ACS PRF Grant No.: 57812-ND7
Project Title: *A Combined Theoretical Simulation and Experimental Study on Electrostriction in Polymer/Ferroelectric Particle Nanocomposites*
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1. Project Progress

In the second year, we have focused on electrostriction in poly(ether-*b*-amide) (PEBAX) multiblock copolymers to understand the fundamental physics of electrostriction in ferroelectric polymers. From the constitutive equation for electrostriction, we get:

$$S_1 = s_{31}T_{31} + Q_{31}P_3^2 \quad (1)$$

where S_1 is the electric field-induced strain along 1 (i.e., stretching) direction, s_{31} is the compliance along the 1 direction, T_{31} is the stress along the 1 direction, Q_{31} is the electrostriction coefficient, and P_3 is the polarization along the 3 direction (i.e., the film normal direction). Here, piezoelectric effect from spontaneous polarization is ignored, because our uniaxially stretched PEBAX film does not have any remanent polarization. From this equation, the first term is the contribution from Maxwell pressure and the second term is the contribution from electrostriction. T_{31} is induced by the Maxwell pressure $T_{33} = D_3^2/\varepsilon_r\varepsilon_0$, were D_3 is electric displacement along the 3 direction. Note, $D_3 = P_3 + \varepsilon_0 E_3$, where ε_0 is the vacuum permittivity and E_3 is the electric field along the 3 direction. The Maxwell contribution should mostly originate from the actuation of soft amorphous phase in PEBAX, whereas the electrostriction should originate from the actuation of the crystalline nylon-12 phase.

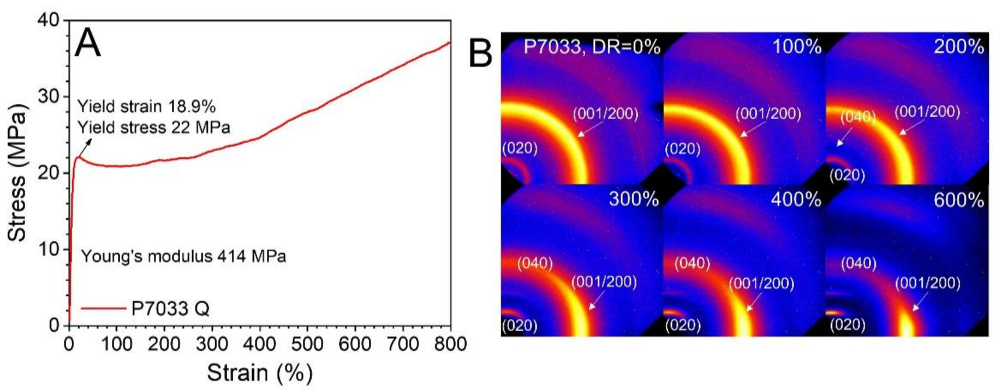

Fig. 1. (A) Stress-strain curve for quenched (Q) P7033 sample. (B) Corresponding 2D WAXD patterns during in-situ uniaxial stretching of Q P7033 at room temperature. The stretching direction is vertical.

Fig. 1A shows the stress-strain curve for the P7033 PEBAX sample with 25 mol.% poly(tetramethylene oxide) (PTMO) at room temperature. The in-situ two-dimensional (2D) wide-angle X-ray diffraction (WAXD) patterns at different stretching ratios are shown in **Fig. 1B**. Beyond 300% stretching ratio, obvious crystal orientation from nylon-12 blocks is observed. At 600% stretching ratio, crystals are highly oriented with the chains along the stretching direction.

The electrostriction study is carried out by simultaneous measurements of electric displacement-electric field (D-E) and S_1-E loops, as shown in **Fig. 2**. At room temperature, D-E loop shows certain ferroelectric hysteresis (**Fig. 2A**). As a result, the S_1-E loops also show broad loops (**Fig. 2B**). Different from poly(vinylidene fluoride) (PVDF)-based terpolymers, this PEBAX sample exhibits negative electrostriction. Namely, upon apply electric film to the film normal direction, the quench and stretched (QS) P7033 film shrinks, rather than expands. When the temperature increases to 75 °C, which is above the glass transition temperature (T_g~45 °C) of the nylon-12 blocks, broad D-E loops are seen in **Fig. 2C**. After subtraction of the AC electronic conduction (the blue horizontal loop), relatively narrow double hysteresis loops are seen with an apparent dielectric constant of 38. The corresponding S_1-E loops become much narrower (**Fig. 2D**). Again, negative S_1 is observed, indicating shrinking of the QS P7033 film, and a 0.4% strain is achieved. It is interesting to see that when the electric field is >160 MV/m, certain saturation in S_1 is reached.

