Abnormal Flow and Viscoelastic Behavior of Poly(ether-block-amide)

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The poly(ether-block-amide) or PEBA studied here is a segmented copolymer with a poly(tetramethylene oxide) as the soft segment, a poly(taulryl lactum) as the hard segment and adipic acid as the joint between the two segments. The copolymer is a thermoplastic elastomer and has been used to produce tubes for toothpaste, antistatic sheets. Our rheological investigation on the elastomer revealed that PEBA exhibited interesting and abnormal rheological behavior such as stress fluctuation after prolonged shearing and abnormal terminal behavior in linear viscoelasticity, which will be presented below.

Figure 1 shows the shear stress evolution of Pebax 3553, a commercial grade of PEBAMA, subject to a prolonged shearing with an aluminum parallel plate fixture upon at 170°C at various shear rates. At low shear rates the shear stress increased in the initial stage, then it maintained at a constant value (denoted as Region I in the inset of the figure) to reach a steady state. However, as the shear rate exceeded a critical value, the stress could only maintain at a constant value for a period of time, then it began to decrease monotonically for a certain period (denoted as Region II) before a stress fluctuation set in (denoted as Region III). It was noted that most of the viscosities measured in Region I at investigated temperatures and shear rates were consistent with the measurements by capillary rheometer. The critical shear rate increased as temperature increased. The number of strains where the stress fluctuation started decreased as the shear rate increased. The stress fluctuation was recoverable by resumption of shear after an interruption. The decreasing trend of the average stress did not mean a permanent destruction of a structure since the melts repeated the overshoot-leveling off-fluctuation shearing behavior after complete relaxation from the stress fluctuation. The fluctuation was independent of materials of the shearing apparatus since shearing with parallel plates of different materials, such as aluminum, stainless steel or Kapton coated showed stress fluctuation. The stress fluctuation might be related to the flow instability originated from stick and slip because the fluctuation ceased when the smooth parallel plates were replaced by serrated ones.

The copolymer also exhibited an abnormal terminal behavior in linear viscoelasticity as shown in Figure 2. At low temperatures the storage modulus decreased monotonically as the frequency decreased. At temperatures higher than 170°C the polymer melt showed a plateau of G' when frequency was lower than 0.5 rad/s. The emergence of the G' plateau implied the occurrence of a structural change. Order-disorder transition or microphase separation of diblock and triblock copolymers exhibited similar plateau or nonterminal behavior, but poly(ether-block-amide) differed from those by following aspects. First, most of the microphase transitions in diblock copolymers were systems of lower critical solution temperature while the segmented polymer behaved like an upper critical solution temperature system, that is, the structure became stiffer as the temperature increased. Second, within the frequency range of G' plateau, G' was still much smaller than G" indicating that the PEBA essentially behaved like a liquid, while melts of diblock copolymers assumed solid like behavior at the terminal frequencies. Atomic microscopic pictures of quenched samples revealed that the plateau was associated with the coarsening of spherical domains. The FTIR studies provided the evidences that the domain coarsening was triggered by the dissociation of hydrogen bonding between soft and hard segments. Upon a temperature raise the soft and hard segments were no longer compatible and separation occurred to introduce morphology of coarse domains with a higher composition contrast against the matrix.