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Research Paper

Investigations of the Influence of Compatibilizer and TiO_2 Filler on the Properties of Thermoplastic Polyurethane/Polyolefins Blends

***Thomas Merlin[1], Kamble Atul D.[2], John Neetha[3]**
[1]Institute of Science and Technology for Applied Studies and Research (ISTAR), Vallabh Vidyanagar, (Guj), INDIA
[2]Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat, INDIA
[3]Matha College of Technology, Ernakulum, Manakkppadi, N. Paravur, Kerala, INDIA

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Abstract: *Melt blending of thermoplastic polyurethane (TPU) with polyolefins (PO) can lower the cost and improve mechanical and chemical properties. Since thermoplastic polyurethane and polyolefins are completely immiscible polymers, property enhancement cannot be attained. Effect of incorporation of polypropylene copolymer (PPCP), TPU-g-MA, TPU-g-AA as compatibiliser on the miscibility of the blends and effect of TiO_2 filler to enhance the mechanical properties were studied. Blends were produced by melt mixing using a single screw extruder. Mechanical and morphological properties were studies. The results show that the blend of thermoplastic polyurethane (TPU)/PO's with suitable compatibiliser and mica gives excellent performance in all aspects.*

Keywords: Polymer blend, TiO_2, filler, morphology, SEM.

Introduction

Blending is important not only for obtaining polymer materials with excellent properties, but for improving their processing capabilities and reducing the product costs. In academic research and industrial applications, multiphase complex systems are now obtained through blending [1]. As the immiscible blends are thermodynamically unstable, compatibiliser must be added to stabilize the morphology. This process of stabilizing polymer blends is commonly called compatibilisation [2]. The incorporation of particulate fillers into polymer matrices has been an extended technique to improve or modify some properties of neat polymers [3]. Traditionally polymers are reinforced with micrometer fillers to gain higher strength and stiffness, to improve solvent or fire resistance and simply to reduce cost. However, these micro fillers also impart several drawbacks such as brittleness and opacity. Nanocomposites, for which at least one dimension of the filler is less than 100 nm, give a new way to overcome the limitations of traditional counterparts [4]. Among many nanocomposites precursors, TiO_2 nanopowder is increasingly being investigated because it is non-toxic, chemically inert, corrosion resistant and of low cost.

It also has high refractive index, broadband UV filter, kills bacteria by photo irradiation and high hardness. Literature has also shown that nanoscale TiO_2 reinforcement brings new optical, electrical, physiochemical properties attained at very low TiO_2 content, which make polymer TiO_2 nanocomposites a promising new class of materials. One can foresee that they will be commercially beneficial for widespread fields. M. Kader et al. studied the effects of fillers on the mechanical, dynamic mechanical and aging properties of rubber-plastic binary and ternary blends derived from acrylic rubber, fluorocarbon rubber, and multifunctional acrylates [5]. As the requirements for the production of new polymers with the best cost/performance balance are increasing, so the research based on the study of polymer blends and polymer-filler composites is extensive [6]. Calcium carbonate ($CaCO_3$), clay, mica and TiO_2 are the inorganic materials which are most widely used as filler in polymers [7, 8, 9, 10, 11]. The incorporation of fillers is done to modify the mechanical properties and morphology of the polymers. This filler improves Young´s Modulus, but it also decreases impact strength, toughness and elongation at break, it is generally accepted that compatibilisers serve as polymeric surfactants for immiscible blends by migration to the interface and thereby lowering the interfacial tension.

In the present study attempts have been made to use particulate TiO_2 as filler for TPU/PO blends with and without compatibiliser, with the objective to investigate the potential of this TiO_2 in bringing about improvements in mechanical, morphological and thermal properties on the of the final compound.

Material and Methods

Low density polyethylene (LDPE), Grade: 24FS040, High Density Polyethylene (HDPE), Grade: MA60200, Polypropylene (PP), Grade: H110MA, supplied by Reliance India Ltd, Baroda. Thermoplastics polyurethane (TPU) with 85 shore A hardness, supplied by Bayer, India. Engage: polyolefin elastomer, grade 8402, supplied by DuPont Dow Elastomers, USA, ethylene vinyl acetate copolymer (EVA) and PPCP (Grade: MI 1530) supplied by Reliance India Ltd, Baroda, commercial TiO_2 filler.

Blending process: The thermoplastic polyurethane and polyolefins were preheated for three hours. The blends of TPU and Polyolefins (PO) with and without compatibiliser were made using single screw extruder. Composition of the TPU/PO blends were 95/5, 90/10, 85/15, 80/20, 75/25 and 70/30 and mixed with 20 parts of each TiO_2 filler on a two roll mill. These blends were grinded and used for making test specimen. Specimens for different mechanical testing were prepared using injection moulding machine.

