STUDIES ON PSU / HDPE BLENDS AND MICA REINFORCED COMPOSITES

by

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Submitted

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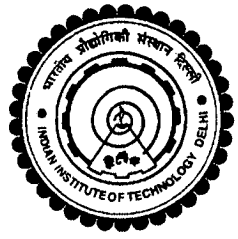

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① Polymers ② Thermal analysis

CERTIFICATE

This is to certify that the thesis entitled **"STUDIES ON PSU/HDPE BLENDS AND MICA REINFORCED COMPOSITES"** being submitted by **Smita Sangam** to the Indian Institute of Technology, Delhi, for the award of degree of **DOCTOR OF PHILOSHOPHY,** is a record of bonafide research work carried out by her.

Smita Sangam has worked under our supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in the thesis have not been submitted in part or in full, to any other University or Institute for the award of any degree or diploma.

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(SMITA SANGAM)

ABSTRACT

Majority of the engineering thermoplastics are characterized by their excellent thermal and dimensional stability, however the applications are limited due to their inferior impact strength, high cost and poor processibility. Poly (ether sulfone) (PSU), is one such engineering thermoplastic with high melt viscosity, low impact strength and chemical resistance. In order to improve these properties and make it more cost effective, blending of this polymer was carried out using a low cost impact modifier HDPE.

The main objective of the study was to investigate the effect of low cost high density polyethylene on the properties of polysulfone in the absence and presence of compatibilser (HDPE-g-MA) .The effect of incorporation of mica on the properties of ternary blend was also investigated. The binary (PSU/HDPE) and ternary (PSU/HDPE/HDPE-g-MA) blends and mica filled composites based on ternary blend (sample CH_{10}) were prepared by melt mixing in twin screw extruder. The composition of PSU/HDPE in the binary blends was varied as 95/5, 90/10, 80/20, 70/30 and 50/50 (w/w) and the blends have been designated as H_5, H_{10}, H_{20}, H_{30} and H_{50} respectively. Neat HDPE and PSU have been designated as H_{100} and H_0 respectively

Ternary blends were prepared to investigate the effect of compatibiliser HDPE-g-MA on the properties of binary blends. These were prepared by mixing PSU/HDPE/HDPE-g-MA (substituting 25 % (w/w) of HDPE by HDPE-g-MA in all the compositions) and composition was varied as 95/3.75/1.25; 90/7.5/2.5; 80/15/5; 70/22.5/7.5; 50/37.5/12.5 etc. The blends were designated by adding prefix 'C' to

binary blend sample designation. For example ternary blend having PSU/HDPE/HDPE-g-MA in ratio of 95/3.75/1.25 composition was designated as 'CH_5'. Preparation of mica filled composites and their characterization was also done with an aim to investigate the effect of filler (mica untreated or treated) on the properties of optimized ternary blend i.e. sample 'CH_{10}' (PSU/HDPE/HDPE-g-MA 90/7.5/2.5).

The results of mechanical, morphological and thermal characterization of PSU / HDPE and PSU / HDPE / HDPE-g-MA blends are described in chapter-3 of thesis. Increasing volume fraction of dispersed phase i.e. HDPE showed improvement in impact strength with an optimum at Φ_d = 0.35 [sample H_{30}]. On the other hand tensile and flexural properties decreased with increasing amount of HDPE in binary blends. The decrease could be due to the addition of low strength material (HDPE) to the matrix. Significant decrease in elongation at break was observed indicating a brittle fracture. The decrease in % elongation may be due to the immiscibility and poor adhesion between the two phases (matrix and the dispersed phase).

