Studies on Effect of Improved *d*-Spacing of Montomorillonite on Properties of Poly(vinyl chloride) Nanocomposites

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Received 19 March 2009; accepted 18 February 2010
DOI 10.1002/app.32717

ABSTRACT: Surface modification of montomorillonite for improvement in *d*-spacing was done by column chromatography with quaternary long chain ammonium salt having cation exchange capacity of 110 meq/100 g. Organically modified montomorillonite (OMMT)/poly(vinyl chloride) (PVC) nanocomposites were prepared through direct melt compounding on a conventional twin screw extruder. Because of improved *d*-spacing of OMMT, the polymer chains get exfoliated in between the plates of clay and dispersed uniformly. The mechanical properties of the nanocomposites were found to be appreciable at 12 wt % loading of OMMT. Moreover, rheological data, such as torque, fusion time, viscosity, and shear rate were also recorded on Brabender Plasticorder. The improvement in mechanical properties with increase in amount of OMMT loading is evidenced from reduction in shear viscosity and torque. Also nanoclay is acting as a lubricating agent with packing effect, which reduces the torque with decrease in viscosity along with increment in elongation at break. Because of soft nature of OMMT and improvement in *d*-spacing the processing of PVC becomes easier, and hence, OMMT is playing a dual role as a (i) good processing aid and (ii) filler. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 148–154, 2011

Key words: poly(vinyl chloride); montomorillonite (OMMT); column chromatography; mechanical properties; morphology study; rheological properties

INTRODUCTION

Nanotechnology is concerned with materials whose structures exhibit significantly novel and improved physical, chemical, and biological properties. Nanocomposites are the first generation of nanotechnology and having lot of valuable applications. Polymeric nanocomposites are the materials that contain dispersed particles in nanometer size in a single or multicomponent polymeric matrix. The nanoparticles may be of size, such as lamellar, fibrillar, tubular, shell-like, spherical, and soforth. The most commonly used nanoparticles are the smectite group mineral, for example, montomorillonite (MMT), hectonite, and bentonite. They have the general family of 2 : 1 layered silicates. Montomorillonite (MMT) is not compatible with most polymers and therefore, it must be chemically modified, to make its surface more hydrophobic. The most popular surface treating agent or intercalent for OMMT is quaternary ammonium salts, which are having cation exchanged capacity with the inorganic cations on the silicate surface. Because of uniform exfoliation of clay at its nanoscale level, this shows high aspect ratio and higher surface area.[1–4] Surface modification of nanoclay enhances a variety of technologies including coatings, environmental, chemical processing, medical, electronic, and sensing applications.

Melt processing is a significant method used for the preparation of polymer-OMMT nanocomposites. In this process, the application of shear during compounding assists exfoliation and uniform dispersion. The melt compounding route would be a powerful approach in the production of polymer- nanocomposites as it is an existing technology and equipment could be utilized and easily scaled to commercial quantities. Various researchers have studied effect of montmorillonite (OMMT) on properties of polymer nanocomposites.[5–17] This article highlights on effect of improved *d*-spacing of OMMT using column chromatography on rheological properties of poly(vinyl chloride) (PVC) nanocomposites. It has been observed that the torque was decreases with increasing the percentage of OMMT, and stock temperature increases as time progresses. This is a drastic change

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Contract grant sponsor: Department of Science and Technology (DST), New Delhi (FASTTRACK Young Scientist scheme); contract grant number: SR/FTP/ETA-58/2008.

Journal of Applied Polymer Science, Vol. 119, 148–154 (2011)

on torque studied on Brabender mixer plasiticorder. Moreover, significant improvements on mechanical and thermal properties have been observed.

EXPERIMENTAL

Materials

PVC (*k* value 57, Reon) is procured from Reliance Industries, Mumbai. Calcium stearate-0.7 phr (Sunwax) and Polyethylene wax-0.5 phr (Byrolub LKO) were used as lubricants. Liquid Tin Mercaptile-3.0 phr was used as a heat stabilizer during processing. Rutile TiO_2-0.5phr was used as a white photoactive pigment. The acrylic based processing aids Paraloid K-400 F-2phr and KM 318 F-2phr were used as ingredients to facilitate processing. The MMT clay is procured from southern clay, Texas. Octadecylamine was used as an intercalent for surface modification of MMT purchased from Aldrich, Mumbai, India.

