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Poly (vinyl chloride) / TiO_2-Poly (methyl methacrylate-co-butyl acrylate) core-shell nanocomposites

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ABSTRACT

In this study TiO_2-poly (methyl methacrylate-co-butyl acrylate) core shell nanoparticles were synthesized using microemulsion polymerization technique. Prepared nanoparticles were utilized as a toughening agent in Poly (vinyl chloride) inorder to improve its impact properties. 5% loading of Impact modifier gave the 41% improvement in tensile strength and 33 % improvement in modulus. Impact strength also increased constantly, result shows no break even at 1 % loading. Core-shell nanoparticles were found to have very good toughening effect on PVC, due to better interaction happening between acrylate and PVC polymeric chains.

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INTRODUCTION

Fillers have important roles in modifying the properties of various polymers and lowering the cost of their composites. The effect of fillers on properties of composites depends on their level of loading, shape and particle size, aggregate size, surface characteristics and degree of dispersion[1]. Recently, polymer-matrix nanocomposite have attracted considerable attention owing to their unique mechanical, optical, electric and magnetic properties; and strong interactions with the matrix resulting from the nanoscale microstructure and extremely large interfacial area between filler and matrix[2-6]. It is well known that the mechanical properties of composites are strongly related to the filler aspect ratio. Thus, layered silicate, like montmorillonite, has been extensively studied in recent years due to its fairly large aspect ratio[7-9]. The polymer/intercalated or exfoliated montmorillonite nanocomposites possess high strength, superior modulus, good heat distortion temperature and superior barrier properties, but their low fracture toughness has greatly limited their applications. The challenge is to find novel methods to increase the fracture toughness[10]. In contrast, nano-sized particles, such as silica and calcium carbonate, filled-polymer composites will possess significant improvements in both rigidity and toughness if the ultra-fine phase dimensions of the nanoparticles are maintained after compounding with a given polymer matrix[10-20]. The homogeneous dispersion of nanoparticles in polymer matrix is very difficult because they have a strong tendency to agglomerate. The sol-gel process provides a method of preparation of inorganic metal oxides under mild conditions starting from organic metal alkoxides[21-25] and allows structural variation without compositional alteration. But the formation of a cross-linked network of organic metal oxides makes it difficult to process, which is a disadvantage that circumscribes the application of this method[12]. Some efforts have been focused to modify the surface of nanoparticles to prepare homogeneously dispersed nanocomposites.

Hergeth and co-workers[26-28] first applied an emulsion polymerization process to encapsulate inorganic particles by a polymer layer, so-called core-shell particles, where the in-situ polymerization of the monomer occurred mainly at the surface of unmodified particles due to the adsorption of monomer on the surface, followed by polymerization in the adsorbed layer.

The polymer of the selected monomer is thermodynamically miscible with the composite matrix; the polymer shell on the particles increases the interfacial adhesion of these inorganic particles with, and also promotes particle dispersion in, the composite matrix[28]. The preparation of core-shell structures has become a fast-growing topic in colloid and materials science[29]. Particles with core-shell structures have diverse applications in coatings, impact modification, bio-separation, drug delivery systems, etc[30-34]. A well established means to improve the toughness of brittle polymer is to incorporate a dispersed rubber phase in order to improve the impact strength[35,36]. Core-shell modifiers can toughen polymer matrix more effectively and are widely used in PC, PMMA, PVC, and SAN[37-40]. Modern polymerization method have led to the possibility of preparing core-shell modifiers with a range of different particle size and desired morphologies. Many of the emulsion polymerization process parameters like hydrophobicity of monomer, the addition sequence of monomer, the initiator type have an influence on the particle morphologies[41-45]. Methyl methacrylate- butadiene styrene (MBS) graft copolymer is known as one of the most efficient impact modifiers for polyvinyl chloride (PVC) and it is added in amount of up to 20%[46-50]. This material has favorable properties for studying rubber toughening, since it provides optical verification of rubber particle cavitations. in spite of the very wide applicability of MBS, data regarding the shell thickness in the core shell impact modifier on the toughening efficiency of PVC are missing. The reason for that is probably the more difficult preparation of laboratory samples and MBS[51].

