

Enhancement of Thermal and Morphological Profile of Polystyrene via Reactive Compatibilization

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Abstract- This research work comprises the goal of improving the thermo-mechanical and morphological properties of Polystyrene (PS). Usually Polymer Blends are made to enhance the good properties of a specific polymer. Here, In order to attain the expected result, the blend films were fabricated through the reactive compatibilization process of two co-reactive polymers i.e. Acid functionalized Aramid (Ar) and Amine modified Polystyrene (APS). Two blend systems, Ar/PS and Ar/APS, were created by simple solution blending and investigated over a range of pristine PS and modified APS ratios. The outcomes has shown that with the increasing percentage of Aramid in both Ar/PS and Ar/APS systems, porosity of copolymers has decreased, which eventually led the to have better strength. Further inspection relayed that an appropriate fraction of Ar is favorable for the enhancement of thermal stability and improved basic copolymer structure. The structural, morphological, thermal and mechanical properties of copolymer were evaluated using FTIR, UTM, TGA, DSC and FESEM. This work is driven towards the enhanced usage and applications of Polystyrene in automobile, construction and packaging industries.

Index Terms- Polystyrene, Aramid, Blends, Reactive Compatibilization, Packaging, Construction, Automobile

I. INTRODUCTION

This project aims to explore morphology and interfacial adhesion of two polymer solutions through Reactive Compatibilization (aramid and PS), and the polymers will be having co-reactive functionalized end-groups. As the statistics show that Polystyrene (PS) covers more than 41% of commodity resin per annum^[1] and is employed in diverse applications ranging from packaging to optical components and foams.^[1-2] On the other hand its poor compatibilization with many polymers, little adhesion to metals, brittleness, insufficient impact resistance and thermal stability up to 250°C reduces^[2] its usage in the automotive and construction industries. Not much of work has been done in this field, especially to enhance the thermo-mechanical properties of Polystyrene.^[3] Our intention is to improve the thermal and mechanical properties of PS by introducing Aramid in it. The method we will opt is reactive compatibilization. Before this process we enhance the reactivity of Aramid by introducing –COCl end group in it. This end group would provide the reaction site and will become the point of attachment with PS, thus forming a graft co-polymer. Merits of this process are quite clear as we expect to get the end product to be thermo-mechanically enhanced, so that its usage can be widened.

II. PROCEDURE

A. Standards and Materials

The objective of the experiment is to create a blend of two immiscible polymers, i.e. Polystyrene and Aramid, by means of simple solution blending apparatus and to test the generated co-polymer by its enhanced properties. Polystyrene (PS) with molecular weight 100,000 was supplied by BDH. Anhydrous Chloride (98%) was received from Organic Compound in the form of fine powder. Multiple Acids were supplied by Merck and used as such.^[4]

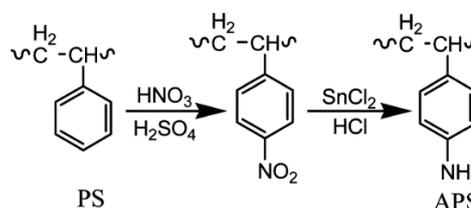
B. Synthesis of Aramid Matrix

Ar was synthesized by the solution polymerization of aromatic diamines and diacid chloride under anhydrous conditions. Two diamines, (1:1 molar ratio), were dissolved in DMA as a solvent under an inert atmosphere. After complete mixing, stoichiometric amount of solution was added at 0°C to avoid any side reaction due to highly exothermic reaction.^[5-6] The reaction between diamine and diacid chloride is very fast; however, an additional 24 h were given for the completion of the reaction. For the end-capping of the aramid solution with the COCl group, an excess of TPC was added with further stirring of 6 h.^[7] The reaction mixture was viscous and brown in color. In order to remove HCl from the aramid solution, stoichiometric amount of TEA was added with constant stirring for 3 h. The precipitates formed were centrifuged, and the pure Ar was separated by decant method.^[8] The structure of synthesized Ar was characterized by FTIR analysis.

