Influence of Processing Conditions on Dual-Phase Continuous Blend System of Thermoplastic Polyurethane with Ethylene-Propylene-Diene Monomer Elastomer

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ABSTRACT: In the present work, we extend the investigation on the influence of processing conditions on the morphology, the mechanical properties, and the rheology of the blends of thermoplastic polyurethane (TPU) and ethylene–propylene–diene monomer elastomer (EPDM). Scanning and transmission electron microscopies show that the dual-phase continuous morphology of the blends was strongly dependant on the EPDM composition, processing temperature, and the shear rates. The network structure of the EPDM domain in TPU matrix became finest and most regular for the blends containing 7 wt % EPDM. It was also found that high shear rate favored the formation of the perfect network structure. Furthermore, the blends prepared at 180°C present finer and more perfect network structure than those at the other processing temperatures. The competition of compatible and incompatible segments of TPU with EPDM during melt blending plays an important role in development of the dual-phase continuous morphology. This was reflected through the influence of processing conditions on the rheological properties, and was also verified by the Davies equation's prediction. The tensile properties present a significant improvement with addition of EPDM, and obtained the optimum value for the blends containing 7 wt % EPDM. The influence of different processing parameters on the mechanical properties is associated with their influence on the morphology, and better tensile properties are obtained in the processing conditions, in which, the finer and more perfect network structure of EPDM domain is presented. These facts confirm that the dual-phase continuous morphology is the main advantage for higher tensile strength, elongation at break, and Young's modulus can be well controlled by different processing conditions for the improvement of mechanical properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5472–5482, 2006

Key words: TPU; EPDM; dual-phase continuous morphology; mechanical properties

INTRODUCTION

Blending of already existing polymers is considered as one of the most successful alternatives and attractive low-cost substitutes for the development of new polymeric materials. Polymer blends obtain a balance (or even synergism) of the desired properties exhibited by the individual components, and is also an efficient way for improving the properties. The most commercial multicomponent polymer systems are two-phase blends that provide advantages over the single-phase systems.[1,2] There is a general agreement that the properties of polymer blends are usually controlled by the properties of the components, morphology of the blends, and interaction between components in the blends.[3–5] Morphology of polymer blends is intimately correlated with the properties of the blending system. The domain size is often used to indicate the extent of compatibility of multiphase polymer systems, i.e., the smaller the domain size, the more compatible are the systems and the better are the mechanical properties.[6–9] The detailed investigation on phase morphological development, phase continuity, and phase stability of polymer blends has been undertaken. The correlation between morphology and mechanical properties has been established.[10,11]

As one of the most versatile engineering thermoplastics with elastomeric properties, thermoplastic polyurethane (TPU) possesses high tensile modulus when compared with rubber, high abrasion resistance, high wear and tear resistance, and resistance to oil and many solvents.[12] Blending of TPU with the other polymers has been of a considerable interest in recent years.[13–18] This interest was caused by the necessity of handling the problems resulted from specific structures of TPU macromolecules, interphase interactions, and microphase transformations

in blending systems based on TPU.[19–21] It is well-known that TPU elastomers are linear multiblock copolymer containing soft and hard segments. The hard segments are based on diisocyanates and a low-molecular weight diol and/or diamine. The soft segments are constituted either by polyether or polyester glycols, which may be extended by diisocyanates.[22,23] Thermodynamic immiscibility of hard and soft segments at low temperature results in a microphase separation, and consequently a domain structure. The hard segments of molecules are connected with each other by intermolecular hydrogen bonding and form domains to act as junctions of physical crosslinking for the soft segments.[24,25] In providing a network of physical junctions in TPU, the hydrogen bond plays a critical role. The hydrogen bonds existing in TPU are labile, and thus can be redistributed depending on thermal effects or owing to modification. The distribution of the hydrogen bonds influences the extent of microphase separation in TPU and the set of properties, typical of these materials.[26,27] It was supposed that the properties of blends of TPU with the other polymers as a second component depended on how the second component influences the extent of microphase separation of TPU. It seems significant to study the role of the second component in which hydrogen bonding is the dominating intermolecular process. Furthermore, Macosko and coworkers[28,29] also explored the compatibilized blends of TPU with amine or maleic anhydride (MA) functionalized polypropylenes. The strategy of reactive compatibilization is based on reactions between the amine/MA groups and urethane linkages or traces of free isocyanates released by thermal degradation of TPU. Such excellent compatibilization can result in significant improvements in the overall mechanical properties.[28,29] Recently, immiscible polymer blends with cocontinuous morphology have been receiving attention from both scientific and industrial communities, since the cocontinuous polymer blends can have a few more advantageous properties, i.e., synergistic mechanical properties, controlled electrical conductivity, or selective permeability, making them ideal for a wide range of applications. Macosko and coworkers have reported the investigations on cocontinuous poly(ethylene oxide) (PEO)/polystyrene (PS), and high density polyethylene (HDPE)/PS blending systems, and developed a novel method for detecting and analyzing the cocontinuity in polymer blends.[30,31] These studies benefited the achievement of cocontinuous polymer blends with the morphological stability.

In our former study, we employed ethylene–propylene–diene monomer elastomer (EPDM) as second component to blend with TPU, and found an interesting cocontinuous morphological structure for these blends, in which a network-type EPDM domain existed in TPU matrix. The experimental results also indicated that EPDM was thermodynamically miscible with the soft segments of TPU and incompatible with the hard segments; therefore, the formation of the network was resulted from the competition of compatible and incompatible segments of TPU with EPDM. This network-type morphological structure enhanced the tensile properties.[32] In the present work, we studied the effect of processing conditions on the dual-phase continuous morphology and mechanical properties of TPU/EPDM blends. Meanwhile, the rheological properties were also evaluated.

EXPERIMENTAL

Materials

TPU (commercial grade: T1180PC), with a hardness of Shore A 64 and estimated hard segment content of 46 wt %, was supplied by Hua Da Chemical, China. The TPU employed in this study is a polyester-based TPU with the hard segments composed of the copolymer of 4,4′-diphenylmethane diisocyanate and 1,4-butane diol. EPDM, with a density of 0.84 g/cm³ and Mooney viscosity ML_{1+4} of 40 at 125°C, was commercially obtained from Dow Chemical, USA.

