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Investigations of the influence of compatibilizer and clay filler on the properties of thermoplastic polyurethane/polyolefins blends

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ABSTRACT

Melt blending of thermoplastic polyurethane (TPU) with polyolefins (PO's) can lower the cost and improve mechanical and chemical properties. Since TPU and PO's 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 clay filler on the mechanical properties were studied. Blends were produced by melt mixing using a single screw extruder. Mechanical and morphological properties were studied. The results show that the blend of thermoplastic polyurethane (TPU)/PO's with suitable compatibiliser and clay gives excellent performance in all aspects.

Keywords: Polymer blend, compatibiliser, clay, filler, morphology, SEM.

INTRODUCTION

It is well-known that blending is important not only for obtaining polymer materials with excellent properties, but for improving their processing capabilities and reducing the product costs. Owing to the needs of academic research and industrial application, most polymer materials are not homogeneous systems any longer, but multiphase complex systems obtained through blending [1]. Immiscible blends are thermodynamically unstable; the 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]. The very large commercial importance of polymers has also been driving an intense investigation of polymeric composites reinforced by particulates, fibers, and layered inorganic fillers [4, 5]. In particular, in the case of layered inorganic fillers, talc and mica had been traditionally attracting the most interest. However, recent advances in polymer/clay and polymer/layered-silicate nanocomposite materials [6, 7] have inspired efforts to disperse clay-based fillers in almost any polymer available, usually expecting that complete exfoliation of the inorganic fillers in the polymer would yield the best performing systems. It has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays [8]. The addition of fillers and reinforcements has played a major role in the polymer industry [9]. Many different types of fillers have been introduced in polymers to provide a synergistic improvement to processability and final product properties like tensile strength, heat distortion temperatures, thermal and electrical conductivities, and enhanced gas barrier properties [10, 11]. It has also been established that addition of high fractions of micron sized fillers has resulted in considerable changes in rheological properties. Examples of these fillers are small solid particles of carbon black, calcium carbonate, glass fibres and talc and their particle size range is usually in the micron-level [10-13]. Over the last two decades, the addition of nano-sized layered silicates in

plastics has been found to offer improvements to the above-mentioned properties with just a small quantity, typically in the range of 3-5 wt%.

MATERIALS AND METHODS

2.1 Materials

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

2.2 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 filler on a two roll mill. These blends were ground and used for making test specimen. Specimens for different mechanical testing were prepared using injection moulding machine.

2.3 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.

2.4 Thermal and morphological properties

Thermal properties of the blends were studied using with Perkin-Elmer, DSC-PYRIS-I differential scanning calorimeter (DSC). 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

3.1. Tensile strength, Tensile Modulus and Elongation

The effectiveness of the clay filler into the blend of TPU/PO's with and without compatibiliser was investigated. In each blend 20 percent of filler was used. Tensile strength of TPU/polyolefins with and without filler and compatibilisers is shown in figure 1a, 1b and 1c using 20 parts loading of the clay as filler. The tensile strength of the TPU/LDPE blends with compatibiliser and clay was found to be higher than the TPU/LDPE blends without clay. PPCP, TPU-g-MA and TPU-g-AA were used as compatibilisers. Similarly the tensile strength of the blends of TPU/HDPE and TPU/PP was found to increase after addition of clay filler in polymer blend matrix.

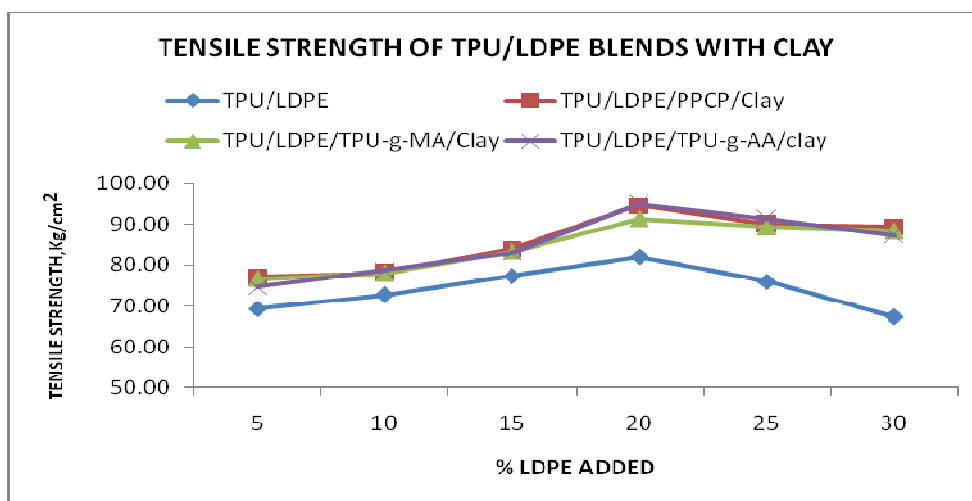


Fig 1a. Tensile strength of TPU/LDPE blends with and without clay & compatibiliser

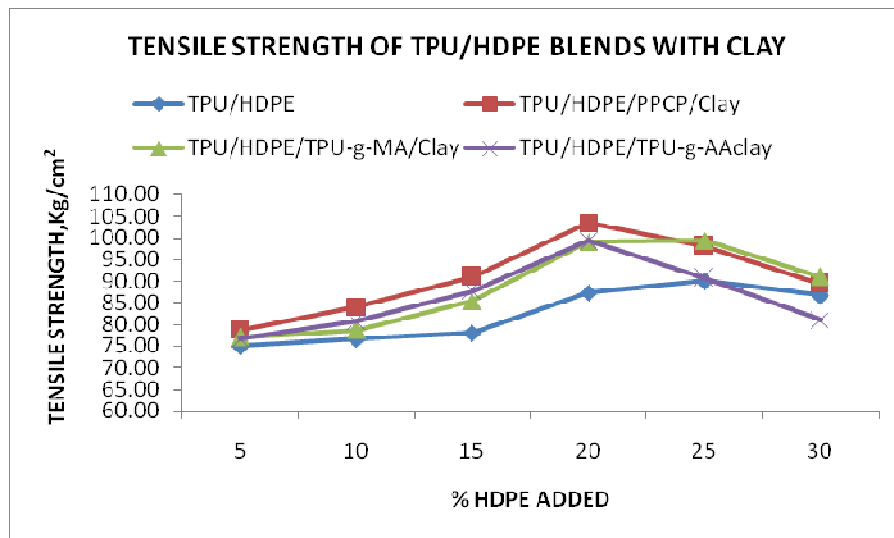


Fig1b. Tensile strength of TPU/HDPE blends with and without clay & compatibiliser

