Effect of Surface Treatment on the Properties of Polypropylene/Nanoboehmite Composites

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ABSTRACT: Boehmite nanoparticles are surface modified with alkyl phosphorous acid to improve their dispersion in polypropylene. Effective grafting is evidenced by NMR, elemental analysis and by the fact that the dispersion ability (or disagglomeration) of grafted boehmite particle in nonpolar solvent is significantly altered. High dispersibility level in PP is obtained with long alkyl chain surface modifiers. The improvement of the nanocomposites thermal stability is correlated with the nanoparticles dispersion level. However, composite with well dispersed nanoparticle did not demonstrate enhanced mechanical properties because of weak polymer/filler interactions with the PP matrix. Better reinforcement is noticed for polypropylene composite loaded with untreated boehmite or treated with shorter alkyl chain. For these composites, the nanoparticles acted as nucleating agents. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 373–381, 2010

Key words: inorganic materials; mixing; nanocomposites; polyolefins; surfactants

INTRODUCTION

In the last 10 years, numerous studies have demonstrated that composite properties can be improved when using nanoscale fillers rather than microfillers. Nanoscale fillers have been reported to improve mechanical properties,[1–3] heat deflection temperature,[4] thermal stability,[5] and fire retardancy.[6,7] Nanoscale fillers can also be used to add new functionalities such as electrical,[8] optical[9] or barrier properties.[10]

Nonpolar polymers such as polyolefins are often used in combination with microfillers such as talc, calcium carbonate, Aluminum trihydrate, or glass fibers in various high volume applications, including automotive components, building materials, or other molded or extruded articles. There is growing interest to (partially) replace microfillers by nanoscale fillers to reduce weight and achieve a better balance of properties. More particularly, nanoboehmite (alumina-monohydrate) can be produced[11] in various shapes such as platelets or rods (Figs. 1 and 2) that would be a good candidate to reinforce commodity polymers due to their morphology and flame retardant properties.[12]

The preparation of polyolefin nanocomposites is technically challenging. Inorganic Nanoscale fillers have a strong tendency to agglomerate due to their poor miscibility in nonpolar polymers. The particles aggregation is driven by the high specific surface area and the difference in surface energy between fillers and polymer. A high energy is required to break-up the agglomerates, making well dispersed nanocomposites difficult to produce. To overcome this technical difficulty, nanoparticles have been surface treated with surface modifiers to improve their compatibility with the polymer matrix.[10,13] The surface modifier has functional groups interacting with the nanoparticles and the polymer matrix trough covalent, hydrogen, or Van Der Waals bonding.

This article focuses on the reinforcement of polypropylene by surface treated nanoboehmite particles. The surface modification of nanoboehmite by organic acids such as sulfonic acid[14] and carboxylic acids[15,16] has already been studied. Phosphonic acids can react with hydroxide groups at metal surface as previously studied by Mutin et al.[17] in case of alumina particles. In the first part, the surface treatment of nanoboehmite by phosphonic and phosphinic acids is studied. Then, the effect of the surface treatment on the properties of the nanocomposite is investigated.

MATERIALS AND METHODS

Materials used for the surface treatment of nanoboehmite

Aqueous colloidal sol dispersion of boehmite nanoplatelets CAM® 9080 with a specific surface area of

Figure 1 TEM images of virgin boehmite nanoparticles platelets produced by a seeded hydrothermal process.

about 80 m^2/g were obtained from the grains and powders division of Saint-Gobain. The concentration of boehmite in the SOL was 10 wt %. The nanoplatelet had a dimension around 150 nm and a thickness around 20 nm.

Octadecyl phosphonic acid $CH_3(CH_2)_{17}PO_3H_2$ (ODPA); Octyl phosphonic acid $CH_3(CH_2)_7PO_3H_2$ (OPA) and Vinylphosphonic acid $CH_2{=}CH_2PO_3H_2$ (VPA) supplied by Rhodia, and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex® 272) supplied by Cytec Industries were selected as surface modifiers (Fig. 3).

Figure 2 TEM images of virgin boehmite nanoparticles rods produced by a seeded hydrothermal process.

Preparation of surface modified boehmites

Surface treatment reactions were carried out in a four liter glass vessel reactor under high shear conditions at 80°C for 3 h. The quantity of surface modifier to achieve a grafting density of about 2 molecules per square nanometer was predissolved in iso-propanol then added to the boehmite SOL. A pH of 5 was adjusted with a 1M solution of NaOH. The solids were dried overnight at 110°C in a regular oven, and crushed into fine powders with a grinder.

Preparation of polypropylene/chemically treated boehmite nanocomposite

A compounding grade of homopolymer polypropylene Profax® 6301 was acquired from Basell. The isotactic polypropylene resin was provided in powder form. The MFR was 12 at 230°C, 2.16kgs weight.

