Effect of Nano-Mg(OH)$_2$ on the Mechanical and Flame-Retarding Properties of Polypropylene Composites

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ABSTRACT: Nano-Mg(OH)$_2$ was synthesized with an *in situ* deposition technique, and its size was confirmed by X-ray diffraction. A polypropylene–Mg(OH)$_2$ composite was prepared by melt-extrusion processing. The addition of a small quantity of a nanofiller (up to 10 wt %) increased Young's modulus up to 433% with respect to the modulus of virgin polypropylene. The addition of up to 4 wt % Mg(OH)$_2$ produced the maximum increase, and a further decrease in the tensile strength was observed with an increase in the concentration of nano-Mg(OH)$_2$. Increases in the hardness and other properties were due to higher nucleation and the intercalation of polymer chains in the nano-layer galleries. The flame-retarding property was demonstrated by the rate of burning. The time required to burn the nanofilled composite was greater than the time required for virgin polypropylene. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 116–122, 2004

Key words: differential scanning calorimetry (DSC); flame retardance; mechanical properties; poly(propylene) (PP); X-ray

INTRODUCTION

Polymer nanocomposites provide exceptional structures and improved thermal properties in comparison with conventional microscale composites. The delaminated versions of nanocomposites offer measurable improvements in the physical properties. The intercalated versions of clay nanocomposites offer reduced flammability but fewer improvements in the physical properties.[1] Inorganic hydrates are commonly used in flame-retardant composite formulations because of their ability to undergo endothermic dehydration under fire conditions.[2–5] There is growing interest in magnesium hydroxide as a flame-retardant filler that does not evolve toxic, gaseous, and corrosive substances upon combustion. Moreover, magnesium hydroxide can be used at higher processing temperatures, and it is well known that an inorganic filler can affect the mechanical properties of a polymer matrix.[6] Nanofilled polypropylene (PP) exhibits an attractive combination of low-cost, low-weight materials and better properties.[7] For improved competitiveness in engineering applications, flame retardancy with nanofillers is an economical option.

In this work, the effect of nano-Mg(OH)$_2$ on the mechanical and thermal properties of PP composites was studied. Nano-Mg(OH)$_2$ was synthesized with an *in situ* deposition method, and the nanoparticle size and crystallization behavior were confirmed with X-ray diffraction (XRD). Differential scanning calorimetry (DSC) thermograms predicted the effects of the addition of small amounts of nano-Mg(OH)$_2$ on the melting temperature of the polymer matrix and the mechanical and thermal properties of PP nanocomposites formed by a melt-intercalation process.

EXPERIMENTAL

Materials

PP (Koylene-grade; melt-flow index = 10 g/10 min, density = 0.91 g/cc; IPCL, Baroda, India) was used for this study. Analytical grades of magnesium chloride (MgCl$_2$) and sodium hydroxide from S.D. Fine Chemical, Ltd. (Mumbai, India), were used for the synthesis of nanoparticles of MgCl$_2$. Poly(ethylene glycol) (PEG; molecular weight = 6000), used to form the complex, was also procured from S.D. Fine Chemical.

Synthesis of the nanoparticles

Nano-Mg(OH)$_2$ was synthesized by an *in situ* deposition technique. MgCl$_2$ (203 g) was placed in 100 mL of
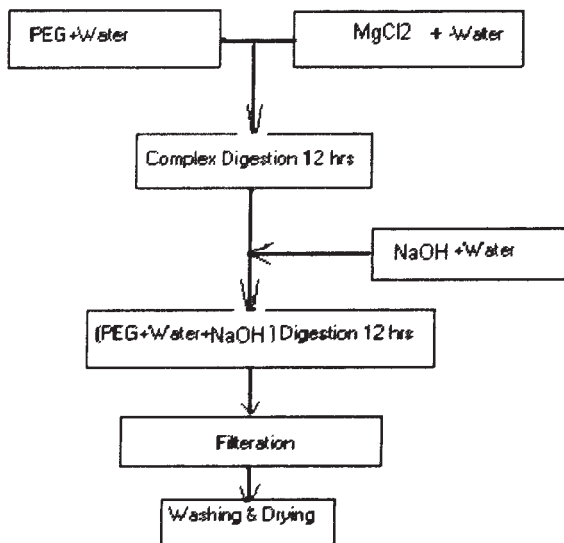
Figure 1 Synthesis of nano-Mg(OH)$_2$ by *in situ* deposition.