Surface modification of MMT

Five grams of MMT was dispersed in water with vigorous stirring at concentration of 5%. An aqueous suspension was achieved. To purify the MMT, the aqueous suspension was kept at room temperature for 24 h. A stoichiometric amount of interfacial agent octadecylamine (7.7 g) was mixed with conc. HCl (2.9 mL) and transferred into an anion exchange column of 35 cm in length packed with cellulose. The time of flow of mixture was $\sim$ 25–35 ml/min. The entire slurry of surface modified clay was passed through nylon filter and collected at receiver. Precipitate was washed three times by flushing the column with hot distilled water. This collected matter was freeze dried to yield a modified organoclay.[18] The improvement in *d*-spacing was observed in XRD of modified and unmodified clay (Fig. 1).

Preparation of nanocomposites

The dry blending of PVC/OMMT with other additives was carried out in a high intensive mixer (Data Processing Plasticorder Model PL-2003) rotating at 50 rpm for 15 min at a temperature of 90°C. Various formulations with filler were carried out to do the comparative study. OMMT was mixed carefully in PVC compounded matrix during the mixing. The dry mix was fed into the conical twin screw extruder through the vibrating pad hopper. The mixing was carried out at 40-rpm screw speed keeping the temperatures of the feed zone, compression zone, and metering zone at 150°C, 160°C, and 170°C, respectively, whereas the temperature of die was kept at 175°C. The compounded materials were extruded through the slit die and the PVC nanocomposites sheets were prepared. The amount of filler loading was in the range of 3–12 wt %.

Mechanical properties testing

The mechanical properties (tensile strength, elongation at break, and Young's modulus) were measured as per ASTM D-638 on UTM supplied by R&D equipment, Mumbai, MS, India. Cross head speed was 5 mm/min. Samples were of standard dumbbell shape. All measurements were performed eight times to obtain an average value.

Scanning electron microscope (SEM)

SEM studies were carried out on CEMECA model SU-30, France to study extent of filler dispersion and agglomeration of nanoclay in to the polymer matrix.

Transmission electron microscopy

TEM (Tokyo, Japan) of nanoclay filled PVC composite was recorded on a Hitachi H-800 transmission electron microscope to study the extent of dispersion of polymer chains inside the plates of the nanoclay.

Atomic force microscopy (AFM)

Multi mode scanning probe microscope model with a nanoscope IIIa controller by digital instrument (Veeco Metrology Group) Santa Barbara, CA, USA was used for the AFM studies. The AFM measurements were carried out in air at ambient conditions (25°C) using tapping mode probe (RTESP) with resonance frequency of 270 kHz was used. Height and phase images were recorded simultaneously at the resonance frequency of the cantilever with a scan rate of 1 Hz and a resolution of 256 samples per line. These images were then analyzed using a nanoscope image processing software (5.30r1).

Hardness test

Hardness of the well prepared PVC nanocomposites was tested on shore-D hardness tester as per ASTM D 2583. All measurements were performed on eight spots of sheet to obtain an average value.

Vicat softening temperature

The vicat softening test was carried out on vicat softening tester (Prolific make, Noida, U.P., India) as per ASTM D 1525. Sample was placed on a specimen support to lowering the needle rod so that it rests on the surface of the specimen. With constant stirring the temperature of the bath was raised at heating rate of 50°C/h for uniform transfer of heat. The temperature at which the needle penetrates 1mm was noted and reported as the vicat softening temperature.

Rheological properties

The rheological data, such as shear viscosity, were collected from computerized Brabender Plasticorder and mixer measuring head at 275°C and rotor speed of twin screw was 40 rpm/min during the compounding of the PVC/OMMT composites.

