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Studies on Nano Kaolin Clay Reinforced PS-HDPE Nanocomposites

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ABSTRACT
Blending of two or more polymers offers a good possibility to modify thermoplastic material so as to improve their properties. Polystyrene and high density poly(ethylene) (PS/HDPE) are two widely used commodity plastics. In this study it is proposed to upgrade the blends by using low cost nano kaolinite clay, a layered type alumina silicate. In order to generate high modulus and strength a polystyrene rich blend PS/HDPE (80/20) was selected for the study. The prepared blends have been characterized for mechanical properties such as tensile strength, tensile modulus etc. Effect of different organo groups grafted kaolin clays at various loadings on mechanical and flow properties were studied. Effect of unmodified clay and modified clays such as amino and dialkylsilane grafted clays were studied. The mechanical tests revealed that tensile properties increased significantly after the addition of nanofiller in comparison to the pure blend. Modification of clay by organic groups has led to better filler dispersion and wetting of matrix. Characterization of tensile fractured specimens done using scanning electron microscopy (SEM).

***Keywords**: Polymer, Nanocomposites, Kaolin Clay, Mechanical Properties.*

1. INTRODUCTION

Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix that is imbedded with inorganic particles which have at least one dimension in the range of 1 to100 nm [1]. Polymer nanocomposites have attracted great interest, because they exhibit enhanced mechanical, thermal, and barrier properties [2]. Polymer blending offers an effective route for the production of new engineering materials, and it is of special interest for the modification of commodity low cost polymers. Polystyrene (PS) and poly(ethylene) (PE) are two of the most widely used commodity plastics in the world. The hybridisation of PS/PE blends with nano structured ingredients should be effective implement in the commercial applications. Commercial success of an immiscible blend requires improvement of interfacial adhesion between the components of blends, necessary to achieve stability of morphology and improvement in mechanical properties. PS is incompatible with PE.

Therefore PS/PE blends exhibits weak interfacial adhesion and poor dispersion of the component, which results in heterogeneous morphology with macro phase separation and poor mechanical properties. Polystyrene and poly (methyl methacrylate) are two examples of high modulus materials that have limited impact resistance, whereas poly(ethylene) and poly(propylene) are two high tough materials that have poor stiffness. An increase in impact strength of PS can be achieved by adding PE which is having high impact strength [3, 4]. For this reason PS/PE blends exhibit more balanced properties which is advantageous for a number of applications, e.g., in packaging where different barrier properties of PE and PS can be beneficially combined. The PS/PE blends are very important for mixed plastic waste recycling [5]. The present trend in reducing the municipal solid waste is to recycle the polymer waste instead of incineration and land filling [6].

In the early 2000s, ternary blends composed of nano clays have attracted particular attention [7]. The study of such ternary blends requires the use of morphological and mechanical characterization techniques. Most published studies on ternary blends composed of nano clay particle dispersed in two immiscible polymer blends have focussed on the compatabilising and reinforcing effects of organoclay. Mehrabzadeh and Kamal et al [8] showed that adding 5% wt. of organoclay in PA-6/PE blends increased the interfacial adhesion between the phases of PA-6/PE. The size of the nano clay particles, the modifications incorporated and the amount nano filler used play a major role in the development of properties of polymer blend [9]. Kaolinite is a mineral that has a wide variety of applications in industry, particularly as filler in

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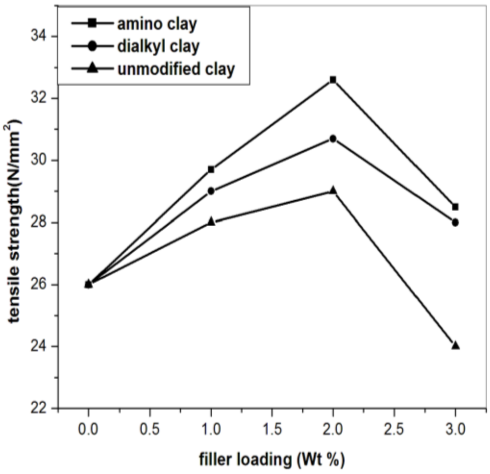

Figure 1: Variation of tensile strength with filler loading.

