

Preparation and characterization of poly(vinyl chloride) calcium carbonate nanocomposites via melt intercalation

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Abstract Calcium carbonate was synthesized by in situ deposition technique and its nano size (35–60 nm) was confirmed by transmission electron microscopy (TEM). Composites of the filler CaCO_3 (micro and nano) and the matrix poly(vinyl chloride) (PVC) were prepared with different filler loadings (0–5 wt%) by melt intercalation. Brabender torque rheometer equipped with an internal mixer has been used for preparation of formulations for composites. The effect of filler content both nano- and micro level on the nanostructure and properties is reported here. The nanostructures were studied by wide angle X-ray diffraction and scanning electron microscopy. The mechanical, thermal, and dynamic mechanical properties of PVC/micro- and nano- CaCO_3 composites were characterized using universal testing machine, thermogravimetric analyzer, and dynamic mechanical analyzer. The results of thermal analysis indicated that the thermal stability of PVC/nano- CaCO_3 composites was improved as compared with corresponding microcomposites, and that of pristine PVC and maximum improvement was obtained at 1 and 3 phr loadings. However, the tensile strength decreased significantly with increase loading of both nano- and micro- CaCO_3 , whereas storage modulus and glass transition temperature increased significantly.

Introduction

In the recent years, organic–inorganic composites, especially nanocomposites, have received great attention because these materials often exhibit spectacular properties. Various nanoscale fillers, including montmorillonite, silica, calcium carbonate, and aluminum oxide, are reported to enhance the mechanical and thermal properties of polymers such as toughness, stiffness, and heat resistance. The mechanical properties of nanocomposites are greatly dependant on the filler's aspect ratio, the surface area, and the interactions between the filler and the polymer matrix, for example, layered silicates and fibers exhibit good reinforcement effects on many polymeric matrices because of the relatively high aspect ratio. However, a relatively high aspect ratio of fillers does not necessarily improve the toughness and sometimes a decrease is also observed. Spherical mineral nanoparticles behave quite differently from layered silicates and fibers. The low aspect ratio and large surface area of spherical mineral nanoparticles could result in strong interfacial interactions between the filler and the polymer matrices. Nanoscale calcium carbonate (nano- CaCO_3) is one of the most common spherical nanoscale fillers used in the preparation of nanocomposites. CaCO_3 can be produced by a variety of methods, including precipitation, dry grinding, and wet grinding. The basic grades of CaCO_3 can be differentiated by changes in the size distribution, particle size, surface area, morphology, surface chemistry, and so on [1–6].

This nanoconcept has been mostly focused on thermoplastic and thermosetting polymers including polyamides, polypropylene (PP), epoxies, and polyesters. The addition of nano- CaCO_3 to composites has been reported to improve the strength, modulus, and toughness significantly. A study

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of PP/nano-CaCO₃ composites revealed a dramatic toughening effect of nano-CaCO₃ on PP. However, the yield strength of PP slightly decreased because of the nucleating effect of nano-CaCO₃ [7, 8].

Relatively a little attention has been paid to poly(vinyl chlorides) (PVC) materials. PVC materials have been extensively used for pipes, doors, windows, and so on in the construction industry. The use of inorganic nanoparticles as fillers such as calcium carbonate and silica not only improves the toughness, electric properties, heat resistance, radiation resistance, and other properties, but also reduces the cost of composites. The effects of inorganic fillers on the microstructure and mechanical properties of PVC composites depend strongly on the particle shape, particle size, aggregate size, surface characteristics, the fraction of fillers, and their degree of dispersion [9–32].

Experimental

Materials

Materials used for the synthesis of nanoparticles of calcium carbonate were CaCl₂, K₂CO₃, and poly(ethylene glycol) PEG. Calcium chloride and potassium carbonate were of analytical grade and PEG (MW 6000 g) was procured from S.d. Fine Chem., Ltd., Mumbai, India. The PVC grade 57GERO68 was obtained from Reliance Industries Ltd., Mumbai, India. Processing aid (PA 20), lubricant processing aid (LI 20), glyceryl monostearate as internal lubricant (LUB 11), PE wax as external lubricant, and organotin stabilizer were obtained from Supreme Industries Ltd., Jalgaon, India. Commercial CaCO₃ (3 μm) was used as filler without any treatment.

Preparation of nanoparticles

The nanosized calcium carbonate filler particles were synthesized using in situ deposition technique as given below [9–11].

