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Core–double shell hybrid nanocomposites as multi-functional advanced materials

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ABSTRACT

In this research work, we report circular type silane modified CaCO₃ (as core) nanoparticles (NP) encapsulated with polystyrene (PS) and polymethyl methacrylate (PMMA) (as double shell layers). These core-double shell [CaCO₃-PS/PMMA] hybrid nanostructures were prepared by a stepwise micro-emulsion polymerization, and characterized by fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy, field emission scanning electron microscopy, elemental mapping, differential scanning calorimetry and thermo gravimetric analysis. These core-double shell hybrid nanostructured composites had perfect nanoscale shape with narrow size distribution (average size 120 nm), smooth surface and non-agglomerated structures. These observations reflected the strong interfacial interaction between silanated CaCO₃-NPs and polymer NPs, which imply the successful grafting of polymer chains onto the surface of silane modified CaCO₃-NPs.

KEYWORDS: Core-double shell nanostructures, Hybrids, Multifunctional properties, Characterization.

1. INTRODUCTION

With rapid extending developments of nanomaterials, the great importance has been recognized to develop multi-functional properties in a single nanomaterial because they are the ideal potential agents in multifunctional application [1]. Moreover, the interaction between nano scaled components can greatly improve performance for application and generate new synergistic properties. One extremely emerging example of nanomaterials is core-shell structured particles which have diverse applications[2] such as photo catalysis[3], biomedical [4], drug-delivery [5], magnetic and silicon semiconductor [6,7], photovoltaic solar cell [8], microelectronic and optoelectronic[9], coatings [10], adhesives[11], pigments [12], super capacitor [13], binders [14], filler for polymers application and biotechnology and material science. It has been reported that integrated properties of such materials are better than those in individual counterparts [15]. Core-shell nanostructures are consisting of a core structural domain with shell layer wrapped over it which may be composed of variety materials including polymer and metals [16].

In last decade, extensive researches have been carried out towards developments, properties investigation and application of inorganic/organic hybrid core-shell nanoparticles. These advanced materials have great importance due to their combined properties of both inorganic nanoparticles and organic molecules. Hybrid core-shell nanoparticles have unique properties; because inorganic nanoparticles can provide the strength while organic shell provides compatibility to the polymer matrix. The preparation of hybrid nanoparticles by micro-emulsion polymerization is an efficient way to prevent their agglomeration and thus significantly enhance the stability of nanoparticles. Core-shell hybrid nanoparticles have been reinforced in variety of polymers, such as polycarbonate (PC), poly (methyl methacrylate) (PMMA), poly (butylene terephthalate) (PBT), and polyvinyl chloride (PVC) to increase the multifunctional properties. Dispersion of core-shell hybrid nanomaterials in polymer matrix results improvement in thermal, rheological and mechanical

properties, which is one of the reasons for their potential applications in some, fields [17-25]. Inorganic nanoparticles have their tendency to get agglomerated because of their high surface area and surface energy. To overcome on this problem traditionally, low-molecular coupling agents or surfactants are mostly used to treat. But this treatment is not mostly effective. Encapsulation of nanoparticles by the polymer i.e. core-shell is the best way to overcome the problem. But a single organic polymer shell will merge with different polymer matrix at the time of processing and the inorganic core would be fixed in between polymer chains and increase the specific properties. But to increase the multi-functional properties of a polymer matrix multifunctional fillers are required, i.e., core-double shell hybrid nanostructures. Single core particles can be encapsulated by two different polymers, i.e. a first single shell would be merged with polymer chains and the second shell would remain itself with core. And when some stresses are applied on the resulting hybrid nanocomposites, the core-shell hybrid nanostructures would penetrate inside the polymer matrix with respect to the stress applied and as a result property would be increased. Recently, we have synthesized nanoparticles of polystyrene (nPS) and polymethyl methacrylate (nPMMA) by modified micro-emulsion process as well as novel atomized micro-emulsion process. These nPS and nPMMA particles were isolated by blending with polypropylene (PP), linear low-density polyethylenes (LLDPE) to study their rheological, thermal and mechanical properties. In our previous work, we have successfully prepared core-single shell hybrid nanomaterials such as nano-calcium carbonate (nCaCO₃)/PS, (nCaCO₃)/PMMA and CaSiO₃/PS [15,26-32] as hybrid nanomaterials with CaCO₃ and CaSiO₃ as core and PS, PMMA as shell prepared by atomized polymerization technique and isolated core-shell nanoparticles were incorporated in PP and high impact polystyrene (HIPS) matrices. In continuation of our previous work, we developed CaCO₃-PS/PMMA core-double shell nanomaterials by step wise microemulsion process with an efficient production. However, to the best