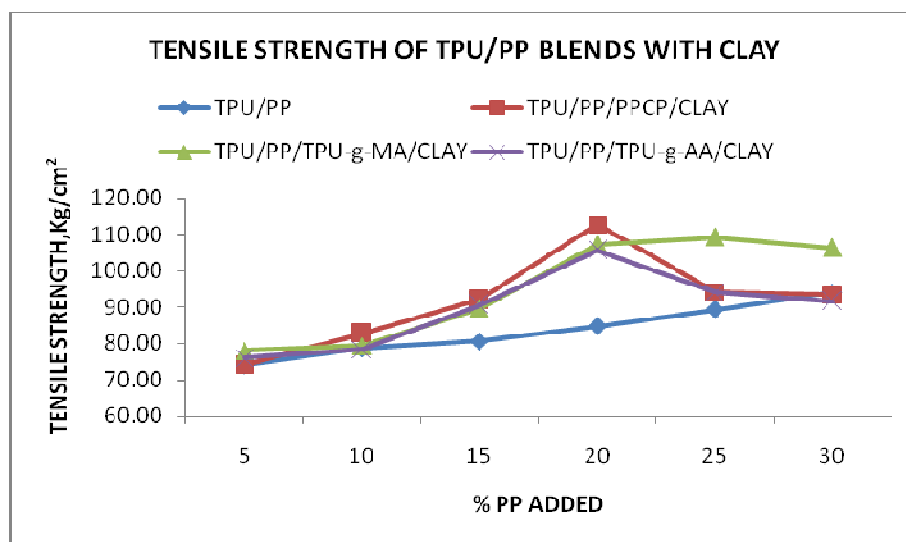


Fig 1c. Tensile strength of TPU/PP blends with and without clay & compatibiliser

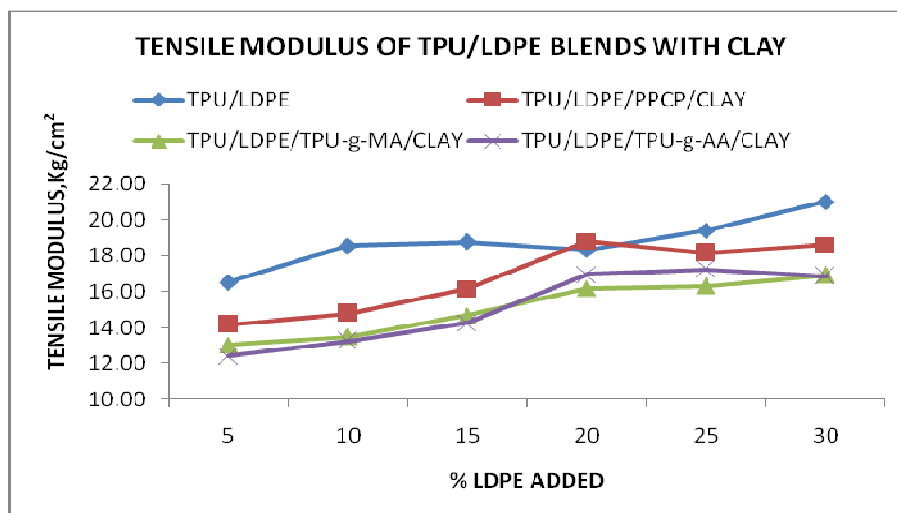


Fig 2 a. Tensile Modulus of TPU/LDPE blends with and without clay & compatibiliser

Figures 2a,2b and 2c show the tensile modulus of the TPU/PO's blends with and without clay and compatibiliser. Addition of the clay in the polymer blends of TPU/LDPE blends increases the tensile modulus of the blends as compared with TPU/LDPE blends without compatibiliser and clay. Similarly, TPU/HDPE and TPU/PP with compatibiliser and clay filler shows improved tensile modulus as compared with conventional blends without clay and compatibiliser. Tensile modulus of the blends increases with addition of polyolefin at certain level then the properties were found to be decrease. When filler is introduced into a polymeric material, the ideal is that it has regular granulometry and its particles are sufficiently small to enable good distribution in the matrix [14]. An increase in tensile properties means that stress has been transferred from the blend matrix to the filler particle.

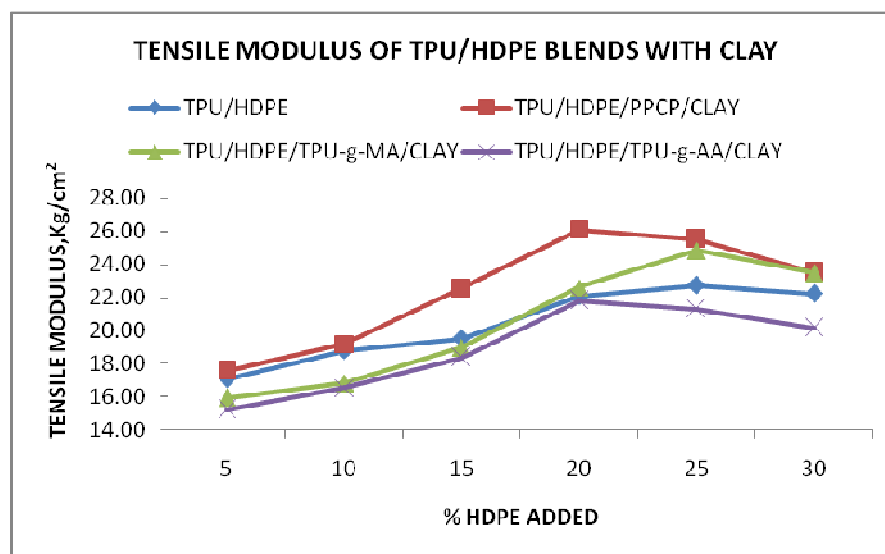


Fig 2 b. Tensile Modulus of TPU/HDPE blends with and without clay & compatibiliser