Analysis of mechanical properties: The tensile strength and tensile modulus of all the blends were carried out at room temperature according to ASTM D-638.The flexural strength and flexural modulus of blends were done according to ASTM D-790.The izod impact strength test of all blends were carried out at room temperature according to ASTM D-256. Shore D hardness of the blends was determined according to ASTM D-2240.

Morphological properties: The fracture surface of the blend samples were analyzed with a Philips, Scanning Electron Microscope (SEM). The surface morphology of the TPU/PO's blends with or without compatibiliser was examined in scanning electron microscope in the inert atmosphere of nitrogen gas.

Results and Discussion

Mechanical Properties

Tensile properties: The effectiveness of the TiO_2 filler into the blend of TPU/PO's with and without compatibiliser was investigated. In each case 20 percent TiO_2 filler was used in blends. Tensile strength of TPU/polyolefins with and without TiO_2 and compatibiliser is shown in figures 1-3 using 20 parts loading of the TiO_2 as filler. The tensile strength of the TPU/PO's blends without compatibiliser and TiO_2 was found lower than compatibiliser and TiO_2 filled TPU/PO's blends. The tensile strength was found to increase with addition of TiO_2 filler in polymer blend matrix in the blends TPU/LDPE, TPU/HDPE and TPU/PP.

Figures 4-6 shows the tensile modulus of the TPU/PO's blends with and without TiO_2 and compatibiliser. Addition of the TiO_2 in the polymer blends of TPU/LDPE decreases the tensile modulus. This may be due to poor dispersion of filler into blend matrix and hence reduction in the toughness of the blend. In TPU/HDPE blends, a slight increase in the tensile modulus was observed. In TPU/PP blends increase the tensile modulus was observed as compared with blend without TiO_2 and compatibiliser. The increased tensile strength/modulus is attributed to the increased toughness of blend by the addition of filler. When filler is introduced into a polymeric material, good dispersion of the filler particle into the polymer blend matrix due to particles are sufficiently small to enable good distribution in the matrix [10].

Percentage elongation of the TPU/PO's blends with TiO_2 filler decreases with increasing amount of polyolefins as shown in figure 7-9. As both TPU and LDPE are flexible in nature, the blend of TPU/LDPE gives more elongation than the TPU/HDPE and TPU/PP blends with TiO_2 filler. The percentage elongation of the TPU/LDPE and TPU/HDPE blends was found to be increased with the addition of TiO_2 into the blend as compared to blend without TiO_2. The decrease in percentage elongation of the TPU/PP blends may be due to poor adhesion between blend matrix and TiO_2.

Flexural properties: Flexural strength and flexural modulus of the TPU/PO'S blends with and without TiO_2 and compatibiliser are shown in the figure10-12 and 13-15 respectively. With addition of TiO_2 in TPU/PO's blends, flexural strength was found to be increased as shown in figure 10-12. In the blends TPU/LDPE, TPU/HDPE and TPU/PP, the flexural strength was found to be increased with addition of TiO_2 filler into the polymer blends as compared to the blends without TiO_2 and compatibiliser.

Flexural modulus of the TPU/PO's blend with and without TiO_2 and compatibiliser is shown in figures 13-15. Flexural modulus of TPU/PO's blends was found to be increased with addition of TiO_2 as compared to the blend without TiO_2 and compatibiliser. Flexural strength and flexural modulus of the blends also increases with addition of polyolefin at the certain level and then dropped. It is well known that the flexural modulus of a filled system depends on the properties of components, fillers and matrix, the flexural modulus of TiO_2 filled TPU/PO's blends is higher than that of conventional blends without TiO_2 and compatibiliser. It could be the good interface between the filler particle and blend matrix that result in better load transfer.

Impact strength: The variations of impact strength of TPU/PO's blends with and without TiO_2 (20 % by wt) and compatibiliser are shown in figures 16-18. The toughening efficiencies of the TiO_2 particles were found to be good in the blends of TPU/LDPE, TPU/HDPE and TPU/PP with compatibiliser. Impact strength of the TPU/PO's blends was found to be increased after the addition of the TiO_2 filler as compared to the blend without filler and compatibiliser. Improvement in the impact strength may be due to the toughness effect of the filler. The uniform distribution of small particles of the TiO_2 blocks the crack propagation in to the polymer blend matrix resulting in increase in the impact strength.

Hardness: Shore D hardness of the TPU/PO's blends with and without TiO_2 filler and compatibiliser is shown in the figures 19-21. As TiO_2 is added in TPU/PO's blends the hardness increases, as TPU is very flexible in nature, polyolefins increases the toughness in TPU/PO's blends matrix along with the filler. TPU/LDPE gives the lower hardness than all other blends such as TPU/HDPE, and TPU/PP blends. An increase in the hardness may be due to the improvement in the toughness of the polymer blends after addition of TiO_2 filler.