RESULTS AND DISCUSSION

Mechanical properties

The effect of OMMT on mechanical properties of PVC nanocomposites is shown in Figures 2–4. It was observed that tensile strength increases with increase in OMMT loading (Fig. 2). Tensile strength at 3 wt % loading in OMMT: PVC composite was observed to be 78 MPa, whereas at 12 wt % loading of OMMT, tensile strength was recorded as 95 MPa. The tensile strength of pristine PVC (73 MPa) was minimum in comparison with PVC nanocomposites. Improvement in tensile strength was due to ordered exfoliation of clay (OMMT) layers in polymer chains, that is, uniformity in dispersion of OMMT along with polymer chains. The increment in Young's modulus was found to be more appreciable at 12 wt % (72 MPa) of loading. Whereas Young's modulus at 3 wt % (64 MPa) loading of OMMT and pristine PVC (62 MPa) was found to be minimal compared with higher % loading (Fig. 3). Elongation at break (Fig. 4) also found to be increased with increased in amount of clay. Elongation at break at 3 and 9 wt % loading of OMMT was recorded as 21 and 30%, respectively. This improvement in mechanical properties, such as tensile strength, Young's modulus, and elongation at break was because of ordered exfoliation of modified clay in polymer chains, which has already been discussed in this text. Moreover, the increment in elongation at break was because of reduction in viscosity of polymer during processing, which provides more strength with maximum elongation and strength. The uniform dispersion, that is, exfoliation of polymer chains in between the two plates of nanoclay was evidenced from SEM (Figs. 5 and 6), TEM (Figs. 7 and 8), and AFM images (Figs. 9 and 10).

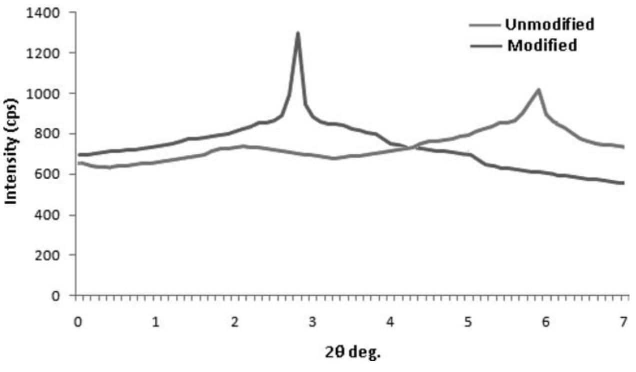

Figure 1 Young's Modulus of PVC nanocomposites.

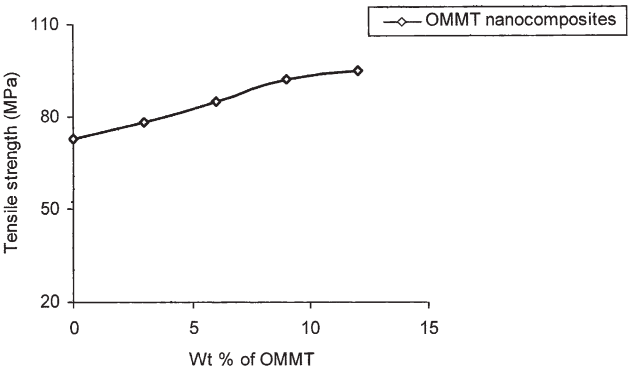

Figure 2 Elongation at break of PVC nanocomposites.

Atomic force microscopy (afm)

The phase images of 3 and 12 wt % loading of nanocomposites are shown in Figures 9 and 10. The phase image of 3 wt % loading (Fig. 9) shows that the nanoclay gets uniformly distributed in the PVC matrix as the dimension of the clay plates is uniform. Hence, the chains of PVC get exfoliated in between the two plates of nanoclay. This result was in line with the SEM of 3 wt % loading of PVC nanocomposites. This uniformity in nanoclay distribution in between the polymer chains was because of presence of polar group on the surface of nanoclay which attracts the PVC having $C^{+\delta}$—$Cl^{-\delta}$ bonds. The photographic image (Fig. 10) of 12 wt % loading of PVC nanocomposites shows intercalation of polymer chains in between the two plates of nanoclay. But intercalation doesn't show any adverse