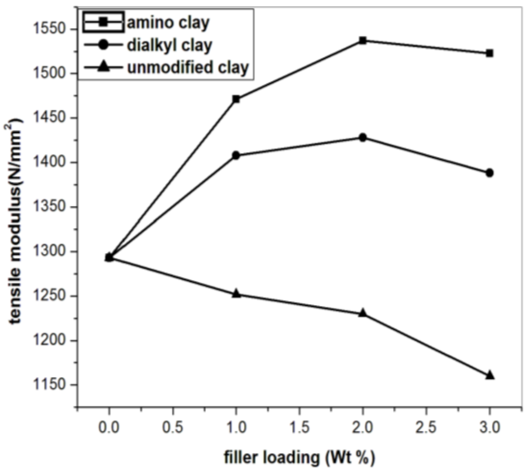

Figure 2: Variation of tensile modulus with filler loading.

paper, plastics, paints, and rubber. Kaolin clay have 1:1 type layered structure: with one side of inter layer space is covered with hydroxyl groups of the $Al_2(OH)_4$ octahedral sheets and other side is covered by oxygen's of the SiO_4 tetrahedron [10] and hence called 1:1 clay mineral. Kaolinite has the potential to be an ideal precursor for the preparation of new nanocomposites materials since it is cost effective compared to montmorillonite clays. A few examples of polymer-kaolinite intercalated nano composites have been reported [11-15]. The physical mixture of polymer and silicate may not form a nanocomposite However nanoclay is naturally hydrophilic whereas PS and HDPE are the hydrophobic polymers. This limits the advantages of incorporation of clay into the polymer matrix. This problem can be resolved by modifying nanoclay chemically with organophillic groups, thereby making it organoclay for better dispersion [16-19]. The aim of the present of the work is to investigate mechanical properties, morphological and processibility of PS-HDPE blended kaolinclay nanocomposites.

2.EXPERIMENTAL

2.1. Materials

Polystyrene (General purpose polystyrene) supplied by Supreme Petro Chem Ltd.; Mumbai, India; MFI-12gm/10 min (200^{o}C/5 kg). High density poly(ethylene) (HD50MA180), Reliance polymers Ltd, Mumbai, MFI-20gm/190^{o}C/2.16kg). Nano kaolinite clay-Nano caliber 100 A (Amino clay), Nano caliber 100 Z (Dialkyl clay) supplied by English India Clays Ltd., India.

2.2.Preparation of the blends

Blends of PS/HDPE containing amino and dialkyl modified kaolinite clay were prepared using a Thermo HAAKE Polylab system equipped with roller rotor operating at 180^{o}C, 30 rpm for 8 minutes. The resulting compound were hot pressed into sheets and cut into pieces. The material was then injection molded using a plunger type injection molding machine with a barrel temperature of 190^{o}C. A pure blend of same composition prepared as above is used as reference.

2.3. Determination of mechanical properties

Tensile and flexural properties were evaluated using Shimadzu Autograph AG-1 series Universal testing machine with a load cell of 10 KN capacity according to the ASTM D 638 at a cross head speed of 50mm/min, cross head separation of 40 mm on dumb-bell shaped specimens and ASTM D 790 at a cross head speed of 5 mm/min on rectangular bar samples respectively. The Izod Impact test on unnotched rectangular bar samples were carried out following ASTM D 256 test method on a pendulum type tester RESIL IMPACT JUNIOR (CEAST).

Melt flow index determined using CEAST Modular Line Melt Flow Indexer ASTM D1238 using a load of 5 kg at 200^{o}C.

2.4. Scanning electron Microscopy (SEM)

SEM was used to investigate the morphology of the fractured surfaces. The tensile fractured surface was sputter coated with gold and examined under Scanning electron microscope. SEM images were taken using a JOEL model JSM 6390LV.

