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IN-SITU ADDITION POLYMERISATION OF STYRENE USING NANOCLAY AND EVALUATION OF PROPERTIES

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ABSTRACT

Polymer nanocomposites have emerged as an area of research in recent years. These nanocomposites exhibit significant improvement in their properties at lower filler content. Polystyrene is a highly commercially potential plastic. The main disadvantage of polystyrene is that it is brittle. To reduce its brittleness nanoclay is added in different proportions. There are different methods for the preparation of polystyrene clay nanocomposites. In this work, in-situ polymerization of styrene with the addition of nanoclay is envisaged. It is proposed to synthesize polystyrene clay nanocomposites with benzoyl peroxide as the initiator. The compatibility of the initiator and the monomer with clay surface was found to profoundly affect the clay dispersion. The effects of the amount of initiator, polymerising temperature and polymerising time on the conversion of styrene were investigated. The mechanical properties mainly impact strength were determined. Mechanical characterization of polystyrene composite was done by determining impact strength, flexural strength and flexural modulus. Study based on processability was also done. Morphological behavior of the composite was investigated using scanning electron microscopy of fracture surface of impact specimen. Thermal behaviour of composite was done using thermogravimetric analyser.

Key words: *polystyrene, nanoclay composites and insitu polymerisation*

INTRODUCTION

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. It deals with structures sized between 1 to 100 nanometres in at least one dimension, and involves developing materials or devices within that size. It is broadly defined as: the creation, processing, characterization, and utilization of materials, devices, and systems with dimensions on the order of 0.1–200 nm, exhibiting novel and significantly enhanced physical, mechanical, chemical, and biological properties, functions, phenomena, and processes due to their Nano scale size. Polymer nanocomposites are a class of reinforced polymers with low quantities (< 5%) of nanometric sized clay particles (Buzea, 2007). These are materials in which nanoscopic inorganic particles, typically 10-100Å in at least one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the performance properties of the polymer. By incorporating nano scale particles into a neat polymer matrix, "Quantumdots" are obtained in a readily processable form. In case the ultra-fine phase dimensions are maintained after compounding with the polymer matrix, the large fraction of the filler atom that reside in the interface would lead to a strong interfacial interaction [2] . As the interfacial structure plays a critical role in determining the composite properties, nanocomposites couple with a great number of interfaces can be expected to possess unusual properties [1]. Uniform dispersion of these nanoscopically sized filler particles (or nanoelements) produces ultra large interfacial area per volume between the nanoelement and host polymer. This immense internal interfacial area and the nanoscopic dimensions between nanoelements fundamentally differentiate PNC's from traditional composites and filled plastics. An interfacial area of 700 m^2/cm^3 can be produced. PNCs provide lighter weight alternatives to conventional filled plastics with additional functionality associated with nanoscale-specific value-added properties (Gowariker, 1986).

MATERIALS AND METHODS

Materials: Materials used for this study were styrene (SHARON ENTERPRISES INDIA LIMITED, Kochi, Kerala), Unmodified clay, amino clay and vinyl clay (M/s English Clay Ltd. Vely, Thiruvananthapuram). After making the test specimens, these were tested for flexural strength (Shimadzu Autograph Universal Testing Machine (UTM)) and impact strength (Resil Impact Testing Machine). Thermal analysis is done in TA-Q 500 series instrument in nitrogen atmosphere for a temperature range of 40^{0}C to 1020^{0}C at 20^{0}C/min and SEM images were taken with JSM 6390 with an accelerator voltage 20 kV on a vacuum atmosphere.

Methods of preparation: Polystyrene prepared by in-situ polymerization [2] from styrene monomer. Initially styrene was washed with 5% NaOH and then with distilled water to remove inhibitors. Then it was polymerized at 90^{0}C. PS obtained was poured into the mould and taken for analysis. During polymerization nanoclay was added in different compositions from 1 to 4%. The experiment also had been done for modified clays (amino and vinyl clay) under the same conditions. Then the samples are tested.