PP and surface modified boehmites was compounded using a 25 mm counter rotative ZSK 25 twin screw extruder. The barrels and die temperatures were set at 230°C. The screw speed was at its higher setting, 900 RPM. The total feeding rate was measured at 20 lb/hr. The composite inorganic particle loading weight was kept constant at 6%.

Measurements

Characterization of the surface modified boehmite

Specimens for elemental analysis were sampled after the reaction from the solution directly in the vessel. The specimens were centrifuged and washed three times. After drying, Inductively Coupled Plasma (ICP) was used to determine the specimen's phosphorus content.

N$_2$ adsorption-desorption isotherm measurements were realized on a Tristar 3000. Samples were dried under inert atmosphere for two hours before

Figure 3 Surface modifiers chemical structure.

TABLE I
**Elemental and BET Results for Boehmite Particles
Surface Treated by Alkyl Phosphonic Acids**

Surface modifier	% P	C_{BET}
Octadecyl phosphonic acid (ODPA)	No data	29.3
Octyl phosphonic acid (OPA)	0.94%	63.2
Vinyl phosphonic acid (VPA)	0.59%	95.4
No surface modifier (Virgin boehmite)	0.00%	180.0

measurement. The coefficient C_{BET} was determined using the BET equation.

Solid state ^{31}P NMR spectra were collected by a Varian UnityPlus-200 NMR spectrometer using cross polarization in conjunction with magic angle spinning (CPMAS).

Dispersibility of treated particle in low viscosity nonpolar solvent

A small quantity of treated particles was mixed with octane in a Horiba® particle size analyzer mounted with an ultrasound probe. The average particle size was then monitored every minute for 8 min to evaluate the particle disagglomeration in the nonpolar solvent due to the ultrasonic energy.[18]

Characterization of the composite properties

Backscattered micrographs were taken by a scanning electron microscopy (SEM) on ASTM bar cross sections to assess the boehmite particles dispersion in the polymer. After etching, the samples were embedded in an epoxy resin.

Thermal analysis was performed with a TA Instruments Q500 TGA to evaluate the effect of boehmite dispersion on the composite thermal stability. All Samples were heated in air between 25 and 800°C at a rate of 10°C/min.

For mechanical testing, the extrudates were injection molded into tensile (ASTM D638- Type I die) and flexural (ASTM D790) bars. The temperature of injection was set at 230°C. Tensile tests were realized on an Instron 4465 tabletop test frame mounted with a 5 kN capacity load cell. Test rate 50.8 mm/min (2 in./min), grip distance 115 mm. Four point bend flexural tests were performed on MTS Sintech 2/G tabletop test frame mounted with a 100 lb capacity load cell.

Differential scanning calorimetry was used to measure melting and crystallization temperatures and corresponding enthalpies. The samples were heated then cooled at a rate of 5°C/min between 25 and 220°C. The data were collected during the second heating/cooling cycle.

RESULTS AND DISCUSSION

Grafting of the surface modifier on the boehmite particles

Elemental analysis showed that washed treated boehmite samples contained phosphorus atoms contrary to untreated boehmite (Table I).

To confirm the grafting of the surface modifier on the boehmite particles, solid state ^{31}P-NMR experiments were performed (Fig. 4). In case of all treated
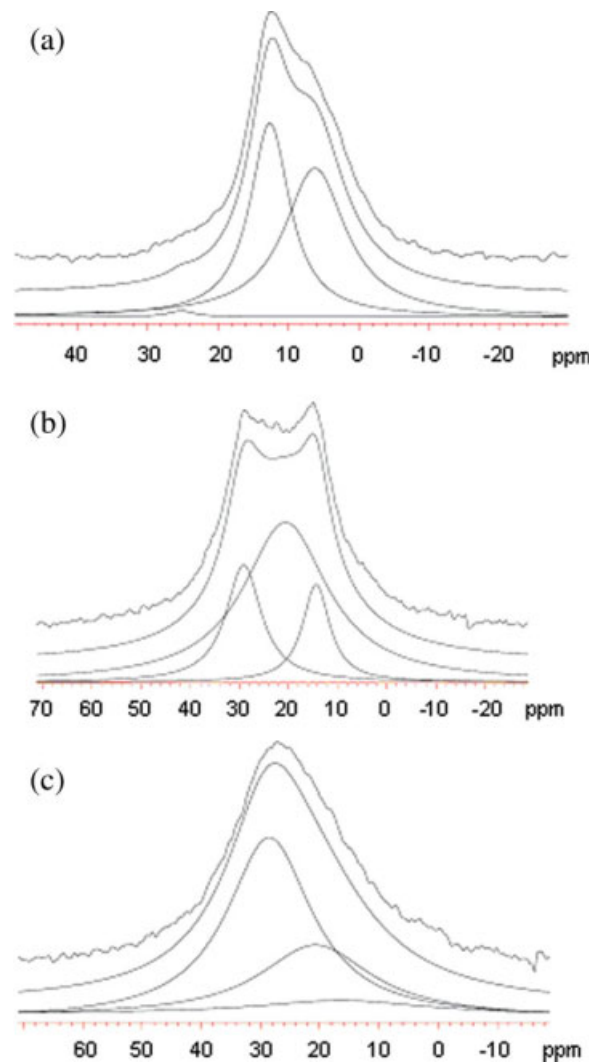