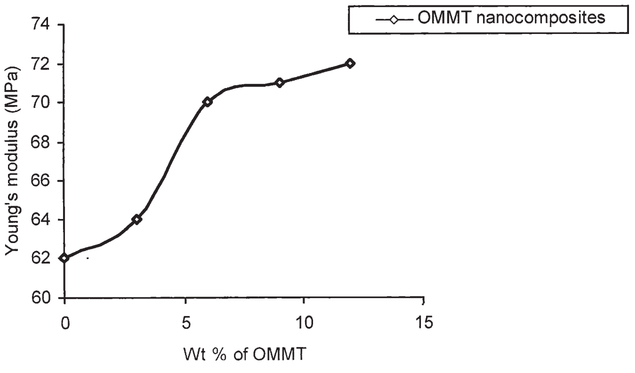

Figure 3 SEM of 3 wt % of OMMT in PVC nanocomposites.

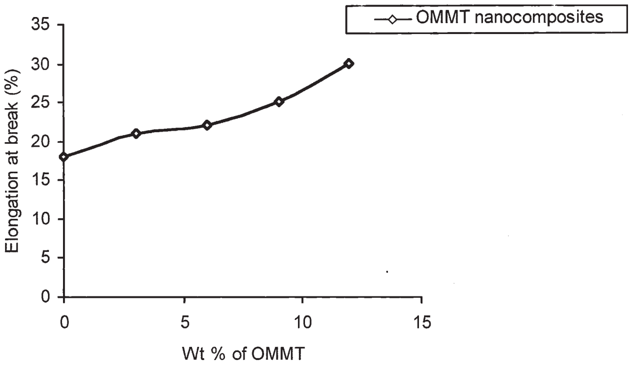

Figure 4 SEM of 12 wt % of OMMT in PVC nanocomposites.

effect on the improvement in properties of PVC nanocomposites.

Hardness

There was continuous increment in hardness with increase in amount of loading of nanoclay in comparison to virgin PVC (Fig. 11). The increment in hardness was more appreciable at 12 wt % of loading in PVC. A total of 3 wt % loading of nanoclay in PVC shows hardness 72, whereas at 12 wt % loading hardness was observed to be 91. This improvement in hardness was found to be more effective compared with virgin PVC (70) and this is because of hard nature of PVC (rigid) with exfoliation of PVC chains in between two plates of nanoclay, which makes the surface of composite very hard because of which the indentation of the indenter was quite difficult.

Vicat softening point (VSP)

The effect of clay content on vicat softening temperature of PVC nanocomposites was shown in Figure 12. The VSP's of PVC nanocomposites show tremendous improvement with increase in clay content. PVC originally in its form was observed to be thermally more stable, but incorporation of nanoclay shows tremendous improvement in thermal stability of PVC nanocomposites. This increase in VSP was because of uniform and ordered exfoliation of clay layer in polymer chains, which creates protective layer on the surface, which shows the shielding effect. This protective layer resists the indentation of indenter inside the composite. As 3 wt % loading of loading of OMMT in PVC composites results VSP 232°C, whereas 12 wt % loading of OMMT in PVC composites shows 313°C, whereas VSP of pristine PVC recorded as 204°C.

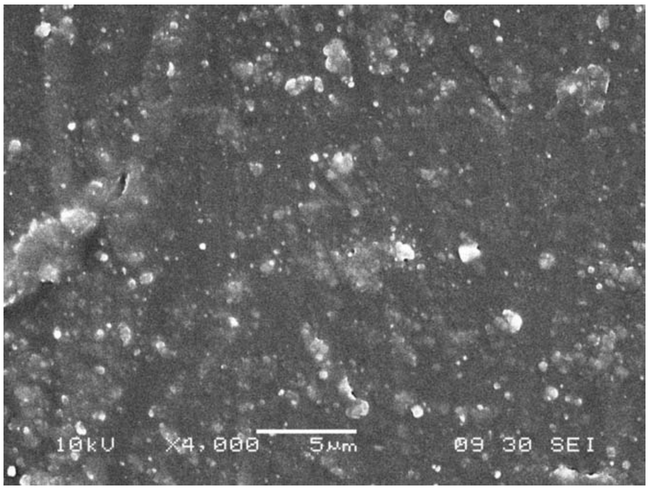

Figure 5 TEM of 3 wt % of OMMT in PVC nanocomposites.

