Effect of Oscillatory Shear on the Interfacial Morphology of a Reactive Bilayer Polymer System

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Introduction

Reactive blending of two or more immiscible polymers with in-situ reactive compatibilizers has been employed for developing new materials with desirable physical and mechanical properties and extensively investigated by many research groups.[1-3] In reactive blending process, mechanical force is usually applied to the materials in order to avoid coalescence and tear the large domain into the small droplet. And there have been many studies on the effect of shear force on the domain size and morphology. [4-5] Most of these research are, however, focused on the properties of whole blend system. In fact, there has been no systematic study on the effect of mechanical force on the interface itself by using model interface. In this study, we try to find the relationship between shear force and and interfacial morphology. And we also try to find the effect of this change of interfacial morphology on the interfacial reaction.

Experimental

We used blend systems consisting of mono-carboxylated polystyrene (PS-mCOOH) synthesized anionically and a poly(methyl methacrylate-*ran*-glycidylmethacrylate) (PMMA-GMA) prepared by free radical polymerization. Molecular characteristics of polymers used in this study are summarized in Table 1.

Table 1. Molecular Characteristics of Polymers employed in this study

Samples	M_w (kg/mol)	M_w/M_n	$\|\eta^*\|$ at 180 °C (Pa·s)	Functionality
PS-mCOOH	135	1.13	8×10^3	~ 1
PMMA-GMA	115.5	1.7	2.5×10^5	~ 12.5

We prepared two plates of each polymer using compression molding. One plate was made of PS-mCOOH, and another plate was consisted of PMMA-GMA. The thickness of each plate is 0.3 mm.

As soon as these two plates with 25 mm diameter are together welded inside a rheometer (Advanced Rheometrics Expansion System: Rheometrics Co.) at 180 °C under nitrogen environment, a time sweep was performed.

To investigate the morphological change of interface with time, the welded plate after reaction at a given time was first quenched into ice/water to fix morphology, then the PS-plate was removed by selective solvent of cyclohexane at 40 °C for 35 h. The interface thickness (or root-mean square roughness) was obtained by atomic force microscopy (AFM: Digital Instrument; D3000). The interface morphology and the existence of micelles formed during the reaction were investigated by transmission electron microscopy (TEM: Hitachi; 7600) on operating at 120 kV.

Results and discussion

Figure 1 gives variations of $|\eta^*|$ of (PS-mCOOH)/(PMMA-GMA) bilayer system with reaction time at 180 °C and $\omega = 0.1$ rad/s for different values of γ_0. With increasing γ_0 from 0.005 to 0.05, the slope of the plots of $|\eta^*|$ versus reaction time at stage I becomes larger. Also, the lag time for the polymer chains to diffuse across the interface at stage II becomes shortened with increasing γ_0. On the other hand, referring to Figure 2, variations of $|\eta^*|$ with reaction time for larger values of γ_0 (> 0.3) are quite different from those for low values of γ_0 (< 0.3). This observation suggests that the oscillatory shearing force with large γ_0 might hinder further chemical reactions even for a long period of reaction at stage III. Namely, with increasing shearing force, the interdiffusion of both polymer chains in the direction perpendicular to the interface might be significantly reduced.

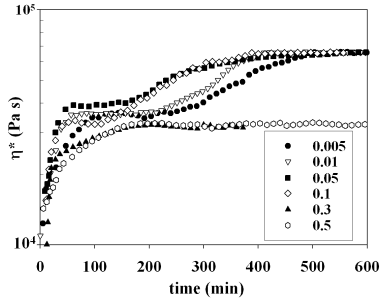

Figure 1. TEM image of a sample that was subjected to chemical reaction for a period of 100 min at 180 °C and $\omega = 100$ rad/s.

Also, we measured the variations of $|\eta^*|$ with reaction time at 180 °C for various values of ω (0.1–100 rad/s) at $\gamma_0 = 0.005$. For $\omega <$ 5 rad/s, the reaction times corresponding to the beginning of stage II and stage III decreased with increasing ω. However, variations of $|\eta^*|$ with reaction time at $\omega = 10$ and 100 rad/s are quite different from those observed at lower values of ω. Namely, at $\omega = 10$ and 100 rad/s the $|\eta^*|$ increases up to 30 min of reaction time, and then decreases approaching a constant value. This is because higher values of ω can break the interface and generate a multilayer of graft copolymer. We can confirm this by TEM study. (see Figure 2)

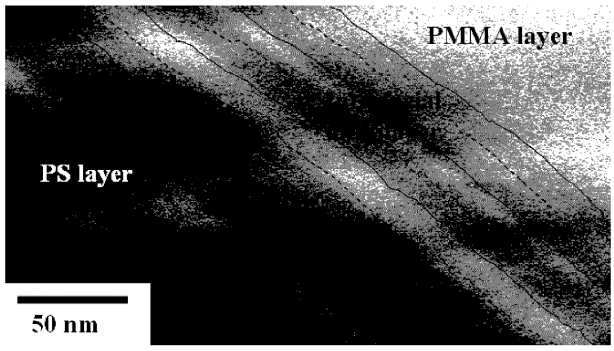

Figure 2. TEM image of a sample that was subjected to chemical reaction for a period of 100 min at 180 °C and $\omega = 100$ rad/s

Conclusions

We have found that the shear force applied on a specimen during oscillatory shear flow has a significant influence on the extent of interfacial reaction and interfacial morphology. The strain amplitude (γ_0) and angular frequency (ω) were found to help enhance the extent of chemical reactions at the interface between the two layers and the generation of an interphase, as long as their magnitudes are small. However, at large values of γ_0 and ω, oscillatory shearing is found to inhibit the diffusion of polymer chains to the interface, thus chemical reactions at the interface.

We have found that during oscillatory shear flow, the application of large γ act as a barrier for the diffusion of reactive polymer chains, which are located away from the interface, to the interface and thus chemical reactions at the interface are restricted. However, when small γ_0 are applied to a specimen subsequent to the application of a large γ_0, chemical reactions take place again at the interface. On the other hand, higher values of ω can break the interface and generate a multilayer of graft copolymer. In this situation, even though a low value of ω was applied again, further reaction did not occur; thus this inhibition becomes permanent obstacle to a further interfacial reactions.

References

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