Preparation of blends

TPU and EPDM were dried in a vacuum oven at 80°C overnight before using. The constituents of the blends with various weight ratios were prepared in a Haake torque rheometer (Rheomix-600P) equipped with an electrically heated mixing head and two noninterchangeable rotors. The processing temperature was set at 160, 180, and 200°C, and the speed of rotor was set at 30, 60, and 120 rpm. Blending time was maintained for 15 min. The sample weight for each blending was controlled at 55 g. Fusion curves of TPU/EPDM blends were analyzed and recorded. The blends were further dried at 100°C before injection molding the test specimens for the determination of mechanical properties.

Scanning electron microscopy

A Hitachi S-4300 scanning electron microscope was employed to study and record the fracture surface of all the blending samples. The sample bars in the form of thin plates were immersed in liquid nitrogen for 5 min and then fractured. The fractured specimen surfaces were etched with boiling tetrahydrofuran (THF) for 2 h, and then coated with a thin layer (10–20 nm) of gold-palladium. The coating was carried out by placing the specimen in a high vacuum evaporator and vaporizing the metal held in a

heated tungsten basket. Scanning electron microscopy (SEM) measurements were performed only on the fractured surface of all the blends.

Transmission electron microscopy

Morphology was also determined by transmission electron microscopy (TEM). Samples were cryogenically microtomed from Izod impact bars perpendicular to the flow direction using a diamond knife. The blend samples were stained with osmium tetroxide (OsO$_4$). A Hitachi H-800 transmission electron microscope was employed to observe these samples.

Measurements of mechanical properties

All blend samples for mechanical property measurements were prepared by pressing in a mold on a hot-press at 170°C and 10 MPa for 4 min, and subsequently on a cold-press at room temperature for another 4 min. The tensile properties were determined with an Instron-1185 universal testing machine using a 5000 Newton load transducer according to the standard of ASTM D-638. All the tests were done at room temperature, and five measurements were carried out for each data point.

Measurement of elastic shear modulus

The elastic shear modulus was measured with a CZ2-NBW-500 torsion pendulum apparatus operating at 1 Hz according to the standard of ASTM D-2236. This test was preferred for small specimen size of 80 × 7 × 3 mm^3. All tests were carried out at room temperature (22–24°C).

### RESULTS AND DISCUSSION

Morphology

The morphologies of the blends prepared at the different processing conditions were investigated by SEM observation. We attempted first to etch the brittle fractured surface with boiling THF or toluene to remove TPU domain or EPDM domain, respectively. Through observing the etched surfaces by SEM, we found that, for the samples etched with THF, the EPDM domain left on the fracture surface could reflect the morphologies more clearly in comparison with the surfaces etched with toluene. Therefore, the SEM micrographs of the surface etched with THF were only presented in this article.

Figure 1 shows the effects of the EPDM content and the rotor speed on morphologies of TPU/EPDM blends prepared at 180°C. In the most of SEM mac-

rographs, a light-color network structure was presented in dark background. As the TPU domain on the surface had already been removed by boiling THF, the network could be considered as the EPDM domain. However, EPDM cannot form perfect network structure in the TPU matrix due to its low content, as shown in Figure 1(a). From Figure 1(b) to (e), the dependence of dual-phase continuous morphology on the EPDM content could be clearly observed. It is noticed that the network structure becomes finer with increasing the EPDM content. For the blend containing 7 wt % EPDM, a perfect and fine network of EPDM domains presents in TPU matrix and the size of mesh goes quite uniform. However, when the EPDM content is greater than 10 wt %, the network structure becomes thicker and the size of mesh looks larger. We have also observed the fractured surface of pure TPU etched with boiling THF by SEM, as shown in Figure 1(f). Its fractured surface exhibits a whole dark background, which is same as the TPU domain of blends observed by SEM. This verifies the fact that the network structure of EPDM in the TPU matrix can be reflected by the SEM micrographs of the fracture surface etched with boiling THF. The dual-phase continuous morphology for the TPU/EPDM blends is also confirmed by TEM with the aid of OsO$_4$ staining due to the double bond in EPDM chains. One may clearly identify a network structure of the EPDM domains in the TPU matrix from the TEM micrographs as shown in Figure 2. It can be observed that, for the blends containing 3 wt % EPDM, the minor phase exhibits a fiber-like shape, which is resulted from deformation of the EPDM domains in immiscible TPU matrix under elongational-flow fields. The fibrillar EPDM domains connect each other to form a network when the EPDM content reach 5 wt %. The network becomes finer with increase in the EPDM content continuously. The phenomena are completely in accord with the results that are observed in the SEM micrographs. It is concluded that the SEM technique employed in this study is fairly effective to investigate the dual-phase continuous morphology for the TPU/EPDM blends.