Morphological Properties: The morphological and particle distribution of TPU/PO's blends with and without TiO_2 sites were studied using SEM. The images of SEM of the blend TPU/PO's with compatibiliser and TiO_2 are shown in figures 22a-22*l*. The presence of cryogenic fracture along the boundaries of the blends without compatibiliser indicates the immiscibility of the two polymers into TPU/PO's blends without compatibiliser and filler. TiO_2 particles are uniformly dispersed within the TPU/PO's blends matrix. Due to good dispersion of TiO_2 filler into the blends, the interparticle distance and blend phase are found to decrease and display significantly finer morphology. This further corroborates that the TPU/PO's with 20 wt % TiO_2 produced relatively improved mechanical properties of the blends. The SEM images also shows that the TiO_2 particles were more reinforced in blends matrix.

Conclusion

Polypropylene copolymer (PPCP), TPU-g-MA, and TPU-g-AA were found to be good compatibilisers for the TPU/PO blends. Addition of TiO_2 as filler was found to improve the mechanical properties such as tensile strength, impact strength, and hardness, but decreases the elongation into the TPU/PO's blends. SEM images shows that the addition of small quantities of compatibiliser and TiO_2 can improve the mechanical properties of the blends studied.

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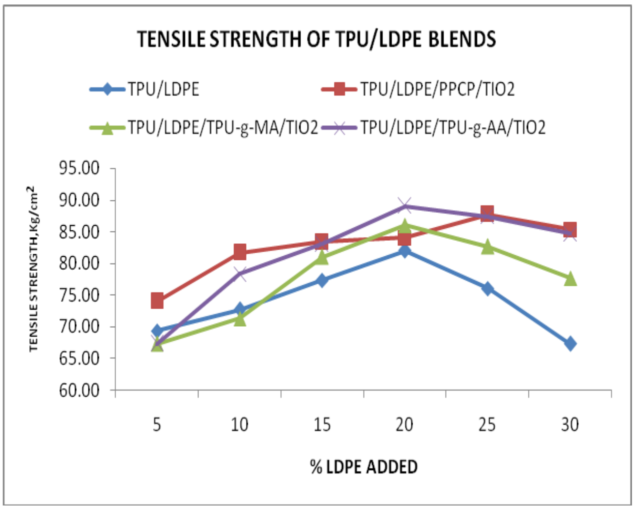

