Determination of thermorheological phase diagram of poly(propylene)/poly(ethylene-\textit{b}-ethylene oxide) blends

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Abstract: The phase diagram of the polypropylene (PP)/poly(ethylene-\textit{b}-ethylene oxide) (P(E-\textit{b}-EO) blends exhibiting upper critical solution temperature (UCST) was experimentally established by using small amplitude oscillatory shear rheology, in which the binodal line was obtained by dynamic temperature ramps and the spinodal temperatures were quantitatively estimated on the basis of the theory developed by Ajji et al. The measurements were carried out in the linear viscoelastic regime in which the material functions are sensitive to phase separation.

Introduction

Polymer blending is an alternative approach to obtain new materials with desirable properties based on commercially available polymers rather than to design and synthesize completely new polymers. Since the rapid growth of commercial polymer blends in the 1980s, the research activity in polymer blends is intensive. According to thermodynamics, polymer blends can be subdivided into immiscible, partially miscible, and miscible blends. Siamese twins could be used as a metaphor for emphasizing the close relationship between the terms “immiscible or partially miscible polymer blends” and “phase separation”. As a result of this close relationship, phase separation behaviors of polymer blends have long attracted the interests of both scientific and industrial communities and polymer blends exhibiting Upper Critical Solution Temperature (UCST) and Lower Critical Solution Temperature (LCST) have been given considerable effort in recent years [1].

The physical origin of phase separation is generally regarded as enhanced elasticity which is believed to be responsible for both the broadening and the failure of time temperature superposition (tTS) principle in polymer blends [2-11]. Although the tTS principle can be used to effectively distinguish the homogeneous region from the phase separated region, they cannot quantitatively determine the critical phase separation temperature. Therefore, it is necessary to develop a new method for
determining the demixing temperature of polymer blends. By using the mean field theory initially worked out by Fredrickson and Larson for block copolymers [12] and later extended to polymer blends by Aiji and Choplin [13] it was revealed that enhanced elasticity in the pretransitional regime affect the linear, as well as the nonlinear, and viscoelastic properties ($G'$ and $G''$) of the blends [14-16]. About the origin of elasticity in the vicinity of phase separation, there are still different interpretations. Kapnistos [15] ascribed the enhanced elasticity to concentration fluctuations as a result of the coupling between thermodynamics and chain mobility forces. Bousmina [17] argued that the interface formed during phase separation introduces a supplementary elasticity into the system due to deformation and shape recovery of the domains on the macroscopic level and confirmed that the interfacial tension is the first cause for the increase of elasticity. Niu et al.[18] argued that the rheological measurement is sensitive to polymer chain reptation, diffusion, and interfacial tension, and thus it is particularly great for detecting concentration fluctuations in the early stages of phase separation. However, rheological measurements in order to be used for determining the phase separation temperatures should fulfill a basic requirement. That is, it should be proven that dynamic measurements do not interfere with thermodynamics and kinetics of phase separation. Many experimental investigations basically agree that small amplitude oscillatory shear (SAOS) does not interfere with the thermodynamics and kinetics of phase separation [19-21] and thus can be used to qualitatively infer the critical phase separation temperature of polymer blends.

In light of the facts mentioned above, extensive rheological studies, both experimentally and theoretically, have been carried out in the last two decades for determining the critical phase separation temperatures of various polymer blends [8,14-18, 22-27]. In these studies, it has been revealed that critical phase separation temperatures obtained with SAOS rheology using dynamic temperature ramp experiments show good accordance with the phase diagram established by turbidity and dynamic light scattering measurements. Therefore, rheological measurements can provide an unambiguous determination of critical phase separation temperature as long as the two components of the blends have different viscoelastic properties.

The ultimate aim of this study is the generation of a mechanically stable three-layer coextruded film consisting of polypropylene (PP) / polyamide (PA) / polypropylene (PP) without a conventional tie-layer. In order to eliminate tie-layers which are used for improved adhesion between two different polymers, a different strategy will be followed: Blending a small amount of a commercially available amphiphilic diblock copolymer poly(ethylene-block-ethylene oxide) (P(E-b-EO)) (up to 5 wt.-%) with PP and bringing it into contact with PA by a coextrusion process. In our preliminary study [28], we showed surface selective enrichment of the block copolymer on the PP film through diffusion and flow processes pointing out that this approach might be useful when performing coextrusion experiments.