It is widely accepted that, for immiscible blend systems, the domain range in size from submicron to hundreds of microns, and spherical, ellipsoidal, cylindrical, ribbon-like, cocontinuous, and subinclusion types of morphologies can be obtained under various conditions. The final morphology obtained is a balance between deformation-disintegration phenomena and coalescence. It is well-known that TPU is constituted of hard and soft segments. The thermodynamic immiscibility between hard and soft segments results in a microphase separation (or say microsegregation) and consequently a multiphase structure; however, a complete macrophase separa-
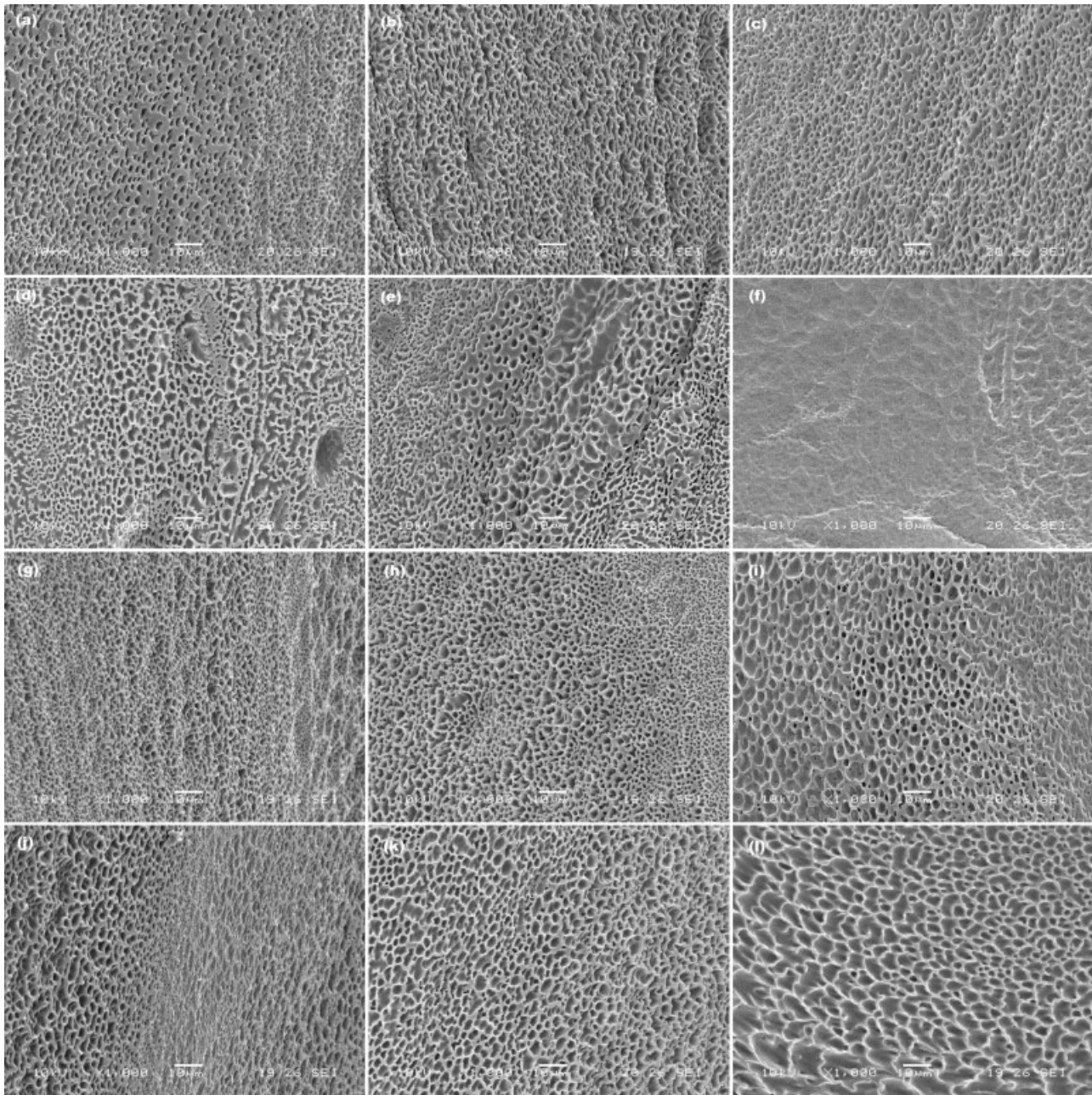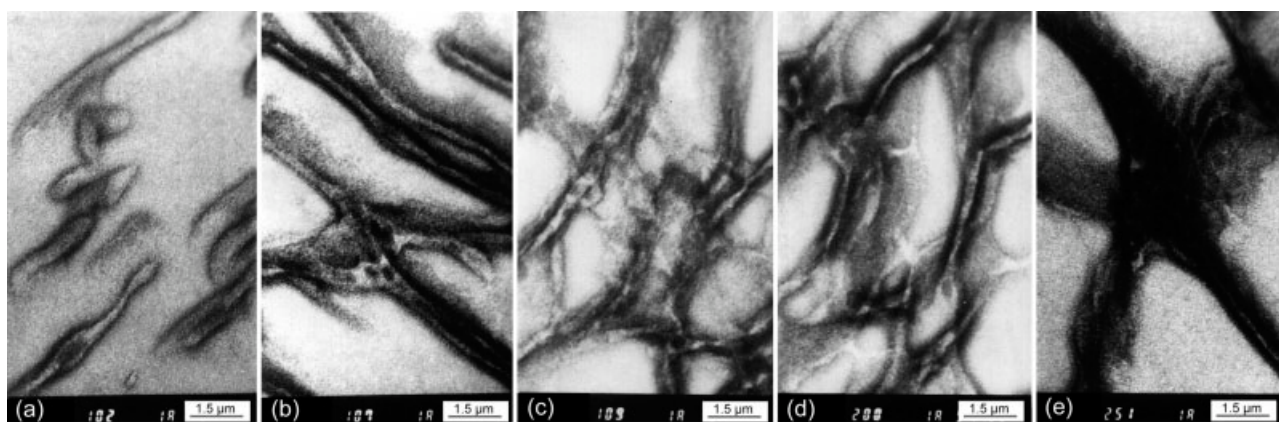
Figure 1 SEM micrographs of the fractured surfaces of TPU/EPDM blends prepared at 180°C with weight ratios of: (a) 97/3, (b) 95/5, (c) 93/7, (d) 90/10, and (e) 80/20 at a rotate speed of 120 rpm; (f) 100/0; (g) 95/5, (h) 93/7, and (i) 90/10 at 60 rpm; (j) 95/5, (k) 93/7, and (l) 90/10 at 30 rpm.

tion of hard and soft segments is prevented by the affinity from hydrogen bonding and steric hindrance between hard and soft segments. Therefore, a large deal of volume is generated in the interfaces between the microsegregated parts. It is no doubt that the EPDM is a nonpolar polymer, and is completely immiscible with the TPU, since the strongly polar hard segments of TPU results in their thermodynamic immiscibility. However, we also found in our former study, that the EPDM is topologically compatible with the soft segment.[32] Therefore, the EPDM is

