

ABSTRACT

The melt blending of nylon-6 and acrylate rubber in an internal mixer like Brabender Plasticorder in the temperature range of 220-235 °C presents a unique way for the preparation of novel heat and oil resistant thermoplastic elastomers. The blends show excellent resistance to oil swelling at elevated temperature (e.g. 150 °C) and its service temperature range can be extended upto 175 °C without much deterioration of the mechanical properties. The blends are reactive in nature and various key properties, like, mechanical, dynamic mechanical, oil and fuel resistance and ageing resistance of the blends are improved significantly with the increase in the extent of the reaction between the two components. The reactive nature of the blend components is reflected in the rise in the mixing torque during melt blending operation. Infrared (IR) and Solid State Nuclear Magnetic Resonance (N.M.R) analysis indicate the chemical reaction between the epoxy groups of ACM and carboxylic acid end groups of nylon-6. Dynamic mechanical analysis of the blends shows a reduction in the $\tan \delta_{\max}$ (the maximum value of $\tan \delta$ at the transition) as well as the T_g (glass transition temperature) of the bulk rubber phase with the level of interaction between the two phases followed by the appearance of a secondary transition at higher temperature region due to the formation of grafted ACM chains. The observed storage moduli of the blends at 50 °C are close to those obtained from Kerner's hard matrix-soft filler model, suggesting the formation of nylon-6 as the continuous matrix, which is further confirmed from the morphology studies. The blends are pseudoplastic in nature and an increase in shear rate decreases the viscosity and increases the extrudate swell of the blends. The morphology study of the extrudate suggests the rupture of ACM phase at high shear rate in the case of uncrosslinked blends, whereas the morphology of the dynamically vulcanized blends is stable against shear stress. The blends are found to be reprocessible at 240 °C without any appreciable degradation of either phase, which suggests its applicability as thermoplastic elastomer. From Thermogravimetric (TGA) studies it is concluded that the melt-mixed nylon-6/ACM blends degrade at a lower temperature as compared to pure nylon-6, indicating a strong interaction between the

polymers at high temperature. To explain the above interaction, the possibility of ester-amide exchange reaction is postulated. Crystallization behavior of the thermoplastic elastomeric reactive blends of nylon-6 and ACM has been studied with the help of X-ray (WAXD) and Differential Scanning Calorimetry (DSC). It is observed that the addition of ACM to nylon-6 results in an increase in the unit cell dimensions of nylon-6 crystals with a reduction in its crystallite size. The presence of ACM also restricts the crystallization process of nylon-6 chains, which results in lowering of T_m (crystalline melting point) and percent crystallinity of nylon-6 phase in the blends. It is found that above 225 °C (i.e. the melting point of nylon-6 crystals) the interfacial thickness, λ of nylon-6/ACM bilayer joints attains the equilibrium value in the range of 40-48 nm within 2 minutes of annealing. The dynamic mechanical thermal analysis of the joints annealed at 200 °C for different times shows broadening of the loss tangent peak corresponding to that of the ACM rubber with the progress of the reaction. Also, the storage modulus of the joints is increased progressively, supporting better adhesion between the two polymers with increasing annealing time. The results of the investigation on the effect of various fillers and plasticizers on the key performance of thermoplastic elastomeric blends based on nylon-6 and ACM indicate that the addition of carbon black and clay reduce the extent of reaction between nylon-6 and acrylate rubber, while silica interacts with ACM chains through covalent bond formation, which increases the overall polymer-filler interaction in the blends. Mechanical properties of the blends are improved very much with the addition of lower amount of carbon black (i.e. 10 to 20 phr.) and higher percentage of silica (30 phr.). Also, the elastic recovery of the blend is very much improved in the case of filled samples. However, the volume swell in ASTM oil # 3 at 150 °C of the blends is well below 10%, which suggests its excellent hot-oil resistance.

Key Words

Thermoplastic elastomer, nylon-6, acrylate rubber, reactive blends, mixing torque, heat and oil resistant TPEs, dynamic vulcanization, swelling, rheology, crystallization, adhesion, fillers, plasticizers, dynamic mechanical properties, ageing, infra-red analysis, ellipsometry, x-ray analysis.