water. PEG (745 g) was diluted with 100 mL of water and was mildly heated for proper mixing. The complex of MgCl$_2$ was prepared with PEG in a 12:1 molar ratio in distilled water. It was heated mildly for the mixing of MgCl$_2$ and PEG for its digestion. Another solution of NaOH was prepared, with 80 g placed in 100 mL of distilled water. The first complex was digested for 12 h; the second complex was added slowly, and the mixture was again kept for digestion overnight. The precipitate was filtered, washed with water, and dried in a vacuum drier.[8–12] Nanosynthesis by *in situ* deposition is shown in Figure 1.

Preparation of the specimens

To study the mechanical and thermal properties of PP filled with nano-Mg(OH)$_2$ particles, we prepared the composites by placing 2, 4, 8, and 12 wt % nano-Mg(OH)$_2$ separately in PP granules. The composite samples with different concentrations of nano-Mg(OH)$_2$ were injection-molded in an injection-molding machine (Gold Coin Polymechplast Machines, Baroda, India); the temperatures were 210°C in the feed zone, 220°C in the compression zone, 225°C in the metering zone, and 230°C in the nozzle.

Tensile testing

Injection-molded tensile specimens prepared according to ASTM D 628 were tested on a UT-2303 universal testing machine (R&D Electronics, Mumbai, India). Testing was performed at room temperature. Young's modulus and the elongation at break (%) were determined at a deformation speed of 5.00 cm/min. The mean value of five measurements was taken.

Impact testing

Injection-molded specimens (notched) were tested on a notch impact tester (Model Precision System, New Delhi, India) according to ASTM D 256 at room temperature. The data represent the average values of five test specimens.