The core-shell impact modifier has a significant effect on its blend with PVC or other polymers, which is the due to the fact that the shell thickness of the core shell modifier influences significantly the interfacial interaction and interfacial layer thickness between the modifier and PVC and other polymer[52]. The modification of hard poly (vinyl chloride) (PVC) by adding another polymer is a well-known method currently in practice. The number of polymers and copolymers applied as PVC modifiers is quite large. Acrylic polymers can be used as PVC modifiers. The acrylic modifiers' comprise homo- and co-polymers of various esters of acrylic and methacrylic acids, graft copolymers of methyl methacrylate, styrene and vinyl chloride on acrylic elastomers[53,54]. These modifiers may be divided into two categories. The first one is an impact modifier which is added to PVC to improve mechanical properties, particularly toughness. The other group is the processing aid, which is used to reduce melt viscosity and to provide processing condition for milling, calendaring and extrusion blow moulding.

The present work deals with synthesis and characterization of TiO_2/ (MMA: BA) core-shell nanoparticles by microemulsion polymerization, and its use as impact modifier for polyvinyl chloride (PVC).

MATERIALS AND METHOD

Methyl methacrylate (purity 99%), butyl acrylate (purity 99%), n-pentanol, ammonium persulphate, sodium lauryl sulphate, toluene and liquor ammonia (30 %conc.) were all procured from S.D Fine Chem. Pvt. Ltd., Mumbai, India. Titanium dioxide was obtained from Kerr McGee Pigments Pvt. Ltd, Australia (rutile grade). Distilled water was used for the reaction. Polyvinyl chloride (K57) was procured from Reliance Industries Pvt. Ltd., Mumbai, India; whereas, lead based one pack stabilizer was obtained from ALA Chemical Pvt. Ltd., Mumbai, India.

Surface treatment of titanium dioxide (TiO_2) powder

The coupling agent aminopropyltriethoxy silane (APS) was mixed in 500 ml of toluene. Titanium dioxide particles (silane coupling agent: TiO_2: 1:3 weight ratio) was added in to the above mixture with continuous stirring at 500 rpm for 10 minutes. Mixture was then subjected to sonication via an ultrasound horn (ACE, 22 kHz) for 1 hour with 5 second pulse and 2 second relaxation at 40 % amplitude. Then the mixture was subjected to mechanical stirring at 1800 rpm for

15 hrs. Finally the surface treated titanium dioxide particles were filtered and washed. Resulting modified nano particles were dried at 110 °C for 24 hours in a vacuum oven.

Monomer destabilization

The monomer methyl methacrylate (MMA) and butyl acrylate (BA) contain hydroquinone, which is an inhibitor. Hydroquinone is used to stabilize the monomer because they react at room temperature. Therefore, to remove the inhibitor before polymerization the monomers were washed twice with 10 % NaOH solution and distilled water using a separating funnel.

Preparation of (MMA-co-BA) pre-emulsion

The pre-emulsion was prepared in a 250 ml beaker in presence of water, surfactant (sodium lauryl sulphate, SLS), co-surfactant (n-pentanol) and monomer (MMA & BA) listed in TABLE 1. Weighed quantity of water was charged in 500 ml beaker and surfactant was added gradually under high speed stirring (1000 rpm). Thereafter, the co-surfactant was added. Then the total quantities of destabilized monomer (methyl methacrylate and butyl acrylate) were added dropwise at 1000 rpm. After complete addition of destabilized monomer the mixture was kept for 1.5 hours at 1800 rpm to get a stable emulsion.