Calcium chloride (111 g, 1 m) dissolved in distilled water (100 mL), whereas PEG (372 g, 0.062 m) separately dissolved in hot distilled water (100 mL). These solutions were mixed properly, and digested gently for 12 h. Solution of potassium carbonate (106 g, 1 m) in distilled water (100 mL) was then added slowly with stirring. The nanoparticles formed were allowed to digest overnight. The nanoparticles were filtered, washed thoroughly with distilled water, till freed from PEG traces, and then dried at 110 °C for 2 h. The filler was heated at about 250 °C for removing traces of moisture before compounding.

Preparation of composites

The PVC compounds were formulated with 2.5 phr of processing aid (PA 20), 2.5 phr of lubricating processing aid (LI 20), 3.5 phr of glyceryl monostearate internal lubricant (LUB 11), 3.5 phr of organotin stabilizer, 2 phr PE wax as an external lubricant filler calcium carbonate variable from 0 to 5% (both nano and micro). These formulations were dry blended in a domestic mixer for 15 min. For preparation of composites, formulations were melt intercalated using a Brabender Plastograph EC equipped with an electrically heated mixing head (W 50 EHT mixer) having 55 cm³ volume capacity and two non-interchangeable rotors. The processing temperature, rotor speed, and blending time were set at 170 °C, 60 rpm, and 10 min, respectively. The sample volume of each blending was kept 90% of the actual volume capacity of the mixer. The variation in torque of composites containing nano- and micro fillers separately and for this purpose the sample mass was kept 62 g. The compounds of composites were obtained in the form of lumps. These lumps were then crushed to get the coarser particles/granules (approximately 3–4 mm size) suitable as feed for injection molding to obtain tensile and impact specimens.

Characterization

The particle size and morphology of synthesized nano calcium carbonate particles were studied using transmission electron microscopy (TEM, Philips Tecnai-20) at an accelerating voltage of 200 kV. Sample of calcium carbonate was dispersed in acetone for sufficient time with ultrasonic wave before analysis for particle size.

The structure of PVC–CaCO₃ nanocomposites was characterized by wide angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). WAXD was performed on X'pert-Pro PANALytical (Philips) diffractometer using Cu K α radiation at a generated voltage of 40 kV and current of 30 mA at 25 °C. The diffractions were scanned from 0 to 40° in the 2 θ range in 0.01° steps with a continuous scan.

To study the dispersion of the filler and the morphology of composites, a tensile-fractured surface was coated with Pd and observed on JEOL 6360 SEM at an acceleration voltage of 10 kV with EDS to obtain the scanning images.

A thermogravimetric analyzer (TGA; Shimadzu Japan, model: TGA-50/50H) was used to analyze thermal characteristics of the PVC/micro- and nano-CaCO₃ composites. The composites were heated from room temperature to 550 °C at the rate of 5 °C/min under nitrogen stream. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed.

Tensile strength was determined by subjecting dumb-bell-shaped specimens (in accordance with ASTM D-638) to a universal testing machine (2302, R&D Equipment, Mumbai, India). The specimens were conditioned for 24 h prior to subjecting to the tensile testing. The load cell of 3000 kg and a crosshead speed of 50 mm/min were employed.

The dynamic mechanical analysis was performed using a Eplexor—150 N Gabo Germany using tension clamp at a fixed frequency rate of 10 Hz in a temperature ranging from 30 to 120 °C, and the heating rate of 2°C/min.

Results and discussion

Particle size analysis

The particle size of the calcium carbonate was found to be in the range of 35 to 60 nm as verified from TEM micrograph of CaCO₃ nanoparticles (Fig. 1).

WAXD studies

The WAXD analysis is a very useful method to describe the extent of intercalation and exfoliation of inorganic nanofiller in the composites.