Hardness

The molded specimens were tested to determine the hardness data with shore hardness (ASTM D 2240 D
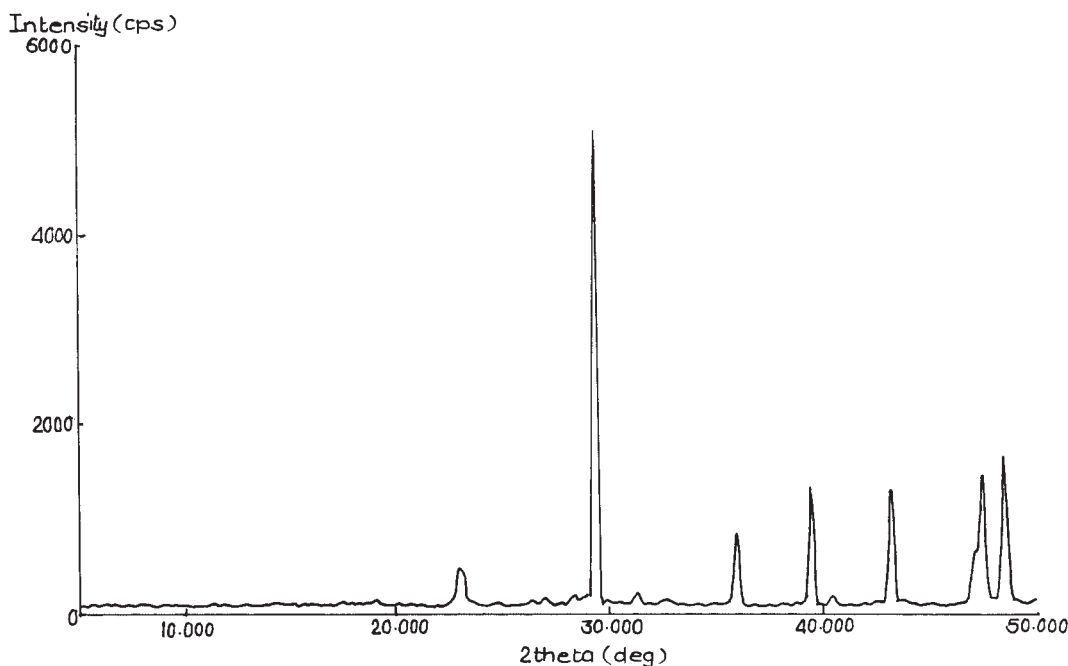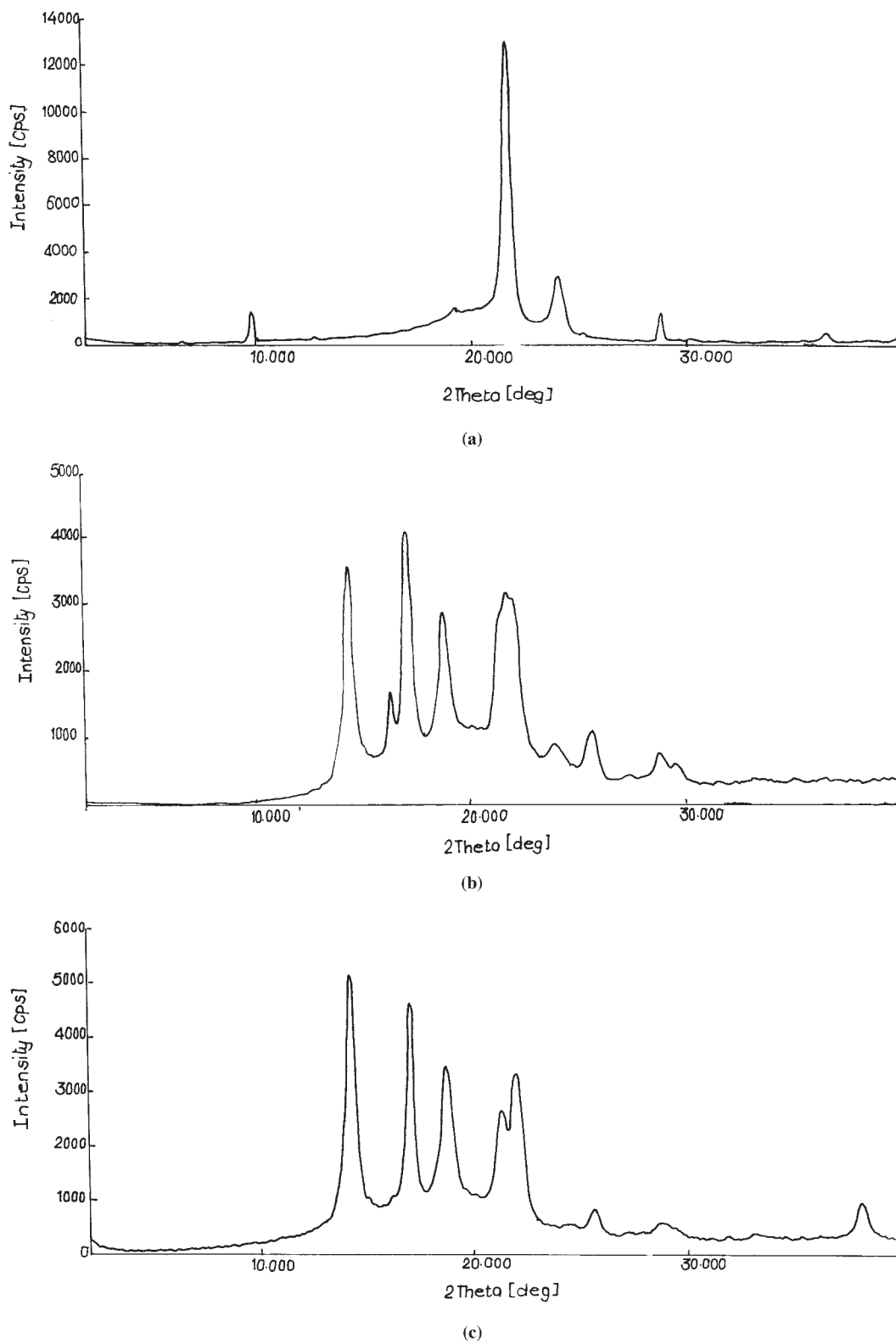

Figure 2 XRD pattern of nano-Mg(OH)$_2$.