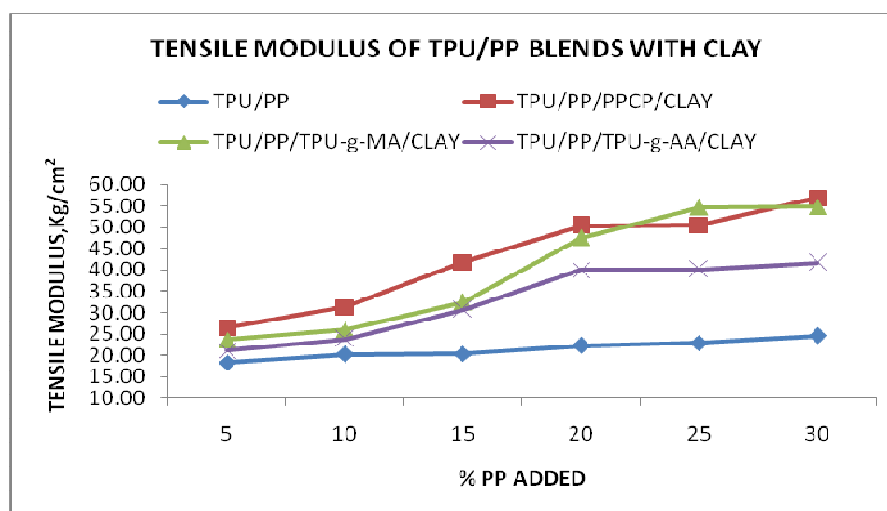


Fig 2 c. Tensile Modulus of TPU/PP blends with and without clay & compatibiliser

Percentage Elongation of the TPU/PO's blends except TPU/PP with clay filler and compatibiliser was found to be more than that of blends without clay and compatibiliser as shown in figure 3a,3b and 3c. The increase in flexibility of TPU and LDPE may be responsible for increased elongation than that in TPU/HDPE. In the figure 3c, TPU/PP blends show decreasing elongation with the addition of clay into polymer blend matrix. The decrease of percentage elongation of the TPU/PP with increasing amount of PP in to the blend may be due to poor interfacial adhesion between two polymers after the addition of clay filler into blend.

3.2 Flexural properties

Flexural strength and flexural modulus of the TPU/PO's blends with and without clay filler and compatibiliser are shown in the figure 4a-4c & 5a-5c respectively. TPU/PO's blends with compatibiliser and clay filler show

increase in flexural strength as compared with blends without compatibiliser and clay filler as shown in figure 4. In each of the blends such as TPU/LDPE, TPU/HDPE and TPU/PP, the clay content was 20 wt %. With increase in the percentage of the polyolefins into polymer blends, flexural modulus of the polymer blends increases up to 20 wt% of Polyolefins contents and beyond 20 % wt it was found to decrease. An addition of clay filler into the blend also increases the flexural strength as compared with blend without clay and compatibiliser. 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 clay filled TPU/PO's blends is higher than that of conventional blends without clay. The increase in flexural properties may be due to the fact that good particle dispersion in the blend matrix enhanced the adhesion between filler and blend matrix.

