Multiple-Shape Memory Polymer Blends Formed by Massive Formation of Interphases via Ultrahigh Plastic Deformation

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The development of advanced shape memory polymers (SMPs) requires the creation of approaches that offer the possibility of forming different temporal shapes as well as changing the corresponding shape memory transition temperatures. A distinctive feature of ultrahigh plastic deformation methods is the possibility of producing polymer blends with a maximum content of interface to form a single broad thermal transition. This can be an attractive way to produce multi-SMPs based on a simple processing technique. Two polymer pairs—glycol-modified polyethylene terephthalate/polylactide (PETG/PLA), glycol-modified polyethylene terephthalate/polybutylene terephthalate (PETG/PBT)—are used to form an immiscible symmetrical blend (50 wt%/50 wt%). Ultrahigh plastic deformation is achieved by high pressure torsion (HPT). HPT leads to intimate mixing of the chains of the respective polymer pairs. Thermomechanical programming successfully enables a triple shape memory effect with fine shape memory parameters.

1. Introduction

Shape memory polymers (SMPs) represent a technologically important class of stimuli-responsive materials in which the response lies in the change of shape.[4] More specifically, the conventional definition of an SMP is a polymer that can be deformed and subsequently fixed in a temporary shape that remains stable unless subjected to an appropriate external stimulus that causes the polymer to recover its original (or permanent) shape. Accordingly, the associated behavior of SMP is called the polymer shape memory effect. Although various forms of external stimuli can be used as the recovery trigger, the most typical one is direct heating that leads to a temperature increase. The potential of SMPs is strongly dependent upon the number of temporal shapes they can efficiently memorize in each shape memory cycle and the ability to tune the shape memory transition temperature(s) for the targeted applications. Currently known SMPs are capable of successful memorization of three, four, and even five different shapes, i.e., are multiple-SMPs. There are many different types of SMPs and more are being developed all the time.[5,15,2,7] At the same time, the development of fundamentally new approaches to the creation of SMPs, including multiple-SMPs, is extremely necessary. We suggest, that homogeneous mixing of immiscible polymers would allow synergistic tunability and significant enhancement of the resulting SMP's potential functions, which could realize new opportunities that would otherwise be impossible to achieve with the individual components on their own or immiscible blends based on them.

Here, we present a new methodology that allows the integration of thermodynamically immiscible polymers in plenty of interfaces within which a multi-shape memory effect can be effectively realized. The results of our previous study[13] have shown that, in principle, it is possible to mix immiscible polymers by shear deformation at high pressure in the solid state. Such conditions are realized in ultra-high plastic deformation methods, i.e., a group of techniques that require very large strains and high pressure.[11] Hence, ultrahigh plastic deformation methods could represent an attractive pathway to multiple-SMPs production, especially as far as easy processing is concerned. High pressure torsion (HPT) was chosen as the method of ultrahigh plastic deformation.

2. Results and Discussion

2.1. Miscibility

In our paper[13] it was shown that the gradual increase in the interaction between the phases due to ultrahigh plastic

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Table 1. T_g, ΔT_g, T_1 values for PET-G/PLA and PET-G/PBT blends before and after HPT processing.

Blend	T_g [°C][a)]	T_g [°C][b)]	ΔT_g [°C][b)]	ΔT_1 [s][c)]
PLA/PET-G	57, 88	60, 90	15,17	0.915, 4.754
HPT-processed PLA/PET-G	75	79	27	0.726, 1.364
PBT/PET-G	52, 88	55, 90	14, 17	2.146, 4.544
HPT-processed PBT/PET-G	72	75	30	1.438, 2.062

[a)] Evaluated by DSC; [b)] Evaluated by DMTA; [c)] Evaluated by solid-state NMR.

deformation resulted in an increase in the interface area and reached a significant fraction of the dramatic billet volume. The more interfacial area is formed, the more intimate the contacts between two immiscible polymers. It should be noted that the interphase has intermediate properties between the two polymers, for example, the glass transition becomes broad between the glass transition temperatures of the two components. The DSC and DMTA results revealed a flat heat capacity response instead of two distinct α-transitions and the combination of the two peaks of loss modulus into one broad peak for PET-G/PLA and PET-G/PBT after HPT blends. **Table 1** lists the corresponding glass transition temperature (T_g) and associated broadness (ΔT_g) values. Moreover, 1H spin-lattice relaxation times in the laboratory frame (ΔT_1) characterizing the individual polymer phases converge very strongly as a result of HPT treatment (Table 1), indicating that the mixing of the polymers takes place at the nanoscale, i.e., in the range of tens of nanometers within the interphase.

