

Nano-Addition of Raw Bentonite Enhances Polypropylene (PP) Properties

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ABSTRACT: Bentonite (BNT) is the cheapest raw material source for making commercial nanoclay, which is approximately 250 times more expensive than BNT. Perhaps this may be one of the reasons why we do not find a translation of good scientific work on polymer nanocomposites into commercial reality. In this work, it is demonstrated that PP nanocomposites were made using 3% raw bentonite via Master batch (MB) route with maleated PP. This product has 9.5% greater tensile strength, 18.6% greater flexural strength, and 27% greater flexural modulus than neat PP. The repeat extrusion of PP/bentonite was carried out, which had beneficial effects on tensile modulus and flexural strength and less so on other properties. This study opens a Pandora's box full of possibilities, such as cheap polymer nanocomposites being available for many different applications. Increase in

the previously mentioned properties of PP-BNT adduct cannot be explained by the nucleation effect of BNT on PP. X-ray diffraction, internal surface area, TGA, and DSC measurements were made on the above samples. Addition of 3% raw bentonite increases the crystallization of PP by 7.5°C (nucleation effect). Since this is just a pilot study, this opens a vast commercial scope for making nanocomposites from raw clays. The stakes for doing this are very high, because BNT is \$0.10/kg and can be available consistently from mineral producers in Gujarat and Rajasthan in India. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1004–1009, 2006

Key words: clay; mechanical properties; nanocomposites; nanolayers; nanotechnology

INTRODUCTION

Polymer-clay nanocomposites possess mechanical properties that set them apart from conventional fiber-reinforced or mineral-filled materials. Property enhancement in nanocomposites occurs at very low clay loadings, < 5 wt %. This means that superior performance can be realized with significant weight savings. The nano-approach calls for a simple, low-cost extension of existing polymerization technologies.

More recently, advances in synthetic techniques and the ability to readily characterize materials on an atomic scale has led to interest in nanometer-size materials. Since nanometer-size grains, fibers, and plates have dramatically increased surface area compared to their conventional-size materials, the chemistry of these nanosized materials is altered compared to conventional materials. Polymer nanocomposites combine these two concepts, that is, composites and nanometer-size materials. The most common filler is montmorillonite (MMT) clay; these nanoclays are unique since they have a platy structure with a unit thickness of one nanometer or less and an aspect ratio in the 1000 : 1 range.

Studies on PP/bentonite composites are very few as most scientists prefer pristine montmorillonite over raw clays. One such recent study deals with the effect of surface treatment of bentonite on the mechanical properties of polypropylene–bentonite composites.¹ The thermodynamics drive the nanometer dispersion of the clay through the polymer and the small amounts of clay do not cause any wear in the equipment. The main strategies for intercalation/exfoliation of nanoclays and formation of polymer nanocomposites are as follows:

Direct intercalation of a preformed polymer into the host clay lattice.

Intercalation of monomer molecules with subsequent chemical, thermal, or photo-induced polymerization *in situ*.

Alternately, intercalates are formed when clay is put in aqueous surfactant solutions, for example, quaternary ammonium surfactants having a long hydrocarbon chain (e.g., commercial nanoclay, Cloisite 15A, 20A, etc.).

Use of swelling agents for intercalation of clay, such as water, glycol, glycerol, poly[ethylene glycol], poly[vinyl alcohol], maleic anhydride [MA], and most important, MA-grafted polypropylene [MA-g-PP] of higher molecular weight. These lead to an increase in interlayer spacing, which can be estimated by X-ray diffraction.

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TABLE I
Suitability of Natural Clay Versus Nanoclay for Making Polymer Nanocomposites

Problem	Effect	Solution
Sourcing of layered clay	Varying composition from place to place.	Stick to one clay type and grade [e.g., vermiculite, bentonite EB].
Choice and cost of clay used [MMT]	MMT is 100's of times more expensive than natural clays.	Bentonite and vermiculite are much cheaper natural clays (10 cents to 30 cents/kg).
Tendency to exfoliate	DC ^b of MMT is much higher than bentonite; hence it is difficult to exfoliate. Cloisite clay is intercalated.	Our work (under patenting) has shown that bentonite has low DC and exfoliates easily by 70–80%.
Organic modification of clay	Possible by i) ion exchange with long chain quaternary ammonium cation. ii) <i>in situ</i> polymerization (many monomer combinations give rise to exfoliation).	Emphasis on physical rather than chemical treatment can lower cost [e.g., ball milling, thermal shock, swelling agents, etc.].
Tuning of compatibilizer	Ratios of clay/compatibilizer/polymer are found by trial & error. There is a need to optimize MFI, acid value, and hydrophobicity of PP-g-MAH. ^c Silanes are expensive to use.	Silane-treated natural clays still require PP-g-MAH for compatibilizing with polymer.
Tuning of clay % in polymer matrix	Higher concentrations (5–10%) cause a reaggregation of clay platelets.	Use of 0.5% to 3% nanoclay suffices in many cases.
Extrusion problems in PP/organoclay	Excess shear causes a reduction in aspect ratio; less shear does not help exfoliation. Reverse exfoliation occurs at temp. \geq 180°C when organoclay begins to decompose, leaving platelet surface bare.	i) use EFM(extension flow mixer) and DEFM(dynamic EFM). Particle size can be reduced thousands of times; ii) However, if you don't have these, try repeated extrusion at a moderate temperature; iii) Use a 2-step method by first making a masterbatch.
Characterization of intercalation or exfoliation	The field of view of TEM is so small that a single platelet can be highlighted while intercalated clusters may be ignored.	X-ray diffraction (XRD) gives information averaged over at least 100 mg of nanocomposite.
Stability of morphology	Morphology of nanocomposite is in quasi-equilibrium, immediately after production.	Product should be stored for one week, then tested and dispatched.