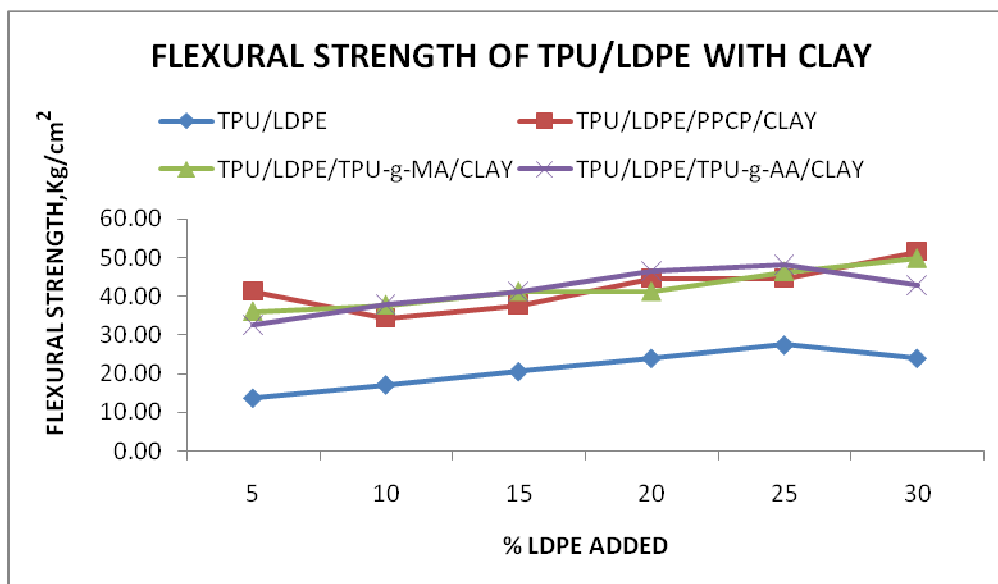


Fig 4a. Flexural Strength of TPU/LDPE with and without clay and compatibiliser

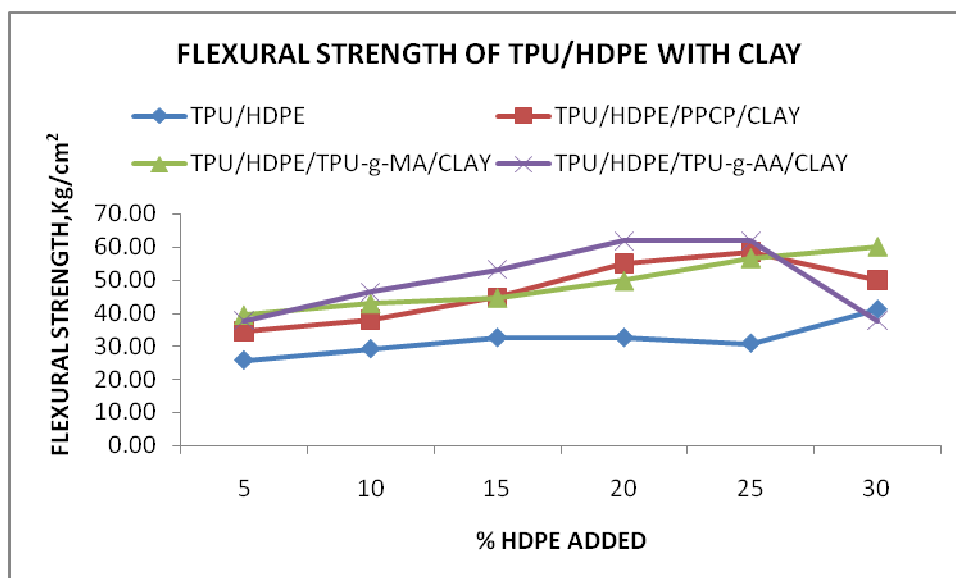


Fig 4b. Flexural Strength of TPU/HDPE with and without clay and compatibiliser

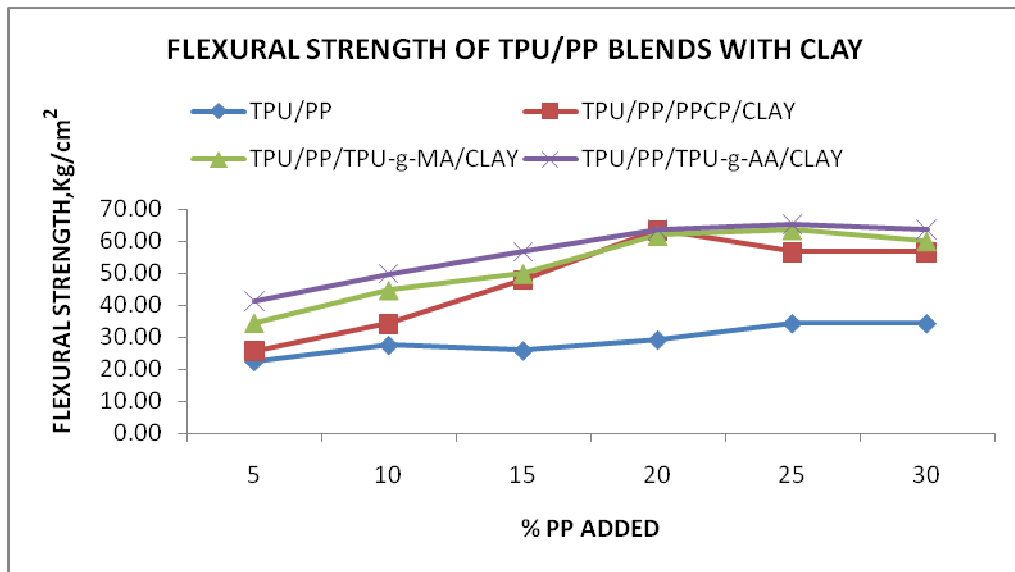


Fig 4c. Flexural Strength of TPU/PP with and without clay and compatibiliser

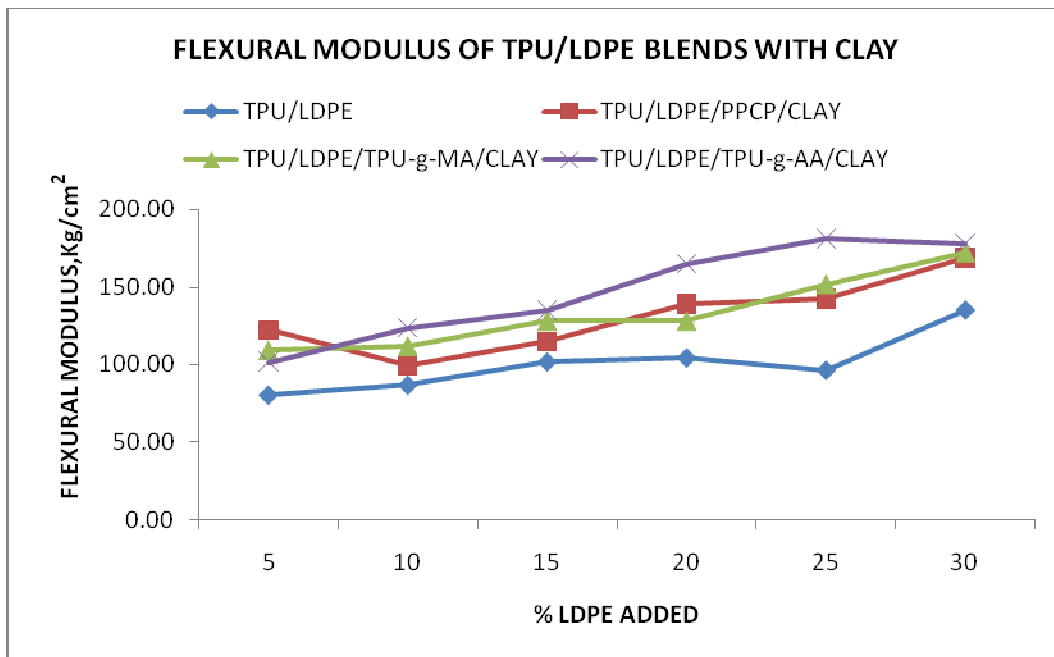


Fig 5a .Flexural Modulus of TPU/LDPE with and without clay and compatibiliser

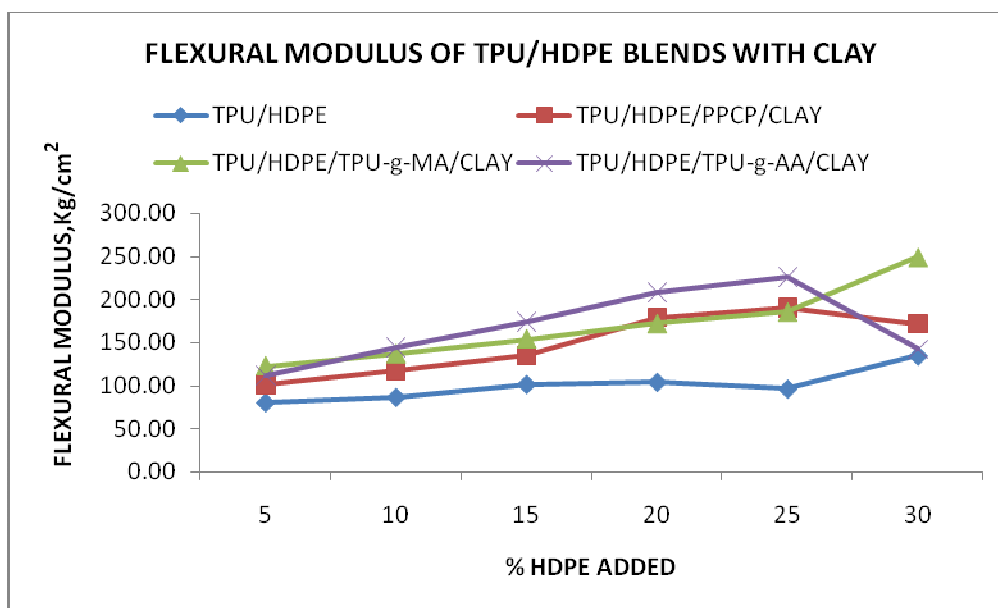


Fig 5b .Flexural Modulus of TPU/HDPE with and without clay and compatibiliser