2.2. Dual Shape Memory Test

The presence of broad thermal and thermomechanical transitions for HPT-processed blends allows for programming of several temporary shapes. It is important that the processes of programming and recovering temporary shapes do not overlap. For this purpose, the quenching temperature at which the high-temperature temporary shape is fixed must be higher than the deformation temperature (programmed) of the low-temperature temporary shape. Otherwise, the programming of one temporary shape would be accompanied by a partial recovering of the other temporary shape of the SMPs. Another important fact to consider is the possible difference between the deformation (programmed) temperature and the transition or switching temperature.[8,9] Usually, an increase in the deformation temperature shifts the recovery temperature to a higher temperature.[10] For the studied systems, at all selected deformation temperatures (60, 70, 80, 90 °C), the difference between the deformation temperature and the transition temperature is 2–4 °C. Based on the obtained data, two successive deformation steps at 60 and at 90 °C were chosen to avoid a possible overlap of programming and recovery processes when implementing a triple shape memory effect.

2.3. Triple-Shape Memory Test

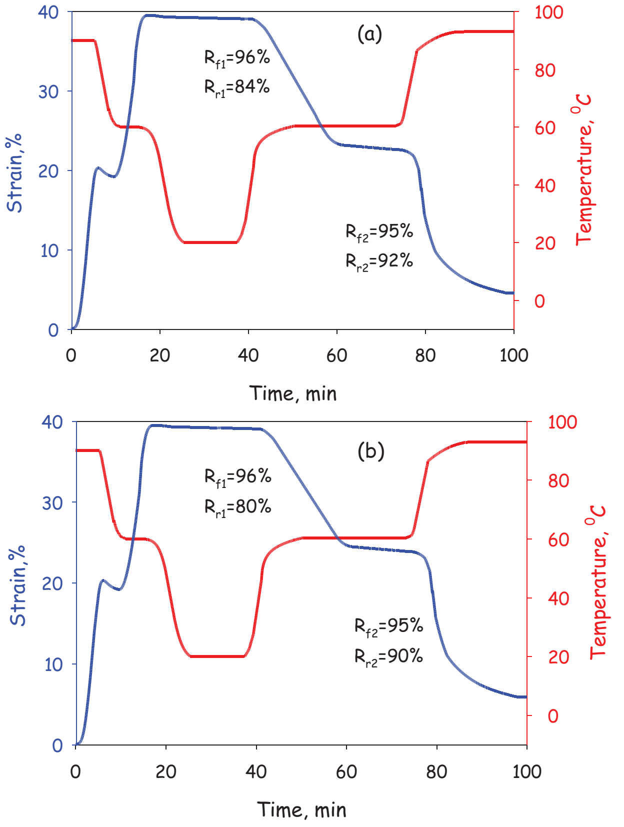

Figure 1. Stress, strain, and temperature of HPT-processed PLA/PET-G (a) and PBT/PET-G (b) blends during triple shape memory cycles.

Figure 1 displays a thermomechanical programming step with the two consecutive deformation steps at two temperatures (60 and 90 °C) and the subsequent shape recovery step under heating at 2 °C min^{-1}. High fixity ratios (Rf1 and Rf2) and high recovery ratios (Rr1 and Rr2) were obtained for temporary shapes 1 and 2, respectively.

3. Conclusion

Two pairs of immiscible polymers PET-G/PLA and PET-G/PBT were subjected to ultrahigh plastic deformation. It was found that such a material exhibits very efficient multiple shape memory properties directly related to the formation of numerous interfaces between both polymers during plastic deformation. We chose shearing by high pressure torsion, a well-known process in metallurgy. The predominant deformation mechanism of both components in a blend was extended by shear, resulting in a dramatic increase of interfaces.