of our knowledge, no study has been reported on the encapsulation of CaCO_3 by double polymer shell layers nanoparticles. Furthermore, we have also focused on improving the performance of the $\text{CaCO}_3/\text{PS}/\text{PMMA}$ core-double shell nanocomposites by enhancing the interfacial adhesion after addition of small amount of core-double shell nanoparticles. Thus, this approach would improve the compatibility of the CaCO_3 nanoparticles with the polymer matrix through the lipophilic polymer layer (PS/PMMA layer) grafted onto the surface of the CaCO_3 nanoparticles. In the present study, we used a stepwise micro-emulsion polymerization to synthesize core-shell hybrid nanostructures of CaCO_3 as a core and PS and PMMA as a shell, the core particles act as “seed particles”, on to the surface of which the shell polymers are supposed to be dispersed. These core-shell hybrid nanostructures can be used as a filler and impact modifier for development polymer blend nanocomposites with different wt. % loading. In this study, structural, surface morphology and stability of the core-double shell hybrid nanostructures are carried out and there results are presented here.

2. EXPERIMENTAL

2.1 Materials

CaCO_3 , with average diameter in the range of 70 nm were procured from Solvay chemicals, USA. Nano CaCO_3 was modified by silane coupling agent as triethoxyvinylsilane (TEVS). Monomers: Styrene (St); Methyl methacrylate (MMA); the initiator: ammonium persulfate (APS); surfactants: sodium dodecyl sulphate (SDS), were procured from Sigma Aldrich, Mumbai, India. St and MMA were treated with 5% NaOH aqueous solution to remove the inhibitor and were distilled under reduced pressure in nitrogen atmosphere prior to start the polymerization. All other materials were of analytical grade, and used further without purification. Deionised (DI) water was used throughout

the all experiments. Solvents like acetone, ethanol and toluene for washing purpose were procured from Sigma Aldrich, Mumbai, India.

2.2 Pretreatment of CaCO₃ nanoparticles

First, desired amount (5 phr w.r.t. weight of CaCO₃) of TEVS was dissolved in acetone. 20 gm of CaCO₃ was dispersed in silane-acetone mixture under mechanical stirring at 500 rpm. Subsequently the mixture was sonicated under probe sonicator [Chrome Tech, India] for 30 min with 5 sec interval time followed by stirring at 500 rpm at room temperature for 2 h. The resulting dispersion was kept for overnight to react TEVS with nCaCO₃. Modified nCaCO₃ were collected by filtration and rinsed several times with acetone and the resulting filter cake was dried overnight at 110 °C under low vacuum [29].

2.3 Synthesis and mechanism of core-double shell hybrid nanostructures

In general, core-double shell hybrid nanoparticles were synthesized using a two-step process, first synthesis of single shell i.e. CaCO₃-PS and then synthesis of the second shell i.e. CaCO₃-PS/PMMA double shell. Typically, CaCO₃ nanoparticles were dispersed in DI water under ultrasonic bath for 30 min. Afterwards, different amounts of SDS, APS, mixture of NH₃+NaHCO₃ and DI water were charged into a reactor equipped with a feeding tube, a thermocouple and stirring impeller. These were kept into oil/water (o/w) atomized microemulsion system with proper surface modification for coating the shell material (Scheme 1). The typical recipes are as follows: 1.5 g SDS was dissolved in 145 g of DI water and kept in beaker to form a clear solution which was sonicated for 30 min. This clear solution was poured into a 1 L stainless steel reactor with an agitator having stirring speed of at 200 rpm. In addition to this, 0.25 g of APS dissolved in 5 g of DI water was added also to the

reactor. The reactor was sealed and the temperature was raised to 75 ± 5 °C to form free radicals. Then, 10 g of stabilizer-free St was added drop wise into the reactor at the rate of 0.02 and 0.09 g/s, respectively and slow stream of purged nitrogen gas was applied through a nitrogen inlet. A constant agitation at reaction temperature of 75 ± 5 °C was maintained throughout the reaction. After the complete addition of St, the reaction was continued to stir for another 1.5 h and stopped by allowing to cool the dispersion to room temperature. A translucent dispersion was formed after the complete polymerization reaction indicated the formation of microemulsion.