Figure 1: Tensile strength of TPU/LDPE blends with and without TiO_2

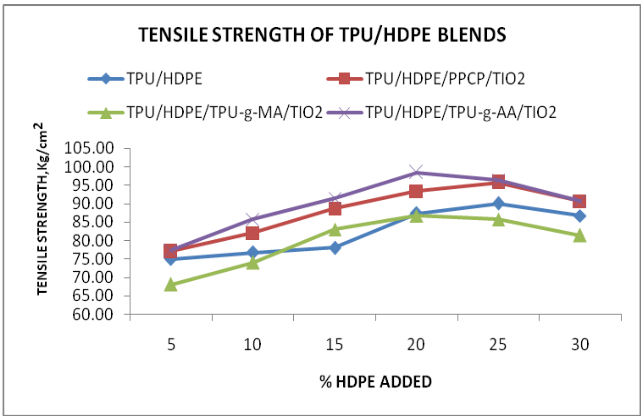

Figure 2: Tensile strength of TPU/HDPE blends with and without TiO_2

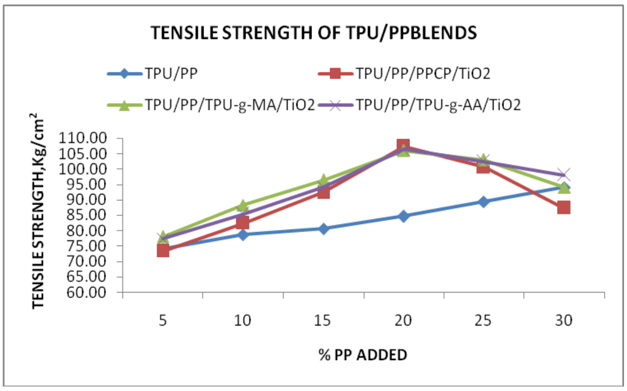

Figure 3: Tensile strength of TPU/PP blends with and without TiO_2

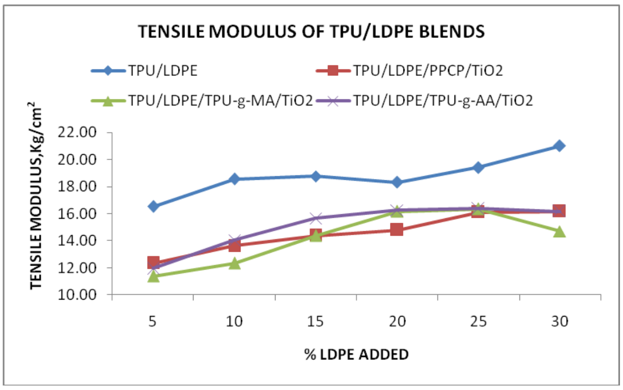

Figure 4: Tensile modulus of TPU/LDPE blends with and without TiO_2

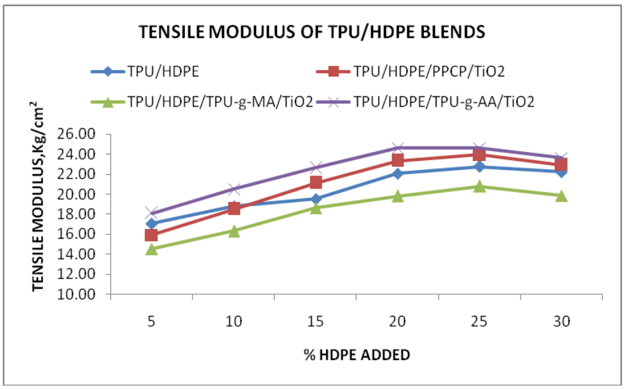

Figure 5: Tensile modulus of TPU/HDPE blends with and without TiO_2

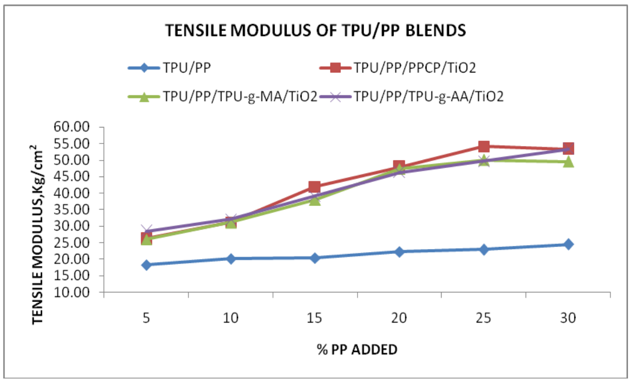

Figure 6: Tensile modulus of TPU/PP blends with and without TiO_2

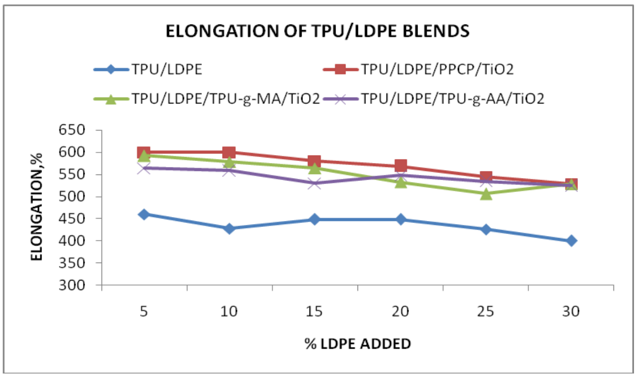

