Compatibilization of Polymer Blends under Conditions of High Pressure and Shear Deformation

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Structural changes in polylactide/polybutylene terephthalate (PLA/PBT) and glycol-modified polyethylene terephthalate/polybutylene terephthalate (PET-G/PBT) polymer blends at a pressure of 1 GPa and room temperature in combination with shear deformation are investigated. High pressure torsion (HPT) is chosen as the compatibilization technique. Based on solid-state NMR data, it is found that the compatibility of immiscible polymers is significantly improved under high pressure conditions in combination with shear deformation. It is assumed that the thickness of the deformed polymer layers decreases to the thickness of the interphase and it can be a fully interphase material.

1. Introduction

Most of the polymer blends currently in use are immiscible. Depending on the composition and manufacturing conditions, they are two-phase or multiphase. Only in very rare cases, when a mixture of two or more polymers has a single glass transition temperature, can it be considered homogeneous. The results of numerous experimental works and theoretical calculations convincingly indicate that all the main properties of the polymer blend depend essentially on the degree of heterogeneity, on the average size of the microsections of each component, and also on the spatial arrangement of the microsections of each component of the blend.[1,2] Compatibilizers, chemical grafting, coupling, or physical modification are used to improve the compatibility and performance of immiscible blends.[3–8] Another focus is on the development of new effective methods for mixing polymers. Of particular interest is mixing at relatively low temperatures, when the mixtures that form have high viscosity, which contributes to the preservation of the structure and morphology formed during mixing for a long time.

The combined effect of high pressure and shear deformation may be a promising way to improve interfacial adhesion between the components of polymer blends. Under such conditions, molecular mixing is unlikely to occur, and compatibilization is improved by intensifying interphase formation, similar to the force assembly in multilayer extrusion.[9] The critical value here is the accumulated shear strain, which should be so large that the polymer inclusions take the form of very thin flakes whose thickness is comparable to that of the interphase.

In the present work, the possibility of homogenization of blends of thermodynamically incompatible polymers—PLA/PBT and PET-G/PBT—by shear deformation at high pressure was investigated. It is known that their mixing by conventional methods (in extruders, mixers) usually results in heterogeneous blends, where characteristic structural transitions can be observed for each of the components of the blend.

2. Results and Discussion

^{1}H spin-lattice relaxation time measurements in both laboratory and rotating frames (T_1, $T_{1\rho}$) using solid-state ^{13}C cross-polarization magic-angle spinning NMR experiments have been chosen as the main method for evaluating the degree of compatibility of polymer blends. It is known that each component of the blend is characterized by its own spin-lattice relaxation time. With improved compatibility, the spin-lattice relaxation times for each of the polymer phases can be expected to converge. For a miscible polymer blend, the relaxation times for both polymers should be the same since ^{1}H spin diffusion occurs between all protons in the blends. Therefore, the difference between the spin-lattice relaxation times should tend to zero. However, for true miscible polymer blends, this value is several tenths to the decimal place of a second.[10–12]

Figure 1 shows the results of measurements of the spin-lattice relaxation times of PLA/PBT and PET-G/PBT blends before and after HPT treatment.

It can be seen that HPT treatment leads to a significant improvement in the compatibilization of PLA/PBT and PET-G/PBT

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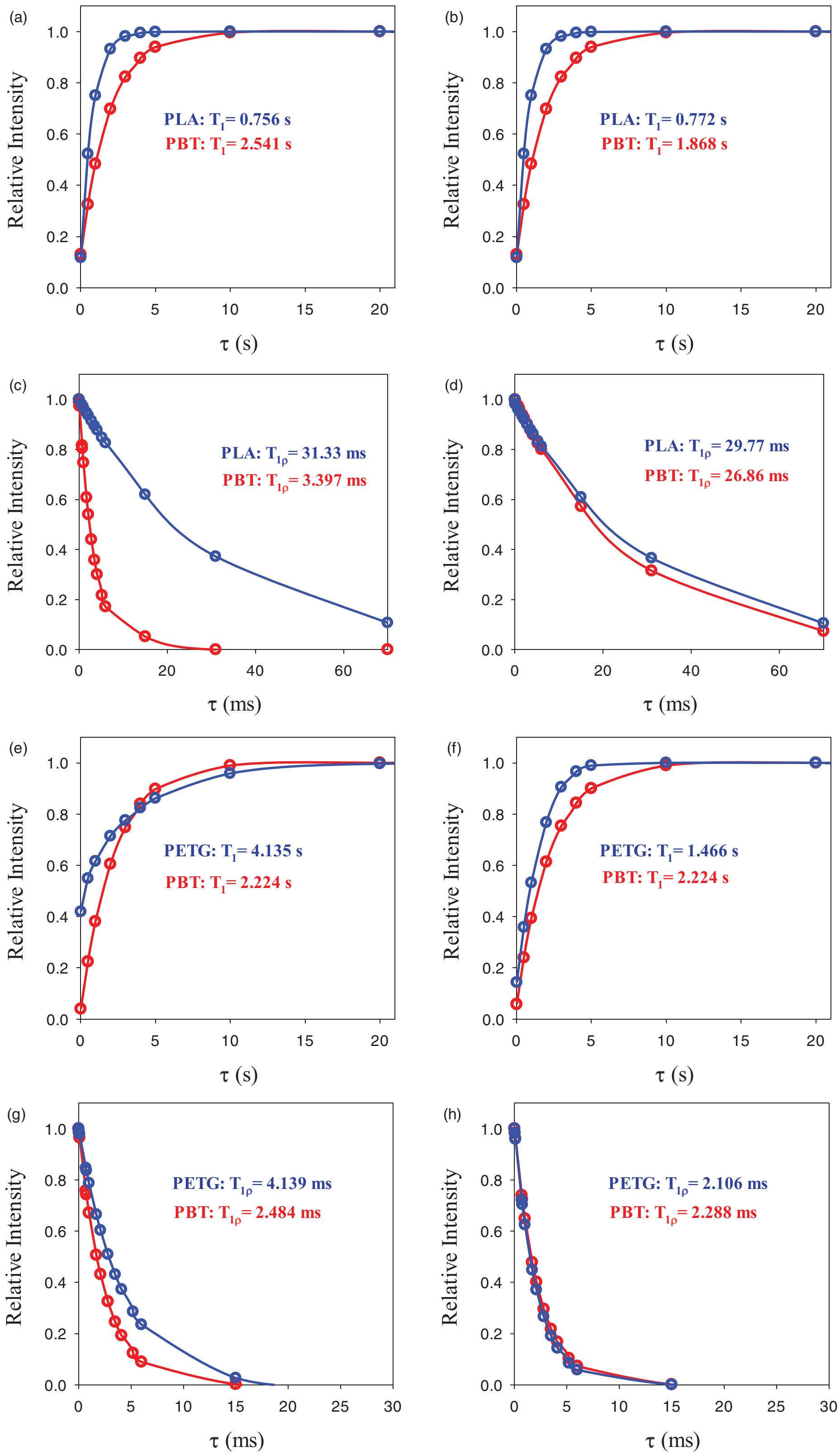