Figure 2a, b shows the WAXD patterns of PVC/micro- and nano-CaCO₃ composites of 1, 3, and 5 wt% of filler. Figure 2a shows minor peaks at $2\theta = 29.0^\circ$, whereas Fig. 2b shows prominent sharp peaks at the same angle, obviously, these peaks are contributed by the filler nano-CaCO₃. The subsiding of peaks at $2\theta = 29.0^\circ$ in Fig. 2a in the case of micro-CaCO₃-filled composites at 1, 3, and 5 wt% indicates fairly good dispersion. While in the case of nano-CaCO₃-filled composites the peaks do not subside instead, they sharpen, and the peak height at $2\theta = 29.0^\circ$

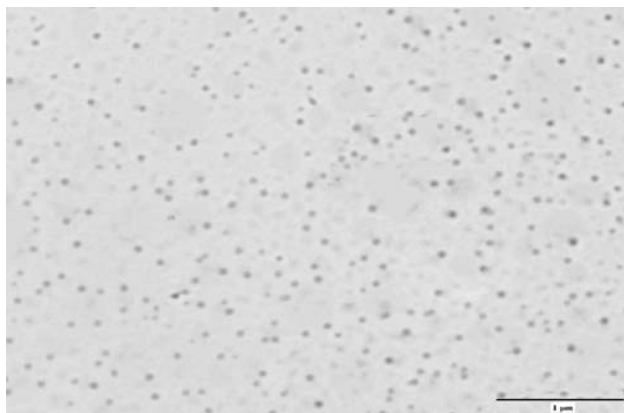


Fig. 1 TEM micrograph of calcium carbonate nanoparticles prepared by in situ deposition technique

increases with increasing content of the filler (1–5 wt%). Therefore it can be concluded that the structure of nanocomposites is intercalated and flocculated and not the exfoliated. This is due to the emerging of peaks instead of subsiding at $2\theta = 29.0^\circ$. This suggested that nano-CaCO₃ did not mix homogeneously because of their high surface energy and there is a strong tendency to form agglomerates. Again these results confirm that melt intercalation of nano-CaCO₃ leads to phase separated system.

Scanning electron micrographs

In order to quantify the relative degree of dispersion of micro- and nano-CaCO₃ particles within the PVC matrix, tensile-fractured surfaces of selected specimens were observed under SEM and their micrographs are shown in Fig. 3a–f.

The study of SEM micrographs revealed that the interface between CaCO₃ particles and the matrix is clear, showing inhomogeneity which suggests that the interfacial adhesion between two phases is poor. Both micro- and nano calcium carbonate aggregate severely in the PVC matrix. It is clear from Fig. 3a–d that the dispersion of filler is good at 1% filler loading for both the composites, whereas the dispersion of microcomposites of 3 and 5% possesses few agglomerates (Fig. 3b, c), and those of nanocomposites possesses more number of agglomerates that too with larger size. The aggregated nano-CaCO₃ particles showed poor compatibility with the PVC matrix. These results are also in accordance with that of WAXD analysis. Thus WAXD and SEM analyses emphasize the need to modify the interactions between PVC and nano-CaCO₃.

Tensile behavior

Figure 4 shows the tensile behavior of PVC/micro- and nano-CaCO₃ composites prepared by melt intercalation.

From the graph it is observed that the tensile strength was decreased monotonously with the increasing filler content. However, the tensile strength for the nanocomposites is lower than that of microcomposites for almost all compositions. With the increasing addition of the nano-CaCO₃ particles, due to the tendency of agglomeration of nanoparticles weak interfacial adhesion existed between the PVC matrix and the nanoparticles, and hence the load-bearing capacity of cross-sectional area of composites decreased, and only a small amount of stress could be transferred from the matrix to inorganic particles, hence tensile strength showed decrement in the magnitude; in this case agglomerated particles easily debonded from the matrix and could not bear any fraction of external load ultimately decreasing the tensile strength. These results are

Fig. 2 WAXD of **a** PVC/micro-CaCO₃ for composites of 1, 3, and 5 wt% of filler and **b** PVC/nano-CaCO₃