greatly distributed in the volume of microsegregated soft segments, while it is introduced into TPU. Owing enough to its high molecular weight and highly flexible molecular chain, the EPDM domains in TPU matrix can easily aggregate when the neighboring microsegregated soft segments are enough close, and then form the physical crosslinking network structure. It is also noted that an optimal concentration of EPDM can result in a perfect network structure. It is obvious that the soft and hard segments of TPU both play important roles in the formation of the
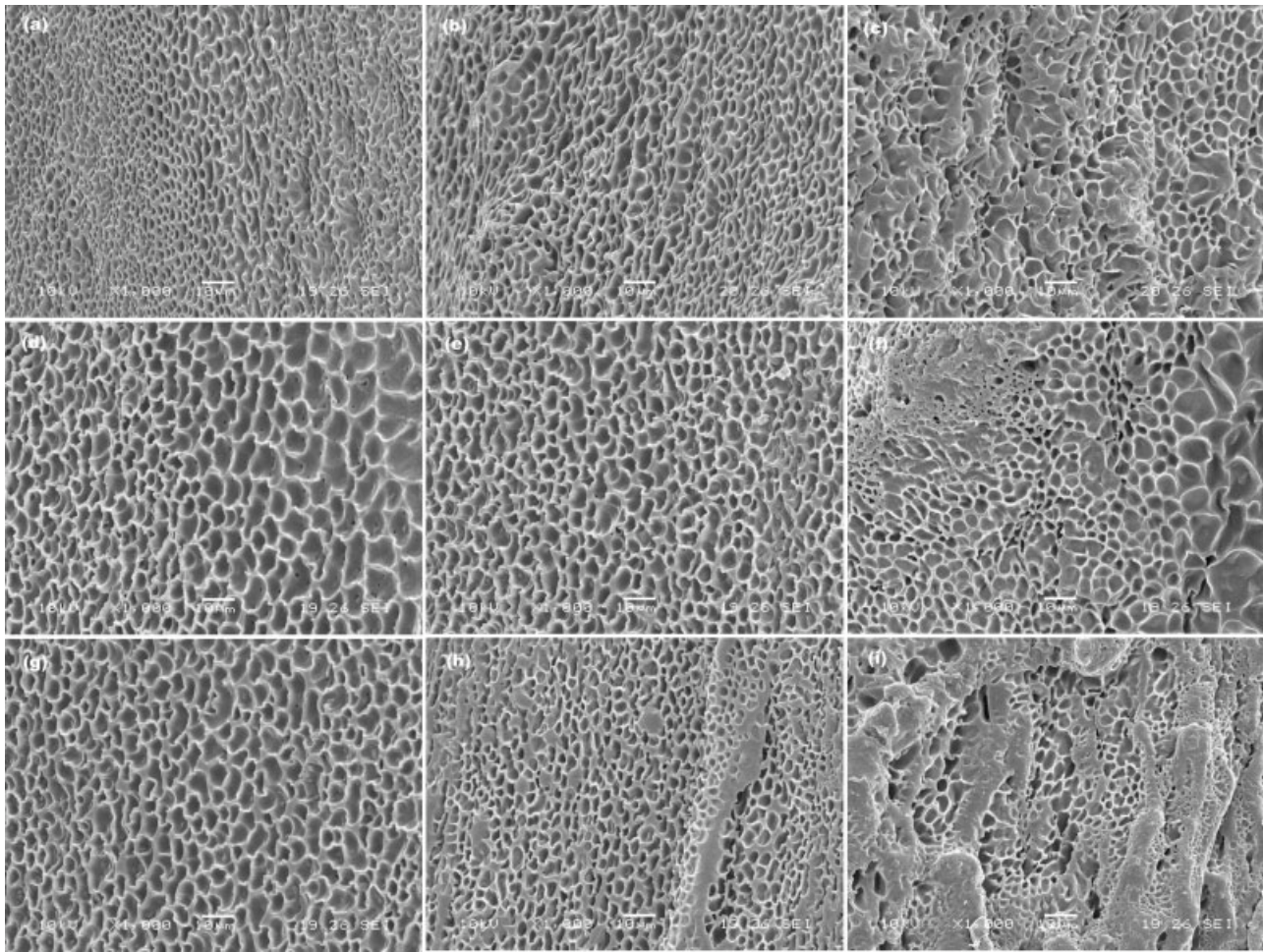
Figure 2 TEM micrographs of the TPU/EPDM blends prepared at 180°C with weight ratios of: (a) 97/3, (b) 95/5, (c) 93/7, (d) 90/10, and (e) 80/20 at a rotate speed of 120 rpm.

dual-continuous morphology. In fact, the formation of the network of EPDM domain is resulted from a competition of the topological compatibility (between the soft segments of TPU and EPDM) and the bulky incompatibility (between the hard ones of TPU and EPDM). However, the topological compatibility between EPDM and hard segments of TPU becomes poor with increasing the amount of EPDM; then the phase separation becomes more serious. As a result, the greater the amount of EPDM in TPU matrix, the larger is the size of EPDM domain. But the perfect network is still kept in an appropriate range of EPDM content. When introducing too much amount of EPDM to TPU matrix (i.e., exceeded 20 wt %), a serious microphase separation happens, thus the network structure is broken.

The similar phenomena with variation of the EPDM content can be found from the blends prepared at rotor speeds of 60 and 30 rpm, as shown in Figure 1. The morphology of TPU/EPDM blends prepared by twin-screw extruder has been reported in our former article. However, only influence of EPDM content on the morphology could be evaluated, as the processing parameters are not alterable significantly. Although the network structure of EPDM in the TPU matrix could be recognized from the samples prepared by twin-screw extruder,[32] it is found that the dual-phase continuous morphology is strongly affected by rotor speed from the samples prepared by Haake rheometer, whose processing parameters (i.e., temperature and shear rate) can be altered flexibly. For the blends with the same EPDM content prepared at rotor speed of 120 rpm, the network of EPDM domain is finest and the size of mesh is smallest; likewise, the blends prepared at 60 rpm exhibit a much finer dual-phase continuous morphology than those prepared at 30 rpm. It is obvious that the higher rotor speed can provide the stronger shear stress and the more effective mixing process.

The effect of shear stress indicates that the domain size is inversely proportional to the applied shear stress. An increase in the shear stress would thereby result in a decrease of the domain size. This makes the EPDM phases dispersed easily as it is the much smaller domain. As a result, the EPDM domain demonstrates a much finer network structure in the TPU matrix at a higher rotor speed. From the SEM micrographs of the fracture surfaces of TPU/EPDM blends prepared at different temperatures and rotor speeds, as shown in Figures 3 and 4, it is clearly observed that the processing temperature affects the morphology. When compared with the samples prepared at 180°C, the blends prepared at 160°C exhibits a thicker network and a more nonuniform dual-phase continuous morphology at any rotor speeds, especially for the blends containing 20 wt % EPDM. However, the blends prepared at 200°C do not comply with the same dependence of the morphology on processing temperatures. Although the network becomes more uniform, the EPDM domain becomes thicker and the size of mesh looks larger, especially in the case of the higher rotor speeds. It is accepted that the viscosity ratio, (the viscosity of the dispersed phase)/ (the viscosity of the dispersed phase), has been shown to be one of the most critical variables for controlling blend morphology. In this case, the viscosities of the TPU and EPDM have different sensitivity to the processing temperature, because two polymers have different flow activation energy. Variation of the processing temperature results in a change of the viscosity ratio, and thus affects the morphology. On the other hand, the processing temperature and the rotor speed determine the morphology through affecting the melt viscosities in different ways during the melt process, and thus a different dependence of the morphology on these two processing parameters is resulted. The following discussion is focused on the dependence of the mixing torque recorded by the

Figure 3 SEM micrographs of the fractured surfaces of TPU/EPDM blends prepared at 160°C with weight ratios of: (a) 95/5, (b) 93/7, and (c) 90/10 at a rotate speed of 120 rpm; (d) 95/5, (e) 93/7, and (f) 90/10 at 60 rpm; (g) 95/5, (h) 93/7, and (i) 90/10 at 30 rpm.