Although the extrusion temperature of the PP used is relatively low being 160 °C, processing temperature for coextrusion has to be adjusted to much higher values (>200 °C) because of the high melting point of the PA to be used. This high discrepancy in processing temperatures led to the question if the PP/P(E-b-EO) blends tend to stay phase separated at high processing temperatures as well. In order to find out this issue, rheological studies have been performed by using rotational rheometry under small oscillatory shear mode and thermorheological phase diagram of the PP/P(E-b-EO) blends has been established.
Theoretical Background

Many studies have shown that $G'$ is very sensitive to the structure evolution that occurs in the early stage of the phase separation process and that there is a sudden change in the slope of the $G' \sim T$ curve as the phase separation temperatures approached [9, 14, 15, 18, 22, 23]. Kapnistos et al. [16] argued that this sudden change can be used for determining the binodal temperatures.

In order to quantitatively assess the effects of thermodynamics on the rheological functions, Ajji et al. [13] extended the earlier theoretical treatment of Fredrickson et al. [12] for block copolymer melts near the order-disorder transition to the case of polymer blends. The critical contribution to the shear stress for near-critical polymer blends is determined by accounting for the effects of strain-induced distribution of order parameter fluctuations to the free energy of the system, through a Fokker-Planck equation. After integration over wave-vector space, the following expressions were obtained for the dynamic storage ($G'$) and loss ($G''$) moduli, respectively.

$$G' (\omega) = \frac{k_B T \omega^2}{1920 \pi} \left[ \frac{1}{3} \left\{ \frac{R_g^2}{\phi N_1} + \frac{R_g^2}{(1-\phi) N_2} \right\} \right]^{\frac{1}{2}} \left[ \frac{1}{\phi b_1^2 W_1} + \frac{1}{(1-\phi) b_2^2 W_2} \right]^{2} \left[ 2 (\chi_s - \chi) \right]^{\frac{5}{2}}$$ (1)

$$G'' (\omega) = \frac{k_B T \omega}{240 \pi} \left[ \frac{1}{3} \left\{ \frac{R_g^2}{\phi N_1} + \frac{R_g^2}{(1-\phi) N_2} \right\} \right]^{\frac{1}{2}} \left[ \frac{1}{\phi b_1^2 W_1} + \frac{1}{(1-\phi) b_2^2 W_2} \right]^{2} \left[ 2 (\chi_s - \chi) \right]^{\frac{1}{2}}$$ (2)

where $\omega$ is the frequency; $k_B$ is the Boltzmann constant; $T$ is temperature; $\phi$ is the blend composition; $N$ is the number of statistical segments; $b$ is the statistical segment length and $W$ is its rate of reorientation; $R_g$ is the radius of gyration; $\chi$ is the Flory-Huggins interaction parameter; and $\chi_s$ designates the interaction parameter at the spinodal. Using the above expressions Equation (1) and (2), the ratio $G'(\omega)/[G''(\omega)]^2$ can be derived as

$$\frac{G'(\omega)}{[G''(\omega)]^2} = \frac{30 \pi}{k_B T} \left( \frac{b_1^2}{36 \phi} + \frac{b_2^2}{36 (1-\phi)} \right)^{\frac{3}{2}} \left[ 2 (\chi_s - \chi) \right]^{\frac{3}{2}}$$ (3)

Assuming that the interaction parameter is given by $\chi = A + B/T$, a linear dependence is, thus, predicted for $[\{G''(\omega)]^2/[T(G'(\omega)))]^{2/3}$ versus $1/T$, with the spinodal temperature, $T_s$, being determined as the intercept with the $1/T$ axis. This procedure has been successfully applied to many polymer blends [9, 14-16, 18, 20, 22, 23, 29]. Using the above information, the complete phase diagram of polymer blends can be obtained.