For perfect double shell encapsulation of CaCO_3 , the possible core-double shell growth mechanism is shown briefly in [Scheme 1](#) and [Scheme 2](#). First, the TEVS as reactive silane coupling agent reacted with hydroxyl group to form covalent bond and to functionalize the hydrophobic surface enough to have a close affinity with PS as a shell. The reaction can be preceding between each $\text{Si-OC}_2\text{H}_5$ group and the hydroxyl groups on the surface of the nanoparticles. When the TEVS molecules were grafted onto the CaCO_3 surface, it contained an unsaturated double bond on the surface of nanoparticles. During polymerization, these unsaturated double bonds of TEVS get copolymerized with unsaturated groups of styrene to covalently graft on the surface of modified CaCO_3 nanoparticles. Consequently, TEVS links the polymer and the CaCO_3 nanoparticles through chemical bonds, and the link results in enhancement of the interfacial adhesion and compatibility between the inorganic CaCO_3 nanoparticles and the polymer matrix. The organic polymer chains of TEVS induce steric hindrance to the association between CaCO_3 nanoparticles and prevent aggregation. Besides synthesis of another shell of PMMA, same process was involved after isolation and drying of CaCO_3/PS core-shell nanoparticles, where PMMA chain growth process is accompanied with the radical transferring to first PS shell macromolecule [[29](#), [30](#), [34](#), [36](#)].

2.4 Isolation of core-double shell hybrid nanostructures

Core-double shell nanostructures were isolated by drop wise addition of the latex into ethanol with constant stirring, and the mixture was kept overnight for uniform dispersion of precipitates. The precipitated particles were filtered under vacuum and washed several times with ethanol/water (1:1) and then dried under vacuum for 48 h at 50 °C.

2.5 Percentage grafting analysis of core-double shell hybrid nanostructures

The stepwise microemulsion polymerization was used for the formation of CaCO₃-PS/PMMA core-double shell hybrid nanostructures using free CaCO₃ nanoparticles, nPS and nPMMA nanoparticles. In order to determine the percentage grafting, it is necessary to separate CaCO₃-PS/PMMA core-double shell hybrid nanostructures from free CaCO₃ nanoparticles, nPS and nPMMA nanoparticles. In a typical analysis, original latex containing CaCO₃-PS/PMMA core-double shell hybrid nanostructures, free CaCO₃ nanoparticles, nPS and nPMMA nanoparticles were dried in an air oven at 120 °C for 2 h. Further, same amount of latex was isolated by acetone under constant stirring and allowed to settle down; as a result free modified CaCO₃ nanoparticles remained in dispersed form. The supernatant solution with free modified CaCO₃ nanoparticles was carefully separated from the residue and centrifuged at 10,000 rpm to get free modified CaCO₃ nanoparticles. It is given by following equation (1), where P is the Wt. of dry latex sample or Wt. of free modified CaCO₃ nanoparticles + nPS + nPMMA + CaCO₃-PS/PMMA and Q is the Wt. of centrifuged free modified CaCO₃ nanoparticles.

$$\% \text{ free modified CaCO}_3 \text{ nanoparticles} = (Q/P) \times 100 \% \quad (1)$$

The modified CaCO₃ nanoparticles, nPS and nPMMA nanoparticles were washed 3 times with DI water/acetone mixture (50/50), vacuum filtered and vacuum dried at 50 °C to get powder form. The

CaCO₃/PS/PMMA core-double shell hybrid nanoparticles were then separated from free nPS and nPMMA nanoparticles by soxhlet extraction method with acetone for 12 h. Equation (2) indicates the % of CaCO₃-PS/PMMA. In equation (2), *R* is the Wt. of CaCO₃-PS/PMMA + free nPS + free nPMMA nanoparticles, and *S* is the Wt. of CaCO₃-PS/PMMA after Soxhlet extraction.