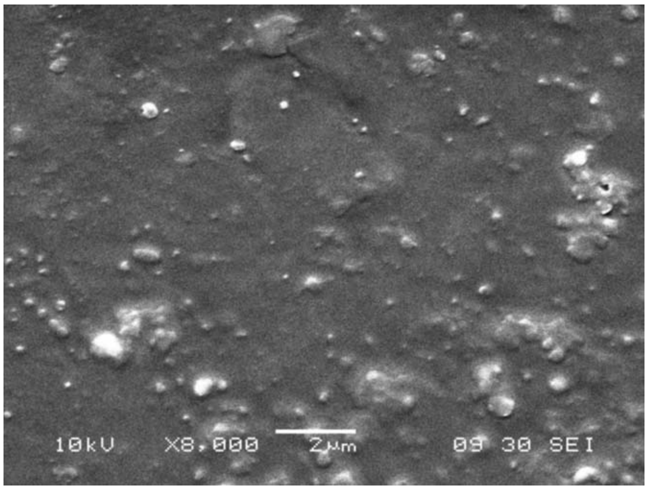

Figure 6 TEM of 12 wt % of OMMT in PVC nanocomposites.

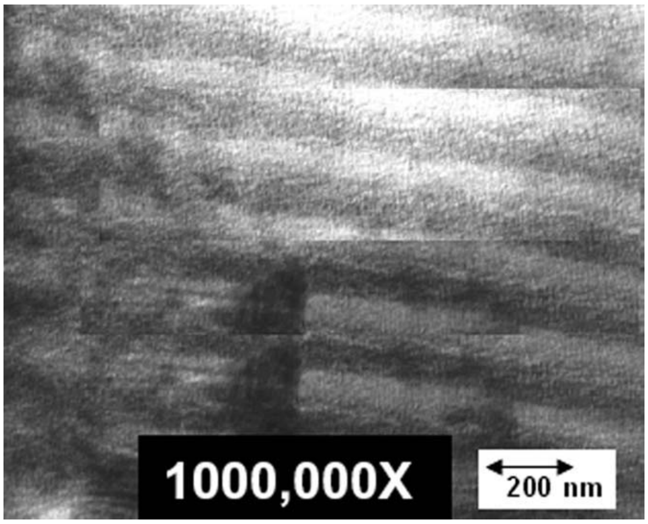

Figure 7 AFM of 3 wt % of OMMT in PVC nanocomposites.

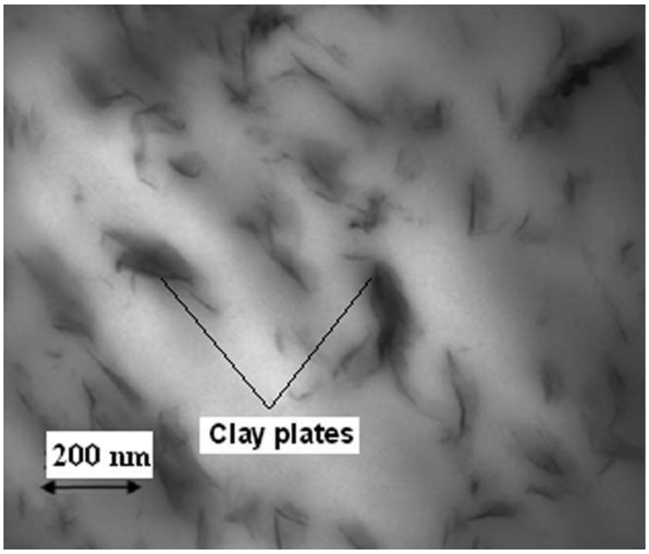

Figure 8 AFM of 12 wt % of OMMT in PVC nanocomposites.