Results and discussion

In order to obtain binodal and spinodal demixing temperatures quantitatively, we have applied the theoretical approach of Ajji and Choplin [13] based on the mean field theory to our studied blend system. Before starting to deal with the results, two important issues which are closely related to each other have to be clarified. According to Kapnistos et al. [15], one single frequency value would suffice for all compositions. Nonetheless, we had to use a different frequency value for each composition in order to observe a change in dynamic moduli. Furthermore, the changes in dynamic moduli were moderately or abruptly depending upon the diblock copolymer content which is addressed below. The reason could be explained as
follows: Block copolymers form micelles above a critical micelle concentration (CMC) because of their amphiphilic properties. It is obvious that the properties and morphology of the micelles change abruptly depending upon the concentration. Considering this fact the block copolymer could be thought of forming vesicles instead of micelles in the PP matrix phase with increasing amount of P(E-b-EO). Besides, it should be considered in this context that frequency ($f$) and wave length ($\lambda$) are inversely proportional according to the equation 4. Probably, individual micelles are detected when worked with blends containing low amounts of the block copolymer. In this case, high frequency values are needed for detection the change in dynamic moduli since the diameter of the micelles is small. Vesicles could be formed with increasing the P(E-b-EO) content and their diameter is much larger than that of the micelles, as depicted in Fig. 1 schematically. Accordingly, lower frequency values are necessary for observing any change in dynamic moduli.

$$\nu = f \cdot \lambda$$

Another aspect related to the issue mentioned above is that a moderate or a sharp change has been observed in dynamic moduli ($G'$ and $G''$) during dynamic temperature ramp experiments as the phase separation temperature is approached for a given composition. Vlassopoulos [14] and Kapnistos et al. [15] argued that the dynamic asymmetry, i.e., the contrast in the glass transition temperatures ($T_g$) between the blend constituents is responsible for the magnitude of the observed effect. According to the literature [30-34], the difference in $T_g$ should be at least 30 °K so that a distinctive change could be observed in the dynamic moduli. There has been a high enough discrepancy observable (ca. 50 °K) in glass transition temperatures of the blend components when calculated using the equation 5. It's obvious for our blend system that observation of a moderate upturn in other compositions different from the blend containing 2 wt.% P(E-b-EO) seems to have nothing to do with the dynamic asymmetry.

$$T_g = \frac{2}{3} T_m(K)$$

Fig .1. Distribution of micelles in the PP matrix phase a. Individual micelles, b. Vesicles.
In this paper, we only give the diagrams of the PP blend containing 2 wt.% P(E-b-EO) as example. Fig. 2 presents the stress sweep experiments of the PP/P(E-b-EO) blend (98/2 w/w). Stress sweep test delivered the following stress values which enables to study in LVE region: 160 Pa (0.5, 1, 2, 3.5, and 5 wt.% block copolymer content), 100 Pa (10 wt.% block copolymer content), and 40 Pa (20 wt.% block copolymer content).

![Stress sweep diagrams](image)

**Fig. 2.** Stress sweep diagrams of the melt-mixed PP/P(E-b-EO) blend (98/2 (w/w)) obtained with the rotational rheometry having parallel plate geometry under nitrogen atmosphere (Frequency value: 16 rad/s, processing temperature: 160 °C (left) and 280 °C (right)).

The time sweep experiments show that all blends checked at 280 °C for 30 min are thermally stable. Time sweep diagram of the PP/P(E-b-EO) blend (98/2) is depicted in Fig. 3 as an example.

![Time sweep diagram](image)

**Fig. 3.** Time sweep diagram of the melt-mixed PP/P(E-b-EO) blend (98/2 (w/w)) obtained with the rotational rheometry having parallel plate geometry under nitrogen atmosphere (Frequency value: 16 rad/s, stress value: 100 Pa, processing temperature: 280 °C).
Fig. 4 displays the change in storage modulus, $G'$, during dynamic temperature ramps for the PP/P(E-b-EO) blend (98/2 (w/w)). It is observed that in the homogeneous region above the critical temperature, $G'$ gradually increases with decreasing temperature, which is due to the slowing down of molecular motion or the increase of intermolecular friction. As temperature further decreases and the phase boundary is approached, $G'$ dramatically increases and a sharp upturn appears, which is thought to be the coupling effect of the decreased molecular chain motion and enhanced elasticity. On the basis of our experimental results, we consider that the concentration fluctuations must have the dominant role to account for the elasticity enhancement because it becomes more significant during the gradual temperature decrease. It is also evident from the diagrams (not shown here) that not only the magnitude of $G'$ upturn but also the temperature range, over which the upturn takes place, strongly depends on the composition of the blend.