$$\% \text{ free nPS and nPMMA in CaCO}_3\text{-PS/PMMA nanostructures} = R - (S / R) \times 100\%$$

$$\% \text{ CaCO}_3\text{-PS/PMMA} = (S/R) \times 100\% \quad (2)$$

The content of shell polymer on modified CaCO₃ nanoparticles was determined by TGA. First free modified CaCO₃ nanoparticles, nPS and nPMMA nanoparticles were separated from CaCO₃-PS/PMMA core-double shell hybrid nanoparticles by the above mentioned method. Approx, 10–12 mg of sample was heated up to 600 °C from room temperature at the rate of 10 °C/min under nitrogen atmosphere at a flow rate of 50 mL/min. Polymer double shells were totally decomposed at 600 °C and CaCO₃ cores remained as residue. Equation (3) indicates the % shell of polymer. In equation (3), *T* is Wt. of CaCO₃-PS/PMMA core-double shell hybrid nanostructures before TGA, *U* is Wt. of residue after TGA.

$$\% \text{ grafted modified CaCO}_3\text{-PS/PMMA nanostructures} = (U/T) \times 100 \%$$

$$\% \text{ shell polymer} = T - (U/T) \times 100\% \quad (3)$$

2.6 Characterizations

Topographical morphology of CaCO₃-PS/PMMA nanostructures was studied by back scattered electron techniques as transmission electron microscope (TEM, Philips CM-200, Eindhoven, The Netherlands) with 75 μA of filament current and 200 kV of accelerating voltage. TEM samples were

prepared by dispersing the material in ethanol and dipping the TEM grid (holey C-foil on Cu grid) into this suspension followed by drying in air to measure the particle size and grafting efficiency of core-double shell nanostructures, while EDS mapping spectra for analyzing elemental composition were recorded on spectrometer attached with the FE-SEM. nCaCO₃, modified nCaCO₃, nPS, nPMMA, nCaCO₃-PS and CaCO₃-PS/PMMA nanostructures were characterized by using X-ray diffractometer (XRD, Bruker D8 Advance, Berlin, Germany) in the range of 10-80°. The samples were placed vertically in front of the X-ray source. The detector was moving at an angle of 2θ while the sample was moving at an angle of θ at the wavelength λ= 1.54 Å (Cu Kα, a tube voltage 40 kV and tube current 25 mA). Functional groups analysis was done by FTIR spectrophotometer (FTIR-8000 Spectrophotometer, Shimadzu, Tokyo, Japan). The number of scans per sample was 25 and resolution of the measurements was 4 cm⁻¹. The recorded wave number range was kept at 500-4000 cm⁻¹. All samples were taken in powder form along with KBr and recorded at room temperature. DSC was carried out to investigate the glass transition temperature (T_g) using a differential scanning calorimeter (DSC-60, Shimadzu, Tokyo, Japan). The temperature was programmed from 30 to 300 °C at a heating rate of 10 °C/min under a nitrogen atmosphere (50 mL/min) to prevent oxidative degradation of samples. The inflection point of the slope of the heat capacity plot was taken as the glass transition temperature (T_g). Thermal stability was determined by a thermo gravimetric analyzer (TGA-50, Shimadzu, Tokyo, Japan). 10 mg of sample was placed on a Pt pan for TGA measurement. The temperature was programmed from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere to avoid thermoxidative degradation. All samples were run and analyzed two times.

3. RESULTS AND DISCUSSION

3.1 FTIR spectra

The nCaCO₃, modified nCaCO₃, nPS, nPMMA, nCaCO₃-PS, nCaCO₃-PMMA and CaCO₃-PS/PMMA nanostructures were further characterized by FTIR spectroscopy in the spectral range of 500-4000 cm⁻¹. In Fig. 1(a), for the spectrum of bare CaCO₃ nanoparticles, the broad absorption band at 3336 cm⁻¹ indicated the presence of -OH on CaCO₃ surface. In Fig. 1(b), modified nCaCO₃ particle, the sharp peak at 1642 cm⁻¹ indicated the presence of unsaturation C=C bond in TEVS attached to nCaCO₃ surface. In general, broad absorption bands in the range 1100–1050 cm⁻¹ were characteristic bands of Si-O-C in TEVS. In Fig.1(c), the absorption bands at 3027, 2885, 1491, 1369 and 756 cm⁻¹ revealed the C-H stretching vibration in aromatic phenyl ring; whereas absorption bands at 2926, 1452 cm⁻¹ were assigned for C-H unsymmetrical and symmetrical stretching vibration of CH₂ in the chain backbone. The specific peaks at 905 and 840 cm⁻¹ were attributed to the amorphous phase present in nPS. From Fig. 1 (d), the FTIR spectrum confirmed the formation of nPMMA, in which absorption peak at 750.33 cm⁻¹ revealed the stretching of -CH₂ bond, while 1147.68 and 1730.21 cm⁻¹ indicated the existence of -C-O and 2949.26 cm⁻¹ for CH₃ in nPMMA. In Fig. 1(e), nCaCO₃/PS core-shell hybrid nanoparticles were characterized by the C-H stretching vibration in aromatic phenyl ring at 3082, 3056, 3027, and 1600 cm⁻¹, whereas absorption bands at 2922 and 2850 cm⁻¹ were assigned to C-H unsymmetrical and symmetrical stretching vibration of CH₂ in chain backbone indicating the existence of PS grafting chains on nCaCO₃ surface. The disappearance of the peak at 1642 cm⁻¹ implied that silane coupling agent had been covalently bonded with St by the unsaturated double bond in the polymerization (Fig. 1f), CaCO₃-PMMA core-shell hybrid nanoparticles showed the stretching of C-H bond in CH₂ group at 2850 and 2992 cm⁻¹ indicated presence of CH₂ group in PMMA backbone. The asymmetrical bending