Figure 7: Elongation of TPU/LDPE blends with and without TiO_2

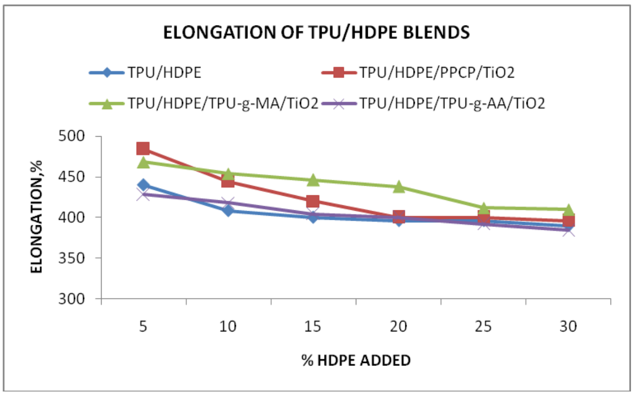

Figure 8: Elongation of TPU/HDPE blends with and without TiO_2

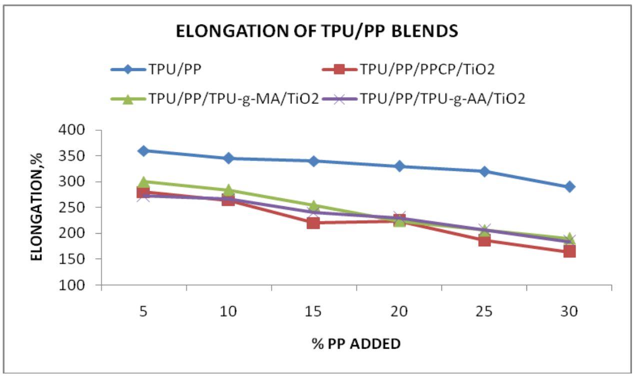

Figure 9: Elongation of TPU/PP blends with and without TiO_2

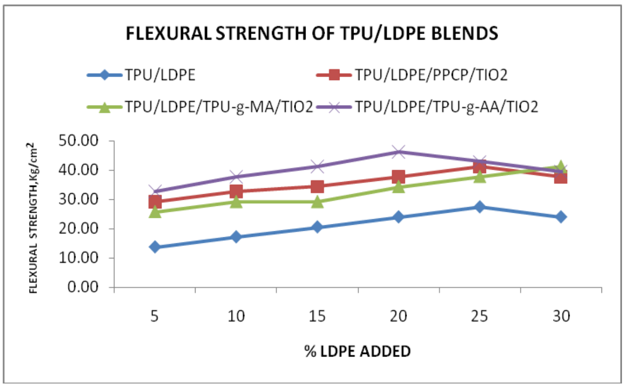

Figure 10: Flexural Strength of TPU/LDPE blends with and without TiO_2

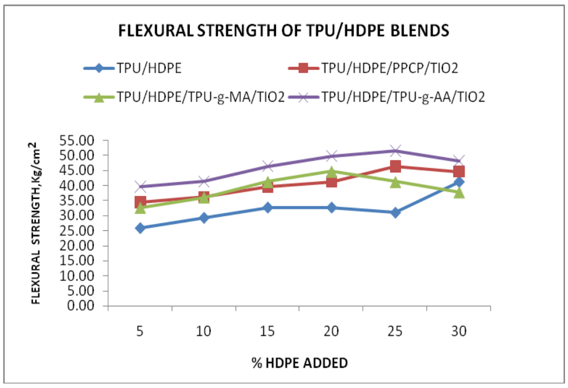

Figure 11: Flexural Strength of TPU/HDPE blends with and without TiO_2

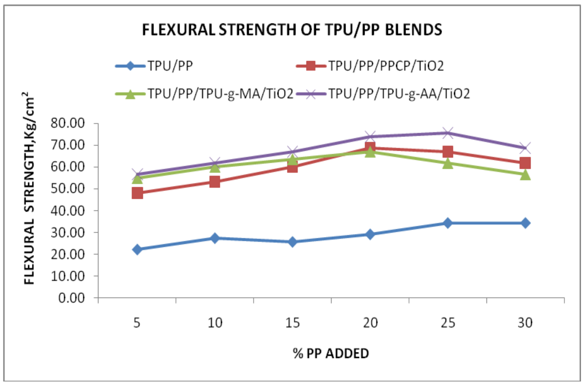

Figure 12: Flexural Strength of TPU/PP blends with and without TiO_2