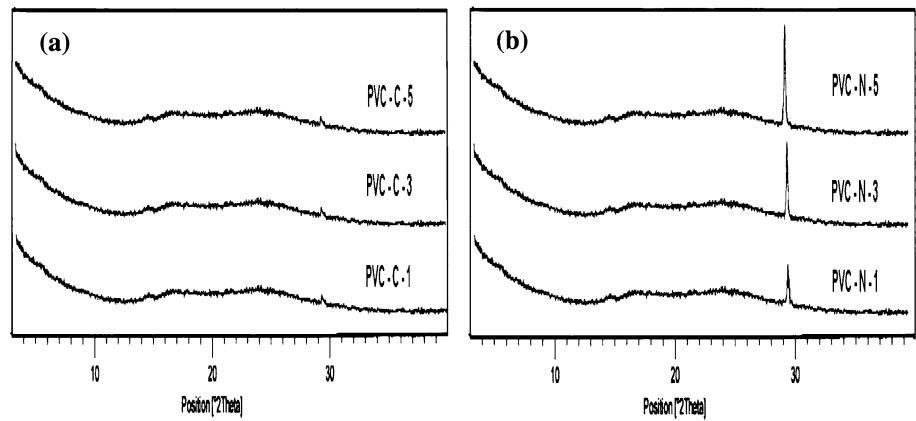
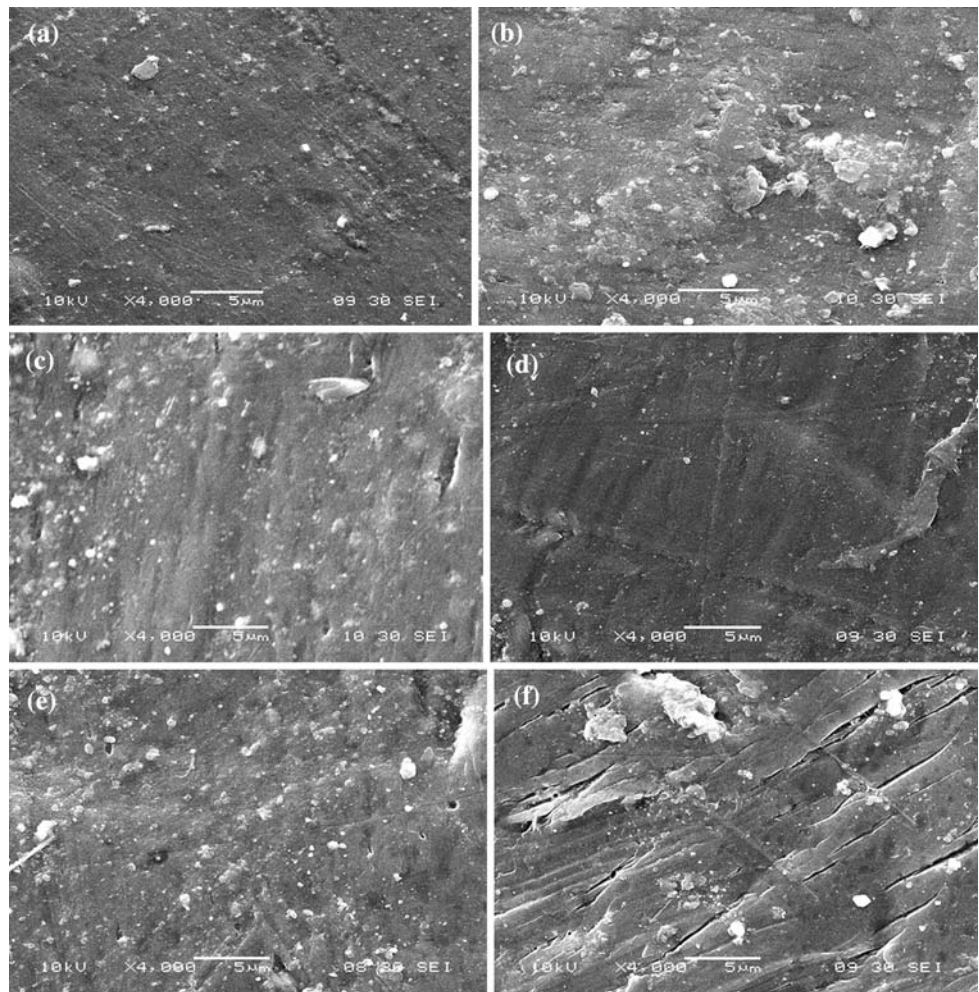


Fig. 3 SEM micrograph: **a–c** PVC/micro-CaCO₃ composites and **d–f** PVC/nano-CaCO₃ composites at 1, 3, and 5 wt% of filler



inconsistent with the results of the research study carried out by Tianbin et al. [16], Sun et al. [5], and Jie et al. [20].

