

Effect of surface functionalization by low-energy ion-beam irradiation on the structure development of a thermotropic liquid crystalline polymer / poly(ether imide) blend.

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Introduction

In-situ composites are blends of thermotropic liquid crystalline polymers (TLCPs) and other thermoplastics, in which the TLCPs are used as reinforcing fillers that are not present as a solid phase during processing of the blends; instead, the fibril shape solid phase is formed when the material is cooled to the solid state ("*in situ*" shaping during processing). In-situ composites have attracted a great deal of interest because they can solve some problems that arise during the processing of conventional fiber-reinforced composites. However, in-situ composites have some drawbacks. One of the drawbacks is that most thermoplastics are incompatible with TLCPs. This incompatibility between the matrix polymers and the reinforcing TLCPs leads to poor interfacial adhesion, which brings about a reinforcing effect less than that expected from the law of mixtures. If any compatibility between the TLCP phase and the matrix polymer is provided, the interfacial tension will decrease, which means less resistance against deformation of the dispersed TLCP phase and good adhesion at the interface. We used low-energy ion-beam irradiation under a reactive gas environment for polymer surface modification[1,2]. Our goal in this paper is to gain an understanding of the structure development of the TLCP phase due to surface functionalization of the matrix polymer.

Materials

The chosen TLCP was an all aromatic liquid crystalline poly(ester amide), Vectra B950 (VB) (a copolymer based on 6-hydroxy-2-naphthoic acid (60%), terephthalic acid(20%), and aminophenol (20%)) produced by Hoechst Celanese Co. Poly(ether imide) (PEI), commercially known as Ultem 1000 (an amorphous polymer made by G.E.), was used as the matrix

Results and Discussion

In this study, we experimentally demonstrated that the ion-beam-assisted gas reaction technique caused surface modification of PEI particles and eminently changed the physical properties of immiscible VB/PEI blends by providing some interactions between the two phases. This interaction is attributed to surface functional groups, (carboxyl groups and

carbonyl groups), added on the surface of PEI particles. Though the modification proceeds at a relatively shallow depth below the surface, the physical properties of the ion-beam irradiated PEI (IBPEI) change modestly because of structural variation (chain scission and recombination, and imide ring degeneration)[2]. The interfacial properties of the VB/PEI blends are also evidently changed due to the improved adhesion at the interface and the reduced interfacial tension (Figure 1).

Rheological data for PEI and ion-beam irradiated PEI melts show almost constant dynamic viscosity values, but IBPEI melt shows slightly higher zero-shear viscosity value, possibly due to the high molecular weight portion produced during the irradiation. IBPEI shows larger modulus values (especially dynamic storage modulus) at low frequency. Comparison of the dynamic viscosity values reveals that blends have lower dynamic viscosity values than the matrix polymers. This indicates the role of a thermotropic liquid crystalline polymer as a processing aid. However, IBPEI blend shows still higher viscosity values than pure PEI blend due to the same reason. Figure 2 gives plots of $\log G'$ vs $\log G''$ for both polymers. Untreated PEI melt shows a homogeneous phase behavior (temperature independence and slope of 2 in the low frequency region) while ion-beam treated PEI melt does not show the same behavior. Though the plot of $\log G'$ versus $\log G''$ is independent of temperature, its slope in the terminal region is less than 2, which should be obeyed if a polymer is to be regarded as being truly homogeneous. Since both criteria are not met, ion-beam irradiated PEI melt cannot be regarded as being truly homogeneous. This implicates that the morphological state does not change with temperature but micro-heterogeneity still exists in the melt. This homogeneity difference disappears in the VB/PEI blend. Dynamic modulus values for both blends show nonlinear behaviors in the low frequency range by mixing with VB having a long relaxation time (Figure 3). Both blends show similar behavior at 330°C. Because of low modulus values for VB, difference in the dynamic modulus values of both blends decreased, but VB/IBPEI blend shows more linear behavior than VB/pristine-PEI blend, which implies a more uniform blend. It is worthy of note that VB/IBPEI blend shows less heterogeneous behavior than VB/untreated-PEI blend. This is attributed to the interaction between IBPEI and VB. More details are discussed below concerned with morphological observation. The interfacial tension was evaluated using an emulsion model (Palierne model[3]). The value of the interfacial tension calculated for the VB/IBPEI blend was less than that calculated for VB/untreated PEI blend, which shows the effect of functionalization on the PEI surface caused by ion-beam-assisted gas reaction.