Figure 4 Characterization of nanoboehmite CAM® 9010 treated with organo-phosphorus surface modifier by Solid State ^{31}P-NMR spectra for (a) VPA ($\delta_{th} = 15.2$ ppm), (b) ODPA ($\delta_{th} = 31$ ppm), and (c) OPA ($\delta_{th} = 31$ ppm). Each NMR spectra is deconvoluted; the top noisier curve represents the experimental data. For VPA surface modifier, the spectra could be deconvoluted into two peaks at 12.6 and 6.2 ppm compared to a $\delta_{th} = 15.2$ ppm (measured in DMSO). For surface modified boehmite grafted by OPA, the spectra can be broken down in three Gaussian curves centered at 29, 20.5, and 14.3 ppm compared to a δ_{th} of 31 ppm. Finally the spectrum for ODPA surface modifier can be deconvoluted in three Gaussian peaks at 28.5, 20.7, and 16.2 ppm compared to a δ_{th} of 30 ppm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
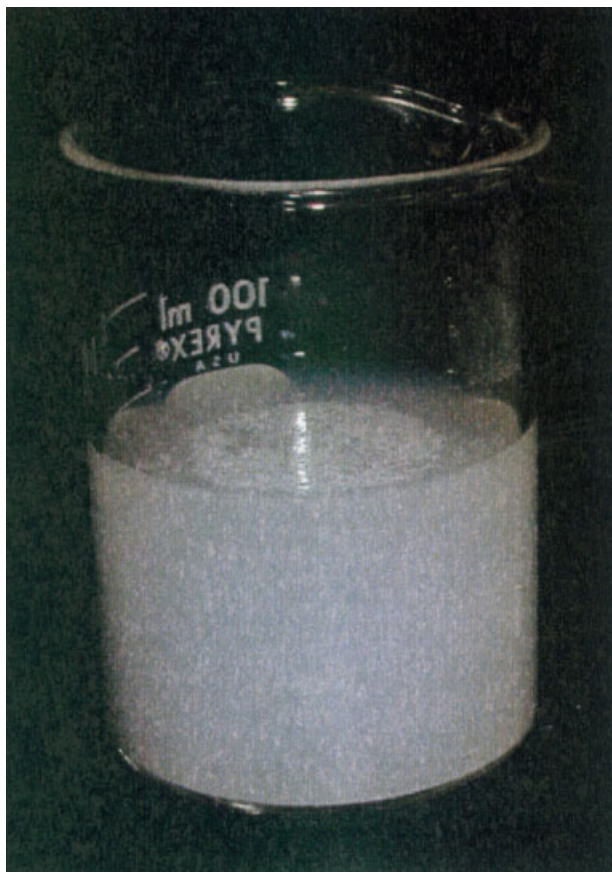
boehmite. The gradual decrease of the C_{BET} value is correlated to the length of the surface modifier's hydrophobic alkyl chain (Table I).

The surface modifier had also a profound effect on the dispersibility of the boehmite particle in a nonpolar solvent. When subjected to ultrasound, boehmite powder treated with Cyanex® 272 (a phosphinic acid with 16 carbon atoms) is desagglomerated. The average aggregate size decreased from 100 μm to less than 1 μm (Fig. 7). Figure 8 summarizes the results for all surface treated boehmite samples. Similarly to the C_{BET} value, the disaglomeration rate was correlated to the surface modifier's hydrophobic alkyl chain. This is probably due to a lower difference in surface energy between the treated particles and the nonpolar solvent.

Properties of polypropylene/surface treated boehmite nanocomposites

Nanoboehmite dispersion in PP

SEM micrograph of PP filled with nontreated boehmite particles exhibits white agglomerates with a

Figure 5 Dispersion in water of nanoboehmite particles after drying. The nanoparticles were untreated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

samples, the phosphorus peak signal is deshielded toward zero compared to the theoretical values for the unreacted surface modifier (δ_{th}).[19] Each spectrum was deconvoluted into multiple peaks by mathematical modeling. Each deconvoluted peak characterizes a phosphorus atom in a different bonding mode.[20] This indicates the surface modifier has reacted with 1, 2, or 3 surface hydroxide group.

