

Thermal Behavior and Morphological and Rheological Properties of Polypropylene and Novel Elastomeric Ethylene Copolymer Blends

Yingwei Di,¹ Salvatore Iannace,² Luigi Nicolais²

¹Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

²Institute of Composite Materials Technology (ITMC-CNR) & Department of Materials and Production Engineering, University of Napoli "Federico II," Piazzale Tecchio 80, 80125, Naples, Italy

Received 3 August 2001; accepted 22 April 2002

ABSTRACT: The thermal behavior including melting and crystallization behavior and morphological and rheological properties of the blends based on an isotactic polypropylene and a novel maleated elastomeric ethylene copolymer were investigated in this work. The addition of an elastomer to polypropylene (PP) was found not to change the PP crystalline structure significantly when cooled quickly from the melt. On recrystallization at a lower cooling rate, the elastomer promotes the formation of β -pseudo-hexagonal PP in PP-rich blends. In elastomer-rich compositions, heterogeneous nucleation is hindered and homogeneous nucleation takes place. These phenomena are revealed by morphology observation: that, with increasing of the elastomer content, the system undergoes PP continuous, dual-phase continuity

and PP-dispersed morphologies. The blend viscosity at a low shear rate range increases continuously with increasing elastomer content and shows positive deviations from the additivity rule. In the terminal zone, the dynamic storage modulus of the blends shows positive deviation from the simple mixing rule and the maximum deviation lies in the composition range of dual-phase continuity which could be caused by a large increase in the interfacial tension. The Cox–Merz rule does not hold for the blends because of the two-phase heterogeneous structure and its variation in steady and oscillatory shear flow. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3430–3439, 2002

Key words: poly(propylene) (PP); morphology; rheology

INTRODUCTION

Polymer modification via blending or compounding has received considerable interest and has become attractive both for industrial application and theoretical interest during the last several decades. Polymer blends have been found to be useful for the preparation of more convenient and available products than by developing new polymers through monomer synthesis and polymerization.^{1,2} Polypropylene (PP) is a thermoplastic widely used in packaging and in the textile and automobile industries because of its good processability. However, its application as an engineering thermoplastic is somewhat limited because of its relatively poor impact resistance, especially at room and low temperatures. To improve its impact toughness and extend its application range, a number of extensive and thorough studies on the toughening of PP have been made in last 20 years, and since then, PP-based blends have been among those most commonly used technologically.³ A significant number of commercial polymers or copolymers for blending with PP have become available, such as the ethylene-

octene copolymer,⁴ the ethylene-propylene copolymer (EPR),⁵ the ethylene-propylene-diene terpolymer (EPDM),⁶ and poly(ethylene vinyl acetate) (EVA),⁷ and continuous efforts are expected to further create more desirable thermal, rheological, and mechanical properties of the PP blends. An example is a new high-impact PP in which a novel polyolefinic elastomeric modifier, Exxelor 1801, used as a minor component, is blended with PP. Indeed, PP/modifier mixtures are now industrially important over the full range of their compositions.⁸

In our recent work, we focused on the blends of PP and Exxelor 1801, which is one of EXXON Chemical's newly developed polyolefinic elastomeric modifiers and can compete against the above-mentioned impact modifiers according to the manufacturer. We present in this article the thermal, morphological, and rheological properties of them. The changes in the multiple morphology and rheological properties of PP as an effect of blending with the elastomer were investigated. The whole compositional range of the blends was studied in order to understand the influence of the elastomer on these changes. Small and wide-angle X-ray diffraction (SAXS, WAXD) techniques were employed to detect their solid-phase behavior and the thermal properties were assessed by the DSC technique. The rheology of the blends was characterized

Correspondence to: S. Iannace (iannace@unina.it).

under steady and oscillatory deformations with a stress-control rotational rheometer. A particular objective was to show the morphology variation with the composition and its associated effect on the thermal and rheological properties.

EXPERIMENTAL

Polymers and blends preparation

Throughout this study, the polymers used were obtained from commercial sources. The isotactic PP (iPP) was manufactured by FINA Chemical, with melt-flow index of 10.8 g/min and density of 0.9003 g/cm³, and the impact modifier was produced by EXXON Chemical under the commercial name of Exxelor® VA 1801 (hereafter referred as E1801), which is a maleic anhydride-functionalized elastomeric ethylene copolymer with melt-flow index of 9 g/min and a density of 0.87 g/cm³.

The blends with different weight fractions of E1801 were prepared in a HAAKE RHEOMIX® 600 mixer attached to a measuring drive unit HAAKE RHEOCORD® 9000. The polymer samples were dried in a vacuum oven at 70°C for at least 16 h before use. Mixing conditions were a 200°C set temperature, 60 rev/min, 50-g-weight sample, and 5-min mixing time. After mixing, the blends were dumped out and compression-molded into about 2-mm-thick plates at 200°C for the following tests. The measurements were carried out on the same part of each of the samples. This ensured that the same sample structure was being examined by the different techniques.

X-ray diffraction studies

The WAXD work was carried out on a Philips X-ray generator and a Philips diffractometer, type PW1710 (40 kV, 20 mA). A tube anode of Cu was used ($\lambda_1 = 0.15406$ nm, $\lambda_2 = 0.154439$ nm). To perform SAXS measurements, a Rigaku-Denki small-angle chamber was attached to the Philips X-ray generator. SAXS patterns were recorded at a scanning rate of 0.5 min/100 s using Ni-filtered radiation.

Morphology examination

The morphology of the blends was examined in a LEICA scanning electron microscopy (SEM) Model S440. Samples were cryogenically fractured in liquid nitrogen, followed by gold coating before their examination.

Thermal analysis by DSC

The melting and crystallization of the blends were analyzed using a DuPont differential scanning calo-

rimetry 2910 DSC in a nitrogen atmosphere. The cooling was provided by a pulsating liquid nitrogen supply. The temperature calibrations were made using the melting onset temperature of pure indium ($T_m^{\text{onset}} = 156.61^\circ\text{C}$) and benzophenone ($T_m^{\text{onset}} = 48.00^\circ\text{C}$). The sample masses varied from 10 to 20 mg and were weighed with an accuracy of 0.01 mg. The tests were run at a heating rate of 10°C/min and a cooling rate of 10°C/min.