According to Fig. 4, the storage modulus, $G'$, and loss modulus, $G''$, seem to have changed equally. Nonetheless, it will be noticed that this is not the case and $G'$ is more sensitive than $G''$ when considered the results of all blend compositions (not shown here).

To determine binodal temperature, temperatures at the inflexion of the related curves ($G'$ vs $T$) have been assigned as binodal temperature. Temperature of 192 °C for the 98/2 blend is marked in Fig. 4 as the guide to the eye. Binodal demixing temperatures of the other blend compositions acquired with dynamic temperature ramp tests are as follows: 214 °C for 99.5/0.5 and 99/1 blend, 196 °C for 96.5/3.5 blend, 194 °C for 95/5 blend, 200 °C for 90/10 blend, and 176 °C for 80/20 blend.

After plotting $\left(\frac{[G''(\omega)]^2}{(G'(\omega)T)}\right)^{1/3}$ vs $1/T$, spinodal demixing temperatures were determined to be 212 °C (99.5/0.5), 214 °C (99/1), 190 °C (98/2), 196 °C (96.5/3.5), 200 °C (95/5), 210 °C (94/6), 215 °C (93/7), 220 °C (92/8), 225 °C (91/9), 230 °C (90/10), 235 °C (89/11), 240 °C (88/12), 245 °C (87/13), and 250 °C (86/14).
192 °C (95/5), 186 °C (90/10), and 176 °C (80/20). Binodal and spinodal temperatures obtained with dynamic temperature ramp experiments were plotted against the block copolymer content and the thermorheological phase diagram was established, as depicted in Fig. 5. According to the diagram, PP/P(E-b-EO) blends show a UCST behavior.

Fig. 5. Determination of the spinodal demixing temperature of the melt-mixed PP/P(E-b-EO) blend (98/2 (w/w)).

Conclusions
In order to assure that the PP/P(E-b-EO) blend is phase separated under the temperature conditions of coextrusion (T > 200 °C), the thermorheological phase diagram of the PP/P(E-b-EO) blends has been established by small oscillatory shear
rheology measurements, concerning a UCST behavior exhibiting system. This diagram shows, however, only the situation under steady-state conditions. Because of the shear stresses during extrusion, it is assumed that phase diagram curve would shift to elevated temperatures. This means that the blends will be phase separated during coextrusion process.

It has been shown for the first time that small oscillatory shear rheology can also be used for determining the critical phase separation temperatures of a high molecular weight polymer containing a low molecular weight diblock copolymer. With the help of this work, the relationship between the theories developed by Frederickson and Larson [12] for block copolymers and by Ajji and Choplin [13] for polymer blends has also been achieved.

**Experimental part**

**Materials**

A random copolymer of polypropylene with 7.5 mole-% ethylene (RB501BF) from Borealis was used as the blend component. P(E-b-EO) with a molecular weight of 2250 g/mol from Aldrich Chemicals Co. was used as diblock copolymer. Molar ratio of EO/E is 2.45 (supplier data).

**Blend Preparation**

According to our concept, diblock copolymer should be pre-blended with the polyolefin used. Otherwise, it would be impractical and expensive on a processing scale to extrude diblock copolymer as a tie layer, especially when more than a few layers are to be produced. Therefore, blends of PP containing different diblock copolymer contents (0.5, 1, 2, 3.5, 5, 10, 20 wt.% P(E-b-EO)) were pre-blended in a co-rotating intermeshing twin screw extruder (Coperion Werner & Pfleiderer ZSK 30, screw diameter D = 30 mm, screw length-to-diameter ratio L/D = 40) at 160 °C and pelletized. The extrusion process was carried out with a screw rotation speed of 100 rpm and a throughput of 4 kg/h.

