



The effect of microstructural evolution during deformation on the post-yielding behavior of self-associated polyamide blends



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ABSTRACT

The deformation-induced microstructure evolution of self-associated polymer blends, i.e., long chain polyamide alloys (LCPAs), was investigated and correlated with their mechanical performance. A PA1012 (soft phase)/PA612 (hard phase) blend was selected for this study. It is interesting that both Young's modulus and yield stress exhibit a nearly linear dependence with composition, which follows a simple additive mixing law. With strong intra-associated hydrogen bonds, the LCPAs studied here were found to be immiscible, but mechanically compatible because of the strong interfacial adhesion of the two constituents. Moreover, when the blend was deformed close to or above its glass transition temperature (T_g), the simultaneous occurrence of fracture reinforcement and toughness was achieved, which was defined as "soft phase-reinforcing-hard phase" (SRH). On the other hand, below T_g , a "hard phase-reinforcing-soft phase" (HRS) mechanical behavior was identified at the expense of elongation at break. Upon uniaxial deformation above T_g , the PA1012 component imparted to the blends a superior fracture stress due to strong strain-induced crystallization effect and the subsequent formation of a microfibrillar structure. However, the PA612 phase contributed little to the improvement of the mechanical properties of the blends. The large discrepancy in the contributions of the blend components to the fracture stress, primarily originates from the flexible nature of the PA1012 chains and the thin crystals nucleated by the already crystallized PA612 phase. However, below T_g , tilt, slippage and fragmentation of the lamellae occur in both phases, which are accompanied by apparent void formation and directly lead to catastrophic fracture. Considering the higher density of hydrogen bonds in PA612, the PA612-rich blends displayed higher fracture stresses as compared to the rest of the compositions. Overall, the distinctive microstructure evolution of the constituent phases and their roles in stress enhancement at large strains have been successfully established. The results presented here shed light on the deformation mechanism of self-associated polymers and offer a new pathway for the development of mechanically reinforcing materials.

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1. Introduction

Characterized by great efficiency and economy, polymer blending has become an alternative to chemical synthesis in manufacturing new materials, and it has been abundantly applied in practice. The miscibility of the constituent components

determines the phase behaviors of polymers, which are generally estimated using the Flory-Huggins theory [1,2]. In terms of this well known theory, most polymers have low miscibility because of the positive Gibbs free energy change due to the restricted entropy effect and the unfavorable enthalpy from repulsive interactions.

The interface compatibility within immiscible polymer blends can be increased only for polymers bearing specific polymer-polymer interactions, such as hydrogen bonding, dipole-dipole and ion-dipole interactions [2,3]. Among them, there are some special pairs sharing similar chemical structures and creating

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strong interactions between the constituent phases, but they exhibit immiscibility, for example, typical binary polyamide blends. Although they are characterized by intensive mutual interactions, these pairs display self-association and are predicted to be different from common immiscible systems, as they may display mechanical compatibility.

Aliphatic polyamide with successive amide groups incorporated in the alkane chains has excellent mechanical and thermal performances [4]. Recently, long chain polyamide (LCPA) with more than ten methylene units between the recurring amide groups has been extensively investigated, particular for even-even series [5–10]. The low hydrogen bonding density due to the small average number of amide groups endows LCPA with flexible chain nature and major advantages such as improved toughness and lower water absorption. To obtain desirable properties, polyamide/polyamide blends have been prepared as an easy way to obtain materials that combine the properties of the different polyamides [9,11,12]. However, most of these blends are confirmed to be phase separated even with strong hydrogen bonding attraction and very similar chemical structures. In the case of even-even polyamide, linear hydrogen bonds that are formed between hydroxyl and amino groups occur in neighboring chains so that the lowest energy can be attained. The polyamide chains, progressively shearing by 13° , create the hydrogen-bonded sheets and they can be stacked in either a progressive or alternative scheme via van der Waals forces [8,13–15]. For this reason, polyamide chains that have similar average number of CH_2 in their diacid and diamine segments are more likely to be arranged together to form linear hydrogen bonds; that is, miscibility is favored, e.g., PA48/PA66 [2]. Otherwise, poor miscibility can be predicted, because of strong intramolecular hydrogen bonding attraction that is characteristic of the inherent self-association feature of polyamides.