Thermogravimetric analysis

One of the most important property enhancements exhibited by polymer nanocomposites is their increased thermal stability at quite low filling level. Representative TGA

curves of PVC/micro- and nano-CaCO₃ composites are shown in Fig. 5 and their numerical data were listed in Table 1. Since the polymer matrix is same for all composites, thermal stability up to 300 °C was common; however, the effect of filler was pronounced at temperature beyond 300 °C, that is, after first mechanistic step of degradation had taken place, this range was approximately 300–550 °C. A measurement of IPDT index allows us to

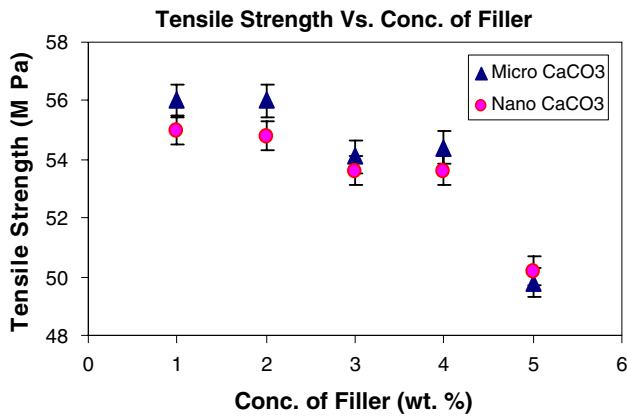


Fig. 4 Tensile strength of composites (micro and nano) with the variation of filler content (1–5%)

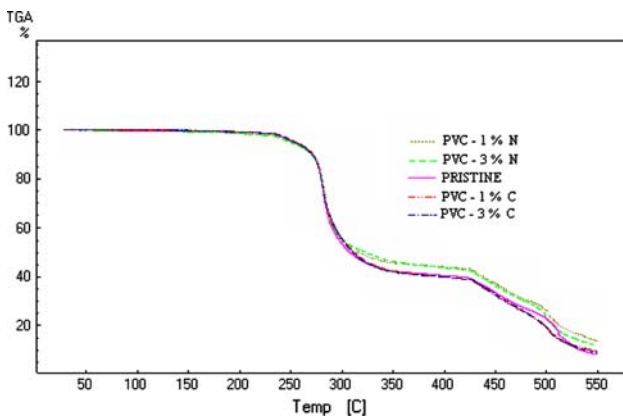


Fig. 5 Representative TGA curves of PVC/micro- and nano-CaCO₃ composites

Table 1 TGA data of PVC/micro- and nano-CaCO₃ composites

Filler (wt%)	PVC/micro-CaCO ₃ composites		PVC/nano-CaCO ₃ composites	
	Onset temperature (°C)	Residue at 550 °C	Onset temperature (°C)	Residue at 550 °C
0	266.4	9.0	266.4	9.0
1	265.5	10.3	266.7	15.0
3	266.0	11.0	268.0	13.0
5	266.7	12.0	267.3	11.0

compare thermal stability based on the area under the thermograms. Apparently the thermograms of PVC 1 and 3% nanocomposites are above the thermograms of pristine PVC and its corresponding microcomposites are in the range of 300 to 550 °C. This indicates that IPDT values will be higher for 1 and 3% nanocomposites indicating that nano-CaCO₃ has favorable effect of enhancing thermal stability to some extent.

Looking at the values of T_{onset} from Table 1, pristine PVC and PVC/micro-CaCO₃ composites did not show variation, whereas those of PVC/nano-CaCO₃ composites showed marginal increase in the values of T_{onset} . As such it was expected to see sufficient increment in the values of T_{onset} of PVC/nano-CaCO₃ because of larger surface area of inorganic nanoparticles coming in contact with the heat sensitive PVC, protecting PVC matrix from the heat by retarding the thermal degradation. Further, the weight residue of PVC/nano-CaCO₃ is higher than that of pristine PVC and their corresponding microcomposites of CaCO₃. Consequently PVC/nano-CaCO₃ composites are expected to show better thermal stability. However, the insignificant increment in T_{onset} of PVC/nano-CaCO₃ composites is due to the formation of large number of agglomerates, and the larger size of agglomerates formed as evident from WAXD and SEM results.