RESULTS AND DISCUSSION

Conversion of Polystyrene: Using Elemental Analysis, % Conversion = (Total PS in gm/ monomer charged)* 100. Around 71% of styrene gets converted into polystyrene. The remaining styrene may get volatilized during polymerization, since the polymerization was done at about 85^{0}C.

Molecular weight determination: Calculation of Viscosity Molecular Weight was done by using the principle based on Markwonikoff's Equation. Viscosity average molecular weight of the PS synthesized in the lab is much lower than that of commercial PS. This is obviously due to the lack of control of temperature, catalyst concentration, removal of heat of polymerization etc. in the case of the synthesis done in the lab (Table 1). We studied the effect of nanoclay loading in polystyrene prepared by in-situ polymerization. The impact strength of PS nanocomposites are increasing with increase of clay content and reaches a maximum at 2% regardless of the type of nanoclay. At 2% of clay vinyl clay has the maximum impact strength, then unmodified clay and then amino clay. The reason behind the higher strength of PS/vinyl clay composite is due to the higher affinity of vinyl clay with styrene which is a vinylmonomer. Flexural Strength of the samples was also calculated using unmodified, amino and vinyl clay.

Flexural Strength: Variations of flexural strength with different weight percentages of different clays that is unmodified clay, vinyl clay, amino clay are listed in table and the results are plotted in graph in figure 2 (Table 2). The flexuiral strength of PS nanocomposites are also increasing with increase of clay content and reaches a maximum at 2% regardless of the type of nanoclay. At 2% of clay vinyl clay exhibits higher flexural strength, then amino clay and then unmodified clay. The reason behind the higher strength of PS/vinyl clay composite is due to the higher affinity of vinyl clay with styrene which is a vinyl monomer[3]. The other two clays that is unmodified clay and amino clay possess lesser value than vinyl clay, the reason is unmodified clay is hydrophilic so it has less affinity to organic styrene and in the case of amino clay, the amino group has low interaction with vinyl monomer styrene.

Flexural Modulus: Variations of flexural modulus with different weight percentages of different clays that is unmodified clay, vinyl clay, amino clay are listed in table 3 and the results are plotted in graph in figure 3.

The flexural modulus of PS nanocomposites are increasing with increase of clay content and reaches a maximum at 2% regardless of the type of nanoclay. At 2% of clay vinyl clay has the maximum flexural modulus then amino clay and then unmodified clay. The reason behind the higher flexural modulus of PS/vinyl clay composite is due to the higher affinity of vinyl clay with styrene which is a vinyl monomer.

Processibility of polymer nanocomposites: Processability of the composites was studied by comparing their MFI. The MFI decreases with increase in clay content up to 2%. This results agrees with the mechanical data observed that the maximum interaction between the polymer and clay occurs at this clay content. Above 2% the flow rate increases due to the agglomeration of the clay particles and agrees with the mechanical properties obtained.

Scanning Electron Microscopy: SEM images of fracture surface of impact strength specimens are analyzed. From the above figures dispersion of nanoparticles can be seen. As a result impact strength; flexural strength and flexural modulus of the polymer nanocomposites are higher as compared to pure polystyrene.

Thermogravemetric Analysis: In the case of pure polystyrene onset of thermal degradation is obtained at 268.99^{0}C and it is completely degraded at a temperature of 413.63^{0}C. In the case of unmodified clay composite onset of thermal degradation is at 268.41^{0}C and it is completely degraded at a temperature of 383.45^{0}C. For modified clay (amino clay) composite onset of thermal degradation is at 347.60^{0}C and it is completely degraded at a temperature of 425.88^{0}C. . For modified clay (vinyl clay) composite onset of thermal degradation is at 376.39^{0}C and it is completely degraded at a temperature of 426.37^{0}C (Fig 5). Thus TGA analyses of all the nanocomposites prepared reveal significant effect of nanoclay addition plays an important role in determining their thermal stability. The addition of clay increased the decomposition temperature of clay composites.