Figure 3 XRD patterns of (a) virgin PP, (b) a 4 wt % nano-Mg(OH)$_2$-filled PP composite, and (c) a 12 wt % nano-Mg(OH)$_2$-filled PP composite.
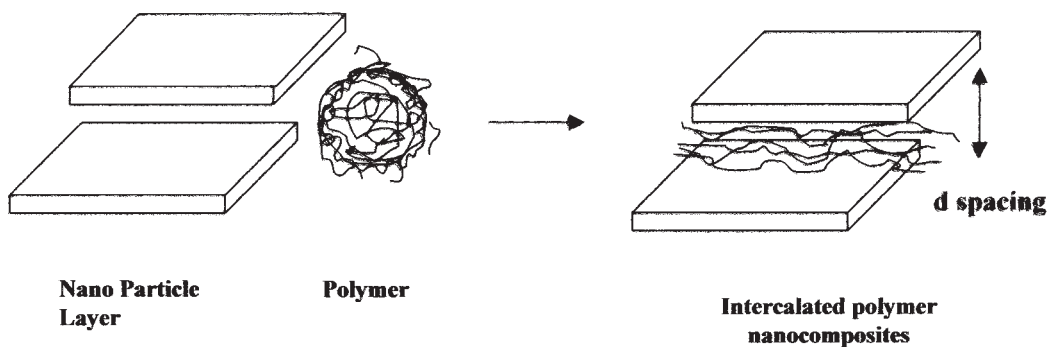
Figure 4 Intercalation of nano-Mg(OH)$_2$ in a PP matrix.

type). The data represent the average values of five test specimens.

RESULTS AND DISCUSSION

Nanosize confirmation by XRD characterization

Figure 2 shows an XRD pattern for Mg(OH)$_2$ synthesized in PEG. Nanosize Mg(OH)$_2$ was confirmed by the XRD pattern with Scherrer's formula:

$$d(\mathring{A}) = k \times \lambda / \Delta 2\theta \cos\theta \qquad (1)$$

where d is the particle size, K is the order of reflection, λ is 1.542, and θ is the diffraction angle. The particle size, based on the ratio of PEG to MgCl$_2$, was 25 nm.

Confirmation of the intercalation of PP with nano-Mg(OH)$_2$ by XRD

The PP–Mg(OH)$_2$ composites were evaluated with XRD, as shown in Figure 3. The d-spacings of virgin PP, a 4 wt % Mg(OH)$_2$–PP composite, and a 12 wt % Mg(OH)$_2$–PP composite were measured with XRD, as shown in Figure 3. The basal spacing was 4.07 nm for virgin PP, 5.16 nm for the 4 wt % Mg(OH)$_2$–PP composite, and 6.19 nm for the 12 wt % Mg(OH)$_2$–PP. Thus, with increasing nanofiller content, the basal spacing increased. Moreover, the intensity decreased as the filler content increased. The intensities of the virgin PP, 4 wt % Mg(OH)$_2$–PP composite, and 12 wt % Mg(OH)$_2$–PP composite were 21.80, 17.14, and 14.30 cps, respectively. These results of increasing basal spacing with decreasing intensity (2θ) confirm higher interlayer spacing with a higher weight percentage of the nanoparticles. This phenomenon revealed that the intercalation of the polymer chains was higher within the galleries, as shown in Figure 4.

Effect of the nanoparticles on the thermal properties of the PP/nano-Mg(OH)$_2$ composites

PP–Mg(OH)$_2$ composites containing Mg(OH)$_2$ nanoparticle concentrations of 4 and 12 wt % were used for

DSC to determine the crystalline nature and variation of the thermal behavior of the composites. A comparison of the DSC thermograms shows that the onset of melting was smoother for the 12 wt % nano-Mg(OH)$_2$-filled composite [Fig. 5(c)]. Although the virgin PP thermogram [Fig. 5(a)] shows a sharp peak, initially there was variation in the heat absorption. The 4 wt % nano-Mg(OH)$_2$-filled composite [Fig. 5(b)] showed an intermediate behavior. This was due to the variation in the heat absorption because the dispersion of the nanoparticles was more even in the PP matrix, which was responsible for even heat absorption, and so a sharp onset could be observed for the nanofilled composites. The values of heat of fusion (ΔH) 78.92 J/g was recorded for virgin PP, and 76.8 J/g was recorded for the 12 wt % nano-Mg(OH)$_2$-filled composite. The peak values of the melting temperatures are approximately the same (165.033, 164.8 and 165.70°C) for the virgin PP, 4 wt % PP composite, and 12 wt % PP composite, respectively. The drastic difference in the melting temperature for virgin PP might be due to the even dispersion of nanoparticles in PP.