vibration of -CH_3 was recorded near 1450 cm^{-1} . The disappearance of the peak at 1642 cm^{-1} implies that silane coupling agent is covalently bonded with MMA by the unsaturated double bond during the polymerization. In Fig. 1 (g), CaCO_3 -PS/PMMA core-double shell hybrid nanostructures were characterized by the asymmetrical bending vibration of -CH_3 was identified near 1450 cm^{-1} of MMA while 756 cm^{-1} revealed the C–H stretching vibration in aromatic phenyl ring of St. The specific peaks at 905 and 840 cm^{-1} were attributed to the amorphous phase present in nPS. It can be inferred from the above results that silane links up the polystyrene and n CaCO_3 nanoparticles through chemical bonds. Consequently, it leads to the enhanced adhesion and compatibility for the PMMA nanoparticles with n CaCO_3 /PS core-shell hybrid nanoparticles [36-38].

3.2. XRD analysis

XRD study was done to determine and to confirm the crystallization phases. Figure 2 showed the XRD patterns of core CaCO_3 , modified CaCO_3 , nPS, nPMMA, CaCO_3 -PS, CaCO_3 -PMMA and CaCO_3 -PS/PMMA. In the case of CaCO_3 , it can be said that phase structures exhibited crystalline structure with high peak intensity of XRD planes as compare to modified and other hybrid nanostructures. In Fig.2 (a), for nano- CaCO_3 , the XRD diffraction planes corresponded to CaCO_3 crystal as calcite. The results demonstrated that the sample was pure phase nanoparticles of CaCO_3 that showed high intensity at $2\theta=29.39^\circ$ corresponds to the reflections from the (104) planes. In Fig. 2 (b), the XRD patterns showed same peaks with lower crystallinity due to the organic coating of silane coupling agent. On the other hand, the XRD pattern of nPS (Fig. 2c) exhibited the broad amorphous peak centred at $2\theta = 19.5^\circ$ and no other peaks were observed. This signifies that a purely amorphous region is present in the nPS. Figure 2 (d) showed the peaks assigned to PMMA/st-PMMA stereo complex. The diffraction peak at 12.5° corresponds to PMMA crystalline structure of

PMMA shell. Both CaCO₃/PS and CaCO₃/PMMA (Fig. 2e-f) samples exhibit a broad amorphous peak centred at $2\theta = 19.5^\circ$ and 12.5° , respectively. In the sample, the broad amorphous peaks and other less intensity are mainly owing to the presence of a relatively amorphous PS and PMMA layer grafted on the CaCO₃ with very nano thin layer. Contrarily, Fig.2 (g) shows that these characteristic peaks of the sample are broad and indicate greater suppression of the crystalline behaviour of the CaCO₃ than that seen in the CaCO₃/PS and CaCO₃/PMMA samples. This increased suppression could be attributed to superior simultaneously grafting of the both amorphous PS and PMMA double shell layers resulting in the constraint of the nCaCO₃ [37, 39-41].

3.3. Structural morphology and EDS mapping of core-double shell hybrid nanostructures

In order to further confirm the formation and the shape of CaCO₃-PS/PMMA core-double shell hybrid nanostructures, TEM and FE-SEM EDS mapping were carried out to characterize the samples. The surface morphology of the bare nCaCO₃, modified nCaCO₃, nPS and nPMMA was studied by TEM, and presented in Fig.3 (a-d). Their morphology was observed circular in shape and the particle surface seems smooth with an average diameter of 80 nm.