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of tensile strength with unmodified and modified clays at different loadings. The increase found up to a filler loading level of 2% and thereafter a slight decrease is found. This shows that an effective interaction of the filler with matrix has occurred. Modification of clay with an organic group has led to better filler dispersion and wetting of matrix. The modification of clay surface by an organic group enhances the hydrophobic character of the inorganic particles

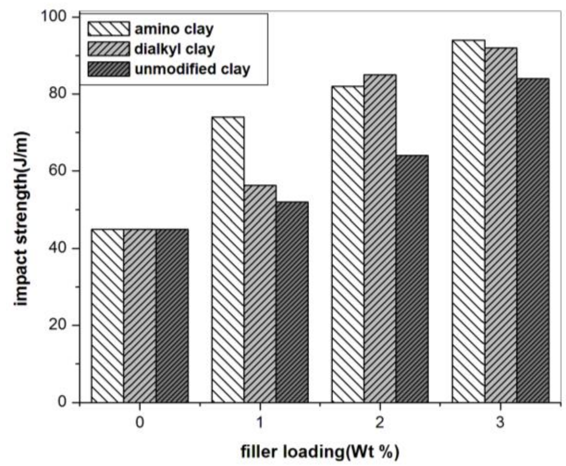

Figure 3: Variation of impact strength with filler loading.

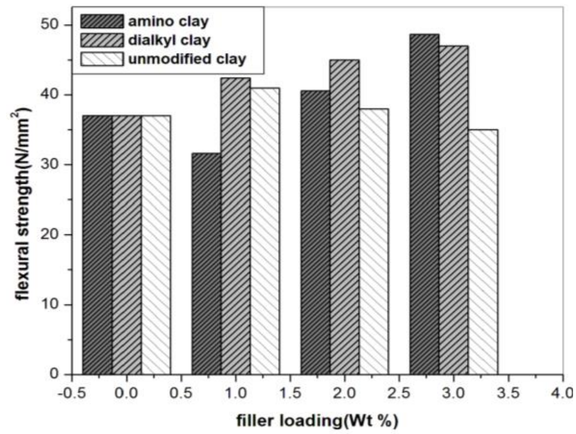

Figure 4: Variation of flexural strength with filler loading

that lead to good interaction with the matrix. The results show that there is an increase of 27%, 15%, 7% in tensile strength of amino, dialkyl, unmodified clays at 2wt. % of nano clay content respectively. The inclusion of fillers in matrix leads to a significant increase in mechanical properties.

Zhao et al. [20] observed the increase in tensile performance by the incorporation of nanofiller. Figure 2 shows the, variation of tensile modulus with filler content. Tensile modulus is also found to increase at 2% filler loading. Tensile modulus shows an increase of 17%, 10% respectively, for amino and dialkyl clay loading at 2 wt.%, whereas unmodified clay shows a decrease in tensile modulus. Svehlova et al. [21] mentioned better filler dispersion leads to a higher modulus. Hence a higher mechanical performance of nanocomposite is an indication of better filler dispersion at 2wt.%. But above 2 wt. % mechanical properties is found to decrease, which is probably due to aggregation of the clay platelets above the critical content.

The use of nanoparticles to improve the toughness of the polymers has been increased recently. Chen et al [22] reported that the fracture toughness of poly(propylene) increased five fold by incorporating nanometer scale $CaCo_3$ and $CaCO_3$ particles acted as stress concentrators to promote toughening mechanism. Nano clay is also used to improve the impact strength [23].

Figure 3 shows the, impact strength of PS/HDPE blends with unmodified, amino and dialkyl modified clays. The impact strength is found to increase steadily with increase in filler loading. The increase in impact strength is found to be at 3 % of amino clay and 3 % with dialkyl clay. For unmodified clay increase is found to low. This may due to the presence of organic modification of clay surface which improved the compatibility between the filler and the matrix. The improvement can be attributed to the increase in toughness of the composite with increasing nano clay content in the range of 3 wt.%. Amine adsorption on kaolin's has been used in industry to produce greater dispersion in polymer systems and to neutralize catalytic surface activity of the clay.