Haake rheometer on the two processing parameters so as to deduce their influence on the morphology.

Rheological properties

The equilibrium torques (recorded after mixing 10 min) of various TPU/EPDM blends recorded in the Haaker torque rheometer at different processing temperatures and rotor speeds are shown in Figure 4. The pure EPDM and the pure TPU exhibit a great difference in torque, which indicates that the former has a much higher melt viscosity than the latter at any temperatures and shear rates in the processing conditions of this experiment. A similar trend of the torque variation as a function of the blending compositions is clearly observed from the blends prepared at three different shear rates and 160°C. The mixing torque of blends increases with an increase of EPDM contents; however, after reaching a maximum value for the blend containing 10 wt % of

EPDM, the torque begins to reduce with a continuous increase of EPDM content. One may also find that higher rotor speed can result in a higher mixing torque for the blend with same blending composition, which also suggests the sensitivity of the viscosities of the blends to the shear rates were quite high at 160°C. The increase in viscosity is due to the entanglement of the molecular chains of both TPU and EPDM caused particularly by EPDM. Because of the enough long and flexible molecular chains, EPDM chains can entangle among themselves and also with the TPU chains. This entanglement impedes severely with the flow of the melt at low shear rates, and consequently, the viscosity becomes higher.[33] However, the disentangling effect is much greater that entangling one at high shear rates, because the repulsion between EPDM chain and the hard segments of TPU arises from incompatibilizaton of both of them.[34] As a result, TPU/EPDM blends showed lower viscosities than pure TPU at high shear rates.
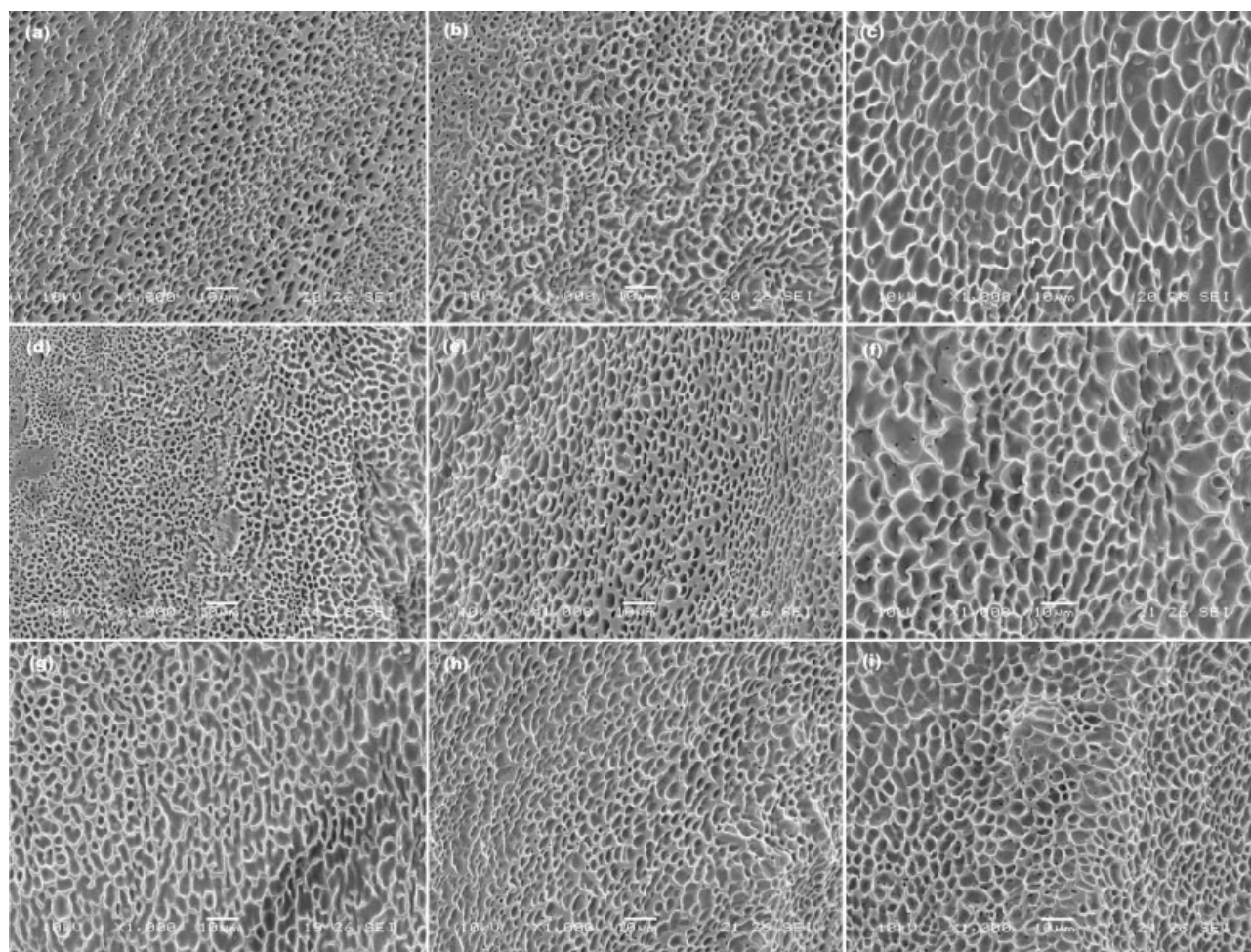
Figure 4 SEM micrographs of the fractured surfaces of TPU/EPDM blends prepared at 200°C with weight ratios of: (a) 95/5, (b) 93/7, and (c) 90/10 at a rotate speed of 120 rpm; (d) 95/5, (e) 93/7, and (f) 90/10 at 60 rpm; (g) 95/5, (h) 93/7, and (i) 90/10 at 30 rpm.

