ABSTRACT

Reactive processing of polymers has attracted the attention of polymer scientists throughout the world in recent years. Reactive blending is one of the processing techniques conventionally and widely used by many industries for achieving the goal of developing new materials. In the present thesis, low-density polyethylene (LDPE) and polydimethyl siloxane rubber (PDMS) were chosen as the blend constituents. They were blended in various proportions in the laboratory but were found to be immiscible. The objective of this thesis is to select a compatibilizer for this immiscible blend system. Ethylene copolymers such as ethylene methyl acrylate copolymer (EMA), Ethylene vinyl acetate (EVA), Ethylene acrylic acid (EAA), an ionomer (Lotek-4200) were tried as the compatibilizers. But it was found that EMA gives the best results for this blend system.

Once the compatibilizer was selected, optimization of the level of the compatibilizer was carried out in the blend system through out entire composition range. The results have been confirmed from physico-mechanical property studies, dynamic mechanical property studies, adhesion studies, phase morphology and X-ray diffraction studies.

The rheological characteristics of different LDPE/PDMS blends without compatibilizer at three different temperatures (160, 180 and 200°C) and four different shear rates (61.3, 122.6, 306.6 and 613.1 s^{-1}) were studied by using Monsanto Processability Tester. The melt viscosity increases initially with an increase in PDMS proportion but decreases at higher proportions of PDMS. The flow behaviour index of the blends decreases with PDMS proportion. The activation energy of flow for the blends decreases with increase in PDMS proportion. The die swell increases with an increase in shear rate but decreases continuously with increase in PDMS proportion.

The rheological characteristics of the blends of poly (dimethyl siloxane) (PDMS) rubber and low density polyethylene (LDPE) compatibilized with poly (ethylene-co-methyl acrylate) (EMA) has been carried out by using Monsanto Processability Tester (MPT) at four different temperatures (160, 180, 200 and 220°C) and four different shear rates (61.3, 122.6, 306.6 and 613.1 s^{-1}) by varying the proportions of EMA copolymer from 0 to 15 wt %. The melt viscosities of these blends are found to be higher than that calculated as per log-additivity rule, indicating a strong interaction between the blend constituents. The activation energy of flow is minimum at 6 wt.% of EMA copolymer. The flow behaviour index (n) of the blends increases with increase in temperature and also with EMA proportion in the blends indicating a decrease in pseudoplastic behaviour of the blends. The die swell characteristics increase with an increase in shear rate as well as with temperature. An increase in EMA concentration in the blends increases the

die swell up to the level of 6 wt.% and then the change is marginal. Surface finish (smoothness of the outer surface of the extrudate) becomes rough with increasing shear rate and the temperature. But it improves with increasing compatibilizer contents. The SEM studies of the compatibilized blends by SEM give co-continuous phase morphology at 6 wt.% of EMA. For other loading of EMA i.e. < 6 wt. % and > 6 wt.%, a two-phase morphology is observed. From all these studies 6 wt.% of EMA is considered to be its optimum loading.

The effect of silica filler on rheological behaviour of the LDPE/PDMS blend in the proportion of 50:50 compatibilized with EMA-g-PDMS have also been studied. A silane-coupling agent, [vinyl tris (2-methoxy ethoxy) silane, (A-172)] was added into the blend system by 10 wt.% of silica filler loadings. All the blends show pseudoplastic flow behaviour i.e. a decrease in viscosity with rate of shear. The melt viscosity increases initially with filler loading (up to 10 wt.%) but then decreases at higher filler loading (>10 wt.%) and higher shear rate,may be due to melt fracture phenomenon. The power law applies to the system and the flow behaviour index (n) of the blends in general increases with increase in temperature but decreases with filler loading. The activation energy of flow for the blends decreases with an increase in silica filler loading. The die swell increases with an increase in shear rate but decreases continuously with increase in silica filler loading. Phase morphology study by SEM shows improved dispersion at 5-10 wt.% of silica filler loading. Surface finish of the extrudate for blend containing 10 wt.% of silica filler is better as compared to that with 20 wt.% of silica filler.

Because of low property range of the compatibilized blend system, the systems were crosslinked with DCP a peroxide, which is well known crosslinking agent for both the constituents, LDPE as well as PDMS. The kinetics of crosslinking reaction using DCP as the crosslinking agent was studied by Differential Scanning Calorimetry and the optimization of the concentration of DCP in the blends for the best technical properties was carried out by Rheometry. The crosslinked blends were subjected to property analysis such as mechanical, dynamic mechanical, thermal, chemical and dielectric property measurements. Some of the properties of the blends such as modulus at 300 % elongation and tensile strength showed sysnergistic effect. Dynamic mechanical analysis of the blends exhibited a composition dependent glass transition temperature and a shift of the T_g towards a higher temperature implying that the blends are miscible even after crosslinking. The formation of a compact network structure through co-crosslinking in addition to compatibilizing action of EMA is the reason for improved properties.