The flexural strength is given in the figure 4. It is found to increase with increase in filler content. Flexural strength increases by about 27 % by usage of modified clays at 3% flexural strength of unmodified clay is found to show a decrease with increase in filler loading. The measured mechanical parameters clearly indicated that a small addition of mineral particles significantly improved PS/HDPE blend properties. The improvement was most visible for modified version of clays. As the clay is organomodified, its surface is organophillic and its surface energy is low. It is found to be more compatible with the polymer matrix. Lower mechanical parameters were observed for the composite with the addition of unmodified kaolinite clay which may be due to agglomeration of fillers.

3.2 Melt flow index test (MFI)

The flow behaviour of nanocomposite was evaluated from Melt flow index test. Knowing MFI is vital to anticipate and control processing parameters during moulding of components. Thepresence of interactions between the polymer chains and the silicate surface may affect the mobility and the rheological properties of the polymer chains. Therefore nanoclay addition may decrease the polymer MFI. The MFI values of PS/HDPE blends with amino and dialkyl modified clay at different loadings and that of pure blend is given in the figure 5. These values appear to be decreasing with increase in filler loading particularly for clay at 2 weight per cent of the filler and there after remains the almost same. As it is shown in the figure 5 the polymer MFI reduced significantly at filler loading of 2 wt. %. This result

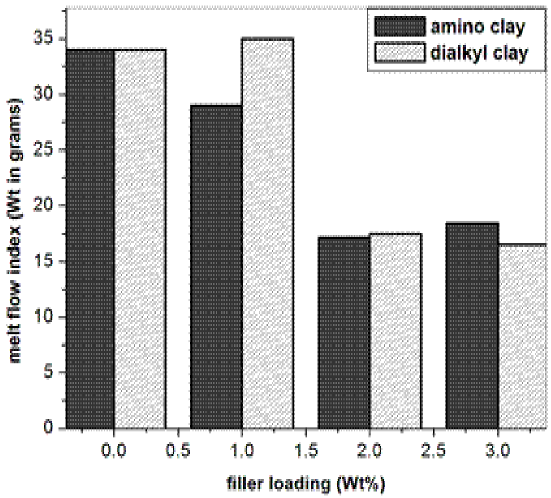

Figure 5. Variation of MFI with filler loading.

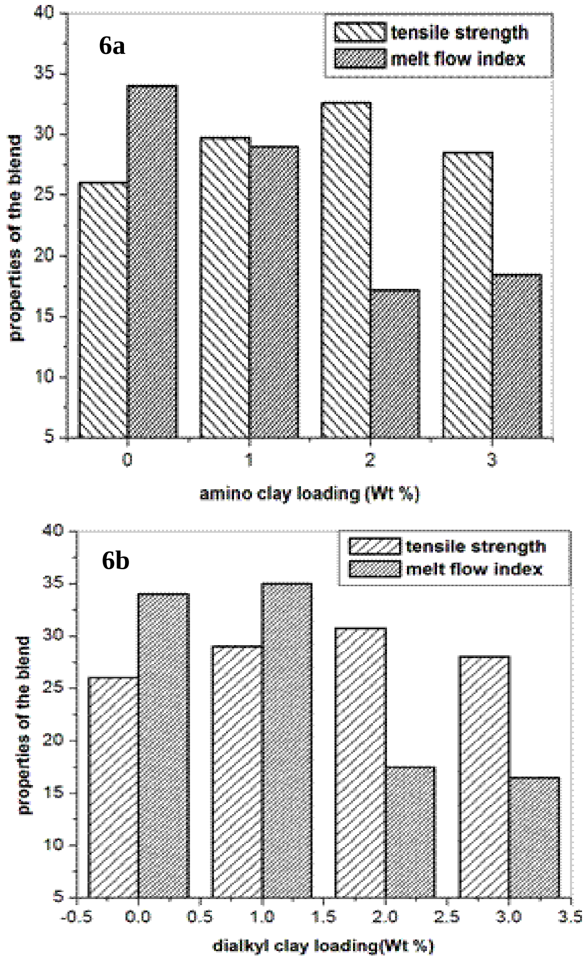

Figure: 6 (a, b).Variation of tensile strength with Melt flow index for amino and dialkyl clay loading.