Rheological properties

The relationship stated from the Brabender Plasticorder is

$$M = CS^a \quad (1)$$

where M is the torque, S is the rpm, and C and a are constants. The above equation resembles the power law behavior, which is given as:

$$\tau = K(\gamma)^n \quad (2)$$

where, τ is shear stress; K, constant; γ, shear rate and n, non-Newtonian flow index. Based on the above two equations, it can be interpreted that the torque recorded on the Brabender Plasticorder is an indirect indication of the shear stress, whereas rotor speed (rpm) is as indirect indication of shear rate. Thus, the viscosity that is given as the ratio of shear stress to shear rate in case of the Brabender Plasticorder and obtained from the ratio of torque to rotor speed (rpm) and is estimated as power law index (n). Figure 11 shows the effect of OMMT loadings on the apparent viscosity at constant shear rate of PVC -OMMT nanocomposites; it is observed that two factors control the viscosity of the PVC -OMMT composites. (1) The viscosity decreases with increase in shear rate, (2) the viscosity is influenced with the blend composition. The viscosity decrease with increased shear rate indicates that the chains are easily deformed and their frictional resistance is not optimum. It is observed that at any shear rate, the higher the filler content lowers the viscosity and the torque during the processing (Fig. 13), subsequently at 12 wt % loading torque increases because of disordered exfoliation of the polymer chains in between the two plates of the nanoclay. The decrease in viscosity is because of the increase in percentage of OMMT clay in PVC. However, the effective decrease in the viscosity with increase in OMMT concentration might be due to lubrication of OMMT during processing of PVC.

The melt flow behavior of the samples can be described by power law index. It is observed that