Mechanical properties of the nano-Mg(OH)$_2$/PP composites
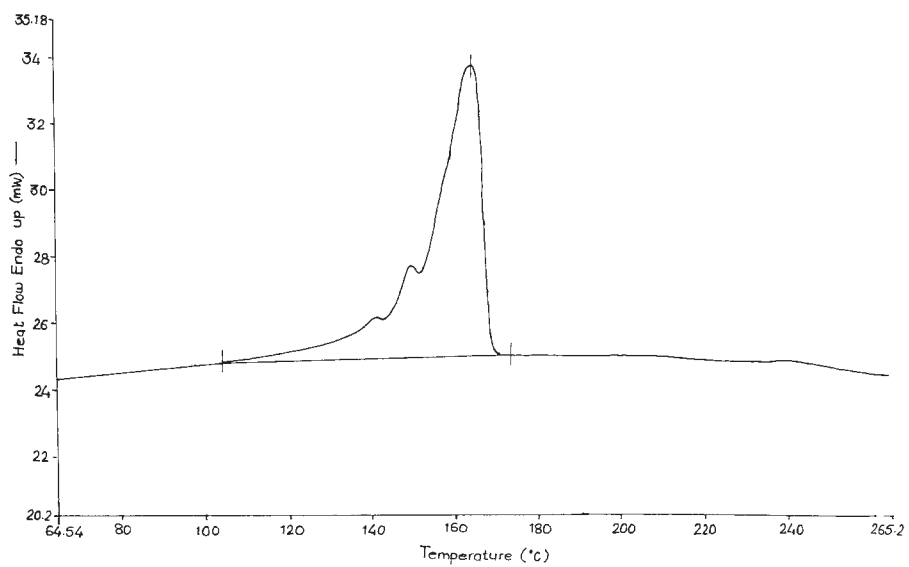
Tensile strength at break

The tensile strength at break of nano-Mg(OH)$_2$-filled composites was measured, as shown in Figure 6. The tensile strength of the nano-Mg(OH)$_2$ composites increased rapidly with increasing nanofiller content from 0 to 4 wt %. Subsequently, as the concentration of the filler increased, there was a reduction in the tensile strength. This decrease was attributed to a possible agglomerization of the nanoparticles. In comparison with the tensile strength of virgin PP, the tensile strength increased by 86% for the composite with a 4 wt % filler concentration.
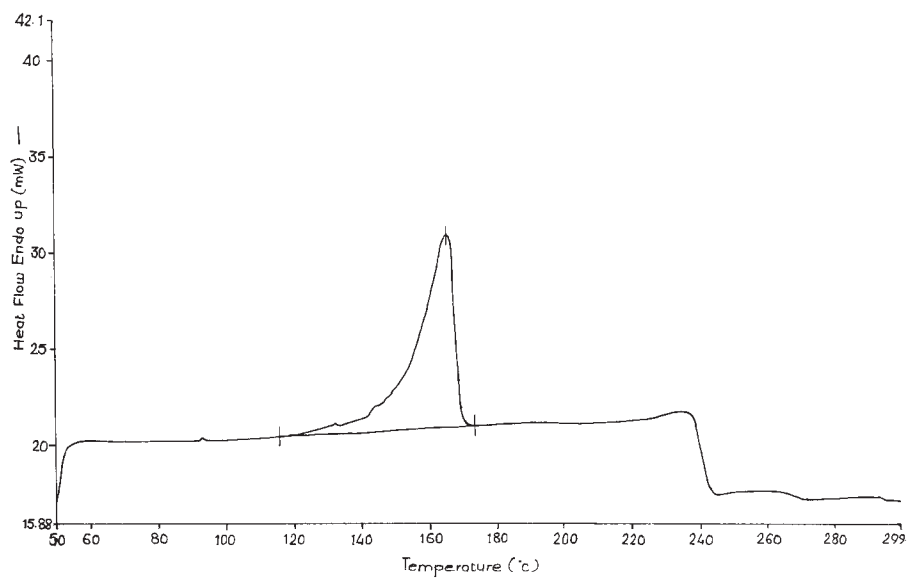
Young's modulus