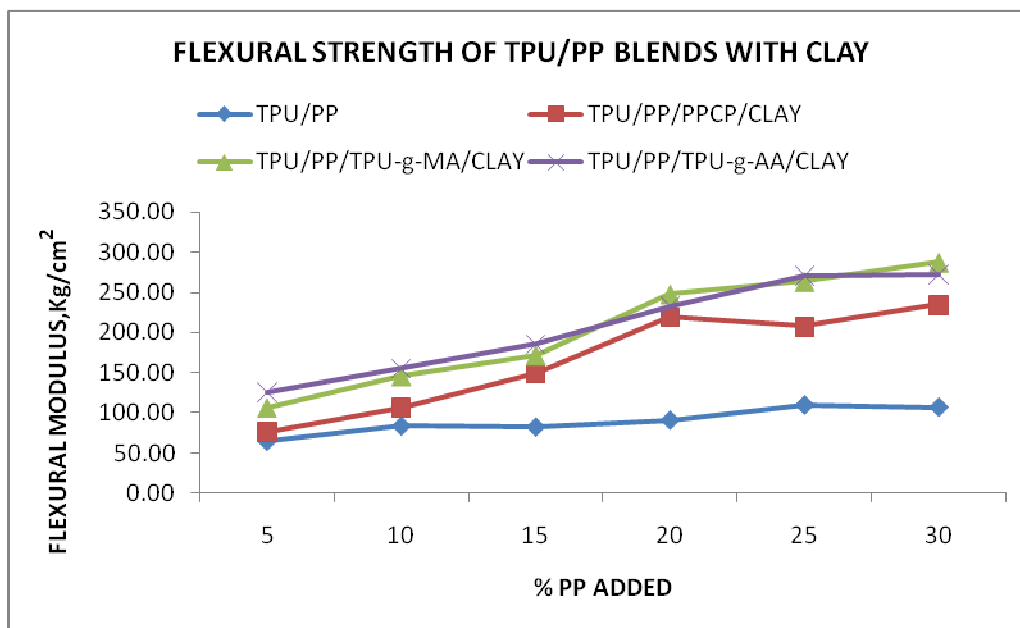


Fig 5c .Flexural Modulus of TPU/PP with and without clay and compatibiliser

3.3. Impact strength

The reinforcement of the clay in to the polymer blend TPU/PO's is shown in figures 6a, 6b and 6c. Addition of the clay filler increases the impact strength of all the blends with compatibiliser as compared with blends without compatibiliser and filler. Addition of the polyolefins in to TPU matrix also increases the impact strength up to certain level of the addition and then found to be decrease. The increase in