Melt rheology

Dynamic and steady-shear rheological measurements were carried out on a Rheometrics Scientific SR500 dynamic stress rheometer. This operates at a controlled stress where the stress is applied to the material and its resulting strain rate is measured. The instrument required only a small volume of material, so rapid temperature equilibrium was achieved. The tests were performed at a temperature of 200°C in a N₂ atmosphere. The samples were found to be thermally stable under these conditions by testing a sample at constant stress for 60 min at 200°C. Before each test, the blends were dried under a vacuum at 70°C for 24 h. Steady and dynamic viscosity measurements were determined using cone/plate and parallel plate geometries, respectively. The cone angle was 0.1 radian and the plate diameter was 25 mm. For the dynamic tests, the strain (γ) values were chosen to perform the experiments in the linear viscoelastic region (LVR), that is, the limiting strain under which the rheological parameters (G' , G'' , η^* , etc.) remained constant. For this purpose, a preliminary study was made at 200°C and the LVR was determined for each blend. The strain amplitude was varied from 0.2 to 10%, to keep the tests within this region over a frequency range of 0.01–100 rad s⁻¹.

RESULTS AND DISCUSSION

Crystalline structure of the blends

It is known that the modulus and strength of a semicrystalline polymer are determined by its crystalline structure and the crystallization behavior of the polymer becomes modified in a blend because of the presence of the other component. Any changes in this structure will result in a change of the properties, so it is essential to determine the effect of elastomer blending on the crystalline structure of iPP as well as on its melting and crystallization behavior. iPP is known to crystallize in several different crystalline forms. It can crystallize into an α -monoclinic, a β -pseudohexagonal, and a γ -orthorhombic form.⁹ The most common form of iPP is the α -monoclinic, with β -pseudohexagonal and γ -orthorhombic formed under special conditions. Quenching conditions can be tailored to ob-

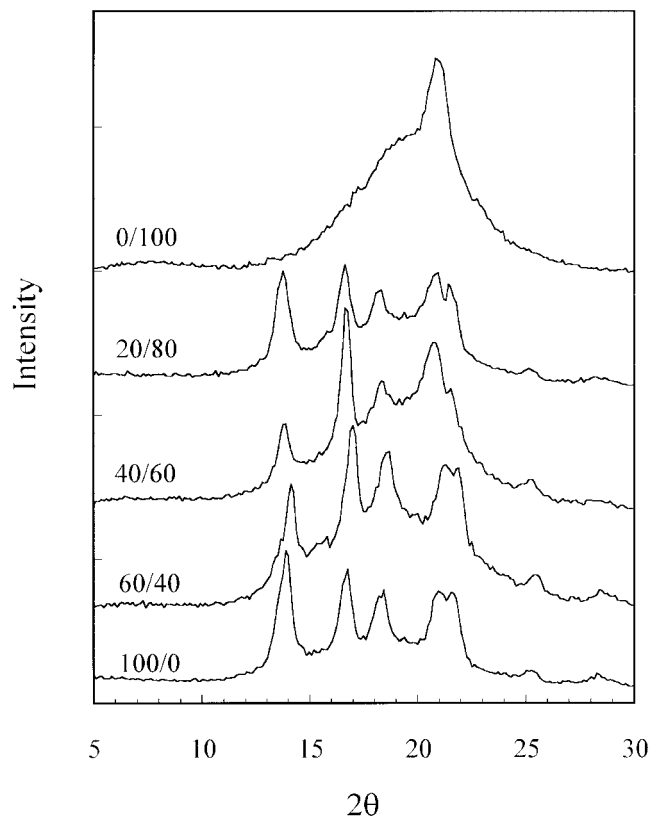


Figure 1 WAXD patterns of PP/E1801 blends.

tain β -form crystal. Nowadays, a number of nucleating agents to achieve the formation of large amounts of the β -form crystal are available.⁹ At atmospheric pressure, the γ -form crystal appears under various conditions, for instance, when the polymer chains are short or in the case of a copolymer with a small amount of ethylene. However, the main way to obtain the γ structure for a high molecular weight homopolymer is to perform crystallization under high pressure.¹⁰ Each of the three crystal forms of iPP has a distinctive reflection in a WAXD scan. These peaks in the WAXD pattern are found between 2θ values of 18–19° for the α -monoclinic structure, 16–17° for the β -pseudo-hexagonal structure, and 19.2–20.05° for the γ -orthorhombic structure.¹¹ The appearance of these characteristic peaks indicates the presence of that particular structure. According to the static WAXD diffractograms as shown in Figure 1, the α -monoclinic modification is not changed pronouncedly and the dominating α -monoclinic modification is maintained with an increasing elastomer content up to 80 wt %. These results were corroborated by the differential scanning calorimetry (DSC) thermograms recorded during the melting of the blends. Figure 2 shows the DSC thermograms of several PP/E1801 blends with different weight fractions of E1801 (for the reason of clarity, not all the compositions are shown). A single peak, characteristic of the melting of α PP, can be

observed about 167°C. The inset of Figure 2 shows a comparison of the melting peak temperatures for PP and its blends. The values of the melting endotherm of PP in the blends are shown to be almost unchanged compared to those of the pure PP. No melting peak was detected at a lower temperature, which would prove the existence of the β -pseudo-hexagonal modification of iPP in the blends. A wide melting peak can be observed, however, at a much lower temperature, around 50°C, for the 50/50 blend, except for the E1801- and E1801-rich blends. This peak shows some kind of structural organization of the E1801 block copolymer, most probably an imperfect crystallization of the polyethylene (PE) blocks.

Although no β -pseudo-hexagonal modification could be detected with either WAXD or DSC, the blends show very interesting behavior during the second melting run after being crystallized at a 10°C/min cooling rate. The thermograms of the blends containing between 10 and 50 wt % elastomer show a distinct melting peak at a lower temperature (Fig. 3; for clarity, not all the compositions are shown). The temperature of this peak corresponds exactly to the melting temperature of β PP (~148°C).¹² Above a 50 wt % elastomer content, the formation of β PP was no longer detected. The amount of β PP was found to decrease with increasing of the fraction of the elastomer. This result shows that the addition of E1801 to PP can induce the formation of the β crystalline form but only in the above-mentioned composition range. It has been found that the β -pseudo-hexagonal can be formed by using special nucleating agents or a temperature-gradient crystallization method.¹³ The elastomer E1801 seems to act as a nucleating agent to achieve the formation of the β crystalline form under a slow cooling rate. However, no unambiguous explanation has been found for this phenomenon up to now. Further investigations will be carried out in our lab to give enough information to explain the observed β nucleation effect of the elastomer by employing several elastomers different in chemical structure.