Figure 4 (a-c) showed CaCO₃/PS, CaCO₃/PMMA and CaCO₃-PS/PMMA nanostructures that were obtained by stepwise microemulsion technique, where St followed by MMA was polymerized around CaCO₃ using SDS as surfactant. The samples demonstrated that core CaCO₃ were completely covered by the thin polymer amorphous shells having 8-10 nm thickness of PS and 25-30 nm thickness of PMMA (Fig. 3c) which adheres strongly to the core within. The particles size increased significantly after PS/PMMA layer adsorption on the CaCO₃ nanoparticles surface. The CaCO₃-PS/PMMA have sizes slightly varying from 115 nm in width, from these observations, it can be inferred that PS is successfully grown around CaCO₃ nanoparticles, which was desirable due to its

high thermal stability, and consistent composite making ability. Furthermore, its one by one growing tendency around each CaCO_3 nano particles is beneficial to reduce the possibility of bare surface touch within CaCO_3 nanoparticles that is a major cause of aggregation. The EDS analysis (Fig.5-8) confirmed the presence of elements, which showed Ca, C and O peaks as well as relative quantities of these different elements in CaCO_3 . The EDS spectra as well as elemental mapping also confirmed the presence of amorphous PS, PMMA and PS/PMMA layers on the surface of the CaCO_3 .

3.5. DSC analysis of core-double shell hybrid nanostructures

DSC thermo grams of nPS, nPMMA, n CaCO_3 -PS, n CaCO_3 -PMMA and n CaCO_3 -PS/PMMA are shown in Figure 9. The DSC curves of the n CaCO_3 /PS and n CaCO_3 /PMMA (Fig.9 c-d) showed slightly higher glass transition temperature ($T_g = 125\text{ }^\circ\text{C}$ and $T_g = 136\text{ }^\circ\text{C}$) than nPS and nPMMA ($T_g = 116\text{ }^\circ\text{C}$ and $T_g = 128\text{ }^\circ\text{C}$, respectively) shown in Fig.9 (a-b). On the other hand, the n CaCO_3 -PS/PMMA showed two different glass transition temperatures ($T_g = 125\text{ }^\circ\text{C}$ and $T_g = 136\text{ }^\circ\text{C}$). The possible reasons for this high T_g of n CaCO_3 -PS and n CaCO_3 -PMMA than that of nPS and nPMMA are (i) strong interfacial interaction between the modified n CaCO_3 as core and the PS and PMMA as double shells. The silane coupling agent chemically grafted the shell with the core, and thus the mobility of the PS and PMMA chains on the particle surfaces was restricted. And from Fig.9 (e) showed two different glass transition temperature of both PS and PMMA which were successfully grafted on the surface of the n CaCO_3 and more energy was needed to transition from a glassy state to a rubbery state. During DSC scanning of core-double shell hybrid nanostructures, the loss of surface energy resulted in energy release.

3.6. Thermal stability of core-double shell hybrid nanostructures

Figure 10 shows the thermal stability of the n CaCO_3 , modified n CaCO_3 , nPS, nPMMA, n CaCO_3 -PS, n CaCO_3 -PMMA and n CaCO_3 -PS/PMMA nanostructures. No significant mass loss was observed