C. Functionalization of Polystyrene

Amine functionality was introduced to PS in two steps, i.e., nitration followed by reduction,^[9-10] producing amino-functionalized polystyrene (APS) (Scheme 1) which served as a reactive compatibilizer, being reactive with COCl end groups of the Ar.

SCHEME 1: Synthesis of APS



D. Blend Preparation

Different proportions of PS or APS were blended with aramid matrix giving Ar/PS and Ar/APS blends. Blend samples were obtained by solution mixing using DMAc solvent. Component polymers, weighed to desired composition, were dissolved in the solvent and stirred until the solution became clear. Subsequently, the solvent was evaporated at high temperature. Before characterization, films were dried at relatively higher temperature under vacuum for 72 h.^[11]

III. RESULTS

A. Spectral Analysis

FTIR is performed to confirm modification of PS to APS and results are discussed elsewhere^[12]. FTIR spectra, of both pure PS and APS blend, were compared. Aliphatic C-H asymmetric and symmetric stretching appeared in both pure Ar/PS and Ar/APS blend. Bands at 1760 cm^{-1} , which denote the CO stretch, are present in both blends, thus, confirming the reactive compatibilization of Ar/APS and Ar/PS through anhydride moieties^[13,14]

Presence of a broad band at 3383 cm^{-1} is a proof of the hydrogen bonded amide N-H. Finally, the peak at 1632 cm^{-1} corresponds to amide C=O which is the confirmation of the amide linkage formed in blend system through reactive compatibilization^[15,16]. Thus, FTIR analysis of Ar/APS film confirmed the formation of the graft copolymer in the APS blend system. The presence of intermolecular hydrogen bonding and graft copolymer, formed in situ at the polymer-polymer interface by amidation reaction between co-reactive groups of engineering polymers, can generate stronger interfacial interactions between blend components^[17].

B. Differential Scanning Calorimetry

The glass-transition temperature (T_g) was taken as the midpoint of the change in heat capacity. In the presence of multiple endothermic peaks, the melting temperature (T_m) was taken as the maximum of the endothermic peak temperature. The melting enthalpy was determined from integration of the peak area of endothermic peaks of blend samples. T_g of pristine PS is about 100°C ^[17] and being amorphous PS is devoid of any melting temperature. By adding Ar and making its compatibilized blend, the T_g has decreased down to 79°C which indicated lowered processing temperature.

C. Morphological Analysis

SEM was performed for Ar/APS and Ar/PS blend samples as illustrated in Figs. 1 and 2, respectively. The objective of this study was to assess the morphological changes in the blend samples with or without reactive compatibilization. PS is an amorphous polymer; therefore, it is immiscible with most of the polymers^[5]. Thus, to improve the compatibilization of PS

and to increase the adhesion of immiscible phases, APS was used as amine compatibilizer to reduce the interfacial tension in Ar/APS blends^[18]. Fig. 1 shows the SEM micrographs of cryogenically fractured surface of 10/90 Ar/APS blend with co-continuous structure. Without compatibilization, the domain size of dispersed phase is very large without amine groups on pure PS, and a discrete interface between two phases can be observed, which suggests poor interfacial adhesion between PS and Ar.

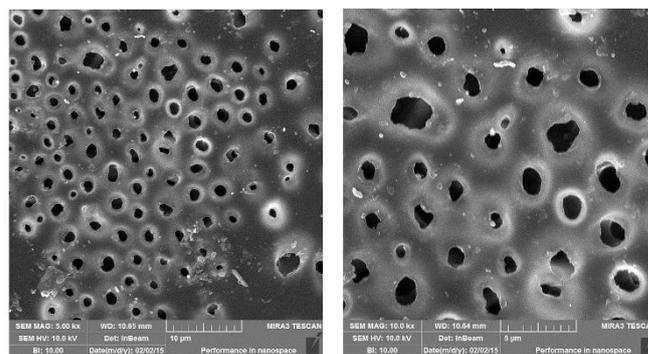


Figure 1: SEM Micrographs of Ar/APS-10/90 blend

There is no bonding at the interface and a droplet-matrix type arrangement is formed in the entire structure.^[19] This provides an explanation for the deterioration of mechanical and thermal properties of the system involving pure PS^[4-6]. Thus, in agreement with the thermal profiles, unmodified PS is immiscible with Ar.