In order to improve the strength and ductility of PSU/HDPE binary blends, compatibilser HDPE-g-MA was used as third component, considering that the maleic anhydride component would interact with the hydroxyl groups of PSU and the HDPE component would show miscibility with the dispersed phase. A mid blend composition 80/20 of PSU/HDPE was used for optimizing the compatibiliser concentration. Substitution of 25 % (w/w) of HDPE by the graft copolymer (HDPE-g-MA) showed optimum set of properties. Ternary blends containing the same volume fraction of dispersed phase (substituted with 25 % of graft copolymer) i.e. PSU / HDPE / HDPE-g-MA were studied

in the same composition range [Φ_d = 0.063 to 0.63] of dispersed phase. Significant increase in the toughness and ductility was observed in these blends over the entire composition range. Four fold increase in impact strength and 13 % increase in elongation at yield was observed at Φ_d = 0.13 [sample CH_{10}]. The modulus values were higher for sample CH_{20} to CH_{50} having Φ_d ranging from 0.24 to 0.63. Improvement in the properties could be due to the emulsifying effect of the compatibiliser leading to decrease in interfacial tension and better adhesion between the matrix and the dispersed phase in the presence of compatibiliser. The experimental data of tensile properties was also compared with the theoretical models. Morphology as determined by scanning electron microscopy showed two phase structure. The size of dispersed phase domains increased with increasing HDPE content in PSU / HDPE blends. The domain size for all the blend compositions decreased in presence of compatibiliser. At a domain size of ~ 1.61 μm, due to better dispersion, optimum increase in the impact strength was observed. The critical volume fraction 'Φ_c' of the dispersed phase for brittle ductile transition was close to the value predicted theoretically by Wu's equation. The inter-particle distance decreased on addition of graft copolymer. The inter-particle distance in ternary blends was less than the PSU/HDPE binary blends. The interparticle distance for sample CH_{10} was 0.92 μm.

The DSC scans showed inward shift in onset melting temperature. The crystallinity of HDPE in the PSU / HDPE binary blends decreased. The decrease was more significant at lower volume fractions of HDPE. The onset of crystallization also shifted to lower temperature and two crystallization exotherms were observed at Φ_d = 0.063 and Φ_d =

0.13 [sample H_5 and H_{10}] of HDPE, indicating lower temperature is required for complete crystallization.

The onset melting temperature, crystallization temperature and crystallinity (%) increased on addition of graft copolymer HDPE-g-MA. This may be due to heterogeneous nucleation of HDPE in the presence of graft copolymer. The glass transition temperature also decreased from 187°C to 180°C at $\Phi_d = 0.63$ [sampleCH_{50}] of HDPE, which can be explained on the basis of plasticization of PSU matrix by HDPE. This may be due to the improved miscibility between the two phases in the presence of graft copolymer.

Wide angle X-ray diffraction studies of the binary and ternary blends also indicated a decrease in the crystallinity of HDPE in PSU matrix. The mean dimension of the spherulite decreased from 232A° to 150A° in the binary and ternary blends.

DMA scans showed two distinct glass transition temperatures i.e. 'T_g' corresponding to HDPE and PSU, at 50°C and 187°C respectively. The 'α' transition of HDPE shifted from 50°C to 57 °C in all the binary blends irrespective of the blend composition, however the intensity of the transition was proportional to HDPE content. The shift of α transition to higher temperature may be due to the reinforcing effect of rigid PSU matrix. An inward shift in 'T_g' of PSU was observed in the binary and ternary blends. The decrease was found to be more significant in the ternary blends. The storage modulus and loss modulus values for ternary blends were higher than PSU/HDPE binary blends

The experimental tan δ values for the binary and ternary blends were comparable.

Thermal stability of binary and ternary blends was determined by thermo-gravimetry in nitrogen atmosphere. A two step degradation was observed in all. First step corresponding to HDPE /HDPE-g-MA at ~ 478°C and second step corresponding to PSU at 534°C. The degradation temperature corresponding to both the components remained unaffected in these blends all the samples were stable upto 450°C.From the mass loss in first and second step the blend composition can be evaluated.

Heat deflection temperature values decreased with increase in the HDPE content however the reduction was not much significant up to $\Phi_d = 0.35$ for both binary and ternary blends.