Figure 1. Spin-lattice relaxation time measurements of initial and HPT-processed PLA/PBT (a–d) and PET-G/PBT (e–h) systems. The observed T_1 recovery and $T_{1\rho}$ decay curves measured for CH_2 of PBT (red) and $–CH_3$ of PLA (blue) in (a, c) initial and (b, d) HPT-processed PLA/PBT systems. The observed T_1 recovery and $T_{1\rho}$ decay curves measured for PAR bonding carbon of PBT (red) and CH_2 of PET-G (blue) in (e, g) initial and (f, h) HPT-processed PET-G/PBT systems.

blends. The T_1 values are quite close to each other. This could indicate that the mixing of the polymers occurs at the nanoscale, i.e., in the range of tens of nanometers within the interphase. The closeness of the $T_{1\rho}$ values also indicates the homogeneity of the HPT-processed PLA/PBT and PET-G/PBT blends at the nanometer scale.

3. Conclusion

Using PLA/PBT and PET-G/PBT blends as examples, it was shown that the compatibility of the polymer components is significantly improved when immiscible polymer blends are subjected to high pressure and shear deformation. It can be assumed that strong shear effect on the components of the blend under high pressure conditions leads to a significant thinning of the polymer layers to the thickness of the interphase. As a result, the specific contact area between the polymer phases increases sharply (the proportion of interphase increases), and the polymer phases are more closely contacted.

4. Experimental Section

Materials: Polylactide (PLA) Luminy L175, having melt flow index, MFI = 8 g 10 min^{-1} (210 °C/10 kg, ASTM D1238), polybutylene terephthalate (PBT) Crastin 6129 NC010 with MFI = 8 g 10 min^{-1} (250 °C/2.16 kg, ASTM D1238) and glycol-modified polyethylene terephthalate (PET-G) Eastar Copolyester 6763 with MFI = 8 g 10 min^{-1} (265 °C 2.16 kg^{-1}, ASTM D1238) were used in the experiments.

Sample Preparation: An initial blend with 50 wt%/50 wt% polymer components was produced on the Flashforge Creator pro three-dimensional printer by alternately depositing layers of blended polymers. A detailed description of the 3D printing process could be found elsewhere.[13]

High Pressure Torsion Setup: Layered polymer samples in the form of a disk with the diameter 12 mm and thickness 3 mm were used. Sample processing was carried out on a self-made HPT installation (W. Klement GmbH, Lang, Austria). Standard semiconstrained anvils with the diameter 13 mm and thickness 1 mm were used. All experiments were performed according to the following scheme. First, the sample was unloaded until the required pressure level was reached. Then, one of the anvils was brought into rotation with a given angular velocity, while the regulator automatically maintained the required pressure level throughout the whole deformation. All experiments were carried out at ambient temperature, the number of revolutions was 10, the rotation speed was 5 rpm.

Characterization: Solid-state NMR spectra were recorded on a Bruker AVANCE III WB 400 MHz spectrometer. The spinning rate for all experiments was 6 kHz. ^{13}C cross-polarization magic-angle spinning spectra were obtained under two-pulse phase modulating proton decoupling. A recycle delay was 2 s. ^{1}H spin-lattice relaxation time measurements both in the laboratory and in rotating frames T_1 and $T_{1\rho}$ respectively were measured at room temperature by saturation recovery method and spin lock method, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

compatibilization, high pressure, high-pressure torsion, polymer blends, shear deformation

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