**Thermogravimetric analysis (TGA)**

Decomposition temperatures of the PP/P(E-b-EO) blends were determined by employing a Perkin Elmer Pyris TGA 7 instrument. Approximately 5 mg sample was weighed onto platin crucible and heated from 50 to 550 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

**Rheological measurements**

In principle, measurement occurs by applying a controlled strain or strain rate to the sample and the resulting stress is calculated from the torque or force. A defined stress can also be applied and the resulting strain rate is measured as in the case of the Dynamic Stress Rheometer (DSR). In this study, a DSR from Rheometrics using parallel plate geometry was employed to perform the rheological tests. In this configuration the polymer sample is placed between two parallel circular discs of radius R, one of which rotates with a given angular velocity, the other one being stationary. The gap h between the discs is adjustable. The sample is tested in a closed chamber under nitrogen atmosphere to avoid undesired reactions such as oxidation during measurements.
Samples for the rotational rheometry were prepared from the blends. The pellets of the PP/P(E-b-EO) blends generated previously in the extruder were pressed into discs using a hydraulic press and a special mould. The discs had a diameter of 25 mm and a thickness of 2.5 mm. The samples were moulded at a temperature of 200 °C during 2.5 min without pressure and 2.5 min under 50 bar. Finally, they were cooled under pressure during 10 min.

Temperature range was chosen by considering the melting and decomposition temperatures of the blends (Table 1). Working temperature on the rotational rheometer changes from 280 °C to 160 °C depending upon the blend composition used. Before the experimental running, the blends were kept at 280 °C for 10 min to eliminate thermal history.

Different test modes are available among which time sweep, stress sweep, and dynamic temperature ramp were applied in this work.

(i) To determine the linear viscoelastic (LVE) region of a molten polymer, a stress sweep measurement was performed while temperature and frequency are kept constant. The moduli are registered as functions of the stress. From a critical stress, $\tau_C$, polymer blend start to show nonlinear behavior and the moduli ($G'$ and $G''$) decline. Stress sweep experiments were carried out at start and end temperatures (e.g. 280 °C and 160 °C for the blend containing 2 wt.% P(E-b-EO)) by using stress values between 0.1 and 5000 Pa and frequency values ranging from 0.1 to 22 rad/s. In principle, the stress value which does not lead to any change in dynamic moduli can be used for further measurements. The stress value was chosen which was obtained during working with start temperature.

(ii) Time sweep experiments were conducted for evaluating chemical, thermal or mechanical stability of the blends by measuring the moduli or viscosity at a constant frequency, stress and temperature over an extended period of time (30 min).

(iii) To determine the binodal phase separation temperature and quantitatively obtain the spinodal temperature of the PP/P(E-b-EO) blends, dynamic temperature ramp tests were carried out at a fixed low frequency and a given stress. The experimental temperature was decreased from 280 to 160 °C with a decrement of 1 °C covering the homogeneous region to the phase-separated region, respectively.

Tab. 1. Decomposition temperatures of the PP/P(E-b-EO) blends prepared by melt-mixing.

<table>
<thead>
<tr>
<th>Polymer blend</th>
<th>Decomposition temperature [ºC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/P(E-b-EO) (99.5/0.5 (w/w))</td>
<td>313</td>
</tr>
<tr>
<td>PP/P(E-b-EO) (99/1 (w/w))</td>
<td>310</td>
</tr>
<tr>
<td>PP/P(E-b-EO) (98/2 (w/w))</td>
<td>305</td>
</tr>
<tr>
<td>PP/P(E-b-EO) (96.5/3.5 (w/w))</td>
<td>295</td>
</tr>
<tr>
<td>PP/P(E-b-EO) (95/5 (w/w))</td>
<td>291</td>
</tr>
<tr>
<td>PP/P(E-b-EO) (90/10 (w/w))</td>
<td>273</td>
</tr>
<tr>
<td>PP/P(E-b-EO) (80/20 (w/w))</td>
<td>261</td>
</tr>
</tbody>
</table>

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References

[33] Colby, R.H. Polymer 1989, 30/7, 1275.