A similar dependence of mixing torque of the blends on blending composition is observed for the blends at the processing temperature of 180°C. However, the sensitivity of the viscosities to the shear rates becomes rather low in comparison of those at 160°C for the blends with lower than 10 wt % EPDM. While the EPDM content is greater than 10 wt %, the sensitivity increases rapidly at rotor speed of 120 rpm. When processing temperature rises to 200°C, trend of the torque variation as a function of the compositions is similar to those at 160 and 180°C. It is also obverted that the sensitivity of the viscosities to the shear rates is fairly high. It is well known that TPU is a polar polymer but EPDM is nonpolar one; therefore, TPU possessed much higher flow activation energy than EPDM. The dependence of viscosity on the shear rate is reflected by the flow activation energy deduced from Arrhenius equation. The viscosity of TPU is not sensitive to the shear rate but relies strongly on the temperature, whereas it is opposite for EPDM. It is obvious that the activation

energy of blends decreases with addition of EPDM into TPU. The greater the EPDM content, the lower is the activation energy. As already mentioned earlier, TPU contains the hard segments with rigid and polar molecular chains. This results in a great interaction among its molecular chains. So TPU possesses high activation energy. On the other hand, EPDM with nonpolar and flexible molecular chain is thermodynamically miscible with the soft segments of TPU. The interfacial free energy (or interfacial tension) between TPU and EPDM decreased during melt blending. It is understandable that the addition of EPDM decreases the polarity of the TPU and the interaction of the molecular chains both inside bulk and at the interface of TPU and EPDM. These explained the dependence of mixing torque on the temperatures and rotor speeds observed in Figure 5.

It is generally believed that the morphology of a blend system is governed by the type of flow (shear or elongation), the viscosity ratio, the composition, the elasticity, and the interfacial tension. Further-
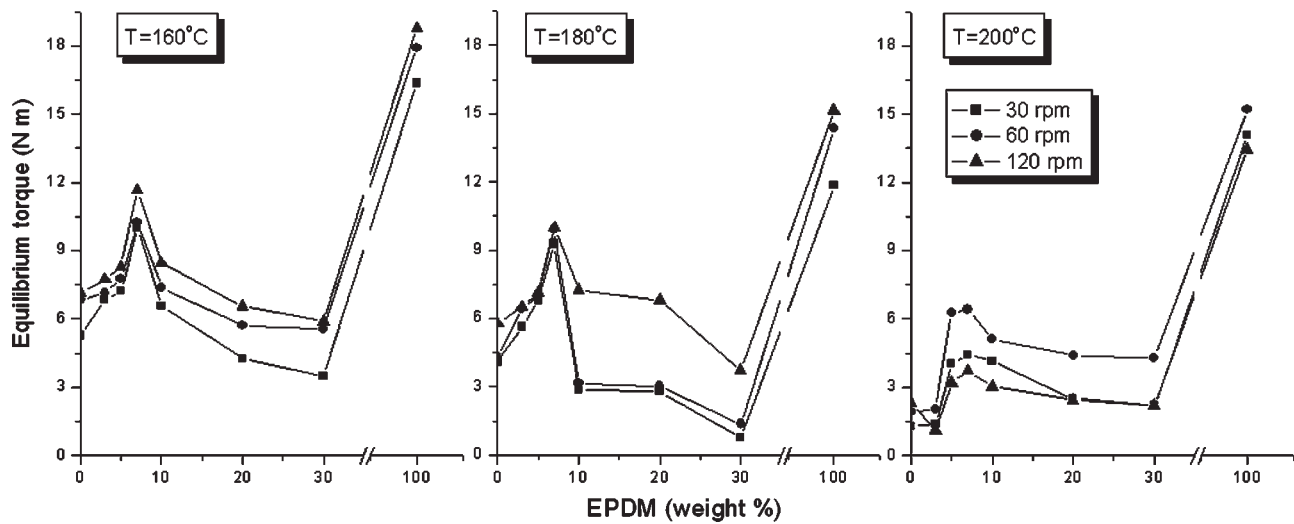
Figure 5 Equilibrium torque of TPU/EPDM blends as a function of EPDM content at different processing conditions.

more, it is important to control the morphology and the phase inversion phenomenon of a blend system at the cocontinuity of the two phases. The formation of the network of EPDM domain is considered as a result of the phase inversion of the minor rubber phase in the major thermoplastic phase during melt blending. This phase inversion is in fact induced by the increase of the viscosity and of the elasticity of the elastomer phase, which considerably changes the viscoelasticity of the major elastomer phase. This can be a reasonable explanation that the behavior of variation of mixing torque with the EPDM content matches the uniformity of the dual-phase continuous morphological structures when the EPDM content is lower than 10 wt %. However, too much elastomer phase results in its aggregation when EPDM content exceeds 10 wt %. This enhances the incompatibility between the elastomer phase and the thermoplastic phase. As a result, the mixing torque begins to decrease along with the degeneration of the dual-phase continuous morphological structures. Otherwise, the shear rate and the temperature play a key role to affect the viscoelasticity of the blends, because the TPU and the EPDM represent the sensitivity to the processing temperature and the shear rate, respectively. Indeed, the nonpolar elastomer phase is mainly influenced by the shear rate at lower processing temperature. The higher the shear rate, the finer is the nonpolar elastomer phase dispersed in TPU matrix. As a result, the morphologies exhibit a significant dependence on the shear rate. However, it can be expected that the higher temperature only produce a significant effect on the thermoplastic phase. This makes a great difference between the elastomer phase and the thermoplastic phase. It is obvious that the high temperature make the blends not favorable to a fine network structure. These have explained

the relationship between the morphology and the rheological properties.