Effect of surface modifier on the hydrophibicity and dispersibility of treated particles

The surface modifier presence has a significant effect on the hydrophobicity of treated boehmite particles as suggested in Figures 5 and 6: boehmite powder treated with OPA could not be redispersed in water contrary to untreated boehmite.

Additional evidence of the effect of surface modifier on the surface polarity was provided by BET measurements. The C_{BET} value is proportional to the average enthalpy of adsorption of the first layer of gas on the surface[21] and was used to characterize the boehmite surface polarity.[22] All treated boehmite samples had a lower C_{BET} value than untreated
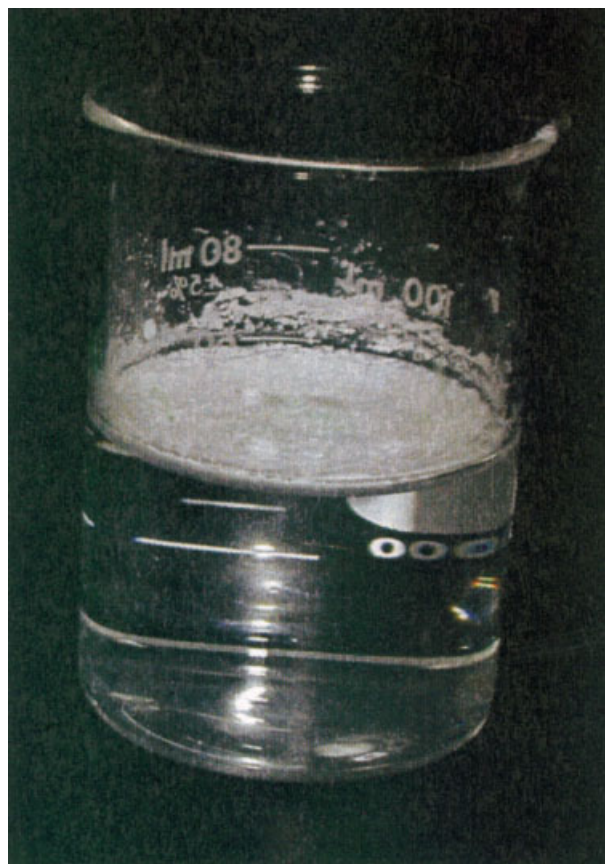

Figure 6 Dispersion in water of nanoboehmite particles after drying. The nanoparticles were treated with OPA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
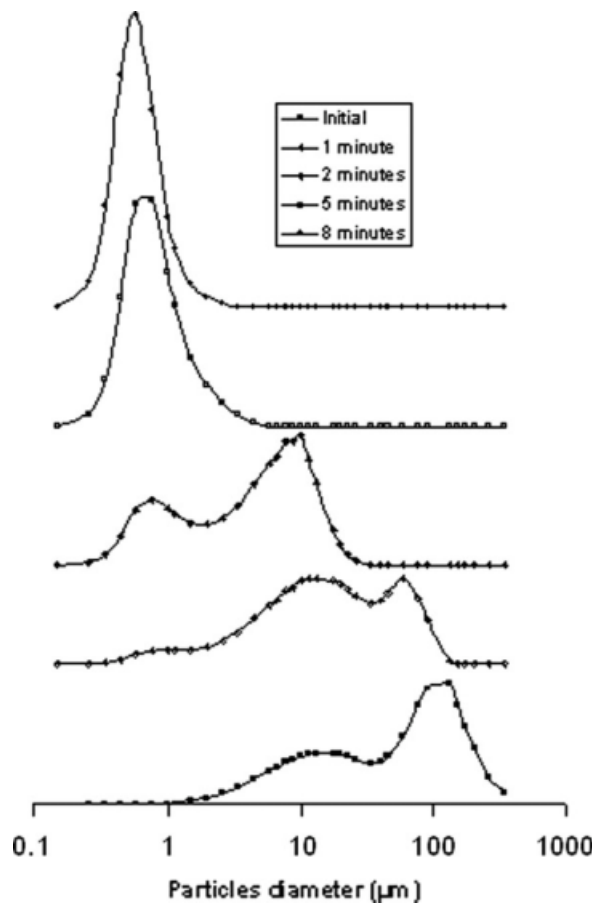
Figure 7 Distribution of particle size measured in octane for boehmite treated by CYANEX® phosphinic acid.