Preparation of TiO_2 core and poly (MMA-CO-BA) shell by microemulsion

The synthesis of core-shell nano particles was carried out by microemulsion polymerization in four necked glass reactor equipped with stirrer, thermometer, nitrogen inlet and a condenser fitted with $CaCl_2$ drying tube. Above reactor was charged with distilled water, core (titanium dioxide), surfactant (sodium lauryl sulphate), co-surfactant (n-pentanol), initiator (ammonium per sulphate), were added in sequence. Then liq. ammonia was added to maintain the pH (7 to 8), to this addition of 15 wt. % pre-emulsion was commenced to initiate seed polymerization. Then after the completion of addition, the solution was heated to 75°C to decompose the initiator. Then heating was continued till a slight blue tint was observed in the reactions mixture which indicates formation point of oligomeric species in solution. The remaining pre-emulsion was then added drop wise over a period of four hours. After the complete addition of pre-emulsion, solution was further heated to 80°C and kept as such for one hour at this point 99% conversion of reactants were obtained. The extent of reaction was computed by determining the non-volatile matter content of the emulsion Ethanol was used as de-emulsifier for this purpose.

TABLE 1 : Recipe for synthesis of core-shell nanoparticles

Reactant	Quantity
MMA	45 ml
BA	12ml
SLS	3.2gm
N-Pentanol	1gm
APS	0.6gm
TiO2	1.67gm
Distilled water	90 ml

Above formulation is based on theoretical Tg, because application is mainly based on Tg of final product. If Tg is below that of room temperature then the formation of film of final demulsified emulsion is possible, however if Tg is above the room temperature then it is useful in formation of powder of final demulsified emulsion. Theoretical Tg of the copolymer is supposed to be 42°C.

The theoretical Tg calculated by FOX equation

1/Tg (copolymer) = M1/Tg + M2 /Tg +…

Method of preparation of PVC nanocomposite

Mixer physically mixed all ingredients (core-shell nanoparticles, lead based stabilizers) and PVC, inorder to prepare a homogeneous mix. After physically mixing, all ingredients were compounded in a two-roll mill at 160°C. After compounding, the mixed materials were compression moulded in the form of a sheet at 170°C. Compressed sheet was cut as per ASTM standards for mechanical testing.

CHARACTERIZATION

X-ray diffraction (XRD) analysis

XRD patterns were taken to analyse the TiO_2 and poly (MMA-co-BA) core-shell systems % crystallinity on a Rigaku mini-flex X-ray diffractometer. Scans were taken in the range from 10° to 60° at a scan speed of 3°/min.

TABLE 2 : Recipe for PVC nanocomposite

Impact Modifier	PVC	Di-butyl Lead Phosphate (DBLP)	Dibasic Lead Sulphate (DBLS)	Epoxidised Soyabean Oil
0 %	100	30	2.5	2
1%	100	30	2.5	2
3%	100	30	2.5	2
5%	100	30	2.5	2

Differential scanning calorimeter (DSC) analysis

DSC of core-shell nanoparticles was carried out to analyze its glass transition temperature, melting temperature and crystallization temperature with a TA Instruments DSC Q 100. Samples were heated from 0°C to 250°C at a heating rate of 10°C/min.

Fourier transforms infra-red spectroscopy (FT-IR) analysis

FT-IR analysis was used to carry out the functional group analysis of MMA, BA and treated

TiO_2. The test was carried out on a PerkinElmer, Spectrum GX equipment. Samples were scanned from 400 to 4000 cm^{-1}.

Particle size analysis

Particle size of emulsion (core-shell) was estimated by Beakman Coulter N-4 plus submicron particle size analyser.

Mechanical properties

Tensile properties (tensile strength, tensile modulus and elongation at break) was measured at ambient condition using a Universal Testing Machine (LR-50K, Lloyds Instrument, UK) according to ASTM D638, at a crosshead speed of 5 mm/min. Charpy Impact Strength was determined at ambient condition according to ASTM D256, using Impact Tester (Avery Denison, UK) employing a 2.7 J striker having striking velocity of 3.46 m/s.

RESULT AND DISCUSSION

X-Ray diffraction analysis

XRD pattern helps know the percentage crystallinity of the prepared TiO_2 core-shell nanoparticles. The XRD pattern of TiO_2/ poly (MMA-co-BA) core shell nanoparticles is shown in Figure 1. The estimated value of percentage crystallinity is 33.21%. The rutile phase titanium dioxide showed an intense peak at 2è =28° which can be seen from the XRD pattern in Figure 1. There is a decrease in crystallinity inspite of the presence of TiO2, because the shell material as poly (methyl methacrylate) and poly (butyl acrylate) are amorphous in nature.