Melting temperatures of crystalline polymers can be related to the size and perfection of their crystal units. Figure 4 shows only slight changes in the melting peak temperature of the components in the melting process after being crystallized at a 10°C/min cooling rate. The melting peak temperature of the α PP decreases only slightly up to 70 wt % elastomer content, which indicates a small decrease in the lamellar thickness. SAXS measurements showed a similarly slight increase of the long period. From the above results, we conclude that the blending of E1801 into PP results in a slight decrease of the size and perfection of the PP crystals and in an increase of the amorphous regions between the lamellae, that is, the presence of the elastomer somewhat hinders PP crystallization. The ob-

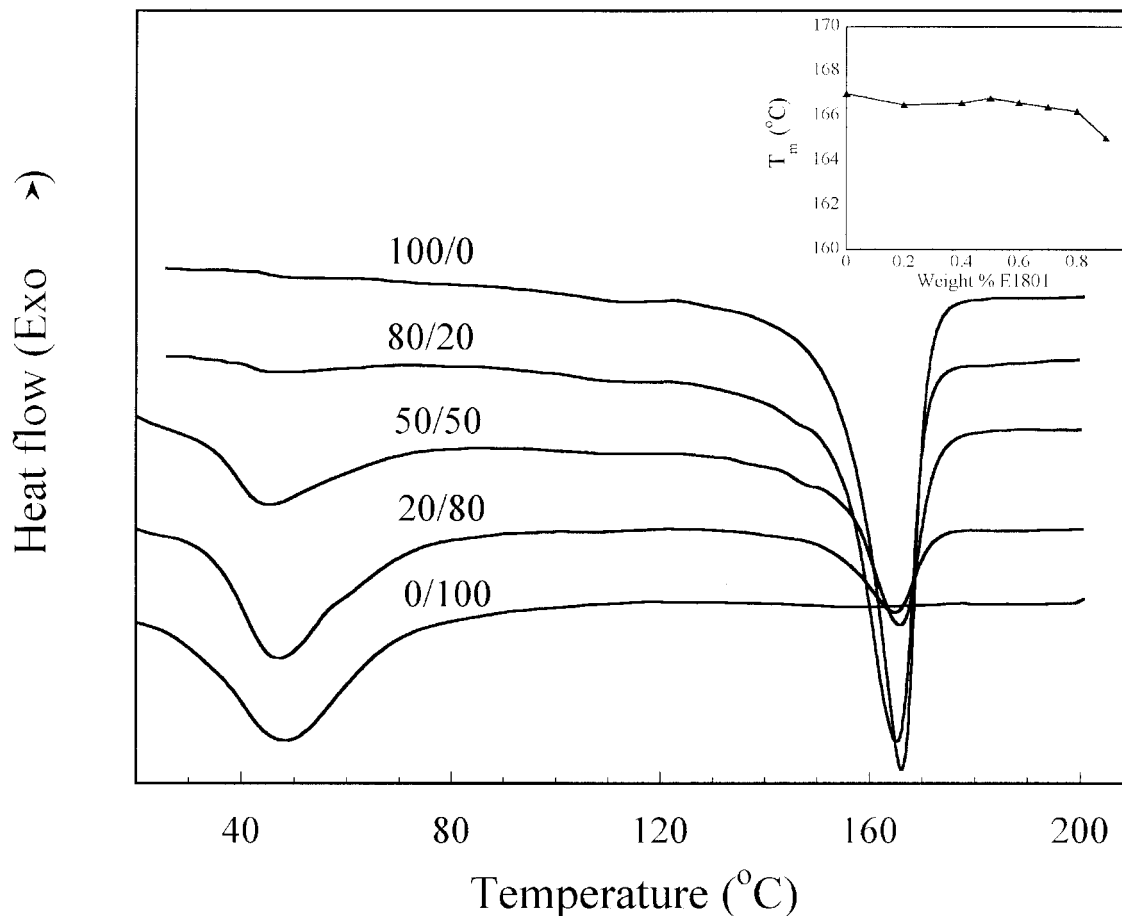


Figure 2 Melting endotherms of PP, E1801, and PP/E1801 blends; inset: melting peak temperature variation with blend composition.

served small nucleation effect of E1801 will influence similarly the size and perfection of the PP crystals.

A similar effect of the blending was observed in the crystallization experiments. The DSC crystallization

exotherms of the PP/E1801 blends are shown in Figure 5. For the PP and 80/20 PP/E1801 blends, a single crystallization peak is observed at about 120°C. However, for 50/50, 30/70, and 20/80 PP/E1801 blends, a

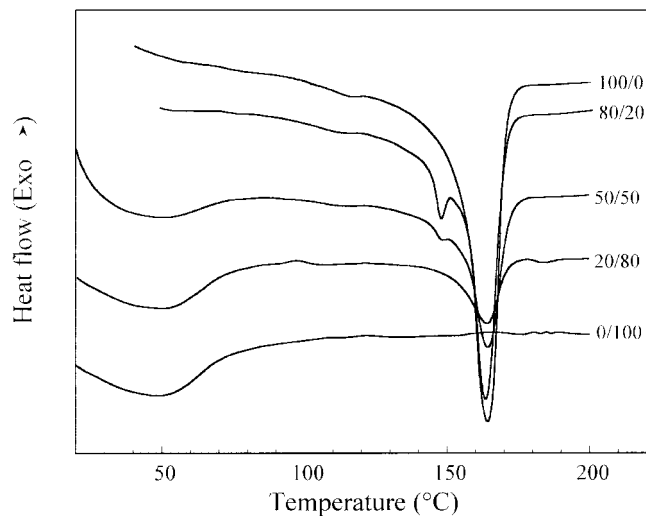


Figure 3 Melting endotherms of PP/E1801 blends crystallized at a 10°C/min cooling rate.

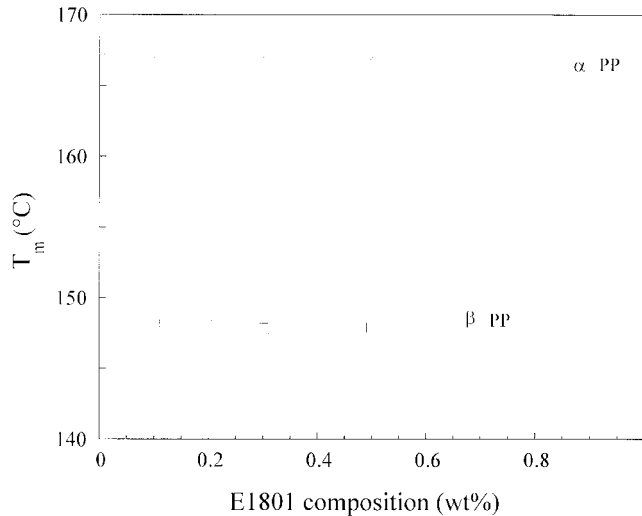


Figure 4 Melting peak temperatures of PP/E1801 blends crystallized at a 10°C/min cooling rate.