toughness may be caused by the good dispersion of the clay filler into blend matrix. Since the clay particles disperse in the blend matrix, blends reduce the brittleness and increase toughness of the blends.

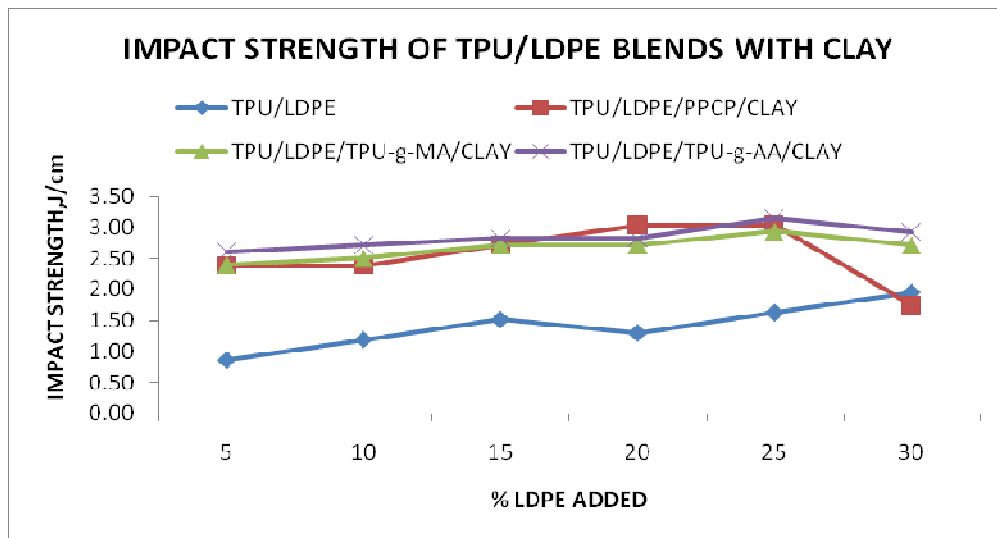


Fig 6a. Impact strength of TPU/LDPE blends with and without clay and compatibiliser

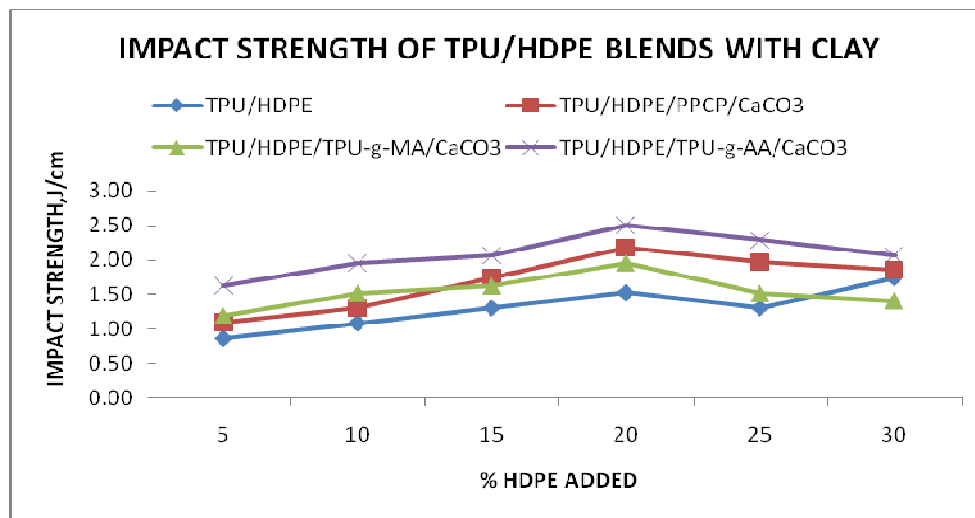


Fig 6b. Impact strength of TPU/HDPE blends with and without clay and compatibiliser

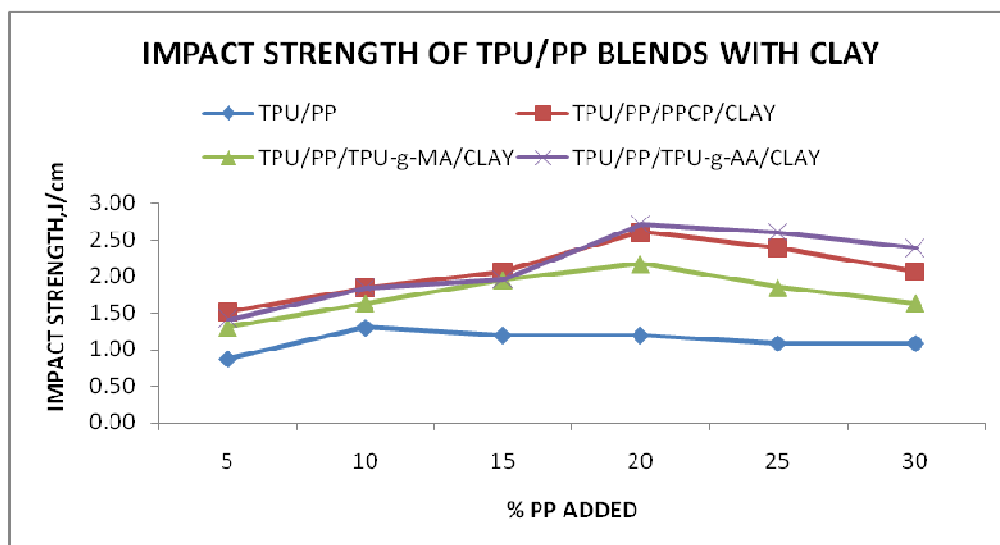


Fig 6c. Impact strength of TPU/PP blends with and without clay and compatibiliser