size larger than 2 μm (Fig. 9). The use of the surface modifier dramatically improved the dispersion of the boehmite particles as shown in Figures 10, 11, and 12. The boehmite particles seem to be structured in small aggregates with a size lower than 500 nm when boehmite particles were treated with OPA and Cyanex® 272.
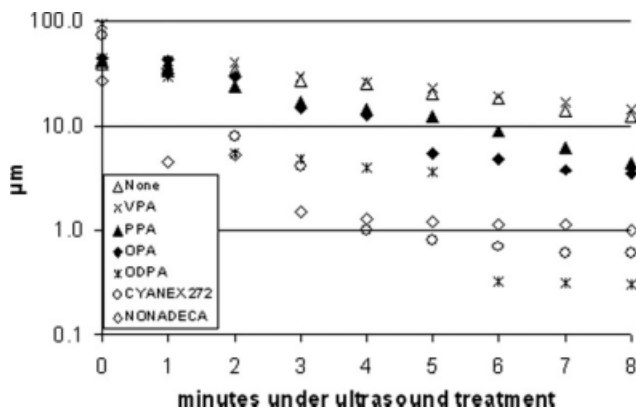

Figure 8 Disagglomeration test in octane: particle size measurement for CAM® 9080 platelets surface modified with various surface modifier.
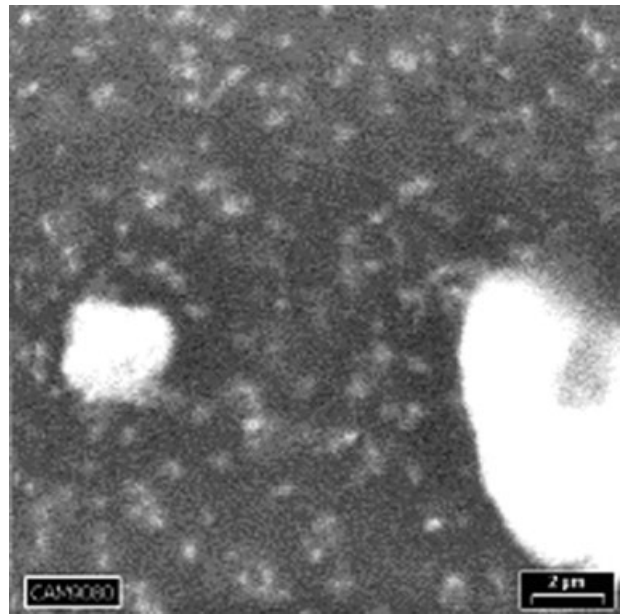
Figure 9 SEM micrograph of nanoboehmite/PP composite at 6% weight loading of untreated CAM® 9080.

Thermal properties

The thermal stability behavior of all boehmite/PP nanocomposites is improved as shown in Table II and Figure 13. The onset degradation temperature is increased by 33°C for PP filled with untreated boehmite particles, by 43, 47, and 64°C for PP filled with boehmite particles treated with OPA, ODPA, and Cyanex® 272 respectively. A good correlation
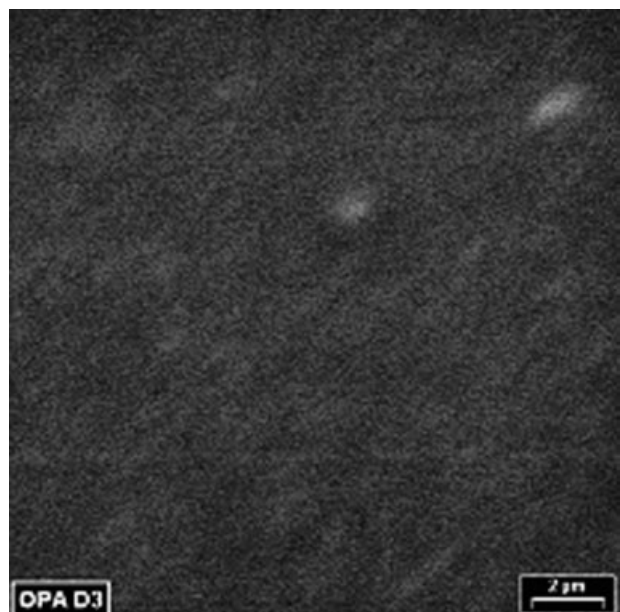
Figure 10 SEM micrograph of nanoboehmite/PP composite at 6% weight loading of surface modified CAM® 9080 by OPA.
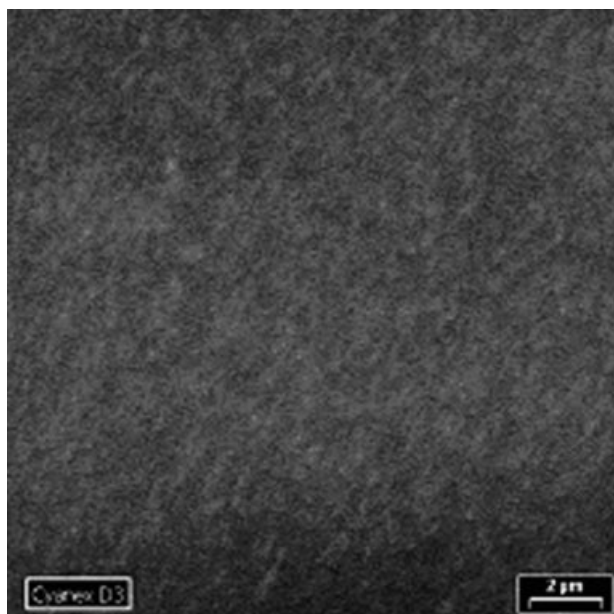
Figure 11 SEM micrograph of nanoboehmite/PP composite at 6% weight loading of surface modified CAM® 9080 Cyanex® 272.

between particle dispersibility and thermal stability was identified.