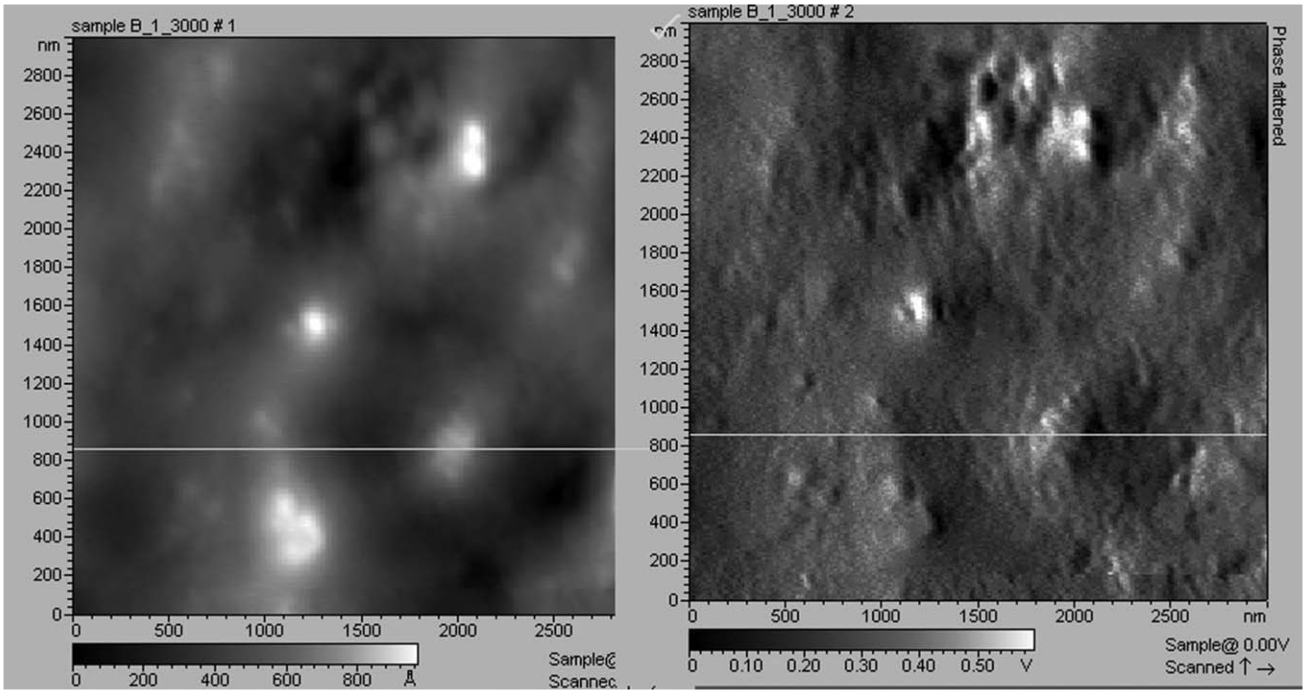

Figure 9 Hardness of PVC nanocomposites.

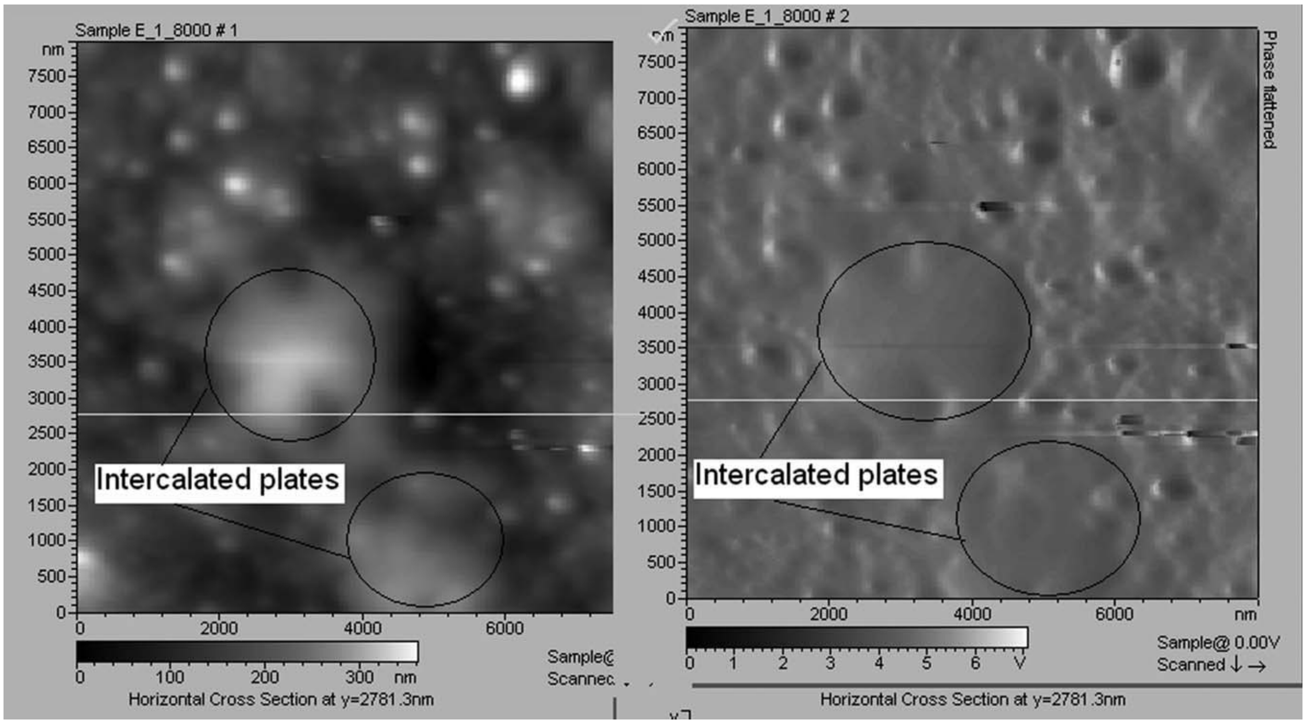

Figure 10 Vicat softening temperature of PVC nano- composites.

shear stress decreases with increase in shear rates, which strengthen the fact that the rate of increasing shear stress is affected by OMMT percentage addition. The data show that the behavior of the melts is highly non-Newtonian, according to the slope of the straight lines used to estimate the value of the non-Newtonian flow index (*n*). This was observed due to lubrication effect of OMMT, which is expected to improve the flow properties of the PVC. Hence melts display a less non-Newtonian behavior with increased OMMT contents. The values of *N* indicate the pseudoplastic nature of the PVC/OMMT blends as $n < 1$, showing that the apparent viscosity decreases as shear rate increases.