3.4. Hardness

Shore D hardness of the TPU/PO's blends with and without clay and compatibiliser is shown in the figures 7a,7b and 7c. As clay is added in TPU/PO's blends the hardness increases as compared with blend without clay and compatibiliser. The improvement of the hardness may be due to the good dispersion of the filler into blend matrix. Hardness of TPU/PP blend was found to be more as compared to TPU/HDPE and TPU/LDPE blends.

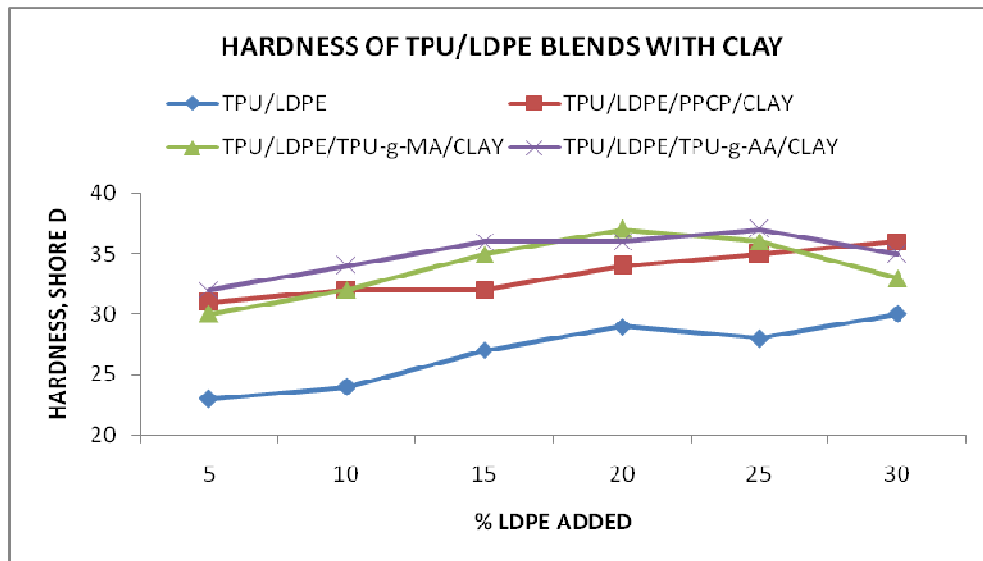


Fig 7a. Hardness of TPU/LDPE blends with & without clay & compatibiliser

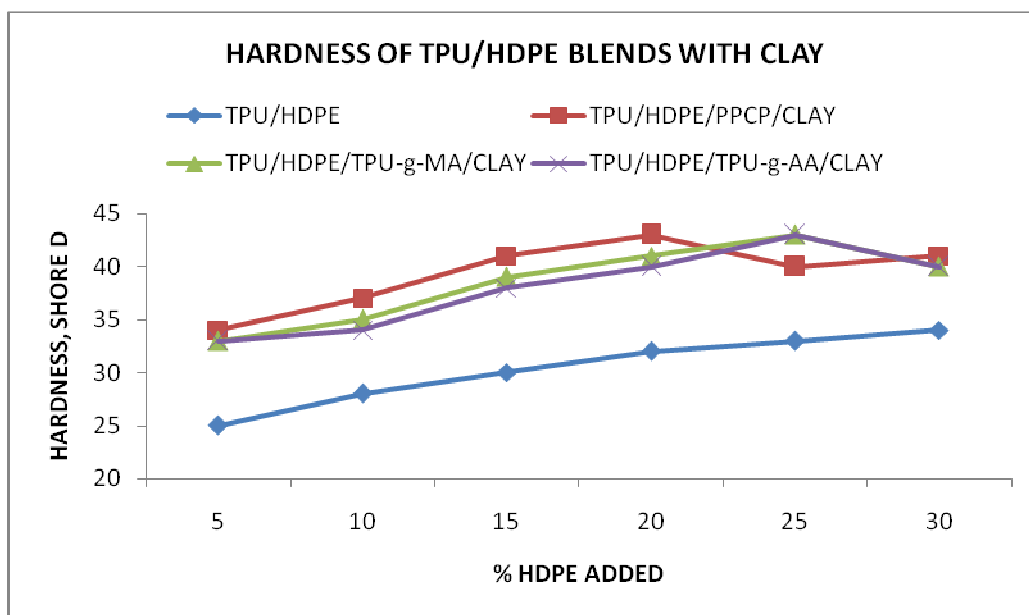


Fig 7b. Hardness of TPU/HDPE blends with & without clay & compatibiliser

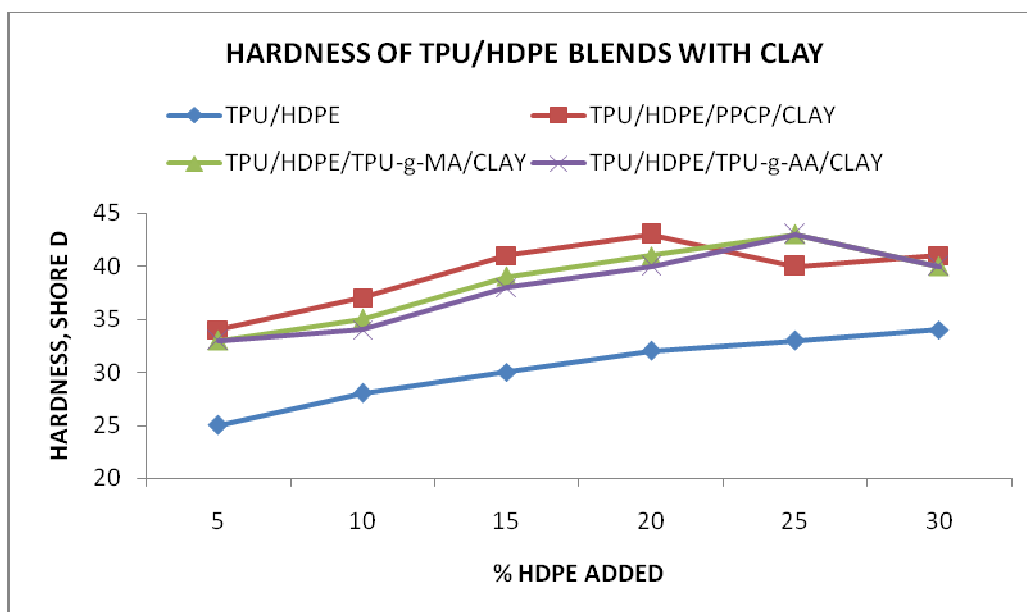
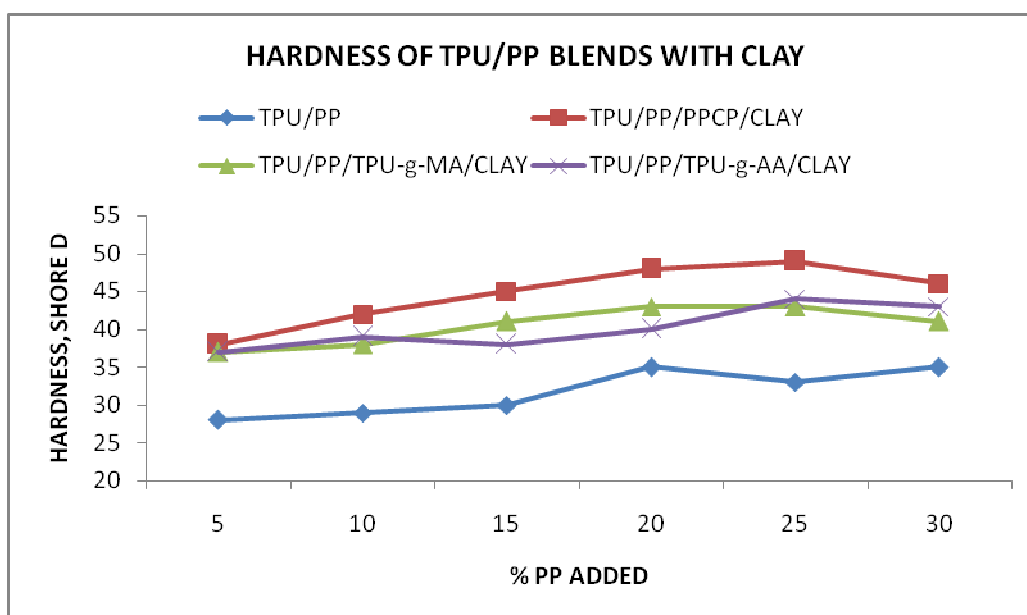


Fig 7c. Hardness of TPU/PP blends with & without clay & compatibiliser



3.5. Morphology of Blends

The morphological and particle distribution in TPU/PO's blends and clay blends sites were studied using SEM and the SEM images are shown in the figures 8a-8l. The presence of cryogenic fracture along the boundaries of the blends without compatibiliser indicates the immiscibility of the two polymers blends. When compatibilisers and calcium carbonate were added into the TPU/PO's blends, the blends display significantly finer morphology. When filler is introduced into a polymeric material, the ideal is that it has regular granulometry and that its particles are sufficiently small to enable good distribution in the matrix. [15]. It is evident that the clay particles are uniformly dispersed within the TPU/PO's blends matrix and no aggregates of filler particles are observed. This further corroborates that the TPU/PO's with 20 wt % clay produced relatively improved properties. The micrograph also shows that the clay particles were more reinforced in blends matrix.