Studies of PSU / HDPE binary and PSU/HDPE/HDPE-g-MA ternary blends show that significant improvement in toughness of polysulfone matrix can be achieved by the addition of HDPE and HDPE-g-MA. The study further indicated that ternary blend PSU / HDPE / HDPE-g-MA (90 / 7.5 / 2.5 by mass) [CH_{10}] showed an optimum set of properties with a reduction in thermal and other mechanical properties (tensile and flexural). In order to overcome the reduction in these properties, mica was used as reinforcing filler. For this purpose, ternary blend i.e sample CH_{10} was selected as matrix and mica powder (untreated) and surface modified with coupling agent were used for the preparation of composites. The filler content was varied from 5 % to 40 % (w/w) i.e. volume fraction (Φ_f) = 0.029 to 0.056

Mechanical properties (tensile and flexural properties) showed increase with filler content. Improvement in modulus by approximately 112 % was observed at $\Phi_f = 0.19$ [sample $CH_{10}M$ (40)] while tensile strength showed an optimum at $\Phi_f = 0.17$ [sample $CH_{10}M$ (30)], the value then decreased, however the parameter remained higher than the

unreinforced matrix [sample CH_{10}]. Composites containing surface modified filler showed better properties than the composites containing untreated mica as filler.

Flexural strength and modulus increased with increase in mica content. An improvement in modulus by 213 % at $\Phi_f = 0.19$ [sample $CH_{10}M$ (40)] was observed. The increase in strength and modulus upon addition of mica filler could be due to greater rigidity imparted by the particulate filler on the matrix. Impact strength decreased by ~ 69 % and elongation by ~ 50 % respectively at $\Phi_f = 0.19$ (untreated mica composites [$CH_{10}M$ (40)]. The decrease in toughness and ductility could be due to the rigidity imparted by the particulate filler to matrix due to which the matrix gets de-bonded from the filler surface leading to generation of stress concentration points and hence rupture was observed at low extensions. Addition of surface treated mica showed an increase in impact strength by ~35 % and elongation at break by ~ 40 % at the same mica loading [sample $CH_{10}T$ (40)].

Scanning electron micrographs of composites showed the presence of flakes having particle of varying length i.e ranging from ~ 7 μm to ~19.5 μm in untreated mica containing composites. In case of composites based on surface modified mica flake size varied between ~ 7 μm to ~ 11.0 μm. Formation of agglomerates was observed at higher loadings of untreated mica filler. Composites with treated mica filler showed better dispersion and adherence of filler particles to the matrix resin. This supports the improved strength properties for the composites containing surface treated mica as filler.

Differential scanning calorimetric studies showed a further reduction in the crystallinity (%) of HDPE in the composites as seen from the heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) values. Inward shift in peak melting temperature and a reduction in

the peak width were also observed supporting the formation of smaller spherulites. The 'T_g' increased from 185°C to 189°C in the composite at Φ_f = 0.19 [sample $CH_{10}M$ (40)]. Addition of surface modified mica further enhanced T_g at all filler loadings. The onset of crystallization was shifted to lower temperature indicating that presence of filler delayed the crystallization of HDPE component.

Thermal stability of composites was evaluated by recording TG traces in nitrogen atmosphere. An increase in the degradation temperature was observed in the presence of mica. This could be due to increase in the viscosity of matrix in the presence of particulate filler and also delay in ignition and flammability due to the presence of mica. As expected wide angle X-ray diffraction studies also showed decrease in crystallinity (%) and spherulite size with increase in the filler content. An approximate reduction by ~ 6 % was observed at Φ_f = 0.19 [sample $CH_{10}M$ (40)]. The spherulitic size at all mica loadings in composites decreased from 150 A° to119A°. The use of surface treated mica resulted in marginal increase in crystallinity by ~2 % for sample $CH_{10}T$ (40).

DMA traces showed two distinct glass transition temperatures corresponding to PSU and HDPE. The 'T_g' corresponding to PSU showed increase from 185°C to 194°C at Φ_f = 0.19 [sample $CH_{10}M$(40)]. The 'α' transition shifted from 58°C to 65°C for sample $CH_{10}M$ (40).

The storage modulus and loss modulus increased with filler content. The tan δ values decreased with increase in mica content. The tan δ values for the surface modified mica containing composites were still less than untreated mica containing composites supporting further reduction in damping.

Heat deflection temperature also showed improvement (~ 8°C) on incorporation of filler. The developed composites showed optimum set of all mechanical and thermal properties at further cost reduction. Composite containing 30 % (w/w) of surface treated mica (sample $CH_{10}T$ (30)) showed maximum improvement in properties and can be considered most suitable for replacement of polysulfone.