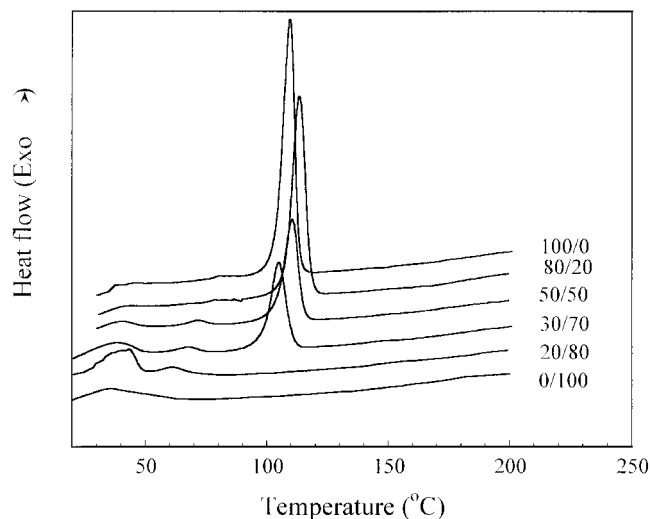


Figure 5 Crystallization exotherms of PP/E1801 blends.

new peak appeared at about 75°C. This multiple crystallization behavior is attributed mainly to the different nucleation process. Also, it is similar to the results of classical droplet crystallization in which crystallization is inhibited until the heterogeneous nucleation occurs.¹⁴ Therefore, the crystallization exotherm of PP about 75°C is attributed to the crystallization by homogeneous nucleation rather than by heterogeneous nucleation, which causes the crystallization exotherm of PP about 120°C. Polymer blends containing a semi-crystalline polymer that shows multiple crystallization behavior have been widely reported.^{15–19} Ghijssels et al.¹⁵ reported that increasing the elastomer content in PP/styrene-butadiene thermoplastic elastomer blends causes the morphology changes and results in a change of the crystallization process. At a certain elastomer content, the elastomer forms the continuous phase, and in the dispersed PP droplets, only homogeneous nucleation takes place instead of the earlier heterogeneous nucleation when PP forms a continuous phase. A similar decrease of the heterogeneous nucleation was also observed by Chun et al.¹⁹ for PP/PC blends in which homogeneous nucleation of PP in PC-rich compositions becomes more dominant than the heterogeneous nucleation when PP makes up the dispersed droplets. From the studies shown above, the multiple crystallization behavior originated in the primary nucleation of the dispersed phase by different nucleation steps.

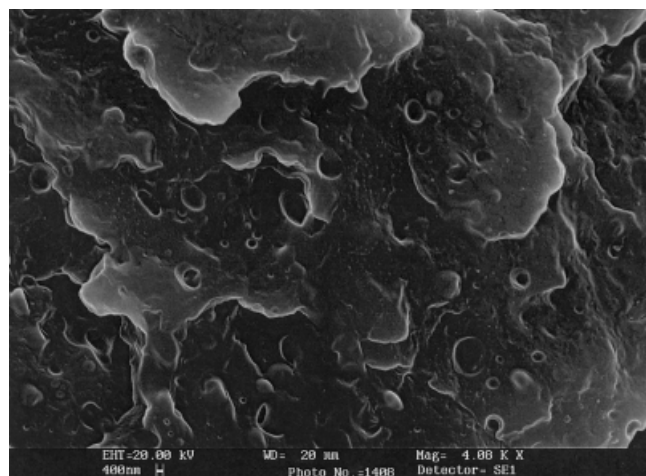
In Figure 5, for E1801-rich blends, the peak area of the crystallization exotherm about 75°C increases as the E1801 content increases, whereas the peak area of the crystallization exotherm at 120°C decreases. This result indicates that homogeneous nucleation of PP in the E1801-rich compositions becomes more dominant than the heterogeneous nucleation when the PP is the dispersed phase in the blend. Above 70 wt % elas-

tomer content, the crystallization of PP at higher temperature was not observed when PP becomes completely dispersed in the E1801 continuous phase and homogeneous nucleation controls totally the PP crystallization process. More details about the morphology variation with the blend composition will be revealed in the next section.

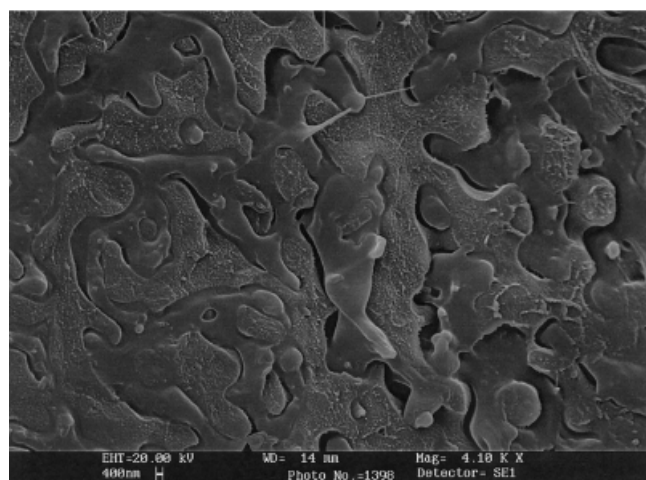
There is practically no change in the crystallization behavior of the E1801. At lower E1801 content, the PP crystallization peak temperature increases slightly (Fig. 5), showing a small nucleation effect of the elastomer. Increased nucleation usually results in decreased spherulite sizes.⁸