4. Experimental Section

Polylactide (PLA) Luminy L175, polybutylene terephthalate (PBT) Crastin 6129 NC010, glycol-modified polyethylene terephthalate (PET-G) Eastar Copolyester 6763 were used in the experiments. In agreement with the self-concentration model for miscible blends developed by Lodge et al.[6] and experimental studies,[10] the maximal broadness of the glass transition was obtained when symmetrical, i.e., 50 wt%/50 wt% polymer blends were used. 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 can be found elsewhere.[13] In HPT, a disc-shaped specimens were placed between two anvils, both of which had a cylindrical cavity with a depth slightly less than the thickness of the specimen. During mixing, one of the HPT anvils was fixed while the other rotates. A pressure of 1 GPa was applied during the HPT process. The polymers were mixed by plastic deformation using simple shear to a true strain of 12.5. In this case, the different initial phases in a binary system were stretched in the shear direction and their thickness was continuously reduced.

The phase mixing efficiency of polymers before and after HPT was investigated by 1H spin-lattice relaxation time measurements both in the laboratory and in rotating frames (T_1, $T_{1\rho}$) using solid-state 13C cross polarization magic-angle spinning NMR experiments. NMR data were obtained using the Bruker AVANCE III WB 400 NMR spectrometer. The thermomechanical properties of rectangular films were characterized using a Q800 DMA (TA Instruments) at a heating rate of 2 °C min^{-1}. Thermal behavior of samples was probed with DSC Q20 differential scanning calorimeter (TA Instruments) during heating with the rate of 10 °C min^{-1}. Thermally-activated shape memory characterization of samples was conducted using the same Q800 DMA instrument with the film tension clamp under controlled strain and controlled force modes. The Log method for dual-SME and triple-SME, which includes the entire set of programs for shape memory studies, was described in detail elsewhere.[5,13]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

interphase generation, multiple shape memory polymers, polymer blends, ultrahigh plastic deformation

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[1] A. Asano, K. Takegoshi, K. Hikichi, *Polymer* **1994**, *35*, 5630.
[2] I. Bellin, S. Kelch, R. Langer, A. Lendlein, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 18043.
[3] V. A. Beloshenko, Y. E. Beygelzimer, Y. V. Voznyak, B. M. Savchenko, V. Y. Dmitrenko, *J. Appl. Polym. Sci.* **2017**, *134*, 45727.
[4] M. D. Hager, S. Bode, C. Weber, U. S. Schubert, *Prog. Polym. Sci.* **2015**, *3–33*, 49.
[5] R. Hosseinnezhad, I. Vozniak, F. Zairi, *Polymers* **2021**, *13*, 1900.
[6] T. P. Lodge, T. C. B. McLeish, *Macromolecules* **2000**, *33*, 5278.
[7] X. F. Luo, P. T. Mather, *Adv. Funct. Mater.* **2010**, *20*, 2649.
[8] Y. W. Luo, Y. L. Guo, X. Gao, B. G. Li, T. Xie, *Adv. Mater.* **2013**, *25*, 743.
[9] M. Sabzi, M. Babaahmadi, M. Rahnama, *ACS Appl. Mater. Interfaces* **2017**, *9*, 24061.
[10] C. Samuel, S. Barrau, J. M. Lefebvre, J. M. Raquez, P. Dubois, *Macromolecules* **2014**, *47*, 6791.
[11] V. M. Segal, *Mater. Sci. Eng. A* **1995**, *197*, 157.
[12] T. Uemura, T. Kaseda, Y. Sasaki, M. Inukai, T. Toriyama, A. Takahara, H. Jinnai, S. Kitagawa, *Nat. Commun.* **2015**, *6*, 7473.
[13] I. Vozniak, V. Beloshenko, A. Vozniak, F. Zaïri, A. Galeski, A. Rozanski, *Polymer* **2023**, *267*, 125653.
[14] J. Wang, J. M. K. Cheung, Y. Mi, *Polymer* **2002**, *43*, 1357.
[15] M. Wei, M. Q. Zhan, D. Q. Yu, H. Xie, M. J. He, K. K. Yang, Y. Z. Wang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 2585.