CONCLUSION

The addition of small amount of nanoclay (3–12 wt %) shows enhancement in properties, such as mechanical, hardness, and rheological. A total of wt % loading of nanoclay shows effective increments in all properties because of ordered exfoliation of clay in polymer chains in between the two intergalleries of nanoclay. The increment in rheological properties was because of nature of OMMT, which shows decrement in torque. Hence, the role of nanoclay was somewhat different and acts as lubricating agents, which reduces the torque with decrease in viscosity along with increment in elongation at break. During processing of PVC, OMMT not only acting as filler but also acting

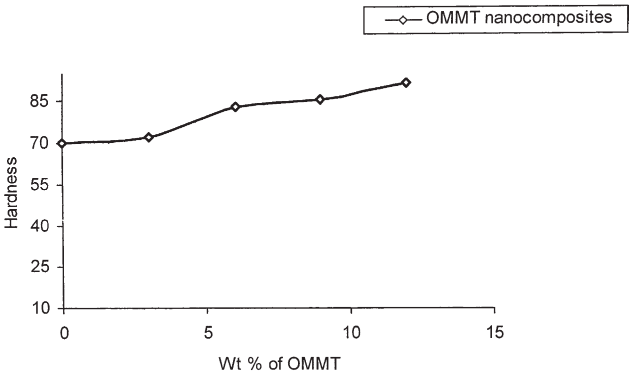

Figure 11 Viscosity of PVC nanocomposites.

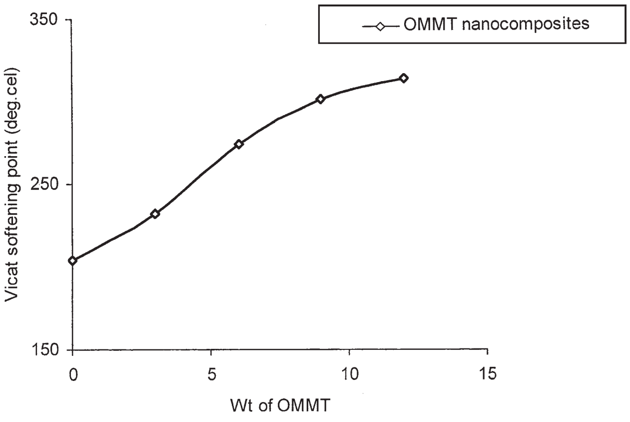

Figure 12 XRD gram of modified and unmodified clay.

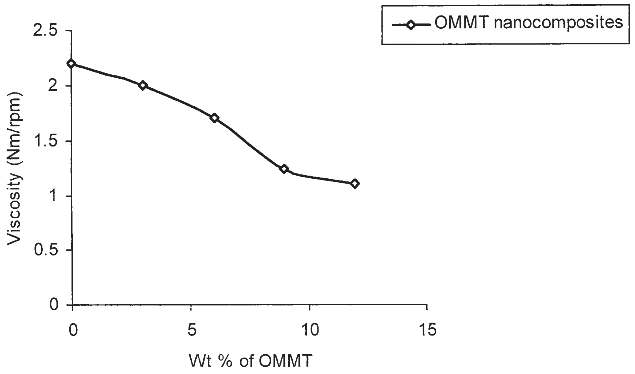

Figure 13 Tensile strength of PVC nanocomposites.

as good processing aid at the time of PVC prosessing. Due lubrication effect of OMMT processing of PVC composites become easier and protect the screw from further damage because of high torque.

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