The relationship between the nano-Mg(OH)$_2$ content and Young's modulus of the PP/nano-Mg(OH)$_2$ nano-
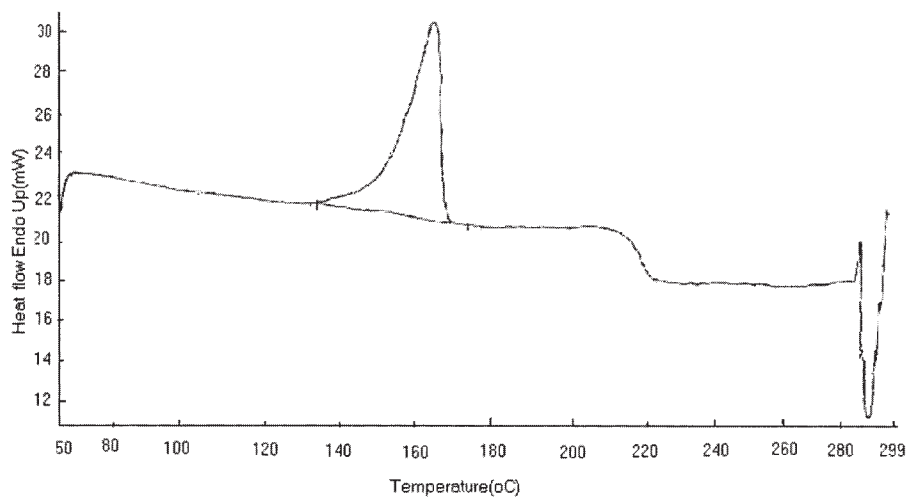
Figure 5 DSC thermograms of (a) virgin PP, (b) a 4 wt % nano-Mg(OH)$_2$-filled PP composite, and (c) a 12 wt % nano-Mg(OH)$_2$-filled PP composite.
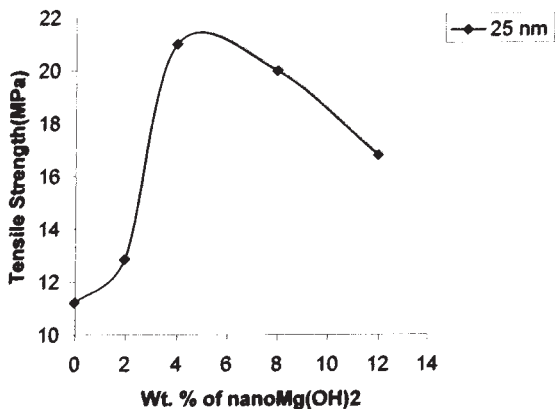
Figure 6 Tensile strength at break of PP/nano-Mg(OH)$_2$ composites with various filler contents.
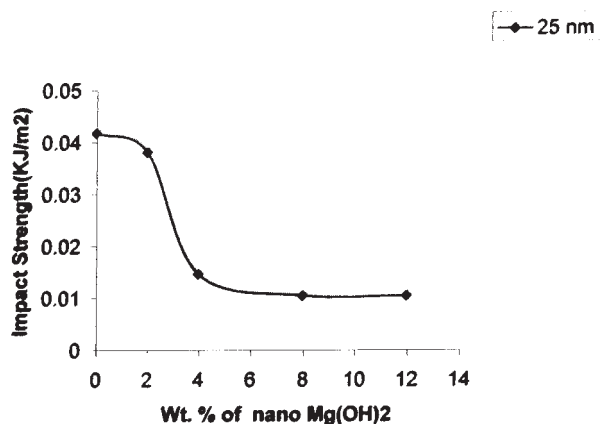
Figure 8 Impact strength of PP/nano-Mg(OH)$_2$ composites with various filler contents.

composites is shown in Figure 7. Young's modulus of nanocomposites increased linearly as the nano-Mg(OH)$_2$ concentration increased. A maximum increase in Young's modulus of 433% was observed for the 12 wt % nanocomposite modulus in comparison with that of virgin PP. This effect might be due to the higher nucleation of the nanoparticles in the PP composite. XRD patterns (Fig. 3) confirmed this fact, supporting the phenomena of intercalation and nucleation. Possible agglomeration at some of the spaces in the matrix could not be confirmed with XRD, transmission electron microscopy could shed some light on this matter.

Impact properties

Figure 8 illustrates the effect of nano-Mg(OH)$_2$ on the impact strength of the PP/nano-Mg(OH)$_2$ nanocomposites. The impact strength decreased as the nanoparticle concentration increased up to 4 wt % Mg(OH)$_2$. A further increase in the concentration of

the nanoparticles did not reduce the impact value much, which remained almost stable. Fracture propagation was more pronounced with the addition of the nanoparticles. It is possible that nano-Mg(OH)$_2$ agglomerated easily into large particles, which could be sites for crack propagation, and acted as a microcrack initiator. However, at a larger filler concentration, the value of the impact strength was not much reduced.