The ultimate properties of polymer blends are affected by many factors including the interface miscibility, the crystallization behavior, the microstructural changes under external force, among others. Considering both the fabrication and application, semi-crystalline polymers are commonly subjected to various external fields, such as stretching, shearing and temperature fields in complicated static or oscillating processes; thus, establishing the relationship between the microstructure evolution and the properties is crucial [16–19]. Many techniques, such as X-ray scatterings and Fourier transformation infrared spectroscopy (FTIR), have been adopted by researchers to shed light on the structural response during external perturbation [20–22]. In poly(ethylene terephthalate) (PET), the super structural evolution and its correlation with the phase transformation during elongation were determined by Hsiao et al. using simultaneous two dimensional small and wide angle X-ray scattering (2D SAXS/WAXS), and a three zones model linking the microstructure and mechanical properties was successfully proposed and found to be applicable to deformations below and above the glass transition temperature (T_g) [23,24]. Jiang et al. revealed the strain-induced structural changes of miscible poly(ϵ -caprolactone) (PCL)/poly(vinyl methyl ether) (PVME) using SAXS. The deformation mechanism of micromolded samples and the role of the amorphous phase upon stretching were proposed. Meanwhile, phase separation was observed at large strains [16,25]. Using in situ polarized FTIR, the individual orientations of poly(-methyl methacrylate) (PMMA)/poly(4-vinylphenol) (PVPh) were quantitatively evaluated by Brisson et al., effectively separating the orientations of the constituent phases [26–28]. However, most of these studies focused on neat polymers, miscible polymer blends and immiscible polymer blends with weak or repulsive interactions between the different species. Knowledge about the microstructure evolutions of the constituent phases is still limited in immiscible polymers characterized by strong attraction between the two

components, especially for those with similar chemical repeating units, mainly due to the challenge of distinguishing the often similar structural responses of the constituent phases. Such self-associating immiscible polymer blends should behave quite differently from other polymer blends.

In this work, the deformation-induced microstructural evolution of self-associated polymers, with particular attention being paid to distinguishing the contributions of the constituent components to the overall mechanical performance, were investigated using *in situ* SAXS/WAXS, differential scanning calorimetry (DSC) and polarized FTIR. PA1012, a characteristic example of the AABB type LCPA with diamine/diacid numbers of $2N/2(N+1)$, was selected as the soft phase, while PA612 was selected as the hard phase within PA1012/PA612 LCPA blends. As it shown in this work, with stronger intra-associated than inter-associated hydrogen bonds, these LCPA blends are immiscible, but display mechanical compatibility due to strong interfacial adhesion. Additionally, when the blend is deformed close to or above its T_g , the simultaneous occurrence of fracture reinforcement and toughness is achieved. Such remarkable mechanical behavior has been denoted as the soft phase-reinforcing-hard phase (SRH) phenomenon. On the other hand, below T_g , a hard phase-reinforcing-soft phase (HRS) mechanical behavior was identified with a reduction of the elongation at break. The microstructural origin of the breaking stress enhancement was successfully revealed by exploring the role of the strain-induced crystallization and the formation of microfibrillar structures in the constituent phases. Based on this research, new insights into the cooperation of the distinctive microstructural evolutions of both components in breaking stress enhancement are obtained, and novel pathways for the development of mechanically reinforced LCPA materials are offered.

2. Experimental

2.1. Materials

PA1012 and PA612 were synthesized from biofermenting sources by Shandong Guangyin New Materials Co., Ltd. PA1012 has ten methylene units in both the diamine and diacid alkane chain sequences. The chemical structures of the two polyamides are displayed in Scheme 1. The molecular characteristics of both polyamides are shown in Table 1.

^a Determined by DSC. ΔH_c was obtained from the first cooling run. ΔH_m was obtained from the second heating run. ^b Determined by DMA. ^c Determined using a Melt Flow Indexer at 235°C in terms of ASTM D1238 (2.16 kg).

PA1012/PA612 blends with weight ratios of 100/0, 80/20, 50/50, 20/80 and 0/100 were prepared using a twin-screw extruder at 240°C for 5 min with a rotating speed of 50 rpm/min. It should be pointed out that, according to our research in transamidation [9], the reaction between PA1012 and PA612 can be apparently occurred above 270°C for 10 min, thus the transamidation can be overlooked in this research. The specimens were first compression molded into flat films and then cut into dumbbell shapes with dimensions (length \times width \times thickness) of $25\text{ mm} \times 3\text{ mm} \times 0.5\text{ mm}$. Prior to the test, the mini dumbbell bars were subjected to the same thermal history.

2.2. SAXS/WAXS measurements and tensile tests

In situ SAXS/WAXS tests were performed at the Shanghai Synchrotron Radiation Facility (SSRF). Using a radiation wavelength of 1.24 \AA and 30 s exposure for both measurements, the scattering patterns were continuously collected. The detector to sample spacings for WAXS and SAXS were 336.5 mm and 1976.6 mm,

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