Thermal stability enhancement has been widely described for several nanocomposite matrix loaded with surface nanoclays and more specifically on nanoclay/PP nanocomposite.[23]

Several mechanisms may explain the good thermal properties of the boehmite/PP nanocomposites. The nanoboehmite platelets may acts radical scavengers,
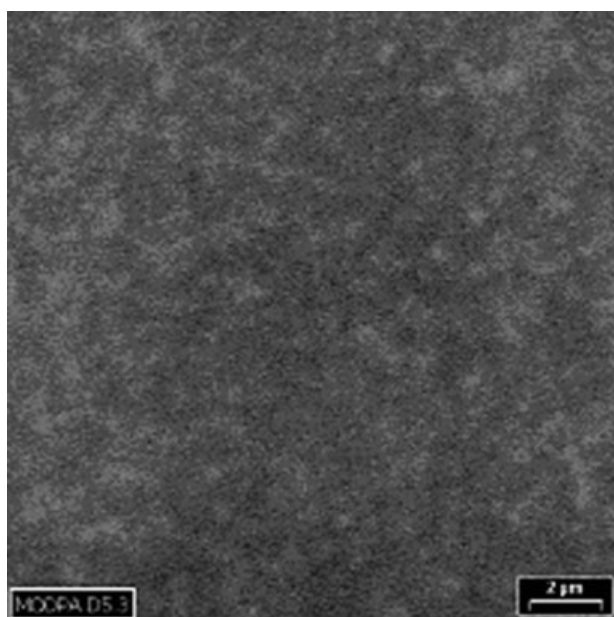
Figure 12 SEM micrograph of nanoboehmite/PP composite at 6% weight loading of surface modified CAM® 9080 by ODPA.

TABLE II
TGA Data of PP/Surface Modified Boehmite Composites at 6% Weight Loading for Virgin PP (Sample PP6301), PP/Untreated Boehmite Composite (sample PP-Boeh) and PP/Boehmite Surface Treated by OPA (Sample PP-Boeh-OPA), ODPA (PP-Boeh-ODPA, and Cyanex® 271 (PP-Boeh-Cya)

Sample I.D	Onset degradation temperature (°C)	Half degradation temp (°C)	Nanoparticle dispersion in PP (from Fig. 13)
PP 6301	282	319	None
PP-Boeh	315	348	Big aggregates
PP-Boeh-OPA	325	356	Few aggregates
PP-Boeh-ODPA	339	372	No aggregates
PP-Boeh-Cya	346	376	No aggregates

or improve the oxygen barrier properties as explained by Wilkie and coworkers.[24] Other mechanisms are more related to the particle and the surface treatment: boehmite is an alumina-monohydrate, which releases water around 250°C; organophosphorous compound are also used as flame retardant additives.[25]

It is expected that the thermal stability measured by TGA be translated into an improvement in fire retardancy. Based on published previous work previously cited, there is a correlation between TGA and cone calorimeter data strongly suggesting that nanoboehmite could be used to improve polymer fire retardancy.

Mechanical properties

No significant improvement in tensile modulus was observed in case of PP nanocomposites samples filled with ODPA and Cyanex® treated boehmite (Fig. 14) and Table III). The ultimate elongation of both samples is very similar to unfilled PP. This
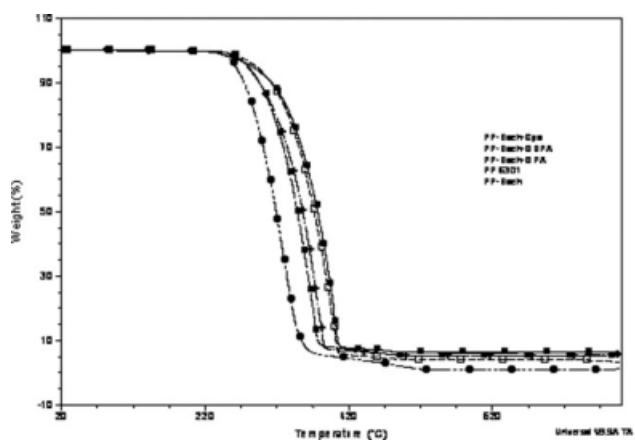

