

Toughening of thermoplastic elastomers via introduction of dynamic bonds

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1 Introduction

Thermoplastic elastomers (TPEs) are a physically crosslinked polymer network that is elastic at ambient conditions but becomes malleable at elevated temperature. One of the most widely used types of TPE is a hard-soft-hard triblock copolymer, where the hard blocks aggregate into a domain which serves as a physical crosslink for the soft middle block. It is important to enhance the mechanical toughness of TPE, as it directly determines the material's reliability and lifecycle. Introduction of the dynamic bonds, which are weaker than covalent bonds and can reversibly associate/dissociate, is the key strategy to increase the toughness of polymeric materials. However, the effects of introducing such dynamic bonds into hard domain and/or soft matrix of TPE are not clear. In this study, we selectively introduce hydrogen bonds (H-bonds) into either or both of hard and soft blocks of TPE and compare their microphase-separated structure and mechanical property, to clarify the capability of H-bonds in each phase on toughening of TPEs.

2 Experiment

The samples were ABA triblock copolymers synthesized by sequential ring-opening metathesis polymerization of functionalized norbornene monomers. The A blocks mainly consisted of the phenyl-bearing monomers, As the dynamic bonding functional group, ureidopyrimidinone (UPy)-bearing monomers were selectively introduced to either or both of the A and B blocks. While the number of UPy monomers in each block was varied, the degree of polymerization the blocks was kept the same among all the samples, by which we could observe the effects of dynamic bonds only. The samples are denoted as TPE(x - y - x) where x and y are the number of UPy monomers introduced in the A and B blocks, respectively. The microphase-separated structure of the triblock copolymers was examined by small-angle X-ray scattering (SAXS) measurements performed at BL-6A, Photon Factory, as well as by atomic force microscopy (AFM) on a thin film sample. Mechanical properties were investigated by uniaxial tensile tests.

3 Results and Discussion

Fig. 1a shows the SAXS profile of the bulk TPEs and AFM phase image of the corresponding thin films. There is an intense peak in the SAXS profile in all the samples. All the samples show the peak at similar q position, indicating that the structures formed in these TPEs are similar in size. The AFM images show densely packed nanometer-scale spots, which is typical of a discrete microphase separated structure formed by block copolymers. Also shown in the

figure is the Fourier-transformation of the AFM phase image. Both methods show a correlation peak at a similar length scale, indicating that both methods probe the same structure. By a combination of AFM and SAXS results we conclude that the synthesized TPEs had spherical microphase-separated structure with a similar size among the samples.

The mechanical property of the TPEs was characterized by tensile tests (Fig. 1b). Introduction of UPy in the soft B blocks (from TPE(0-0-0) to TPE(0-20-0)) increases the stress in an entire strain region while that in the hard A blocks (TPE(0-0-0) to TPE(5-0-5)) does not affect the curve at small deformation. However, if UPy is added to the A blocks in addition to UPy in the B block (TPE(0-20-0) to TPE(5-20-5)), the stress is enhanced even at small deformation. This suggests that the introduction of UPy in both the hard and soft phases is more than just the addition of each effect: there is a synergistic interaction between UPy in the hard domains and soft matrix that further enhances the mechanical resilience of the TPE.

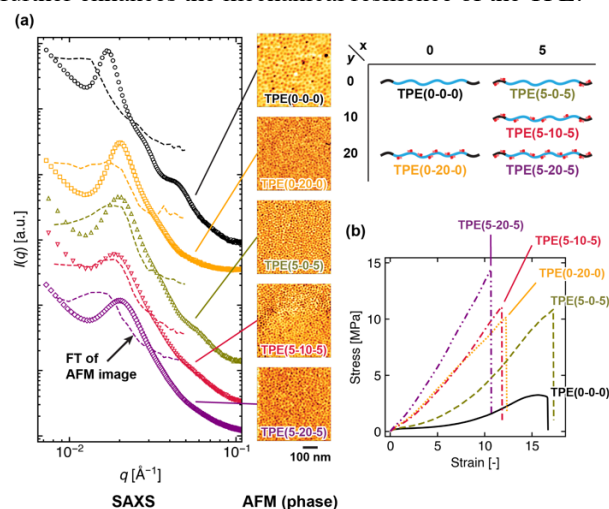


Fig. 1: SAXS profiles and AFM phase images (a) and the stress-strain curves (b) of the TPEs.

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Research Achievements

1. Kawana, S.; Nakagawa, S.; Nakai, S.; Sakamoto, M.; Ishii, Y.; Yoshie, N.; "Interphase synergistic effects of dynamic bonds in multiphase thermoplastic elastomers", *J. Mater. Chem. A*, **7**, 21195-21206 (2019).

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