Thermo-Mechanical Study of TPU Nano-fibers

Electrospun thermoplastic polyurethane (TPU) nanofibers are known to contract considerably (~ 40%) upon heating up to ~ 90°C. This work investigates this thermomechanical behavior and the nanofiber shape memory capabilities. During the electrospinning process, the polymer system undergoes marked stretching, which can be partially preserved in the final state of electrospun nanofibers, due to extremely rapid solvent evaporation. Structural analyses of this phenomenon have shown that neither the confinement nor the extreme processing conditions can explain the fibers contraction. A broad thermal transition indicating the presence of a mixed phase of hard segments dispersed in the soft segment matrix was observed. The polymer was found to be amorphous and the contraction was attributed to the destruction of non-crystalline hard segment clusters. The shape memory effect was studied in TPU films as a model system, by applying classical thermomechanical cycles (programming and recovery). The films were able to fix the applied deformation during long-term storage at room temperature, well above the material's calorimetric glass transition temperature and in absence of a percolated structure of hard domains. The mixed phase was found to give rise to a very broad relaxation spectrum dominated by long relaxation times, which explains the suppression of strain recovery at room temperature. The shape memory effect of electrospun fibers is therefore attributed to the non-equilibrium state matrix induced by electrospinning, similar to a programming stage, followed by recovery of the stored strain upon heating, resulting in the observed contraction in electrospun TPU fibers. Finally, the potential of the thermoresponsive fiber mats as reliable time-temperature indicator (TTI) was demonstrated with a simple model device in which the fiber mat was designed to release a liquid dye as an indication of the time-temperature history.