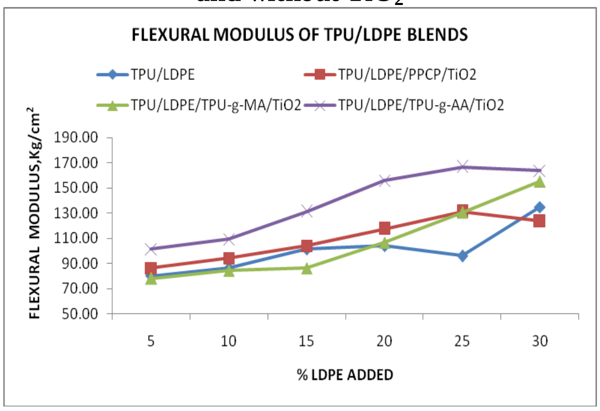

Figure 13: Flexural modulus of TPU/LDPE blends with and without TiO_2

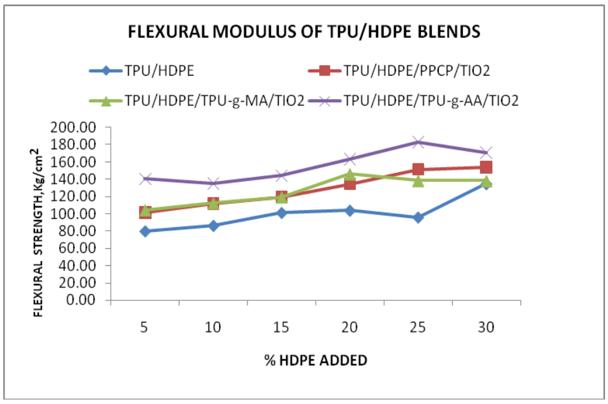

Figure 14: Flexural modulus of TPU/HDPE blends with and without TiO_2

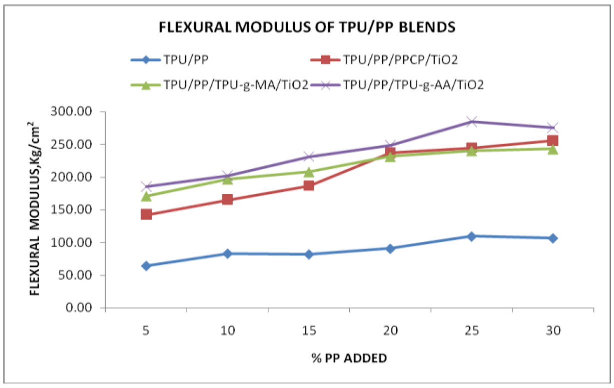

Figure 15: Flexural modulus of TPU/PP blends with and without TiO_2

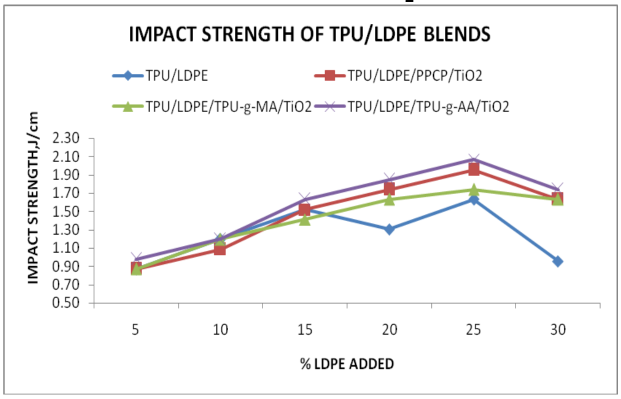

Figure 16: Impact Strength of TPU/LDPE blends with and without TiO_2

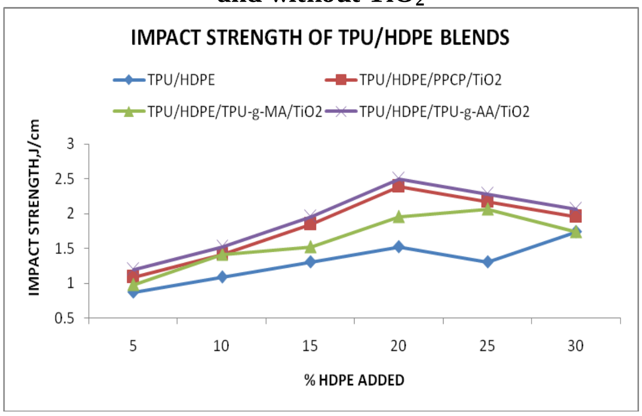

Figure 17: Impact Strength of TPU/HDPE blends with and without TiO_2

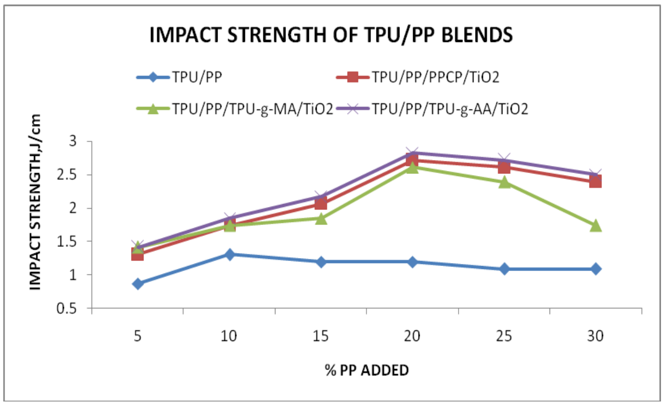

Figure 18: Impact Strength of TPU/PP blends with and without TiO_2