The titanium dioxide alone has percentage crystallinity of 45.86 % as seen from literature. Owing to the coating of shell on its surface the percentage crystallinity decreased up to 33.21%.

Differential scanning calorimetric analysis

Differential scanning calorimeter (DSC) is generally used for the determination of glass transition tem-

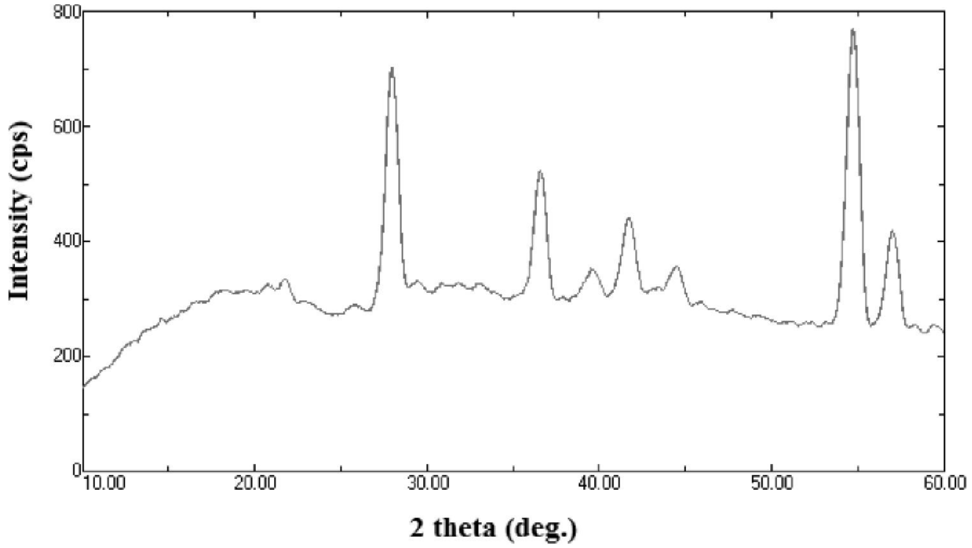

Figure 1 : XRD pattern of core-shell nanoparticles

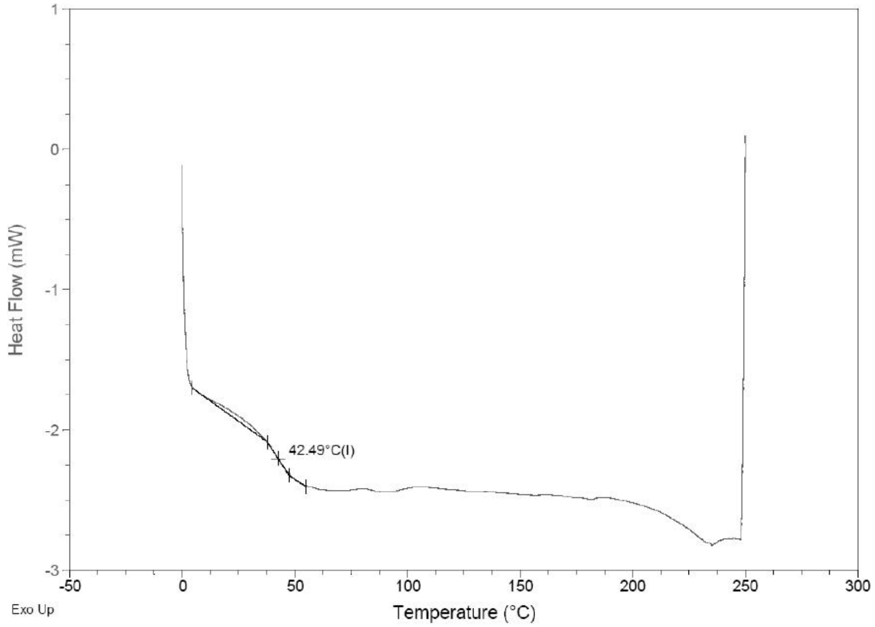

Figure 2 : DSC thermogram of core-shell nanoparticles

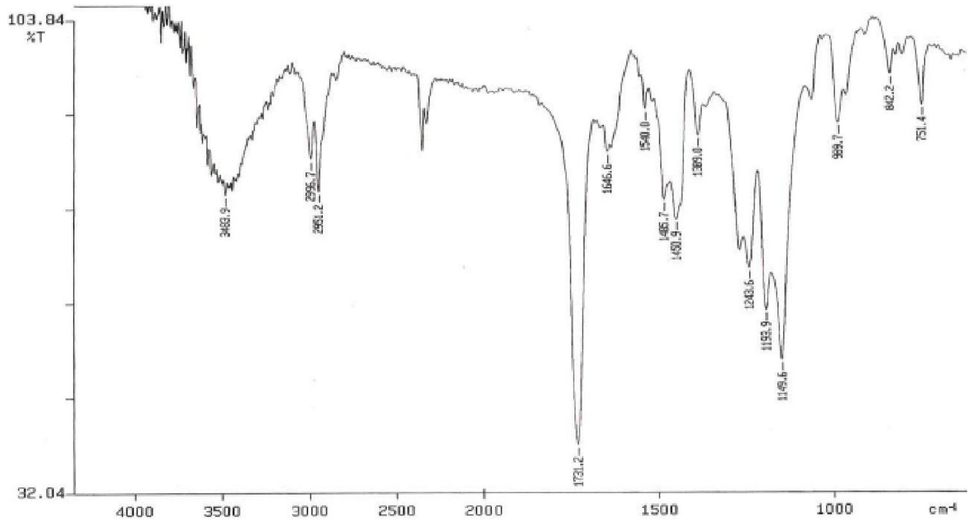

Figure 3 : FT-IR spectra of core-shell nanoparticles.

perature (Tg), melting temperature (Tm), and crystallization temperature (Tc). From DSC we conclude that the theoretical Tg is equal to practical Tg, making ussure that 100% conversion of reactants to product has taken place through the reaction. From the Figure 2 it shows that the practical Tg is equal to theoretical Tg.

Fourier transforms infra-red spectroscopy (FT-IR) analysis

FT-IR spectra of the core shell nanoparticles is shown in Figure 3 which corresponds to the aminopropyltriethoxy silane treated TiO_2 with a poly (MMA-co-BA) shell.

The vibration absorption at low frequency such as 751.4 cm^{-1} and 842.2 cm^{-1} shows the existence of Ti-O-Ti backbone. The peak around 3400 cm^{-1} and 3600cm^{-1} is the characteristic peak for surface hydroxyl on TiO_2. The absorption band in 1149.6 and 1243.6 cm^{-1} occurs in the spectrum of silica coated TiO_2 which is due to the presence of aminopropyltriethoxy silane. The stretching at 1646.6 and 1731 cm^{-1} shows the presence of C=O in MMA and BA backbone, and aliphatic functional group such as CH_2, the stretching at 2951.2 and 2996.7 cm^{-1} shows the presence of the methyl group CH_3, also the absorption peaks at 1149.6, 1193.9 and 1243.6 cm^{-1} shows the C-O bond which present in