reveals that the penetration of the polymer chains into the interlayer space of the organoclay is greater at composition beyond 1%. Consequently the interaction between the polymer chains and the silicate layer should be stronger in it compared to others. A comparison of tensile strength and MFI of blends with modified clays at different filler loading is given in the figure 6(a,b). From figure 6(a,b) it is evident that as tensile strength increases the melt flow index decreases. And the MFI values are less for amino clay than compared to dialkyl clay, which is an indication of more penetration of polymer chains into amino modified clays silicate layer compared to dialkyl clay, which may be the reason for increase in tensile strength for amino modified clays compared to dialkyl modified clays. High level of interaction between the modified nanoclay and the polymer matrix is responsible for increase in properties

3.3. SEM Analysis

In a two phase system such as PS/HDPE, morphology is a major determinant of properties. Thus the shape size and spatial distribution of the dispersed phase along with the interfacial characteristics decide the mechanical properties. The control of phase morphology is the key issue when the desirable mechanical properties have to be imparted to the polyblends. In an incompatible blend premature failure occurs when subjected to a mechanical load due to lack of adhesion between the two. The tensile measurements give an idea about the maximum load bearing capacity of the material. The influence of modified clays on the mechanical properties of PS/HDPE blends has been investigated. SEM micrographs of the fractured surfaces of materials are given in the figures 7-9. Scanning electron micrographs of pure physical blend of PS/HDPE revealed a particular two phase morphology. The sharp edges of particles and holes on the fractured surface indicate poor interfacial adhesion [24]. The coarse morphology of the blends and detachment of dispersed particles confirmed bad adhesion at the interface between the homopolymers [25] and pointed to incompatibility, which is likely to stem from the high interfacial tension occurring between the composites during the melt mixing process. SEM micrographs of blend with amino clay exhibited a more homogenous morphology compared to others with clay particles on it. The distinction between two phases was scarcely detectable. The SEM micrograph of dialkyl clay is found to exhibit a fibrillar type morphology which may lead to improvement in properties.

4. CONCLUSIONS

The study covers the effect of kaolin clay particles on the mechanical, morphological and processing features of PS/HDPE blends. Incorporation of organo modified kaolin clay increase interfacial adhesion with the matrix. Tensile strength and tensile modulus is found to increase with 2% clay loading. Impact strength is found to increase at 3 % of filler loading. Flexural strength is found to increase with increase in filler loading. The MFI is

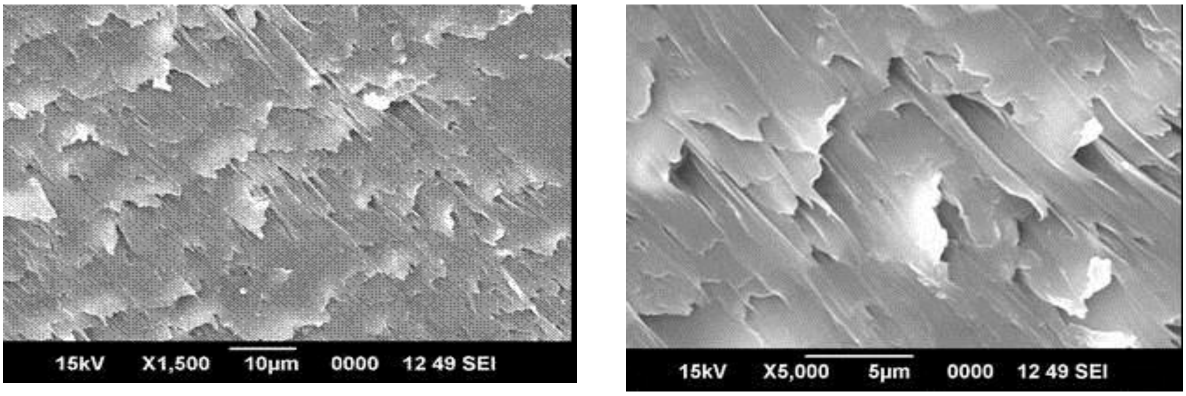

Fig:7(a) Fig:7(b)