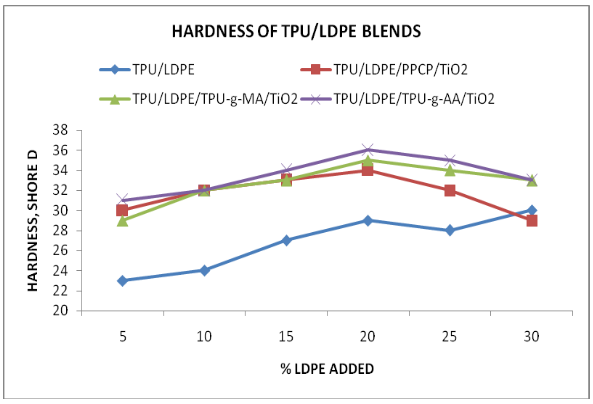

Figure 19: Hardness of TPU/LDPE blends with and without compatibiliser and TiO_2

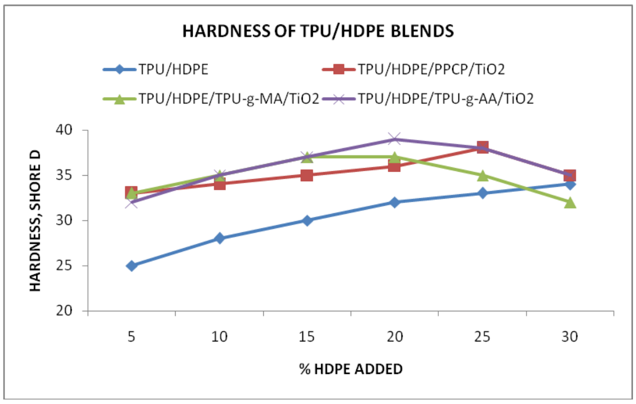

Figure 20: Hardness of TPU/HDPE blends with and without compatibiliser and TiO_2

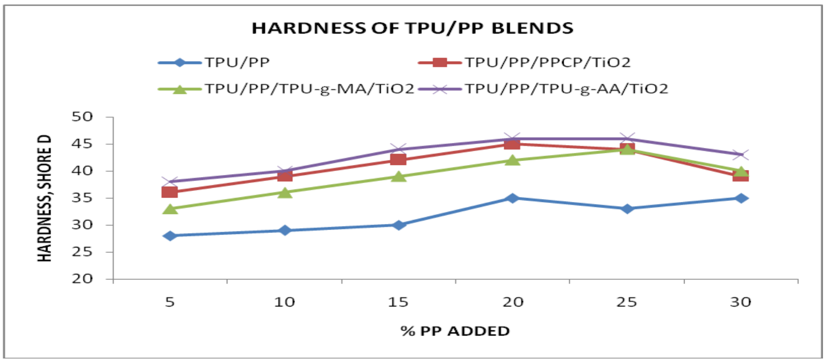

Figure 21: Hardness of TPU/PP blends with and without compatibiliser and TiO_2

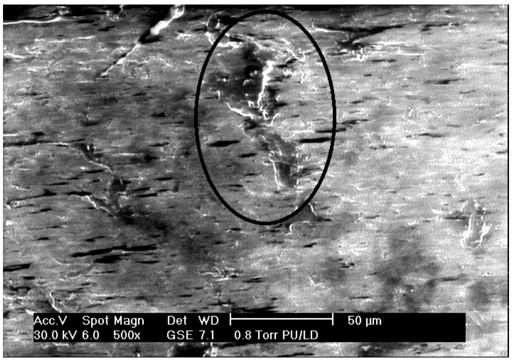

Fig 22a: SEM of TPU/LDPE

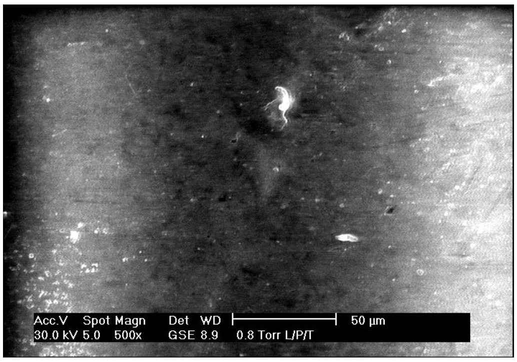

Figure 22b: SEM of TPU/LDPE/PPCP/TiO_2

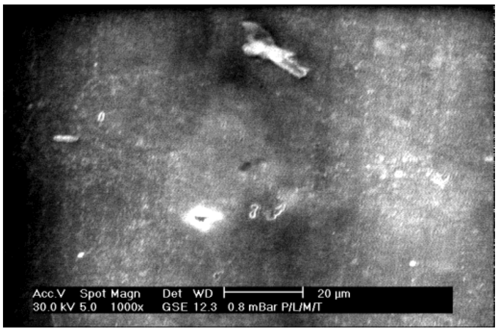

Fig 22c: SEM of TPU/LDPE/TPU-g-MA/TiO_2

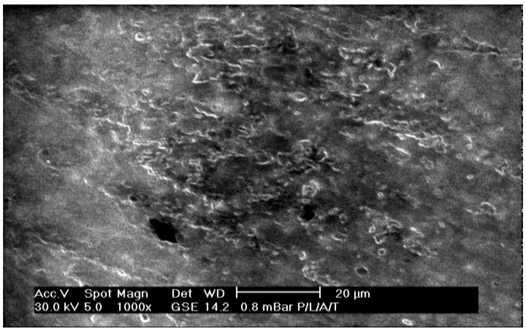

