

ABSTRACT

In the current era, the advancement of technology imposes continuous demands for the smart versatile materials that concurrently show strength, flexibility as well as easy processability. In this context, the development of new thermoplastic elastomeric blends is inevitable. Having been motivated by this fact, the present thesis work demonstrated the development of smart thermoplastic elastomeric blend from polyvinylidene fluoride (PVDF) and hydrogenated nitrile rubber (HNBR) which was responsive to electric field. Before studying the electromechanical properties, an exhaustive investigation was carried out on rheological properties, morphology, crystalline microstructure and dielectric relaxation spectroscopy. Both the rheological studies and the morphological analysis described the formation of thermoplastic elastomeric blends (TPEs) when the rubber content was varied in between 50 to 70 wt%. In the thermoplastic elastomeric blends, rubbery HNBR formed interconnected droplets dispersed in the matrix of PVDF showing yield in complex viscosity and a secondary plateau in complex modulus in the lower frequency range of the linear viscoelastic region. After the dynamic vulcanization (TPVs), complex viscosity and storage modulus significantly increased in the lower frequency region due to the formation of ligament-like network which connected the rubbery droplets. In order to find out how the rheological properties changed during the time of mixing or dynamic vulcanization, TPEs and TPVs were taken out at different times and their oscillatory and steady shear rheological properties were investigated. Interestingly, both the TPEs and TPVs were shear sensitive and the morphology changed significantly after each processing step. Droplet like structure was observed after mixing and compression molding whereas lamella-like structure was formed after milling and injection molding. The change in morphology showed a significant effect on mechanical properties. Compression molded samples (TPEs and TPVs) depicted higher elongation with moderate tensile strength; on the other hand, tensile modulus increased significantly after the injection molding. 30/70 (w/w) ratio of PVDF/HNBR TPEs, prepared by compression molding, showed very high elongation (~1600%) which is not generally observed for TPEs. The size distribution of the dispersed phase, cure kinetics, and dynamic mechanical properties were also investigated. Both the TPEs and the TPVs were recycled without much alteration in the mechanical properties. Apart from the experimental work, molecular dynamics and dissipative particle dynamics simulation were employed to predict the properties like glass transition temperature, interaction parameter, morphology and the results were compared with the experiments. Lamella-like crystals were discerned for both the PVDF and its TPEs and TPVs by small angle X-Ray scattering and microscopy. Above the crystalline melting temperature, HNBR suppressed the mobility of PVDF and the effect was increased with the HNBR content. Interestingly, after the complete crystallization, HNBR segments were expelled out from the lamella, and crystal long period remained intact; however, the electron density contrast between the crystalline and the amorphous regions was reduced. When HNBR phase was crosslinked, the crystallization became faster and the electron density contrast increased. IP (interfacial polarization) relaxation of PVDF, caused by the permittivity difference between the crystalline and the amorphous phase, was absent for the TPEs and the TPVs, whereas IP relaxation of HNBR, arising due to permittivity difference between the acrylonitrile group and the long methylene sequence, shifted to the higher frequency. The shift was higher at higher HNBR content and decreased when HNBR was crosslinked. 30/70 (w/w) ratio of PVDF/HNBR TPEs showed maximum planar actuation of 5% and could be visible by bare eyes. For the planar actuation test, no pre-stretching was required which minimized the complicity in designing the actual devices. The TPE also gave 0.6 mm bending actuation at a low electric field of 20 kV/mm. Addition of 10 wt% barium titanate (BT) nanofiller, the planar actuation was increased to 10%; whereas at 5 wt% BT loading, dielectric strength was maximum and it also showed the bending actuation of 0.9 mm at 20 kV/mm. In essence, the study provides a promising and unexplored alternative of developing electromechanically active thermoplastic elastomeric blends.

Keywords: Polyvinylidene fluoride, Hydrogenated nitrile rubber, Thermoplastic elastomeric blend, Electroactive polymer, Structure-property, Simulation.