Hardness

The relationship between the nano-Mg(OH)$_2$ content and the hardness of the PP/nano-Mg(OH)$_2$ nanocomposites is shown in Figure 9. The hardness of the nanocomposites increased linearly with an increase weight percentage of Mg(OH)$_2$. Above a 4 wt % concentration, the PP composites showed significantly increasing hardness. An approximately 50% increase in the hardness value for nano-Mg(OH)$_2$ was observed in comparison with that of virgin PP.
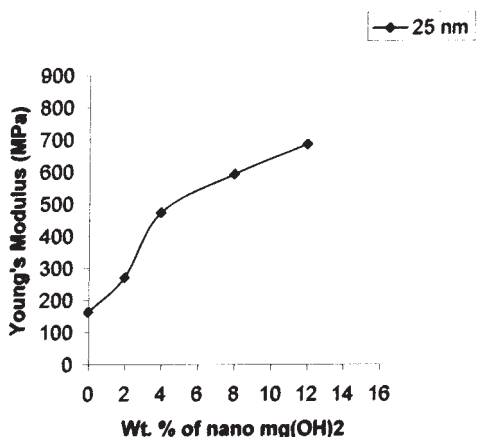
Figure 7 Young's modulus of PP/nano-Mg(OH)$_2$ composites with various filler contents.
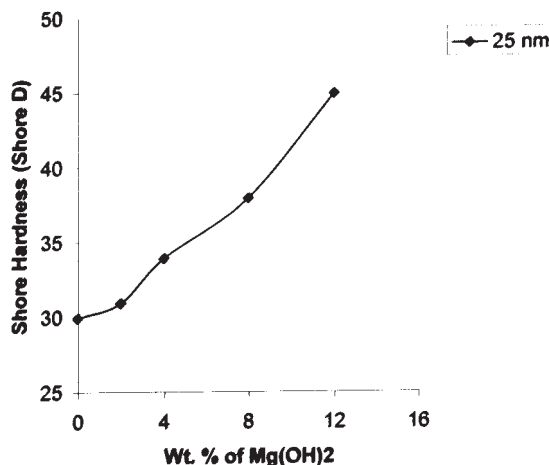
Figure 9 Shore hardness (D) of PP/nano-Mg(OH)$_2$ composites with various filler contents.
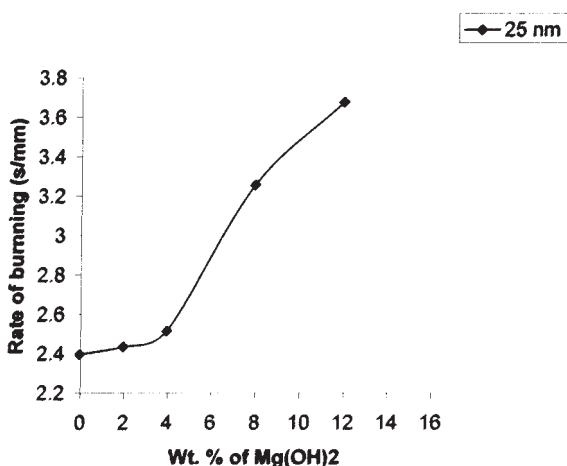
Figure 10 Flame retardancy of PP/nano-Mg(OH)$_2$ composites with various filler contents.

Flame-retarding properties

The relationship between the nano-Mg(OH)$_2$ concentration and the rate of burning for the PP/nano-Mg(OH)$_2$ composites is shown in Figure 10. The burning rate per second was reduced as the nanofiller composition increased. This reduction in the flammable property was 35 wt % with respect to the rate for PP. The reduction in flammability was due to the endothermic nature of Mg(OH)$_2$, which was evenly dispersed in the PP matrix

CONCLUSIONS

Substantial improvements in the mechanical properties were obtained by the addition of small amounts of nano-Mg(OH)$_2$. The addition of nano-Mg(OH)$_2$ at a concentration of 12 wt % to PP led to an increase in Young's modulus of as much as 433%, a 50% increase in the hardness, and a 35% improvement in the flame retardancy of PP. This improvement was due to the even dispersion, in PP, of nano-Mg(OH)$_2$, which was endothermic in nature and intercalated and nucleated the polymer chains.

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