Mechanical properties

The tensile strength and elongation at break of TPU/EPDM blends as a function of EPDM composition prepared at different temperatures and rotor speeds are presented in Figures 6 and 7. The EPDM suggests a typical elastomeric behavior with a tensile strength of 11.2 MPa and an elongation at break of 1580%, but the pure TPU presents much higher values of 40.5 MPa for tensile strength and 960% for elongation at break, respectively. It was observed that the tensile strength and elongation at break present the similar trend of variation as a function of the EPDM composition at any processing temperatures and rotor speeds. At first, they increase with introduction of 3 wt % EPDM into TPU. The tensile strength and elongation at break kept gradually increasing with the increasing of the EPDM content, and both present the maximum values with addition of 7 wt % EPDM to TPU. It is accepted that the network of EPDM in TPU matrix plays a critical role on the enhancement of the tensile properties of blends. The EPDM network can provide a backbone for blends to resist cracking. The finer and more perfect the network, the more powerful is the resistance to cracking. As a result, a more effective enhancement could be achieved and higher tensile strength and elongation at break were obtained. However, the network structure became worse and was finally broken with continuously increasing the EPDM content, which resulted in a higher incompatibility of EPDM and the hard segments of TPU. When the content of EPDM exceeded 7 wt %, the tensile strength
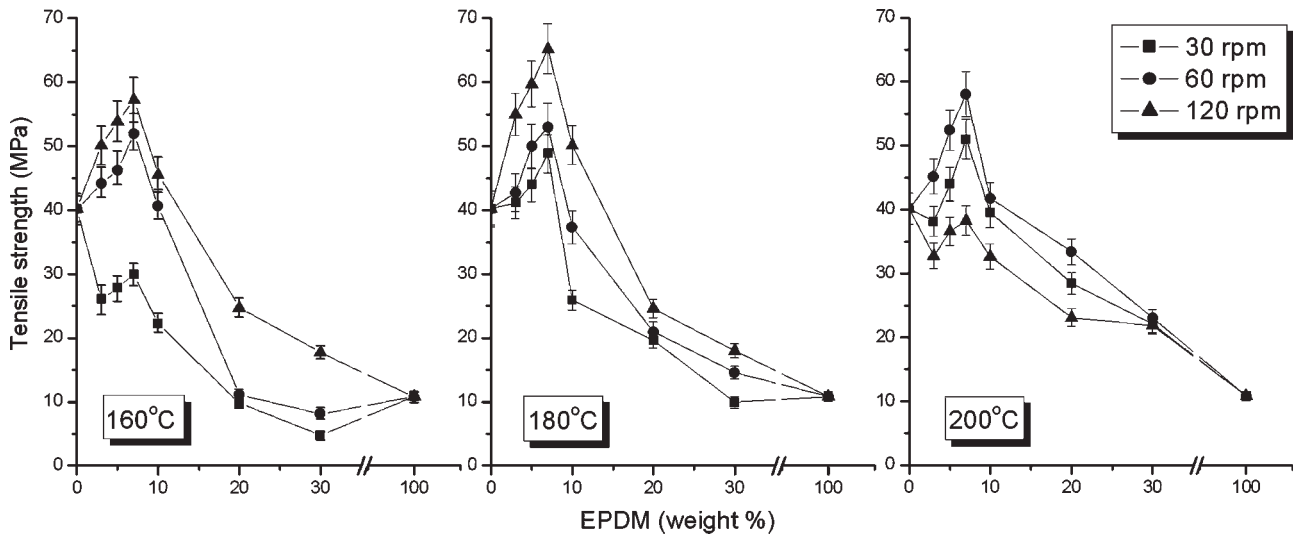
Figure 6 Tensile strength of TPU/EPDM blends as a function of EPDM content at different processing conditions.

and elongation at break begin to decrease. Figure 8 illustrated a similar trend of the variation of the Young's modulus with the EPDM composition. However, the Young's modulus first decreases with the addition of 3 wt % EPDM, and then begins to tail after the trend of the variation of the tensile strength and elongation at break with EPDM composition. The same arguments can be also brought with regard to the Young's modulus of TPU/EPDM blends. It is understandable that the perfect level of network structure also contributes to improving the Young's modulus of the blends.

The influence of the processing temperatures on mechanical properties cannot be dissociated from their effects on the morphologies. As observed preciously, the blends prepared at 180°C present more uniform and finer network structures than those pre-

pared at 160 and 200°C; therefore, their mechanical properties are superior to those from the other two processing temperatures. One may also find that the blends prepared at 200°C achieve better tensile properties than that at 160°C, owing to their more perfect network structure. The effect of the shear rates on the tensile properties is also associated with their effect on the morphologies. As we discussed in the first section, the higher shear rate can provide better dispersion ability for blends, and thus, result in a finer and more uniform network structure. As a result, the blends prepared at the higher rotor speed achieve the better tensile properties. These results indicate that the dependence of the mechanical properties on the processing conditions is identical with the dependence of the morphology on processing conditions.
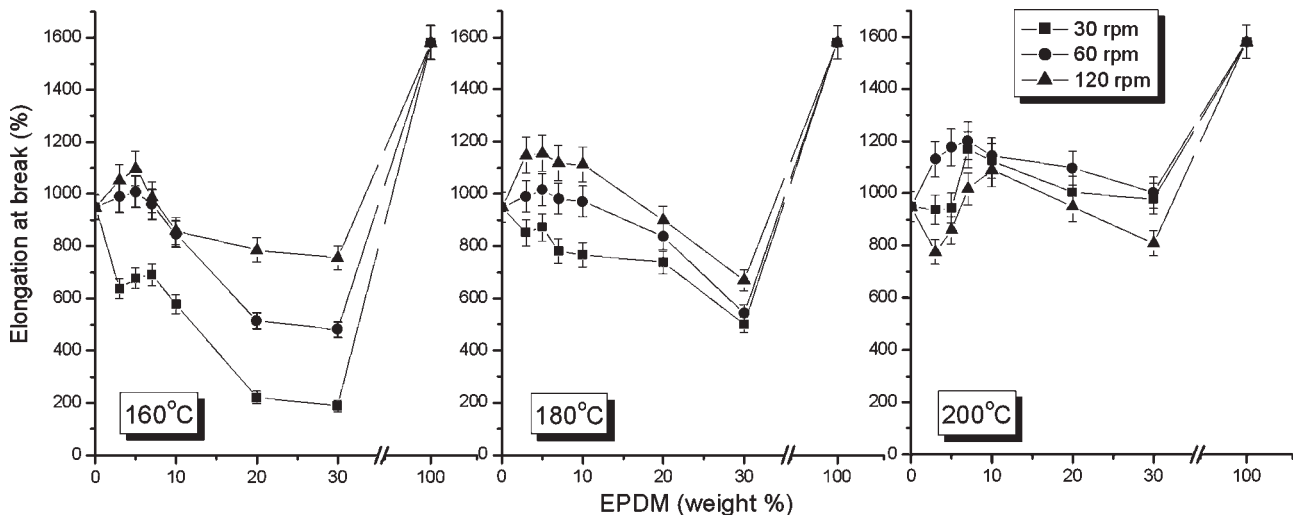