Figure 13 TGA thermograms of virgin polypropylene (-○-), composites PP/nanoboehmite untreated (-■-) and surface treated by OPA (-▼-), ODPA (-□-) and Cyanex (-●-).
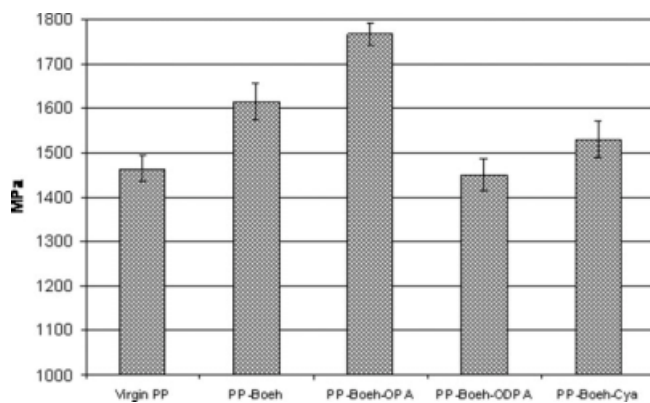
Figure 14 Tensile modulus of PP/boehmite nanocomposites measured on ASTM bars.

Figure 15 DSC thermograms acquired during cooling of Polypropylene composites loaded with 6% of boehmite nanofiller.

suggests a weak interaction between the PP and the ODPA or Cyanex® treated boehmite.

On the other hand PP nanocomposite samples filled with untreated boehmite and OPA treated boehmite have higher modulus than unfilled PP by 10 and 20% respectively. The ultimate elongation of both samples is much lower than unfilled PP: 40 and 7% compared to 400%. This suggests the presence of polymer/filler interaction between the PP and untreated and OPA treated boehmite.

Thus the surface treatment (or its absence) can have a strong effect on the interaction between the polymer and the nanoboehmite particles.

Differential scanning calorimetry

DSC measurements were performed to further investigate the interactions between the nanofillers and the polymer matrix.

All PP/boehmite nanocomposite have higher crystalline peak than unfilled PP (Fig. 15 and Table IV).

In case of the PP filled with ODPA and Cyanex® treated boehmite the crystalline peak is shifted only by 7.3 and 4.7°C respectively. No secondary crystalline peak is observed.

In case of PP filled with untreated boehmite and OPA treated boehmite the primary peak is shifted to higher temperature by 10.2 and 8.4°C respectively. In addition a secondary peak is observed at a temperature about 7°C higher than the primary peak. The detection of crystallite peak by DSC at higher temperature is an evidence that nanoboehmite particles promote crystallization and act as nucleating agent. Covering nanoboehmite with long alkyl chain surface modifiers lessens the ability of the particle to introduce heterogeneous nucleation sites.

Multiple DSC peaks are often an indication of different crystalline phase. For example several crystalline phases were previously reported for boehmite/polyamide nanocomposites.[26,27] The XRD spectra of the nanocomposite in Figure 16 with untreated boehmite shows that the α-phase is predominantly present. There is no evidence of a peak at a 2θ angle of 20° characteristic of the γ-phase. It is difficult to conclude if the β–phase is present because the characteristic peaks at 2θ angles of 16.2 and 21 are often confounded with the main α-phase. However, the XRD spectra of the untreated boehmite exhibit a small shoulder at 16.2° which is not observed in the virgin PP sample nor in the untreated boehmite sample. Finally, the relative intensity of the α-phase peaks at 2θ angle of 14° and 17° decreases

TABLE III
Tensile Properties at Room Temperature for Several PP/Boehmite NanoComposites. Standard Deviations Are in Between Parenthesis

Sample I.D	Tensile strength (MPa)	Ultimate elongation (%)	Flexural modulus (MPa)
PP6301	31.7 (±0.2)	395.5 (±0.1)	2000 (±80)
PP-Boeh	32.8 (±0.3)	7.4 (±0.1)	2370 (±250)
PP-Boeh-OPA	33.3 (± 0.2)	39.4 (±36.1)	2590 (±310)
PP-Boeh-ODPA	30.9 (±0.6)	366.5 (±58.3)	2000 (±20)
PP-Boeh-Cya	31.3 (±0.2)	380.7 (±0.1)	2150 (±50)

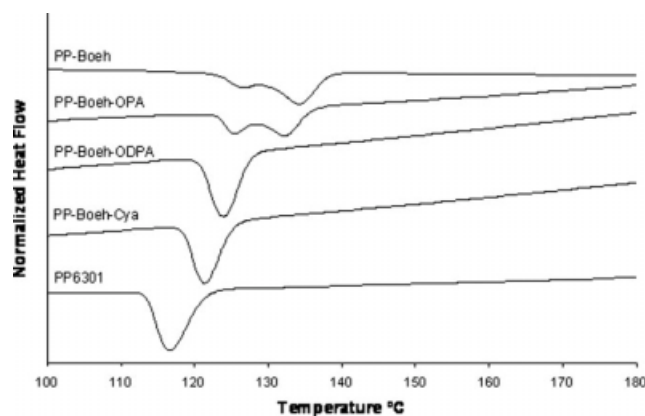Error Bars for Tensile and Flexural Moduli Are Given for a Significance Level of 0.05 (95% Confidence interval).