Morphology observation

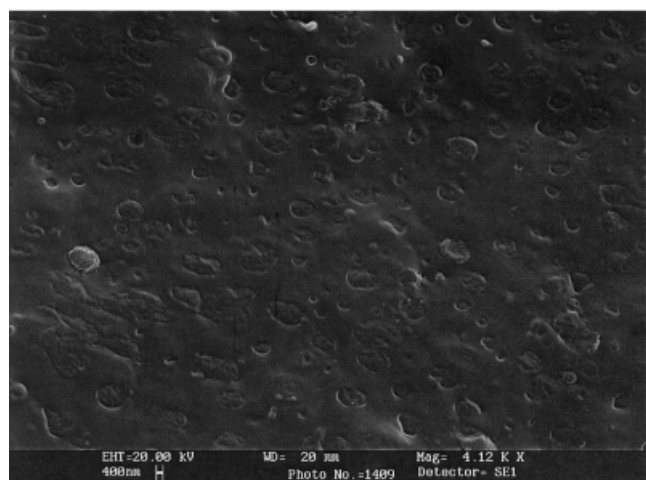
The cross-sectional surface of PP/E1801 blends was studied using SEM. At room temperature, PP and E1801 are immiscible, so blending of the two polymers will result in a dispersed two-phase structure. Micrographs of 0.2, 0.5, and 0.8 weight fractions of E1801 in the PP/E1801 blends are shown in Figure 6(a–c), respectively. The phase separation between the PP-rich phase and the E1801-rich phase is clearly observed. At low E1801 content, which is generally used to improve the low-temperature impact strength of PP, the elastomer forms droplets dispersed in the PP. The two phases show good adhesion due to a strong interaction of the amorphous phase in E1801 and that in PP as reported in other PP/elastomer blends.⁸ The size of the dispersed particles depends on the relative PP/elastomer viscosity and on the conditions of the mixing. At large E1801 content (= 80 wt %), as can be expected, the elastomer is the matrix and PP droplets are dispersed in it [Fig. 6(c)]. It appears that phase inversion takes place at an intermediate blend ratio. Figure 6(b) shows the blend morphology at an intermediate composition range: Both components formed continuous phases. In this micrograph, both PP and E1801 seem to form continuous phases. However, closer scrutiny reveals that the structure of this blend is not perfectly regular, but contains regions with different compositions and different continuous phases. In some areas, E1801 is the continuous phase in which PP droplets are occluded, while there are regions where PP is the continuous matrix containing E1801 islands. This kind of transitional morphology was also observed in polystyrene (PS) and poly(methyl methacrylate) (PMMA) blends.²⁰ In this composition range, composition alone does not define the structure, and the size, shape, and distribution of these regions also depend on the relative viscosity of the components and on the blending conditions. A regular dual-continuity structure is a rarely attainable final form of this morphology.²¹ Although the composition limits of this transitional morphology are hard to define precisely, in our study, the completely dispersed structures were



(a)



(b)



(c)

Figure 6 SEM micrographs of PP/E1801 blends with different compositions: (a) 80/20; (b) 50/50; (c) 20/80.

detected below a 0.20 and above a 0.80 weight fraction E1801 content. In the former case, a continuous PP phase was observed, while in the latter, a continuous

E1801 phase was achieved. The definite limits of transitions from one structure to the other cannot be determined; however, we must note the fact that the special melting and crystallization behavior of PP was also observed in these composition ranges. A maximum in the amount and melting peak temperature of β PP was observed at 20 wt % E1801 content. At 50 wt %, evidence of the coexistence of continuous and dispersed PP phases is provided by the appearance of two PP crystallization peaks in Figure 5. Above 70 wt % E1801 content, the main PP crystallization peak disappeared and only the homogeneous nucleation crystallization peak remains, which has been already related to a completely dispersed PP phase.¹⁵ From these observations, the conclusion can be drawn that the compositions where the transitions take place are really at about a 0.20 and a 0.7 weight fraction E1801 content and that dispersed morphology results in special crystallization and melting phenomena for the PP/E1801 blends used in this study.

It is well known that rheological properties of viscoelastic polymer blends reflect their morphology.²² The following rheological study will show the reflection of the above-observed morphology on the steady and dynamic shear properties for the PP/E1801 blends.

Rheological properties

Rheological properties of multiphase systems are strongly influenced by the morphology, which depends on several parameters such as the composition of the blend, shear rate, and elongational strain rate during mixing, viscosity and elasticity of both phases, interfacial tension, and time of mixing.²³ Rheological properties are therefore essential in order to relate the morphology of the phase-separated state to the processing of multiphase systems. Figure 7 illustrates the steady shear viscosity variation with the shear rate for the PP/E1801 blends with different proportions. As seen and as expected for the whole range of the explored shear rate, the pure components and their blends exhibit a decrease in the viscosity value with an increasing shear rate, that is, PP, E1801, and PP/E1801 blends are pseudoplastic melts. It is also observed that PP presents a lower viscosity than that of E1801 at low shear rates, and as the E1801 content increases, the viscosity of the blend systems tends to increase. The differences in melt viscosity could be explained by the intermolecular interaction of different molecular chains and the composition.

As the result of a greater degree of chain branching in E1801 and the polar maleic anhydride functional group grafted to the backbone of E1801, PP/E1801 blends were expected to exhibit a greater entanglement density than that of PP. In the near-zero shear viscosity (low shear rate) region, which is of special