Good adhesion at the interface enables the stress to be transmitted to the dispersed VB phase and to deform it. Hence, extra energy is consumed by plastic deformation of the VB. Also, extra energy is consumed in the tensile extension process to overcome the larger frictional force due to better adhesion. As a result, the tensile strength of the system increases (Figure 4). However, the improvement in mechanical properties was not so much eminent as the compatibilizer added system. This implies that surface functionalized PEI does not provide such a strong interaction as a reactive compatibilizer and /or the reaction did not occur sufficiently to provide enough compatibilizer. High viscosity of PEI, thus low chance of encounter between the reactive functional groups, is ascribed to be the possible reason.

References

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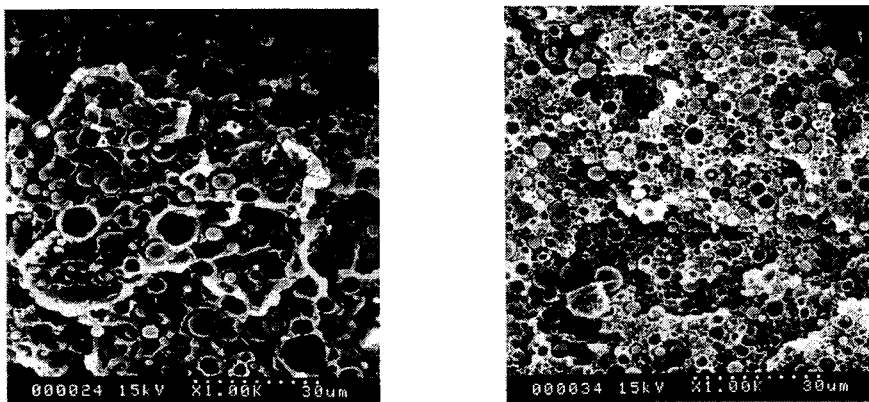


Figure 1 SEM micrographs of the fractured surfaces (A) untreated VB/PEI blend (B) VB/IBPEI blend.

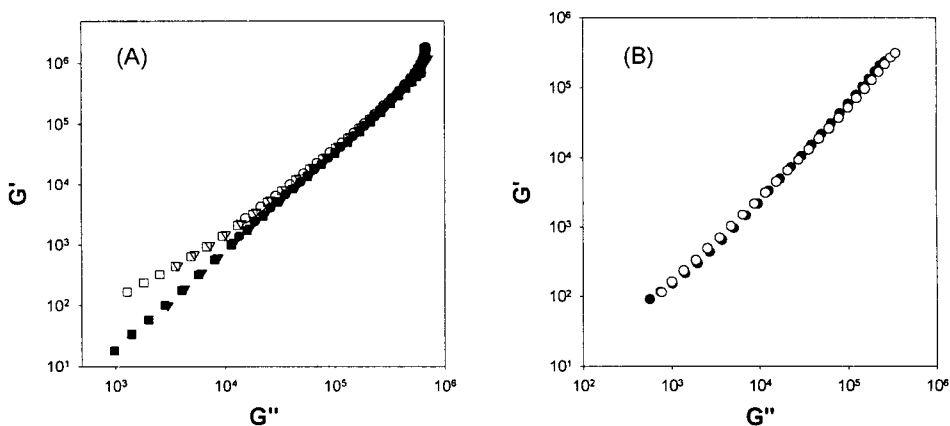


Figure 2. (A) $\text{Log}G'$ versus $\text{Log}G''$ for untreated PEI (open symbols) and IBPEI (filled symbols). (B) $\text{Log}G'$ versus $\text{Log}G''$ for untreated VB/PEI blend (open symbols) and VB/IBPEI blend (filled symbols).