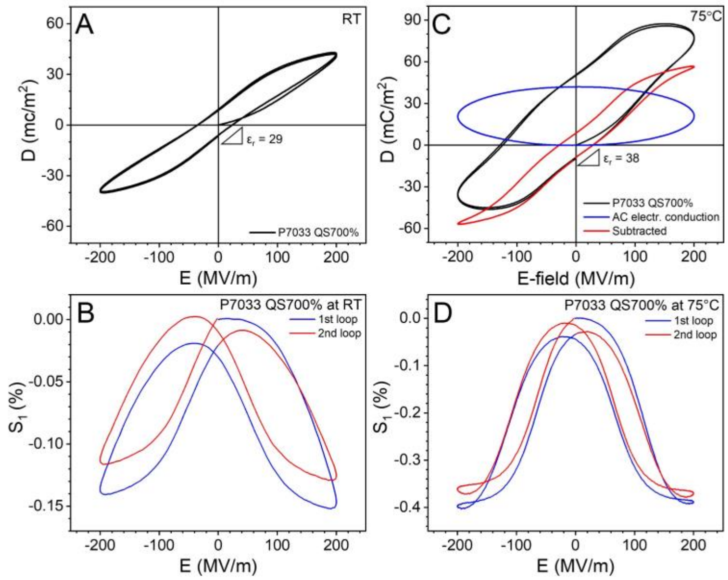

Fig. 2. Simultaneous measurements of (A,C) two continuous bipolar D-E and (B,D) longitudinal strain (S_1) loops for the QS700% P7033 sample at 200 MV/m at (A,B) room temperature and (C,D) 75 °C, respectively. For D-E loops, subtraction of AC electronic conduction (shown as the blue horizontal loops) from the experimental data (black loops) results in neat ferroelectric loops (red loops).

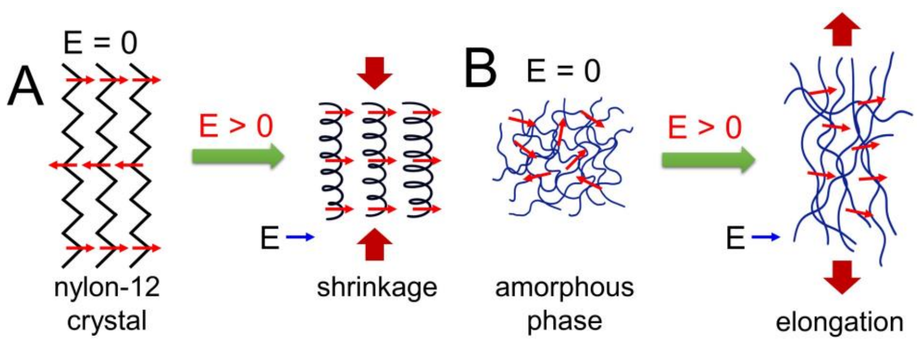

Fig. 3. Schematic models of (A) crystalline phase and (B) amorphous phase in uniaxially stretched PEBAX films upon the application of a high electric field. The stretching direction is vertical and the electric field is along the normal direction (the blue arrow) of the stretched film. Small red arrows represent the amide groups.

The negative S_1 electrostriction in QS P7033 can be understood using the proposed mechanism in **Fig. 3**. First, nylon-12 crystals contain antiferroelectric arrangement of amide dipoles. Upon electric poling, every other dipoles are twisted to orient in a parallel mode. As a result of twisted chain conformation, the crystal will shrink in the chain direction (**Fig. 3A**). Meanwhile, there is also Maxwell pressure, primarily squeezing the random amorphous phase, which include both amorphous nylon-12 and PTMO to elongate the sample (**Fig. 3B**). Under high enough poling electric field, the Maxwell elongation overwhelms the nylon-12 crystal shrinking, a saturation of shrinking S_1 is obtained.

2. Program Impact

This project has initiated a new direction of the PI's research in the fields of electromechanical actuation, which results in a grant application to NSF. A visiting PhD student has been working on the project and trained for scientific research.

3. Publications

Wongwirat, T.; Wang, M.; Huang, Y.; Treufeld, I.; Li, R.; Laoratanakul, P.; Manuspiya, H.; Zhu, L. Mesophase structure enabled electrostrictive property in nylon-12-based poly(ether-*block*-Amide) copolymers. *Macromol. Mater. Eng.* **2019**, *304*, 1900330.