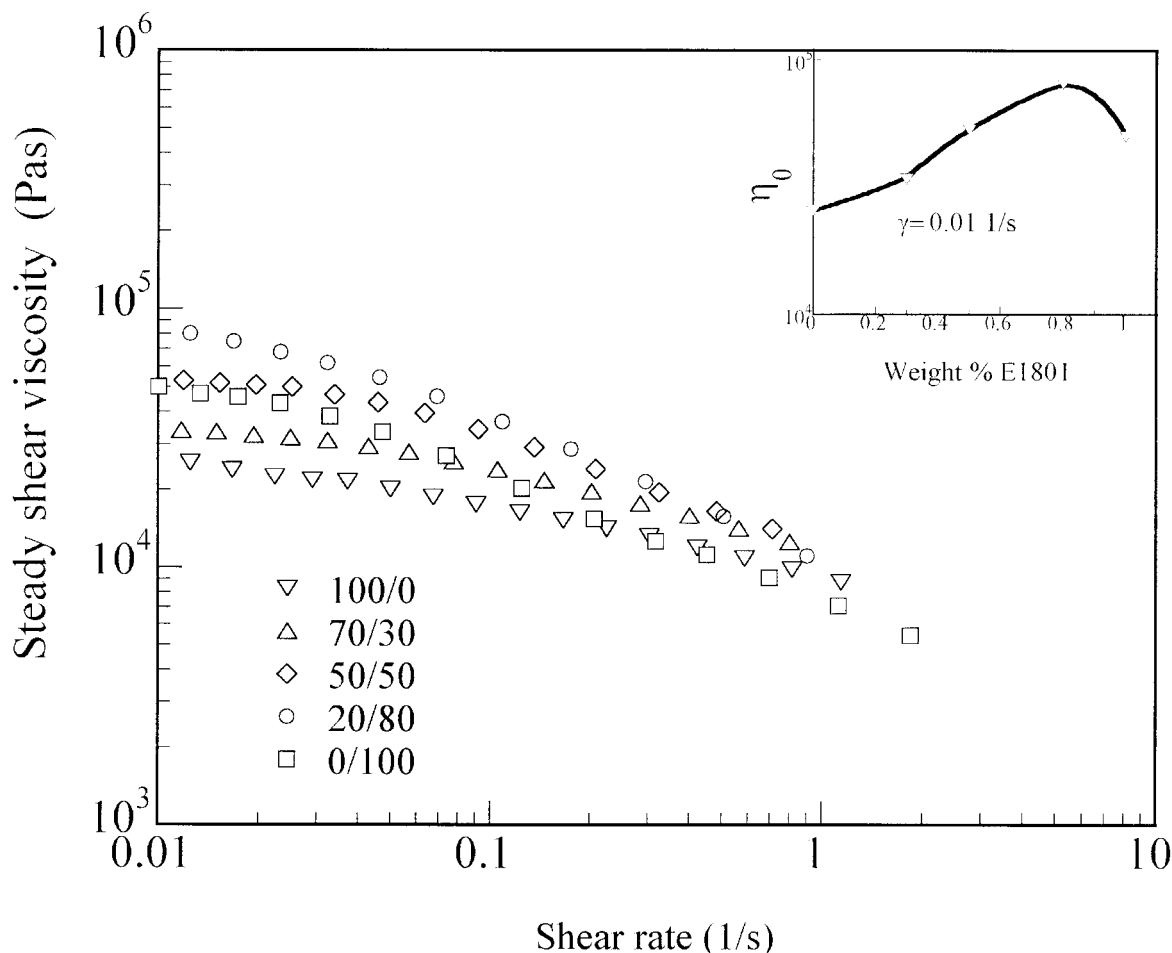
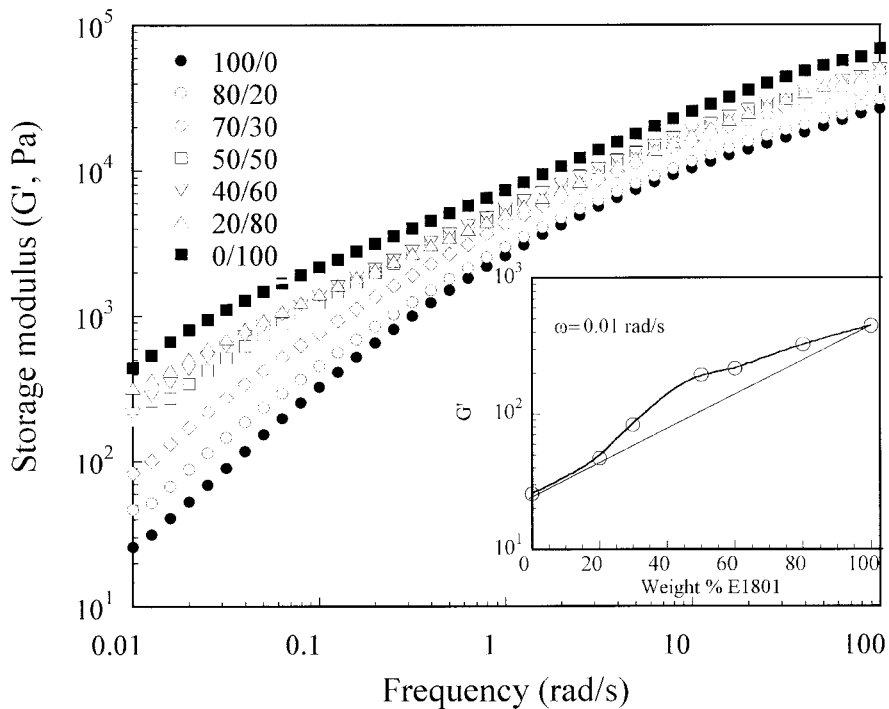


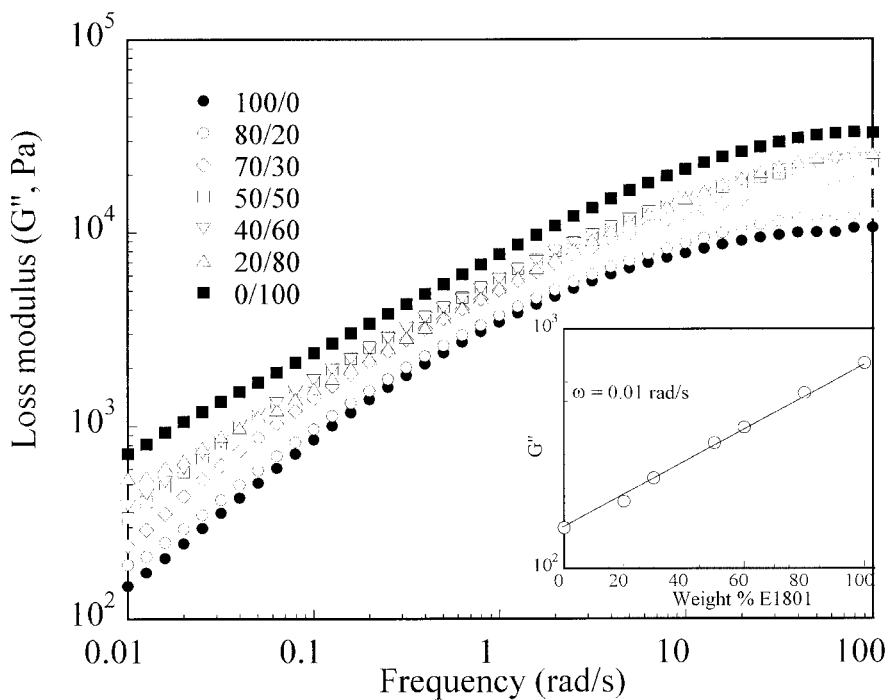
Figure 7 Steady shear viscosities of PP/E1801 blends at 200°C; inset: compositional dependence of steady shear viscosity at low shear rate range.

interest for polymer characterization and where the rheological response depends on the size of the macromolecular random coil and specific interactions among molecules, the blend viscosity increases with an increasing amount of E1801. At the low shear rate region, as shown in the inset of Figure 7, the shear viscosity of the PP/E1801 blends has larger values than those of the simple mixing rule, that is, they are positive deviation blends (PDBs). It has been found that immiscible polymer blends often show positive deviation in the blend viscosity as a function of the blend composition. However, there are also exceptions; one example was reported by Martuscelli et al. which showed negative deviation for the blends of PP and ethylene-*co*-propylene (EPR).^{5,24} Although factors governing the compositional dependence of the complex viscosity for miscible or immiscible blends are not fully understood, they appear to be characteristic features of many polymer blends.²⁵ We attribute the PDB behavior for PP/E1801 blends to the morphological effect of the phase-separated structure and the increased intermolecular interaction in them.