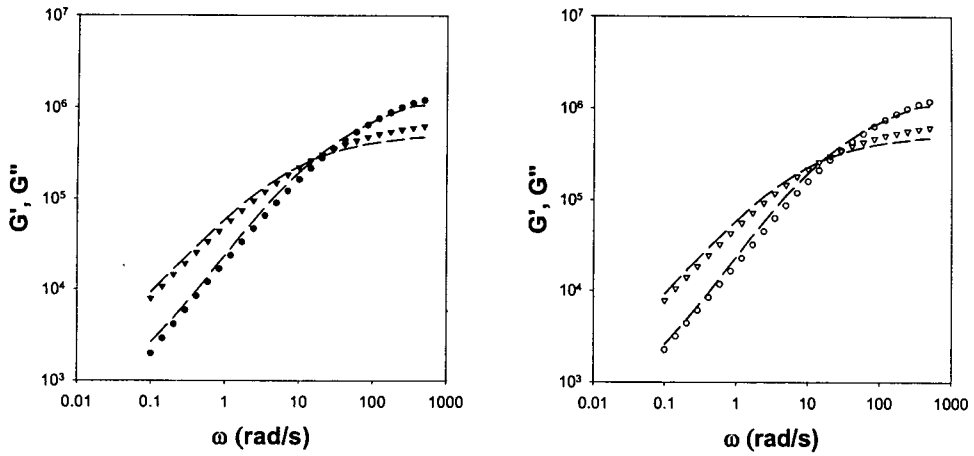


Figure 3. Comparison of model predictions with experimental data: (A) untreated VB/PEI blend at 3300C. (B) VB/IBPEI blend at 3300C. Dashed lines are model predictions. Symbols are experimental data (G' (∇) and G'' (\diamond)).

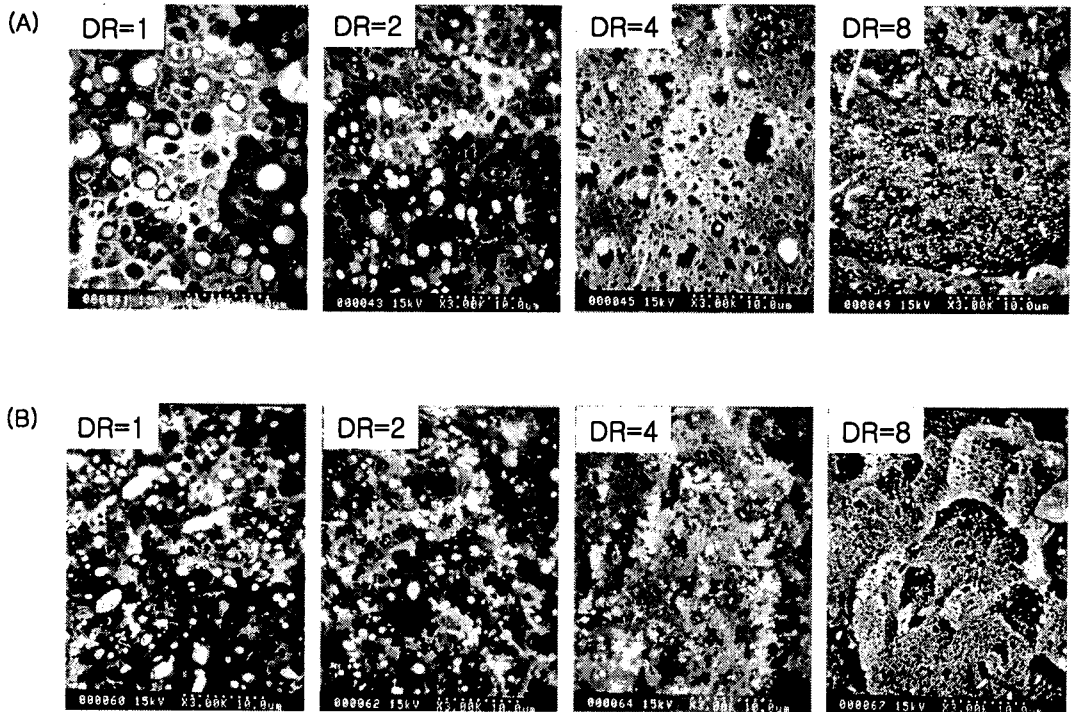


Figure 4. SEM micrographs of the fractured surfaces (A) untreated VB/PEI blend (B) VB/IBPEI blend at different draw ratios.