect of dynamic cure is a smaller decrease in modulus as the temperature is increased and the dynamic cured composition continues to exhibit sufficient dynamic modulus from T_g of EPDM to the melting point of PP even after the melting point of pure PP has been surpassed.
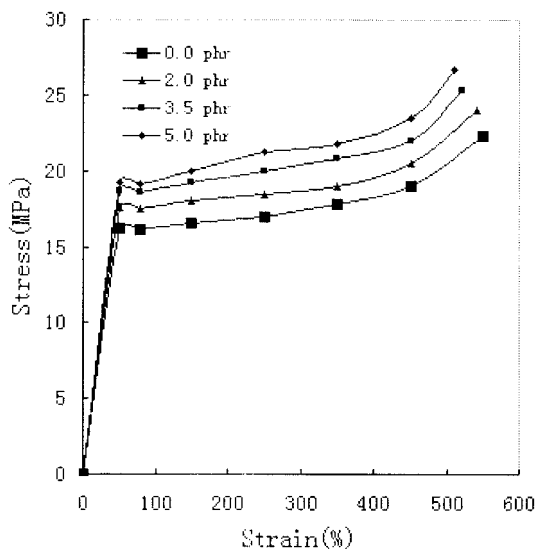
Figure 4 Tensile stress—strain curves of dynamically cured EPDM/PP blend at various curing agent levels.

Mechanical properties

The stress–strain curves and the ultimate tensile strength of the EPDM/PP blends at various curing agent levels are shown in Figures 4 and 5. It is apparent that, as the amount of curing agent is increased, stress increases with strain sharply following Hookean law, and then, after passing through the yield point of the PP, the stress–strain curves pass through a rubber (EPDM) plateau, reaching a breaking stress in each curve and the ultimate tensile strength follows a slight increase, which is in agreement with dynamic modulus as a function of temperature. It is explained in terms of variation of both crystallinity degree of PP and crosslinking density of EPDM. Crystallinity degree of PP decreases and crosslinking density of EPDM increases with increasing curing agent content. The combined effect of the above two factors results in a slight increase of ultimate tensile strength of the blend. The elongation at break with curing agent content is shown in Figure 6. As the amount of curing agent increased, the crosslinking degree of
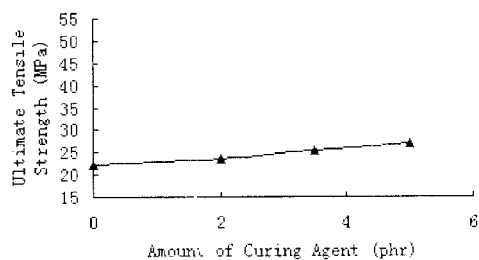

Figure 5 Effect of curing agent level on the ultimate tensile strength of dynamically cured EPDM/PP blend.
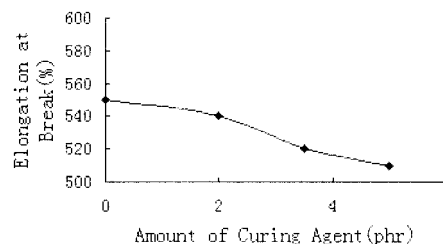

Figure 6 Elongation at break versus curing agent level for dynamically cured EPDM/PP blend.

EPDM increased and the crosslinked EPDM particles then acted as stress concentration points, leading to a decrease of elongation at break and an increase in ultimate tensile strength.

CONCLUSION

Comparative studies of microstructure, rheological behavior, and viscoelastic and mechanical properties were carried out as the amount of curing agent is increased for EPDM/PP blends (60 : 40). Dynamically cured EPDM/PP blend is composed of two phases (i.e., EPDM and PP phase). As the level of curing agent is increased, EPDM phase changed from dispersed phase to continuous one, and again to dispersed phase, and PP phase remained continuous phase throughout.

The melt viscosity of dynamically cured EPDM/PP blend increases with increasing curing agent level, yet the difference in the viscosity of the blends tends to drop at high shear stresses. As the amount of curing agent is increased, the dynamic modulus of the blends increases slightly, T_g of EPDM increases, and T_g of PP almost remains unchangeable. EPDM/PP blend showed enhancement in yield stress and ultimate tensile strength with the increase in curing agent levels, in the case of elongation at break; the relationship is the reverse of that expected, however.

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