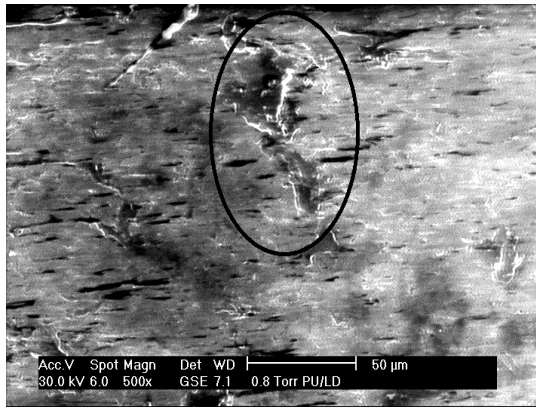


Fig 8 a.TPU/LDPE

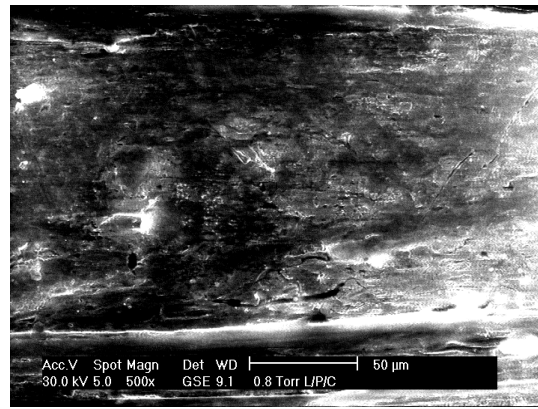


Fig 8b.TPU/LDPE/PPCP/clay

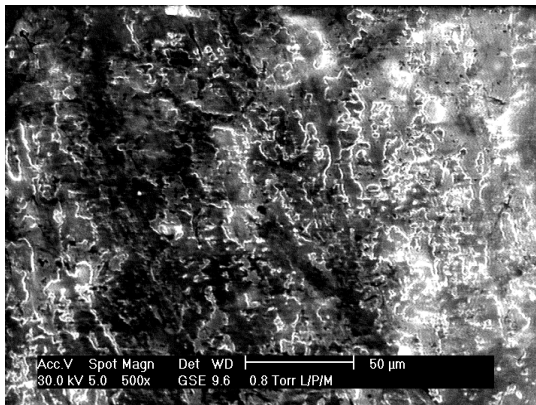


Fig8c.TPU/LDPE/TPU-g-MA/clay

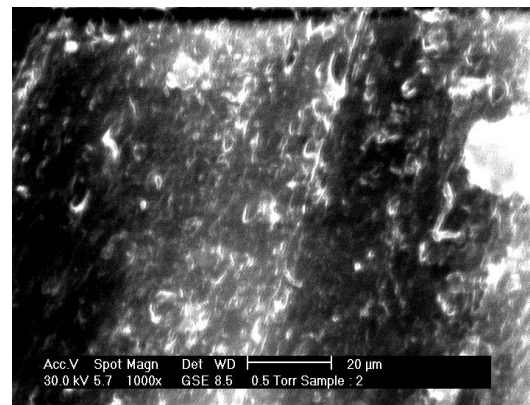


Fig8d.TPU/LDPE/TPU-g-A/clay

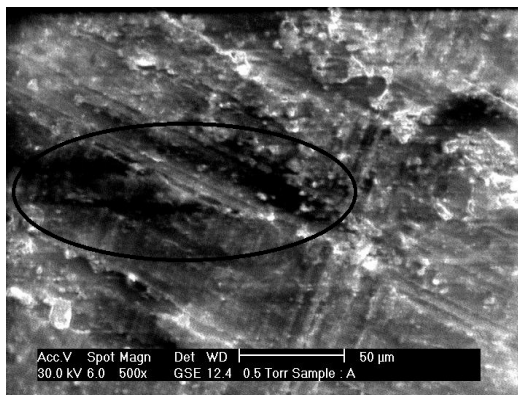


Fig8e. TPU/HDPE

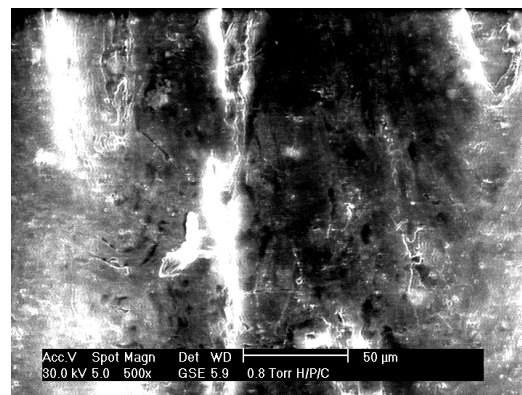


Fig8f. TPU/HDPE/PPCP/clay

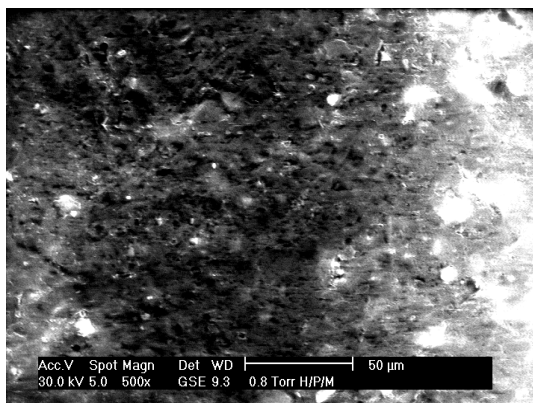


Fig8g.TPU/HDPE/TPU-g-MA/clay

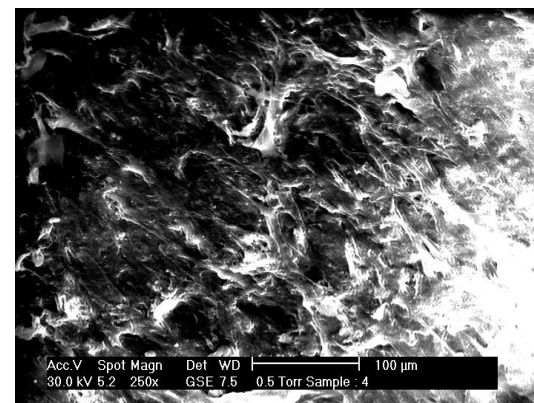


Fig8h. TPU/HDPE/TPU-g-AA/clay

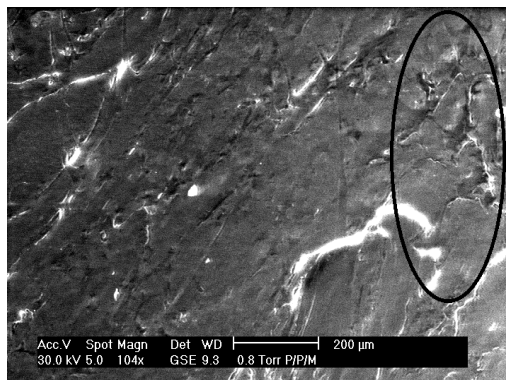


Fig8i. TPU/PP

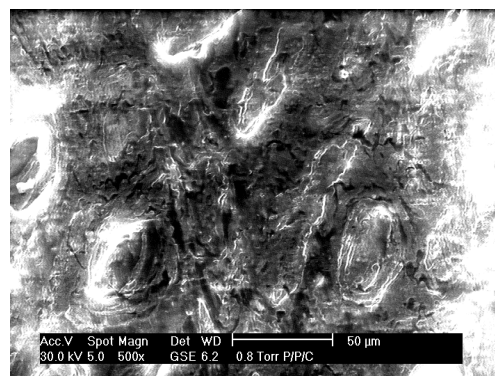


Fig8j. TPU/PP/PPCP/clay

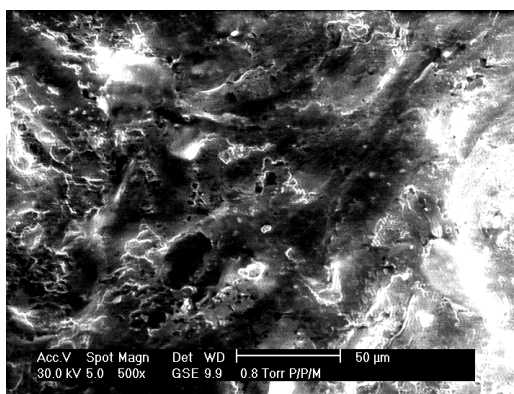


Fig8k. TPU/PP/TPU-g-MA/clay

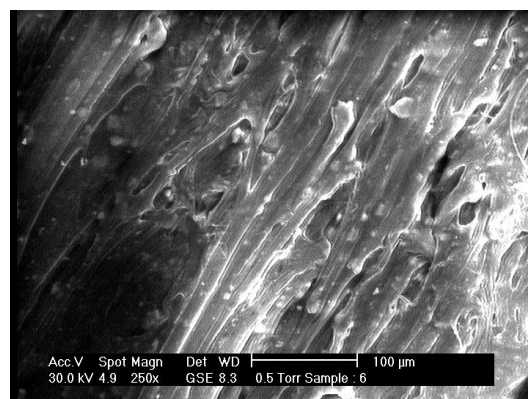


Fig8l. TPU/PP/TPU-g-AA/clay

CONCLUSION

Polypropylene copolymer (PPCP), TPU-g-MA, and TPU-g-AA were found to be good compatibilisers for TPU/LD, TPU/HD and TPU/PP blends. The mechanical properties of the blends such as tensile strength, impact strength, and hardness were found to increase after addition of clay filler. SEM images show very good dispersion of clay filler into the blend matrix and so it can be concluded that clay can be used for improving mechanical properties of the TPU/PO's blend.

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