As well known for the polymer materials, they all behave more or less solidlike (elastic) and liquidlike (viscous) depending on the rate at which they are being deformed. This behavior is related to the fact that strained macromolecules tend to pull back to the original shape. The dynamic storage modulus, G' , is related to the elastic behavior of the materials and may be considered as the amount of the stored energy. The dynamic loss modulus, G'' , represents the amount of dissipated energy. The dependence of G' and G'' on the frequency measures the relative motion of all molecules in the bulk and can give important information about the flow behavior of melts. In Figure 8(a,b), the dependence of the storage modulus, G' , and the loss modulus, G'' , of PP/E1801 blends on the investigated frequencies are compared, respectively, with those of the pure polymers. It is observed that the storage modulus or elastic storage of the strain energy of E1801 is higher than that of PP, and at a low-frequency range (terminal zone), G' increases with an increase of the E1801 proportion in the blends. The insets of Figure 8(a,b) depict, respectively, the G' and G'' variation



(a)



(b)

Figure 8 Storage modulus (G') and loss modulus (G'') variations with frequency (ω) for PP/E1801 blends at 200°C: (a) storage modulus; inset: compositional dependence of G' at low frequency; (b) loss modulus; inset: compositional dependence of G'' at low frequency.

with the blend composition at the low-frequency regime, in which a large positive deviation from the linear addition for G' in the whole composition range is shown. In contrast to the storage modulus, G' , the loss modulus, G'' , was not affected so significantly, as

shown in the inset of Figure 8(b) in that not much deviation from the simple mixing was observed. Because G' is associated with an index of melt elasticity,²⁶ the results shown in Figure 8(a) imply that the elasticity of PP is enhanced by the addition of an elas-

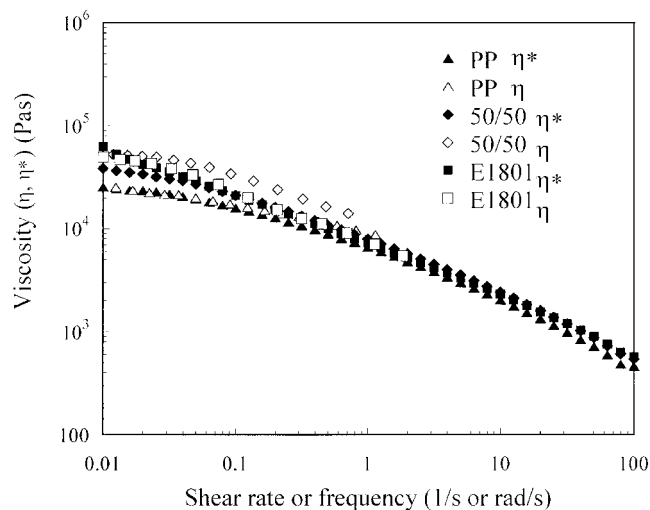


Figure 9 Comparison of complex viscosities (η^*) and steady shear viscosities (η) of PP/E1801 blends at 200°C.

tomers at low frequencies. In the terminal zone, the gradient of the G' curves also decrease as the elastomer content increases. This indicates that the relaxation time of the blend was prolonged by increasing the E1801 content. It has been reported that the “enhanced elasticity” and “prolonged relaxation time” at low frequencies for immiscible polymer blends are related to the phase-separated morphology of the blend.^{20,23,27–32} On the other hand, the loss modulus has been shown to be either insensitive or very weakly sensitive to phase separation. According to the above studies, the results shown in Figure 8(a,b) are the reflection of the two-phase structure of PP/E1801 blends as viewed in Figure 6.

The dynamic modulus of immiscible polymer blends may depend on the domain size, interfacial tension, and/or concentrations of the dispersed phase. The composition corresponding to the maximum deviation from linear additivity in the G' -composition graph [inset of Fig.8(a)] was found to lie in the composition range of dual-phase continuity as shown in Figure 6(b), which could be caused by a large increase in the interfacial tension.²³ As the frequency increases, the G' values become close to each other and all approach a plateau at high frequency. The reason for this is that in this region, that is, in the longer time scale, the response becomes dependent upon the local structure and the local structure of PP and its blends are similar, except for the few branch points.

The Cox–Merz rule predicts that the magnitude of complex viscosity (η^*) should be comparable with that of the steady shear viscosity (η) at equal value of frequency (ω) and shear rate (γ).²⁵ Figure 9 gives a comparison among the η^* and η of PP, the 50 wt % E1801 blend, and E1801 at 200°C. PP and E1801 appear to obey the rule, whereas the blends clearly show a deviation (for a clear comparison, not all blends are

shown). The empirical Cox–Merz rule has been shown to be applicable for flexible polymers, but it seems to be invalid for materials with ordered structures such as liquid crystalline materials and suspensions.^{33,34} It has been reported that the rule may not hold when morphological influences have to be considered.^{20,35} The domain deformation of the immiscible PP/E1801 blends under oscillatory and steady shear is extremely different. In oscillatory shear, the small strain amplitude does not substantially alter the droplet shape of the dispersed phase and yields a linear viscoelastic response, whereas the steady shear produces much larger strain amplitude. Owing to the fact that the morphological state of a two-phase PP/E1801 blend depends strongly on the intensity of the deformation applied, its response to dynamic and steady shear will not overlap. There is no reason one should expect that the rheological properties measured from steady shear will coincide with those measured from dynamic oscillatory shear. This leads us to understand what is shown in Figure 9: that the Cox–Merz rule does not hold for the PP/E1801 blends. This is also a reflection of the two-phase heterogeneous structure for PP/E1801 blends on the rheological properties. Li et al.³⁵ characterized the rheological properties of different PP blends. In spite of both matrix materials obeying the rule, their immiscible blends failed clearly, which was attributed to gross phase separation. The influence of the morphological factor has also been confirmed by other studies of two-phase polymer blends for which the Cox–Merz rule was not obeyed.²⁰

CONCLUSIONS

Blends of iPP and an elastomer, Exxelor VA 1801, were prepared by melt blending and their thermal, morphological, and rheological properties were investigated. The combined WAXD, SAXS, and DSC results showed that there were only slight changes in the crystalline structure of PP in the blends quickly cooled from the melt. Under a lower crystallization process, the elastomer promoted the formation of β -pseudohexagonal modification in the PP-rich blends. In the E1801-rich blends, the crystallization process of PP slowed down and double crystallization peaks were observed; one is the typical crystallization exotherm (heterogeneous nucleation) and the other is the new crystallization exotherm (homogeneous nucleation). Above 70 wt % elastomer content, PP crystallization is controlled totally by homogeneous nucleation when PP becomes the completely dispersed phase.