CONCLUSION

The significant factor that determines the improvement of properties in polymer by the incorporation of nanoclay is its distribution in the polymer matrix. . The uniform dispersion of nanofillers in the polymer matrices is a general prerequisite for achieving desired mechanical and physical characteristics. Benzoyl Peroxide is used to initiate the reaction where the appropriate dispersion of nanoclay is observed. When nanoclay was added to styrene, its strength has been increased and reaches a maximum with 2% nanoclay. And at the same time impact strength has been increased for modified clay than that of unmodified clay.

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Table 1. Viscosity average Mol.Wt comparison

In-situ polymerized PS	Commercial PS
8871	39,953

Table 2: Variation of flexural strength for different types of clay

Samples	Flexural Strength (N/mm^2)
Pure PS	3.03
PS + Unmodified clay	5.21
PS + Vinyl clay	6.31
PS + Amino clay	5.68

Table 3: Variation of flexural modulus for different types of clay

Samples	Flexural Modulus (N/mm^2)
Pure PS	1165.70
PS + Unmodified clay	4153.70
PS + Vinyl clay	7443.82
PS + Amino clay	6244.10

Table 4: Comparison of impact strength and Melt flow index with vinyl clay added polystyrene

PS+VC	Impact Strength (J/m)	Melt Flow Index
0	9.08	127.00
1	11.74	78.26
2	18.32	36.86
3	13.95	150.00
4	9.90	188.00

Fig 1: Variation of impact strength with different types of clay loadings

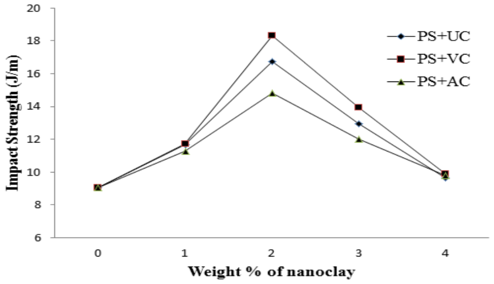


Figure 2: Comparison of flexural strength of different clays

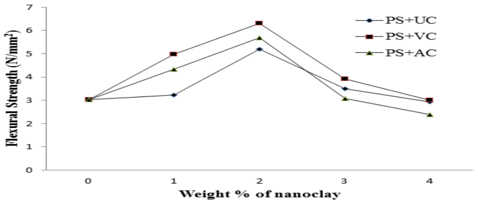


Figure 3: Comparison of flexural modulus of different clays

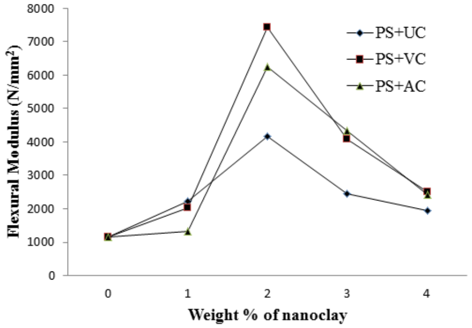


Figure 4. SEM (Scanning electron microscopy) of pure PS and PS with 2% of vinyl clay

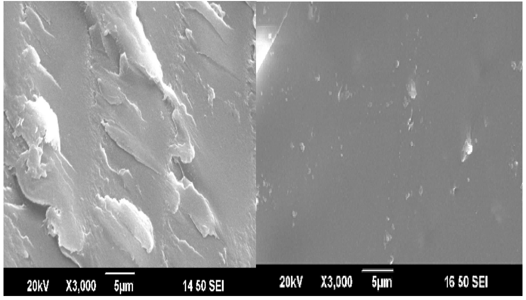
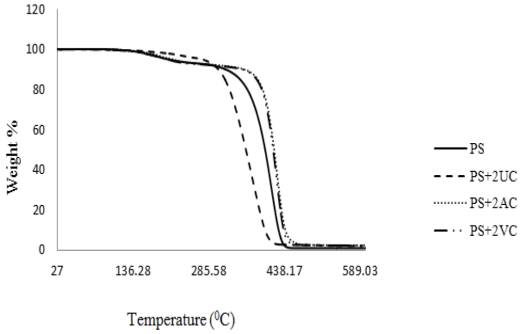


Figure 5: TGA analysis of different clay types with polystyrene



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