below 370 °C, however, at higher temperature, the degradation of the organic layer becomes apparent due to the greater mass loss. There no change in the onset decomposition temperature (d_{on}) of the nCaCO₃ was observed, but slightl change shows in the onset decomposition temperature (d_{on}) of modified nCaCO₃ and percentage weight loss (W_L) (1.2 %) was found (Fig. 10 b), which was due to the decomposition of silane coupling agent and adsorbed water on the particles surface. A remarkable difference was observed in the thermal behavior of the nPS, nPMMA, nCaCO₃-PS, nCaCO₃-PMMA and nCaCO₃-PS/PMMA (Fig.10 c-g). Nano-CaCO₃-PS and CaCO₃-PMMA core-shell particles (Fig. 10 e-f) showed higher thermal stability (d_{on} at 390 °C and 386 °C, respectively) with minimum weight loss ($W_L = 65\%$ and 62%) than pure nPS and nPMMA (Fig. 10 c-d) particles (d_{on} at 370 °C and 369 °C with 100 % W_L). The synthesized nano CaCO₃-PS/PMMA core-double shell hybrid nanostructures showed two step degradation (Fig.10 g). Initial decomposition occurred within the range of 30-180 °C. Further, approximate 4 % W_L was reported at 200 °C, while the second step degradation occurred between the range of 180-350 °C and only 12% W_L occurred at 310 °C. Finally last step degradation observed between 310-600 °C and only 76 % W_L was reported at 600 °C. The different behaviors further supported the existence of a strong interaction between the modified CaCO₃ core and the PS/PMMA double shell with the help of silane coupling agent. The W_L of the CaCO₃-PS/PMMA core-double shell hybrid nanostructures between 310 and 600 °C was used to calculate the amount of grafted PS/PMMA on the modified CaCO₃. The extracted CaCO₃-PS/PMMA core-double shell hybrid nanostructures showed 68 % grafting.

4. CONCLUSION

Core-double shell hybrid nanostructures of CaCO₃-PS/PMMA were synthesized by an efficient step wise microemulsion polymerization. The TEM micrographs of the resulting materials showed

perfect core-double shell morphology of CaCO₃-PS/PMMA, while XRD and FTIR spectra confirms the interaction of the CaCO₃ as core and PS/PMMA as double shell. Moreover, the core-double shell hybrid nanostructures demonstrated higher thermal stability and T_g than that of pristine nPS and nPMMA. Hence, encapsulation of CaCO₃ by double shell layers of PS and PMMA hybrid nanostructures endow the multifunctional properties in a single hybrid system. Similarly, the use of core-double shell layers hybrid materials can be suggested as a movable filler, impact modifier, and lubricating agent for polymer hybrid blend system. Further studies on the relationship between the CaCO₃-PS/PMMA filled polymer blend nanocomposites [CaCO₃/PS/PMMA filled polylactide] and their mechanism indicating polymer matrices along with their detailed investigations of the physico-mechanical (multifunctional) properties will be future prospective of this work.

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Captions for Figures

- Figure 1** FTIR spectra of (a) bare CaCO_3 nanoparticles, (b) TEVS modified CaCO_3 nanoparticles, (c) nPS, (d) nPMMA, (e) CaCO_3 -PS, (f) CaCO_3 -PMMA, (g) CaCO_3 -PS/PMMA core-double shell hybrid nanostructures
- Figure 2** XRD diffraction pattern of (a) bare CaCO_3 nanoparticles, (b) TEVS modified CaCO_3 nanoparticles, (c) nPS, (d) nPMMA, (e) CaCO_3 -PS, (f) CaCO_3 -PMMA, (g) CaCO_3 -PS/PMMA core-double shell hybrid nanostructures
- Figure 3** TEM micrograph of (a) bare CaCO_3 nanoparticles, (b) TEVS modified CaCO_3 nanoparticles, (c) nPS, (d) nPMMA
- Figure 4** TEM micrograph of (a) CaCO_3 -PS, (b) CaCO_3 -PMMA, (c) CaCO_3 -PS/PMMA core-double shell hybrid nanostructures
- Figure 5** FE-SEM and EDS mapping of bare CaCO_3 nanoparticles
- Figure 6** FE-SEM and EDS mapping of TEVS modified CaCO_3 nanoparticles
- Figure 7** FE-SEM and EDS mapping of CaCO_3 -PS core-shell hybrid nanostructures
- Figure 8** FE-SEM and EDS mapping of CaCO_3 -PS/PMMA core-double shell hybrid nanostructures
- Figure 9** DSC thermo grams of (a) nPS, (b) nPMMA, (c) CaCO_3 -PS, (d) CaCO_3 -PMMA, (e) CaCO_3 -PS/PMMA core-double shell hybrid nanostructures
- Figure 10** TGA curves of (a) bare CaCO_3 nanoparticles, (b) TEVS modified CaCO_3 nanoparticles, (c) nPS, (d) nPMMA, (e) CaCO_3 -PS, (f) CaCO_3 -PMMA, (g) CaCO_3 -PS/PMMA core-double shell hybrid nanostructures
- Scheme 1** Reaction mechanism of the formation of nano- CaCO_3 /PS/PMMA core-double shell Hybrid nanostructures
- Scheme 2** Mechanism of step wise microemulsion polymerization.



