In the two-phase dispersed morphology of the blends, the minor component formed the discrete phase and the major component formed the continuous phase. In the intermediate composition range, a dual-continuity morphology was observed and each continuous phase was found to contain some amount

of the other component dispersed in it, which resulted in the double crystallization exotherm for PP.

The rheological study showed that PP/E1801 blends were pseudoplastic and positive deviation blends. At low frequency as the E1801 content increased, the PP/E1801 blends showed enhanced elasticity and a prolonged relaxation time which were caused by the two-phase separation structure. The most significant enhancement composition lies in the composition range of dual-continuity for which the increased interfacial tension at this composition range may be the reason. The applicability of the classical Cox–Merz rule on the blend system was examined. Both PP and E1801 were found to follow the rule. By contrast, the rule does not hold for PP/E1801 blends also due to the morphological features.

One of the authors (Y. D.) would like to express his appreciation to the Italian Ministry of Foreign Affairs for the Government Fellowship for the academic year of 1999–2000.

References

1. Utracki, L. A. *Commercial Polymer Blends*; Chapman & Hall: London, 1998.
2. Paul D. R.; Newman S. *Polymer Blends*; Academic: New York, 1978.
3. *Thermoplastic Elastomers: A Comprehensive Review*; Legge, N. R.; Holden, G.; Schroeder, H. E., Eds.; Hanser: New York, 1987.
4. Da Silva, A. L.; Rocha, M.; Coutinho, F. M.; Bretas R. *J Appl Polym Sci* 2000, 75, 692.
5. D'Orazio, L.; Mancarella, C.; Martuscelli, E.; Cecchin, G.; Corrieri, R. *Polymer* 1999, 40, 2745.
6. Wal, A.; Nijhof, R.; Gaymans, R. J. *Polymer* 1999, 40, 6031.
7. Ramirez-Vargas, E.; Navarro-Rodriguez, D.; Medellin-Rodriguez, F. J.; Huerta-Martinez, B. M.; Lin, J. S. *Polym Eng Sci* 2000, 40, 2241.
8. Pukanszky, B.; Tüdös, F.; Kallo, A.; Bodor, G. *Polymer* 1989, 30, 1399.
9. Busse, K.; Kressler, J.; Maier, R.; Scherble, J. *Macromolecules* 2000, 33, 8775.
10. Angeloz, C.; Fulchiron, R.; Douillard, A.; Chabert, B. *Macromolecules* 2000, 33, 4138.
11. Bond, E. B.; Spruiell, J. E.; Lin, J. S. *J Polym Sci Part B Polym Phys* 1999, 37, 3050.
12. Varga, J.; Garzo, G.; Ille, A. *Angew Makromol Chem* 1986, 142, 171.
13. Meille, S.; Ferro, D.; Brucker, S.; Lovinger, A.; Paden, F. *Macromolecules* 1994, 27, 261.
14. Wundelich, B. *Macromolecular Physics*; Academic: New York, 1976; Vol. 2.
15. Ghijssels, A.; Groesbeek, N.; Yip, C. W. *Polymer* 1982, 23, 1913.
16. Aref-Azar, A.; Hay, J. N.; Marsden, B. J.; Walker, N. *J Polym Sci Part B Polym Phys* 1980, 18, 637.
17. O'Malley, J. J.; Crystal, R. G.; Erhardt, P. F. *Block Copolymer*; Plenum: New York, 1970.
18. Frensch, H.; Jungnickel, B. *J. Collid Polym Sci* 1989, 267, 16.
19. Chun, Y. S.; Jung, H. C.; Han, M. S.; Kim, W. N. *Polym Eng Sci* 1999, 39, 2304.
20. Han, J. H.; Chin, C. F.; Li, D. J.; Han, C. D. *Polymer* 1995, 36, 2451.
21. Bu, W.; He, J. *J Appl Polym Sci* 1996, 62, 1445.
22. Okada, O.; Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 2699.
23. Jeon, H. S.; Nakatani, A. I.; Han, C. C. *Macromolecules* 2000, 33, 9732.
24. D'Orazio, L.; Mancarella, C.; Martuscelli, E. *Polymer* 1991, 32, 1186.
25. Hsieh, T. T.; Tiu, C.; Hsieh, K. H.; Simon, G. P. *J Appl Polym Sci* 2000, 77, 2319.
26. Utracki, L. A. *Polymer Alloys and Blends*; Hanser: New York, 1990.
27. Kapnistos, M.; Hinrichs, A.; Vlassopoulos, D.; Anastasiadis, S. H.; Stammer, A.; Wolf, B. A. *Macromolecules* 1996, 29, 7155.
28. Gramespacher, H.; Meissner, J. *J Rheol* 1992, 36, 1127.
29. Takahashi, Y.; Noda, I. In *Flow-Induced Structure in Polymers*; Nakatani, A. I., Dadmun, M. D., Eds.; American Chemical Society: Washington, DC, 1995.
30. Kitade, S.; Ichikawa, A.; Imura, N.; Takahaschi, Y. *J Rheol* 1997, 41, 1039.
31. Kernick, W. A.; Wagner, N. J. *J Rheol* 1999, 43, 521.
32. Chopra, D.; Vlassopoulos, D.; Hatzikiriakos, S. G. *J Rheol* 1998, 42, 1227.
33. Gillmor, J. R.; Colby, R. H.; Hall, E.; Ober, C. K. *J Rheol* 1994, 38, 1623.
34. Kalika, D. S.; Giles, D. V.; Denn, M. M. *J Rheol* 1990, 34, 139.
35. Li, S. C.; Jarvela, P. K.; Jarvela, P. A. *Polym Eng Sci* 1997, 37, 18.