Phase Morphology and its Role on Tensile Properties in Ternary Blends of PP/PC/SEBS

Hadis Goodarzi, Omid Moini Jazani, Mohammad Reza Saeb

1Department of polymer Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
2School of Chemical Engineering, University of Isfahan, Isfahan, Iran
3Department of Resin and Additives, Institute for Color Science and Technology, Tehran, Iran

Email: O-moini@yahoo.com, Saeb-mr@icrc.ac.ir

Received 2012

ABSTRACT

This work deals with phase morphology in ternary blends of polypropylene (PP)/ polycarbonate (PC)/ poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) based on PP continuous phase and also its consequence on tensile properties. Firstly, two types of conceptual models have been employed to foresee the type of morphology based on interfacial tension of polymer pairs. Scanning electron microscopy has been used to witness the predicted morphology; however, the relative interfacial energy model was the only theoretical relation which agreed with observed morphology in PP/PC/SEBS ternary blends. The composition of mentioned blends varied and the tensile properties were measured. It has been found that the blend composition has significant influence on the size of microstructures followed by its consequence on tensile characteristics.

Keywords: Ternary Blends; Morphology Prediction; Polypropylene; Polycarbonate; SEBS

1. Introduction

There have been tremendous demands for polymer blends since three decades ago because polymer blends can be considered as potent multicomponent systems which can represent enhanced qualities while keeping the producing price sufficiently low. In other words, producing new polymers undergoes a lot of efforts and costs, whereas mixing molten polymers would be easier and might have more flexibility regarding desired characteristics.

The hottest point regarding blending polymers is the prediction of the ultimate properties which highly depends on the morphology of multicomponent systems. This issue is more important while preparing ternary blends due to variety of phase morphologies in these systems. To predict the type of morphology, many works have been already performed based on thermodynamic of polymer blends [1-3]. However, there have been limited conceptual models to be considered for this task. Interfacial tension is a good measure of affinity of polymers together. All the predictive models in ternary polymer blends are based on interfacial contribution; on the way in which, a semi-quantitative tool can roughly pursue the morphology evolution. Generally, it has been observed that for the blend systems containing two minor phases, three distinct types of phase morphology have to be specified [4]. For some ternary systems, one of the minor components forms an encapsulating layer around domains of another minor component, whereas in other systems two minor components may form independent phases separately. The third type is the intermediate case, where mixed phases of the two components are formed without any ordered structures. In order to predict the tendency of one minor phase to encapsulate the second one, the alternative form of Harkin’s equation can be used as follows:

\[ \lambda_{AC} = \gamma_{AC} - \gamma_{AB} - \gamma_{BC} \]  

where \( \gamma_{AC} \), \( \gamma_{AB} \), and \( \gamma_{BC} \) are the interfacial tensions of each polymer pairs, respectively and \( \lambda_{BC} \) is defined as the spreading coefficient for the shell forming component B on the core of component C. The index A corresponds to the matrix continuous phase. As a rough estimation through ternary polymer blends, whenever the \( \lambda_{BC} \) is positive, the B-phase encapsulates the C-phase. In a similar way:

\[ \lambda_{BC} = \gamma_{BC} - \gamma_{AB} - \gamma_{AC} \]  

It means that, when \( \lambda_{CB} \) is positive, the component C will also encapsulate component B. However, if both \( \lambda_{CB} \) and \( \lambda_{BC} \) are negative, components C and B will tend to form two separate dispersed phases within the matrix component A. In the intermediate region, where \( \lambda_{BC} = 0 \), stack morphology may result, in which component B partially eliminates the interface between component C and the matrix.

Besides above mentioned general model, Guo [1,2] and co-workers presented a new model to predict the morphology of ternary blends, based on free energy calculation through the multi-component system, including either surface tension or interfacial area of each component. They claimed that the most stable morphology is the one exhibiting the least free energy of all possible pairs. Guo’s Relative Interfacial Energy (RIE) equations are as below:

\[ (RIE)_{BC} = (\sum A\gamma_{AC}) B / K = (1 + x)^{0.5} \gamma_{AC} + \gamma_{BC} \]  

(3)

\[ (RIE)_{CB} = (\sum A\gamma_{BC}) C / K = [x^{0.5} \gamma_{BC} + (1 + x)^{0.5} \gamma_{AC}] \]  

(4)

\[ (RIE)_{AC} = (\sum A\gamma_{AC}) A / K = x^{0.5} \gamma_{AC} + \gamma_{BC} \]  

(5)

where \( x \) is equal to \( x = V_B/V_A \). \( \gamma_{AB} \) is the interfacial tension between two phases and "K" is a constant. Both models, the spreading coefficient and the relative interfacial energy, have
been widely used by different researchers to predict the ternary blends morphology. However, there have occasionally been unexpected deviations as a result of uncertainty of conceptual models based on assumptions involved, at the same time experimental errors arising from interfacial tensions measurements, especially in case of rheological methods.