TABLE IV
Phase Change Temperature and Time to Crystallization for Nanocomposites Loaded with 6% of Modified and Untreated Nanoboehmite

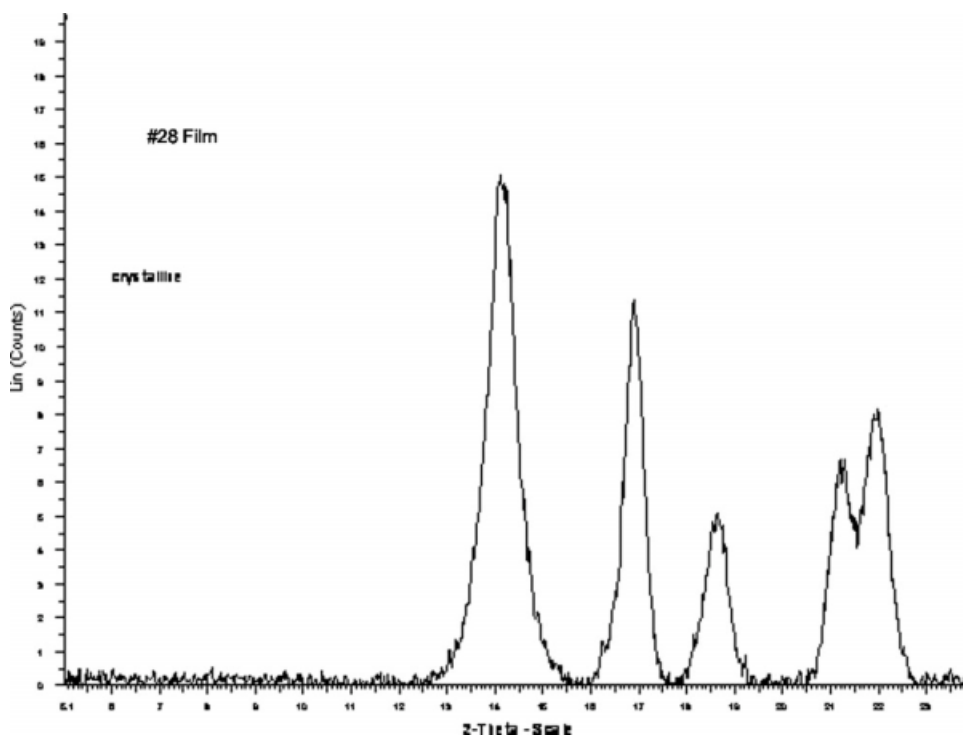| Sample I.D	Crystalline temperature (°C)	Melting temperature (°C)
PP 6301	116.7	161.8
PP-Boeh	134.2−126.9	166.1
PP-Boeh-OPA	132.1−125.1	166.2
PP-Boeh-ODPA	124.0	166.1
PP-Boeh-Cya	121.4	164.5

Figure 16　XRD spectra of polypropylene loaded with 6% of untreated nanoboehmite (sample PP-Boeh).

significantly from the virgin PP to the sample with untreated boehmite. This reduction may indicate a preferential orientation of the crystal induced by the nanoparticle.[28]

In summary, nontreated nanoboehmite or nanoboehmite treated with short alkyl chains act as nucleating agents due to polar polymer-filler interactions. This also leads to higher tensile modulus and lower ultimate elongation as seen in the previous paragraph. On the other hand nanoboehmite treated with long alkyl chains do no act as nucleating agents and do not change the mechanical properties of the nanocomposite (same tensile modulus and ultimate elongation than PP).

CONCLUSIONS

Nanoboehmite particles were surface modified by alkyl phosphonic/phosphinic acid in order improve their dispersibility in nonpolar environment. When surface modifier with long alkyl chains is used, the dispersibility of the treated particles in the nonpolar polypropylene is greatly improved.

The authors found the thermal stability of the nanoboehmite PP nanocomposite is significantly enhanced even at a low loading level and is correlated to the dispersion level.

The nanoparticle's surface treatment strongly affects the polymer mechanical properties. When the boehmite is not treated or treated with a surface

modifier with short alkyl chain, the nanocomposite has higher modulus, and lower ultimate elongation suggesting stronger filler-polymer interactions. In this case the nanoparticles act as nucleating agents during the crystallization of the polymer.

When surface modifiers with long alkyl chains are used, the mechanical properties of the nanocomposite are hardly altered suggesting weak filler-polymer interactions. In this case the surface treated particles have limited nucleating effect.

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