Thermogravimetric analysis of the pure components and the blends were carried out by a thermal analyzer. The thermogravitograms and derivatograms of the blends show that the thermal degradation takes place in two stages, where as neat LDPE shows a three stage degradation and neat EMA and PDMS rubber show only single stage degradations respectively. Kinetic studies of the blends and pure components depict that the degradation follows a first order kinetics. Activation energy at 10 % degradation have been determined using Freeman and Carroll's method and is found to be maximum (41 kcal/mol) for the blend containing 6 wt % of EMA. Half life period at 200°C have been evaluated by the Flynn and Wall method and is found to be maximum for the blend containing 6 wt % of EMA.

The thermal ageing was carried out in air oven at 150°C for 2, 5 and 7 days. The percent retention of T.S. and 300 % modulus decrease with time of ageing but increase with PDMS proportion in the blends. Percent retention of elongation at break (E.B.) decreases with time of ageing but increases slightly with the increase of PDMS proportion. With the incorporation EMA compatibilizer in the same 50:50 blends of LDPE and PDMS, percent retention of T.S., 300% modulus and elongation at break increases with EMA concentration and become maximum at 6 wt.% of EMA. However beyond 6 wt.% of EMA concentration in the same blend the percent retention for all these properties falls. As the proportion of PDMS increases in the blends the ageing behaviour improves due to inherent higher thermal stability of PDMS. With incorporation of EMA copolymer in 50:50 blends of LDPE and PDMS, the dispersion of the blend constituents improves up to 6 wt.% of EMA, with further increase in EMA proportion a separate phase of EMA-g-PDMS is formed so a slight reduction in ageing properties is observed.

The electrical properties such as volume resistivity, dielectric strength, permittivity and loss tangent were studied for the different LDPE/PDMS blends. The volume resistivity of the blend system decreases with PDMS proportion due to the presence of impurities in PDMS. With the incorporation of EMA copolymer in 50/50 LDPE/PDMS blend, the volume resistivity increases and attains a maximum value at 6 wt.% of EMA copolymer. This is because up to 6 wt.% of EMA copolymer it helps in compatibilizing LDPE and PDMS leading to better bonding between the two polymers. It is found that the dielectric strength continuously decreases with the PDMS proportion and EMA concentration in the blends. This is due to the presence of impurities (silica filler, moisture etc.) in PDMS and polar nature of EMA.

It is found that the relative permittivity (dielectric constant) increases with the increasing concentration of silicone rubber in the blend. But it decreases initially with an increasing concentration of EMA compatibilizer in LDPE/PDMS 50:50 blends. The initial decrease in relative permittivity with an increasing concentration of EMA copolymer may be due to compatibilization effect. But above 6 wt.% of EMA compatibilizer a separate form of EMA-g-PDMS is formed, which is somewhat continuous in nature, so conductivity of the system increases. The relative permittivity is found to decrease with increasing temperature up to around 107°C for 50:50 blends containing different proportion of EMA, beyond which the rate of change of permittivity with temperature is very high. This particular temperature corresponds to the melting of crystallites present in LDPE. The matrix softening at high temperature leads to enhanced contribution of ionic conduction as well as interfacial polarization to relative permittivity.

Acid and alkali resistance properties of crosslinked alloys of low-density polyethylene (LDPE) and polydimethyl siloxane (PDMS) rubber with EMA copolymer as the compatibilizer have been investigated. Tensile properties of the individual components and the blends before and after treatment with different acids and various concentrations of an alkali are reported. Treatment with nitric acid has resulted in severe deterioration of tensile properties of all samples compared to all other acids studied. Retention of tensile properties of all the blends studied is found to improve significantly as compared to the reference sample the PDMS rubber. This has been further supported by the scanning electron microscopic studies.

KEY WORDS

Reactive blending, Compatibilizer, Phase morphology, Lap shear adhesion, Impact strength, Additivity rule, Rheology, Cure kinetics, Synergistic effect, Dielectric loss tangent, Glass transition temperature, Activation energy, Degree of crystallinity, Co-crosslinking, Acid and alkali resistance properties.