There have also been many reports in the literature on account of mechanical properties, especially works done by Lusinov and coworkers [3]. The results have shown that the size of dispersed domains as well as the type of morphology can affect the ultimate properties, sometimes significantly. Some models previously used for binary blends have been generalized for ternary systems in terms of matrix-disperse and co-continuous well defined morphologies.

This work deals with prediction of morphology is ternary blends based of polypropylene (PP), in which, polycarbonate (PC) and poly (styrene-b-ethylene-co-butylene)-b-styrene) (SEBS) are appended as minor constituents. Based on previous works done by other researchers, a maleated SEBS (SEBS-g-MAH) has been appended to the blend to enhance the ultimate properties via morphology improvement. Two different compositions are prepared to study the role of such parameter on resultant properties. Two different compositions of PP/PC/SEBS were prepared, according to supplier. The polycarbonate (PC), as the first minor constituent, contains a 50/50 weight content of SEBS and SEBS-g-MAH, namely 70/15/15 and 80/10/10 in which, the secondary phase had affinity to the PC domains.

2. Experimental

2.1. Materials

Isotactic polypropylene homo-polymer (PP), 550J supplied by Arak petrochemical company (Iran) was used as the continuous phase with melt flow index of 3 g/10min at 230°C and 2.16g, according to supplier. The polycarbonate (PC), as the first minor phase was provided from Bayer Co. (Germany) with trade name of Makronol® 2858 and melt flow index of 10 g/10min at 300°C and 1.2g. The second minor constituent, poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS), was a tri-block copolymer and supplied by Shell Chemicals under trade name of Kraton® G1652. According to the supplier, this component contains 29% styrene and has molecular weight; styrene block 7000, EB block 37500 and melt flow index of 5 g/10min at 5kg and 230°C. The maleic-anhydride grafted SEBS (SEBS-g-MAH) tri-block copolymer was used as compatibilizer which had affinity to the second minor phase. This matter under trade name of Kraton® FG1901x supplied by Shell Chemicals (29% styrene, nominal weight of grafted maleic anhydride= 1.8± 0.4%, MFI: 22 g/10min, 5kg, 230°C).

2.2. Sample Preparation and Characterization

Ternary blends were prepared using a Brabender co-rotating twin-screw extruder (D=2cm, L/D=40) at a rotation speed of 130 rpm. The temperature profile along the barrel kept unchanged as 230-235-240-245-250-255°C, respectively from hopper to die zones. Two compositions of PP/PC/SEBS were prepared, namely 70/15/15 and 80/10/10 in which, the secondary phase contains a 50/50 weight content of SEBS and SEBS-g-MAH, based on our previous works. Thus, the blends are actually quaternary systems. It should be noted that the compatibilizer (SEBS-g-MAH) has only affinity to the rubbery phase of SEBS, based on chemical structures, therefore, we used ternary blend instead of quaternary in the current work. The tensile stress-strain test was carried out using Galdabini testing machine with cross head speed of 50 mm/min according to ASTM D638. The morphology of fracture surfaces was studied by using AIS-2100 scanning electron microscope of SERON under nitrogen atmosphere. Prior to the SEM studies, the impact samples were fractured in liquid nitrogen and consequently were etched by cyclohexane for 24h to remove SEBS and SEBS-g-MAH minor phases. Then, the etched samples were gold sputtered to make the samples conductive.

3. Results and Discussions

According to Wu, the interfacial tension of polymer pairs can be calculated using surface tension of constituent polymers. The surface tension of any matter has two components, namely polar and dispersive. The details of the method and calculations have mentioned elsewhere [5]. In the current work, the surface tension of each component, γ_i, and interfacial tension coefficients, γ_{ij}, for binary pairs were calculated at 256, using polar and dispersive contributions of surface tension and harmonic mean equation, respectively. As EB is the major part of SEBS chains (about 70 % by weight), the surface tension of SEBS was roughly replaced by the one estimated using the surface tension data of EB. Table 1 represents the surface tension of each component as a function of temperature, at the same time the interfacial tensions of all possible polymer pairs calculated using method developed by Wu. The spreading coefficients, λ_{CB} and λ_{BC}, were consequently calculated using equations 1 and 2, as shown in Table 2. According to interfacial data represented in Table 1, there is an inherent tendency between PP and SEBS components, whereas the blend of PP and PC is thermodynamically the most incompatible one among all possible pairs. This suggests that PC may form as a core and SEBS encapsulates the PC domains.