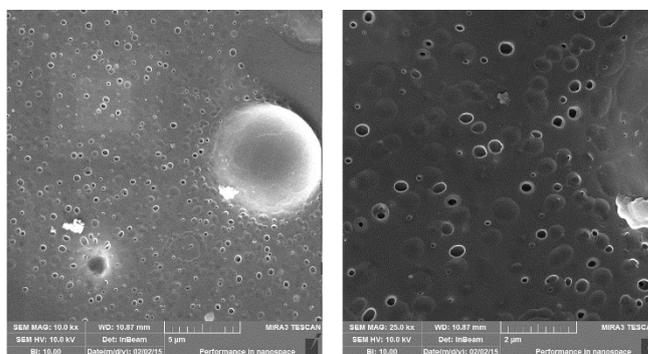


Figure 2: SEM Micrographs of Ar/PS-10/90 blend

All the particles debonded from the matrix are visibly free on the cryo-fractured surfaces. Moreover, surface roughness of particles is an indication of good interfacial adhesion between the blend components but in Fig. 1 surfaces of the particles are smooth lacking any apparent roughness^[20]. The morphological analysis of the functionalized system was performed for Ar/APS-10/90 (Fig. 1) and Ar/PS-10/90 (Fig. 2). With the addition of Ar, the surface of the blends becomes coarse, which is a typical characteristic of compatibilized blends.^[4-7,21] By the addition of APS, the domain size distinctly decreases, and the phase boundaries disappear in the Ar/APS blend. The distinction of the phases is not possible because they are completely miscible with each other resulting increase of entropy and stability of the system

according to Flory Huggins theory^[16]. There are no globules of one system in the other rather they are indistinguishable from each other. From this observation, we can state that APS plays the role of an effective compatibilizer between the immiscible PS and Ar components^[22].

IV. DISCUSSION

Optimal thermal and morphological profiles were depicted by 10-wt. % APS blend, which demonstrated a decrease in T_g value which serves to facilitate processability without deteriorating thermal stability. The plasticization effect of 10-wt. % PS blend will result in cost efficient processing, requiring less fuel consumption. Plasticization effect of reactively compatibilized Ar/APS blends can be studied for ternary blends. Additionally, Rubber toughening of PS can be performed, via reactive compatibilization, to improve mechanical properties of PS.

V. CONCLUSION

PS was successfully amine functionalized (APS), as characterized by spectroscopic analyses i.e. FTIR, confirmed that APS was reactively compatibilized with PS to yield Ar-co-APS copolymer. T_g of the blends was lowered by blending thus facilitating processability. Moreover, Polymeric blend systems show enhancement in the thermal, processing and morphological properties by reactive compatibilization. In-situ reactive compatibilization form Ar-co-APS copolymer with the reduced interfacial tension thus stabilized morphology. The presence of intermolecular hydrogen bonding in APS/PS-co-Ar blends further augmented the compatibilization effect.