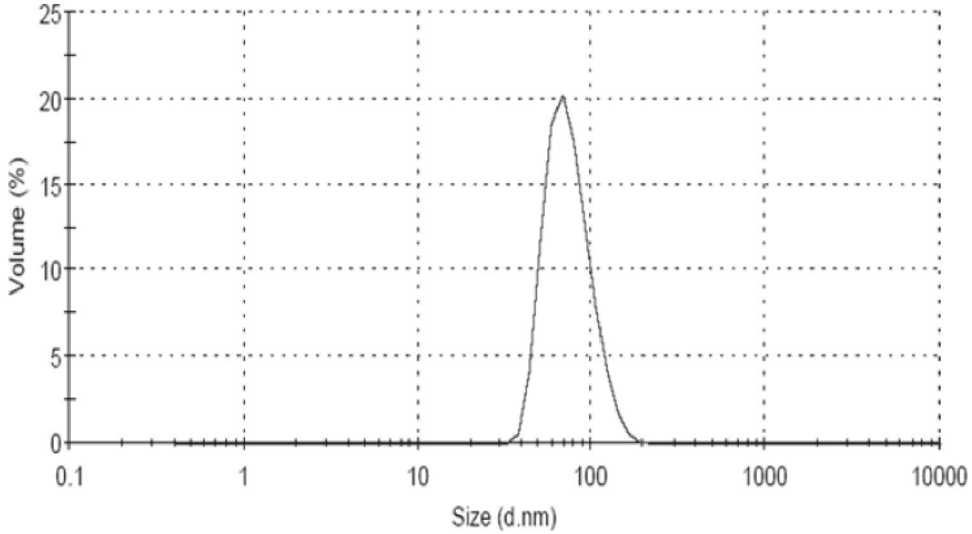

Figure 4 : Particle size of core-shell nano particle.

backbone of MMA/BA. The peaks at 2951.2 and 2996.7 cm^{-1} are characteristics for PMMA/BA. The stretching at 3483 cm^{-1} is characteristic peak of NH_2 which is present in aminopropyltriethoxy silane.

Particle size analysis

Particle size and polydispersity index of the prepared core-shell is 75.21 nm and.0132 respectively. From Figure 3, it is confirmed that the particle in nano sized due to the microemulsion polymerization.

Mechanical property

The mechanical properties of nanocomposites depends on many factors, including the aspect ratio of the filler, the degree of dispersion of the filler in matrix resin and the adhesion at the filler matrix interface and extent of exfoliation. TABLE 1 shows the loading of synthesized impact modifier were added at diff ratio from 0%, 1%, 3%, and 5 %.

From TABLE 3 it can be seen that with the increase in loading of the synthesised impact modifier modulus of PVC nanocomposite also increased (increased up to 33.04 %) because the synthesised impact modifier has the core –shell geometry and the shell is made up of copolymer of methyl methacrylate and butyl acrylate, which are compatible with polyvinyl chloride. So it increased the interaction between each other improving the interfacial adhesion between polyvinyl chloride and copolymer of methyl methacrylate and butyl acrylate.

TABLE 3 : Mechanical properties of PVC nano composites

% loading of the core-shell nanoparticle	Young Modulus (MPa)	Tensile Strength (MPa)	%Elongation at Break	Impact Strength (J/m)
0	1502.2	41.25	12.24	11.2
1	1719.5	47.77	17.25	No Break
3	1963.4	57.6	21.25	No Break
5	1998.4	58.20	22.05	No Break

Tensile strength also increased with increase in impact modifier concentration and it increased up to 41.09%. Impact modifier contains butyl acrylate and it is amorphous material and it shows the rubber like nature after polymerization also the butyl acrylate having Tg -45 which also shows the rubber like nature. PMMA having the good compability with PVC due to specific interaction of a hydrogen bonding type between carbonyl group (C=O) of PMMA and hydrogen from (CHCl) group of PVC.

Impact strength of PVC nano composite increased with increase in impact modifier content from. TABLE 3 shows the without (0%) impact modifier the samples broke at 11.2 J/m; however as the impact modifier concentration increased there is no break even at 1 % loading of impact modifier, due to the core material content inorganic material and the inorganic particles act as stress concentration points and retard crack propagation to become destructive. When particle volume fraction increases, the distance between particles superimposes each other, which is important for local plastic deformation within the composite and the absorption of impact energy.

CONCLUSION

TiO2/ poly (MMA-co-BA) nanoparticle with core-shell structure was synthesized by microemulsion polymerization. Synthesized impact modifier has significant effect on Tensile strength and impact strength. 5% loading of Impact modifier gave the 41% improvement in tensile strength and 33 % improvement in modulus. Impact strength also increased constantly, result shows no break even at 1 % loading.

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