Figure 7(a,b): Scanning electron micrographs of PS/HDPE (80/20) blend at two different magnifications**.**

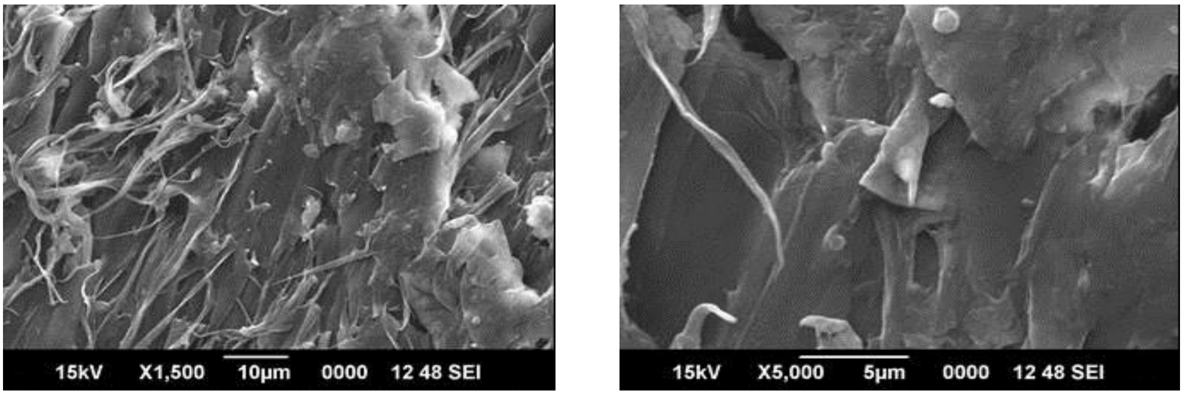

Fig:8(a) Fig:8(b)

Figure 8 (a,b): Scanning electron micrographs of PS/HDPE blend (80/20) containing dialkyl clay at two different magnifications.

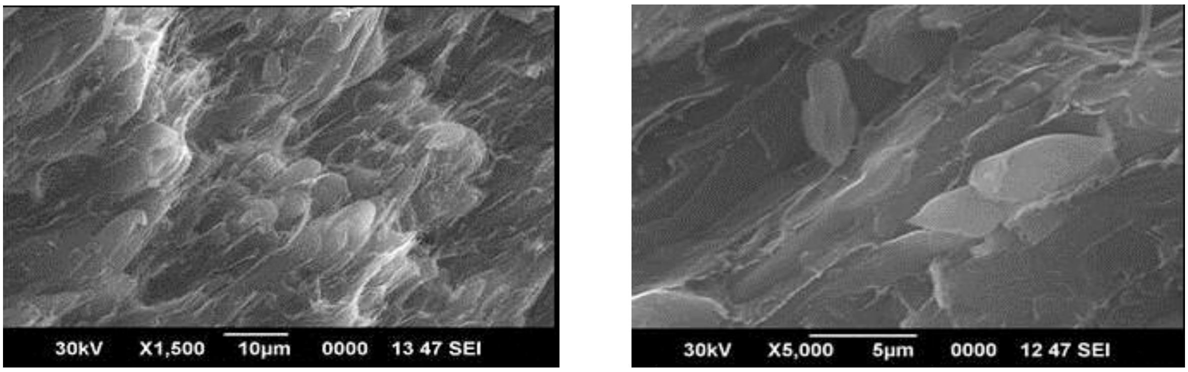

Fig: 9(a). **Fig: 9(b).**

Figure9 (a,b): Scanning electron micrograps of PS/HDPE blend (80/20) containing amino clay at two different magnifications.

found to decrease at filler loading beyond 1% which indicates the penetration of polymer chains at the interlayer space of clay particles. The improvement in mechanical parameters for modified clays can be related to a good dispersion of mineral particles in the polymer matrix, amino modified clays shows overall better performance as revealed by the morphology. Thus low cost kaolinite clay can be used as a suitable modifier of plastics.

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