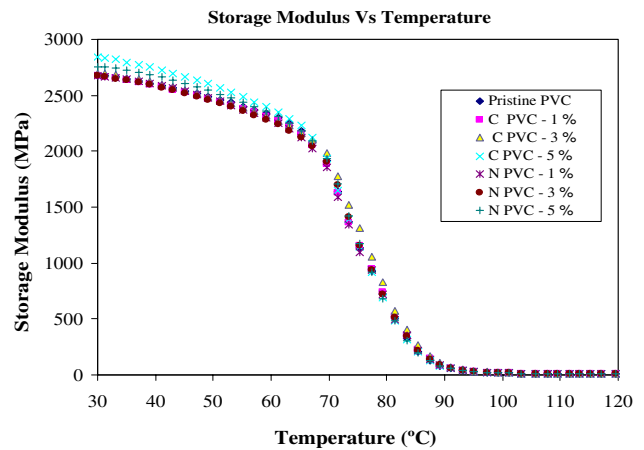


Fig. 6 Variation of storage modulus with respect to temperature for Pristine PVC and PVC/micro- and nano-CaCO₃ composites at 1, 3, and 5 wt%

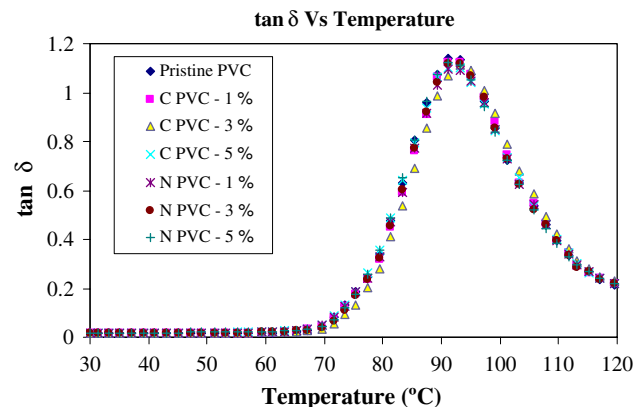


Fig. 7 Variation of $\tan \delta$ with respect to temperature for Pristine PVC and PVC/micro- and nano-CaCO₃ composites at 1, 3, and 5 wt%

Table 2 T_g of PVC/micro- and nano- CaCO_3 composites

Filler (%)	T_g of PVC/micro- CaCO_3 composites ($^{\circ}\text{C}$)	T_g of PVC/nano- CaCO_3 composites ($^{\circ}\text{C}$)
0	91.2	91.2
1	91.6	92.0
3	93.3	91.4
5	93.3	91.1

Dynamic mechanical analysis

Dynamic storage modulus and $\tan \delta$ as a function of temperature for pristine PVC and PVC/micro- and nano- CaCO_3 composites are plotted in Figs. 6 and 7, respectively. It is observed that the storage modulus (E') of microcomposites is slightly higher than that of PVC/nanocomposites and pristine PVC in the glassy region. Moreover, the magnitude of storage modulus is higher with the increasing content of micro- CaCO_3 in the same (glassy region). A similar trend is observed in the case of glass-transition temperature obtained from $\tan \delta$ versus temperature curve as onset of the curve of these composites. In general, the nanocomposites did not show significant variation in storage modulus as well as in glass-transition temperature, rather the trend is mediocre compared to pristine PVC and microcomposites; this unexpected viscoelastic behavior again accounted for non-uniform distribution of nanoparticles and the formation of agglomerates causing inhomogeneous interactions of organic matrix and the inorganic filler (Table 2).

Conclusions

Nano- CaCO_3 particles were successfully synthesized using in situ deposition technique and the particle size was obtained in the range of 35 to 60 nm confirmed by XRD and TEM techniques. The PVC/micro- and nano- CaCO_3 composites were prepared by melt intercalation. The impact of nanoparticles on dispersion, thermal, dynamic mechanical, WAXRD, and tensile behavior was studied and compared with microcomposites. From the results of WAXD and SEM, it was confirmed that dispersion of filler was not proper in PVC matrix, and hence the structure of PVC nanocomposites was intercalated and flocculated. The tensile strength of both the micro and nanocomposites was decreased with the increasing CaCO_3 content. The storage modulus of both composites was found to be slightly higher than that of pristine PVC. The glass-transition temperature of both the composites was also slightly higher than pristine PVC. Further the onset degradation temperature of PVC/nano- CaCO_3 composites was marginally

higher than microcomposites and pristine PVC. Thus, this study shows that there is poor interaction and dispersion between PVC and the nano- CaCO_3 filler. Fine dispersion (without significant particle aggregation) and adequate interfacial adhesion are essential if high performance is to be achieved. To achieve fine dispersion, fillers may be prepared as paste (high-viscosity liquids) in any of the plasticizer, which are required for specific PVC formulations. Surface treatment of fillers can be another approach to modify the interfacial adhesion in polymer composites.

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