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REFERENCES

- [1] C. Manas, K.R. Salil, Industrial Polymers, Specialty Polymers, and Their Applications, Taylor and Francis, 2008, pp. 30–31.
- [2] K. Carlborn, L.M. Matuana, Functionalization of wood particles through a reactive extrusion process, *J. Appl. Polym. Sci.* 101 (2006) 3131–3142.
- [3] J.W. Plunkett, Plunkett's Nanotechnology and MEMS Industry Almanac, Plunkett Research Ltd., 2006.
- [4] S. Shabbir, S. Zulfiqar, Z. Ahmad, M.I. Sarwar, In situ reactive compatibilization of aramid/polystyrene blends using amine-functionalized polystyrene, *Polym. Eng. Sci.* 48 (2008) 1793–1800.
- [5] S. Shabbir, S. Zulfiqar, I. Lieberwirth, A. Kausar, M.I. Sarwar, Compatibilizing effect of functionalized polystyrene blends: a study of morphology, thermal and mechanical properties, *Surf. Interface Anal.* 40 (2008) 906–913.
- [6] S. Shabbir, S. Zulfiqar, S.I. Shah, Z. Ahmad, M.I. Sarwar, Synthesis, morphology and properties of self-assembled nanostructured aramid and polystyrene blends, *J. Phys. Chem. B* 114 (2010) 13241–13248.
- [7] S. Shabbir, S. Zulfiqar, M. Ishaq, M.I. Sarwar, Miscibility studies of PVC/Aramid blends, *Colloid Polym. Sci.* 286 (2008) 673–681.
- [8] G.S. Rule, T.K. Hitchens, Fundamentals of Protein NMR Spectroscopy, Springer, Netherlands, 2006.
- [9] L.D.S. Yadav, Organic Spectroscopy, Kluwer Academic Publishers, Dordrecht(NL), 2005.
- [10] K.R. Sharma, Polymer Thermodynamics: Blends, Copolymers and Reversible Polymerization, first ed., CRC Press, 2011.
- [11] J.S. Higgins, J.E.G. Lipson, R.P. White, A simple approach to polymer mixture miscibility, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 368 (2010) 1009–1025.
- [12] L.M. Robeson, Polymer Blends: A Comprehensive Review, Hanser, Munich, 2007, pp. 24.
- [13] Z.-H. Wu, Y.-Q. Zhao, G.-Z. Zhang, Z.-T. Yang, J.-P. Qu, Multifractal analysis on dispersion of immiscible high-density polyethylene/polystyrene blends processed via polymer vane plasticating extruder, *J. Appl. Polym. Sci.* (2013), <http://dx.doi.org/10.1002/APP.39434>.
- [14] R.P. Singh, M. Zhang, D. Chan, Toughening of a brittle thermosetting polymer: effects of reinforcement particle size and volume fraction, *J. Mater. Sci.* 37(2002) 781–788.
- [15] Y.-J. Wang, W. Liu, Z. Sun, Effects of glycerol and PE-g-MA on morphology, thermal and tensile properties of LDPE and rice starch blends, *J. Appl. Polym. Sci.* 92 (2004) 344–350.
- [16] U. Ratanakamnuan, D. Aht-Ong, Preparation and characterization of low-density polyethylene/banana starch films containing compatibilizer and photosensitizer, *J. Appl. Polym. Sci.* 100 (2006) 2717–2724.
- [17] X. Wei, Y. Lu, L. Huang, Mechanical properties and morphology of UHMWPE/PC/HDPE-g-MAH blends, *Polym. Plast. Technol. Eng.* 50 (2011) 190–195.

[18] L.M. Matuana, J.J. Balatinecz, R.N.S. Sodhi, C.B. Park, Surface characterization of esterified cellulosic fibers by XPS and FTIR spectroscopy, *Wood Sci. Technol.* 35(2001) 191–201.

[19] C. Koning, M.V. Duin, C. Pagnouille, R. Jerome, Strategies for compatibilization of polymer blends, *Prog. Polym. Sci.* 23 (1998) 707–757. S. Shabbir et al. / *Thermochimica Acta* 573 (2013) 213–219

[20] M. Kazayawoko, J.J. Balatinecz, L.M. Matuana, Surface modification and adhesion mechanisms in wood fiber-polypropylene composites, *J. Mater. Sci.* 34(1999) 6189–6199.

[21] M. Liu, Z. Liu, S. Ding, S. Li, L. Zhang, Graft copolymerization of oleic acid on low-density polyethylene in the molten state, *J. Appl. Polym. Sci.* 90 (2003) 3299–3304.

[22] C.A. Orr, A. Adedeji, A. Hirao, F.S. Bates, C.W. Macosko, Flow-induced reactive self-assembly, *Macromolecules* 30 (1997) 1243–1246.