Figure 7 Elongation at break of TPU/EPDM blends as a function of EPDM content at different processing conditions.
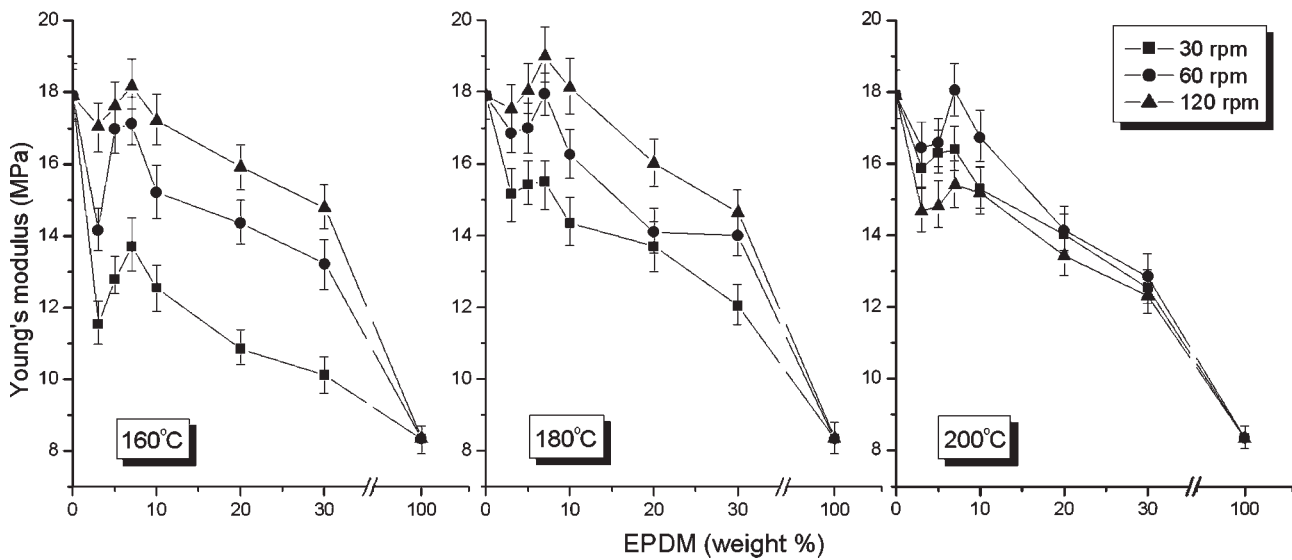
Figure 8 Young's modulus of TPU/EPDM blends as a function of EPDM content at different processing conditions.

The information about phase continuity of TPU/EPDM blends in different processing conditions can also be yielded qualitatively from the mechanical behavior study by using the corresponding theoretical models, which have been evolved by Kerner et al.[35] The first two theories assume spherical particles dispersed in an isotropic matrix. But Davies and coworkers proposed a relation by assuming that two components with shear modulus G_1 and G_2, respectively, have been mixed to obtain a new blend with shear modulus G, as expressed in the equation[36]

$$G^{1/5} = \phi_1 G_1^{1/5} + \phi_2 G_2^{1/5} \qquad (1)$$

where ϕ is the volume fraction of phase 1 or 2 as indicated. It suggests that this equation is best suited to morphologies, which have cocontinuity of both phases at all $0 < \phi_2 < 1$. Figure 9 illustrated the shear moduli of the TPU/EPDM blends measure at low frequency (~ 1Hz) by means of a torsion pendulum apparatus as well as the theoretical data calculating from the modulus of each phase by Davies equation as a function of volume fraction of EPDM. The shear modulus of the blends falls away from the modulus of TPU (MPa), as the content of EPDM is increased and approaches that of EPDM (MPa). It is interesting to note that all the experimental data fit the Davies equation basically, suggesting that the blends most probably have dual-phase continuity. However, these experimental data have still been found to deviate slightly below Davies's theoretical curve. The Davies model is based on actually perfect interpenetrating network (IPN) structure, as IPNs exhibit significantly stiffer than the two continuous phases formed in physical blends. Moreover, the derivation of the Davies equation considers domain–

domain interactions, the deviation of the experimental data from the Davies curve can also be imputed to poor domain–domain interactions resulted from immiscibility of TPU and EPDM. The influence of the processing conditions on dual-phase continuity can also be evaluated in a qualitative way through comparing the dependence of the experimental and theoretical data (the dynamic shear modulus) on the volume fraction. It is evident that the farther the shear modulus derivate from the Davies curve, the poorer is the network structure. These are in agreement with the actual morphology as shown in Figures 1–4.
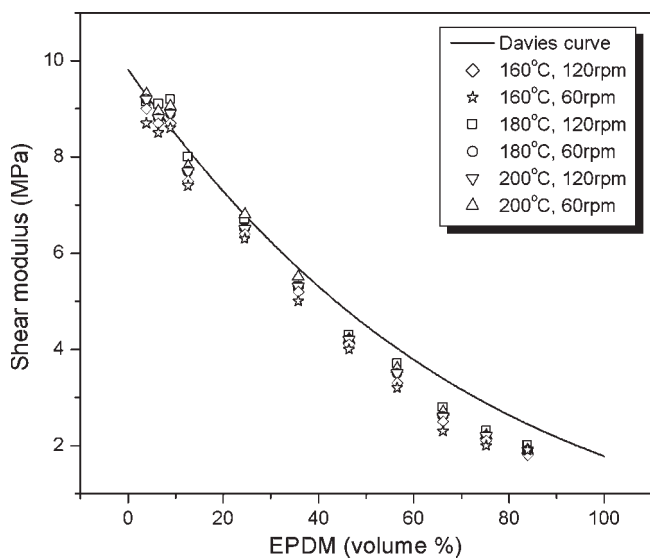

Figure 9 The elastic shear modulus of TPU/EPDM blends as a function of EPDM content at different processing conditions. The solid line is theoretical curve refer to the Davies equation, and open symbols are experimental points.

CONCLUSIONS

The influence of processing condition on the morphology, the mechanical properties, and the rheology of the blends of TPU and EPDM was intensively investigated. The dual-phase continuous morphology of the blends was governed by the EPDM composition, processing temperature, and the shear rates. The network structure of the EPDM domain in TPU matrix became finest and most regular for the blends containing 7 wt % EPDM. It was also found that high shear rate was favorable to the formation of perfect network structure. Furthermore, the blends prepared at 180°C present finer and more perfect network-type morphology than those at the other processing temperatures. The competition of compatible and incompatible segments of TPU with EPDM during melt blending plays an important role in the dual-phase continuous morphology development. This was verified by the Davies equation's prediction, and was also reflected through the influence of processing conditions on the rheological properties. The tensile properties present a significant improvement with addition of EPDM, and obtained the optimum values for the blends containing 7 wt % EPDM. The influence of different processing parameters on the mechanical properties is associated with their influence on the morphology, and better tensile properties are obtained in the processing conditions, in which, the finer and more perfect network structure of EPDM domain is presented. This confirms that the dual-phase continuous morphology is the main advantage for higher tensile strength, elongation, and Young's modulus, and can be well controlled by different processing conditions for the improvement of mechanical properties.

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