Fig22d: SEM of TPU/LDPE/PPCP/TiO_2

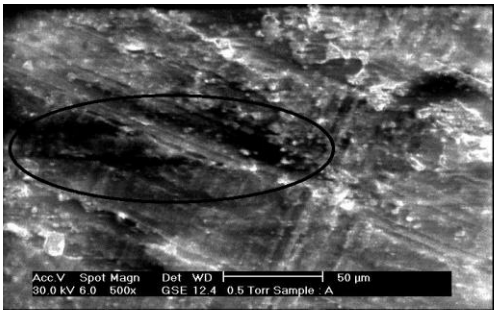

Fig 22e: SEM of TPU/HDPE

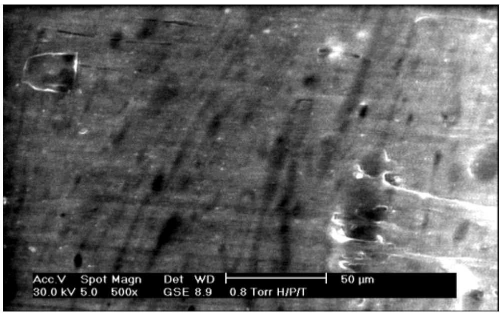

Fig22f: SEM of TPU/HDPE/PPCP/TiO_2

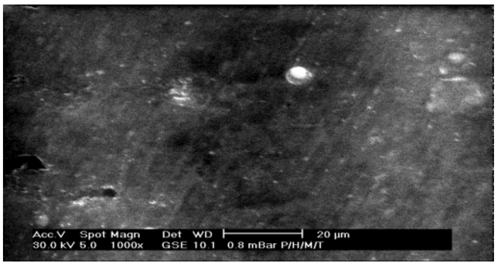

Fig 22g: SEM of TPU/HDPE/TPU-g-MA/TiO_2

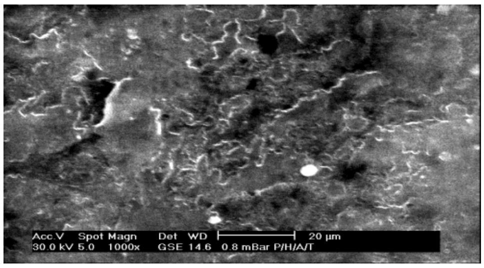

Fig22h: SEM of TPU/HDPE/TPU-g-AA/TiO_2

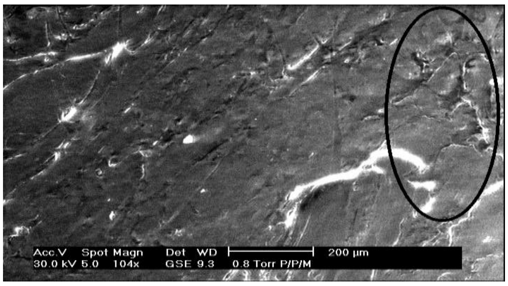

Fig 22i: SEM of TPU/PP

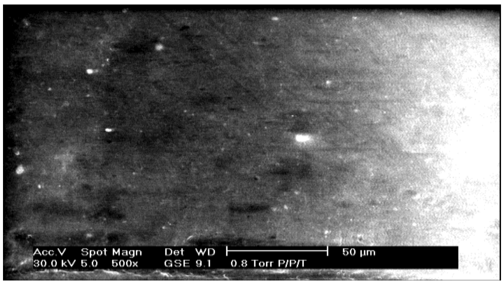

Fig22j: SEM of TPU/PP/PPCP/TiO_2

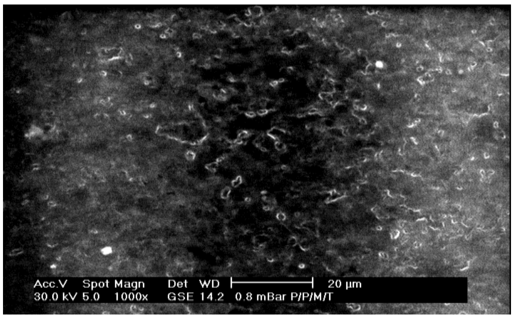

Fig 22k: SEM of TPU/PP/TPU-g-MA/TiO_2

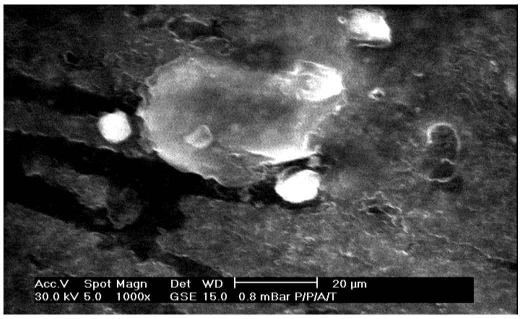

Fig22 *l*: SEM of TPU/PP/TPU-g-AA/TiO_2