According to spreading coefficient values in Table 2, both λ_{CB} and λ_{BC} are negative; hence, both minor components, PC and SEBS, form as dispersed domains in the matrix of PP. It should be, however, mentioned that the value of λ_{BC} is very small.

Table 1. Surface tension as a function of temperature and Interfacial tensions estimated using Wu equation at 255 °C.

<table>
<thead>
<tr>
<th>Polymer pair</th>
<th>Surface and Interfacial Tension Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/SEBS</td>
<td>γ_{PP} 30.5-0.056T; γ_{SEBS} 34.56-0.045T</td>
<td>1.21</td>
</tr>
<tr>
<td>PP/PC</td>
<td>γ_{PC} 44.1-0.06T; γ_{SEBS} 34.56-0.045T</td>
<td>7.03</td>
</tr>
<tr>
<td>PC/SEBS</td>
<td>γ_{SEBS} 34.56-0.045T</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2. MORphology predicted by spreading coefficient model.

<table>
<thead>
<tr>
<th>Ternary system</th>
<th>Spreading Coefficient Predictive Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spreading coefficient (mN/m)</td>
</tr>
<tr>
<td>PP/PC/SEBS</td>
<td>Continuous phase is PC</td>
</tr>
</tbody>
</table>

a. C phase is the SEBS and B phase is the PC.
close to zero corroborating incomplete encapsulation of SEBS around PC domains. Another finding is that $\lambda_{CB}$ is too much lower than the other one, corroborating tendency of formation of core-shell morphology.

Table 3 represents the relative interfacial energies for 70/15/15 PP/PC/SEBS ternary blends, calculated using equations 3-5.

According to these data, the morphology in which the C-phase (SEBS) encapsulates the B-phase (PC) has the least value of relative interfacial energy (RIE), the dominant thermodynamically case, among all possible cases. The same trend was observed for 80/10/10 ternary blends. This is in contrary to the spreading coefficient which predicted that either B or C phases remain dispersed in PP matrix; even though, calculations demonstrated a small driving force for the PC to encapsulate the SEBS distinct domains. To validate the predictability of the mentioned models, the morphology of blend was observed for both composition ranges. The morphology of 70/15/15 and 80/10/10 ternary systems are compared in Figure 1. Figure 1 demonstrates that PC particles are engulfed by the SEBS minor components in the presence of reactive SEBS-g-MAH component. It should be mentioned that using this compatibilizer results in complete encapsulation, similar to what have already been observed by other authors for PA-6/PC/SEBS ternary systems compatibilized by the same reactive constituent [6]. Thus, predictive models based on uncompatibilized ternary system can successfully estimate the phase morphology in these multicomponent systems. Another founding is that as the blend composition changed from 70/15/15 to 80/10/10; the smaller particles appeared in the matrix of PP. Hence, the particle size of PP/PC/(SEBS+SEBS-g-MAH) highly depends on the blend composition.

Table 4 contains tensile data of both mentioned compositions. Accordingly, altering the composition from 70/15/15 to 80/10/10 results in higher mechanical characteristics. Comparing the morphology and mechanical data illustrates that smaller core-shell domains in the 80/10/10 systems causes increase in mechanical properties. Also, this blend represents higher toughness compared with 70/15/15 one, studied in previous works [7]. Therefore, there is a relationship between microstructure and tensile properties in ternary blends of PP/PC/(SEBS+SEBS-g-MAH). Actually, maleated SEBS has higher affinity toward SEBS rather that PC. Nonetheless, increasing the PP matrix, at the same time decreasing minor domains in 80/10/10 system led to enhanced tensile properties. This behavior is attributed to finer morphology in the assigned composition.

4. Conclusion

Blends of PP/PC/SEBS with various compositions were prepared using twin-screw extruder in the presence of reactive compatibilizer of SEBS-g-MAH. The type of morphology was first predicted using conceptual models as spreading coefficient and relative interfacial energy. The mentioned models were theoretically in agreement with observed morphology by scanning electron microscopy. However, the spreading coefficient model proposed two dispersed model, it has been roughly found that incomplete encapsulation might occur in the ternary blends without reactive compatibilizer. Two compositions; namely 80/10/10 and 70/15/15, was chosen to investigate morphology-tensile properties relationship. It was found that finer composite droplets (PC domains encapsulated by SEBS and maleated SEBS) in 80/10/10 system result in higher tensile properties, i.e. tensile modulus, yield stress and elongation at break.

REFERENCES