^a MMT = Montmorillonite.

^b DC = Degree of crystallinity.

^c PP-g-MAH = graft copolymer of PP and maleic anhydride.

Nanoclay is melt-blended with MA-g-PP to generate a preintercalated composite masterbatch [PICM]. PICM is diluted by blending with PP to give PP nanocomposite [PPNC].

Polypropylene nanocomposites are still challenging due to the lack of affinity of organophilic PP for hydrophilic clay. In these systems, only partial exfoliation has been possible. Other thermoplastics, such as poly(ethylene oxide),² poly(methyl methacrylate),³ polybutadiene acrylonitrile,⁴ polydiacetylene,⁵ poly(ϵ -caprolactone),⁶ polystyrene,^{7,8} polyimide,^{9,10} and poly(ethylene terephthalate),¹¹ have since been used to synthesize polymer-clay nanocomposites by different methods. Polypropylene-clay nanocomposites have also been actively studied by researchers from Toyota.^{12–15} Polymer-clay nanocomposites have been successfully produced by extrusion.¹⁶ A wide range of

thermoplastics, from strongly polar polyamide 6¹⁷ to styrene,¹⁸ have been intercalated between clay layers. However, polyolefins, which represent the biggest volume of polymers produced, have so far only been successfully intercalated to a limited extent.¹⁵

The performance of nanocomposites is related to the degree of delamination of the clay in the polymer matrix, which increases the interaction between the clay layers and the polymer. Table I gives a comparison of the suitability of nanoclay and natural clay in the strategies to be adopted for making a polymer nanocomposite.

EXPERIMENTAL

Materials

Polypropylene homopolymer (PPHP, AMI 120N, IPCL, Baroda, Gujarat, India), maleated polypropylene (MAPP, Optim P-415, % of grafting 1.0, from

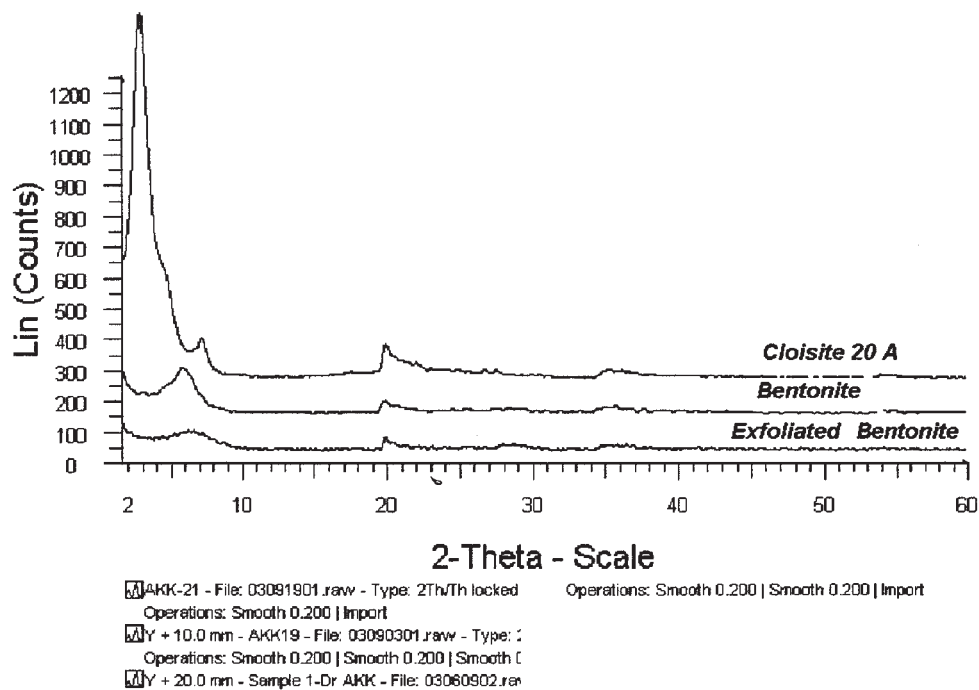


Figure 1 X-Ray diffractograms of Cloisite 20A, bentonite, and exfoliated bentonite.

M/S Pluss polymer Pvt. Ltd. New Delhi, India), and bentonite clay (sodium based bentonite EB grade, M/S Shree Mahalaxmi Chemicals, Bombay India) were used as received.

Preparation

PP-Nanocomposites were prepared by (i) the single step melt process using maleated polypropylene (MAPP) as a compatibilizer (10% by wt) between raw dry bentonite clay (3% by wt) and polypropylene homopolymer, and (ii) through the masterbatch route (MB). In the MB route, raw dried bentonite clay and MAPP were dry mixed in the high speed mixer in the ratio of 1 : 4. It was then melt mixed in the single screw extruder (L/D : 25/1) attached to a Brabender Plasticorder (PLV-151, Brabender OHG, Duisburg, Germany) in the temperature profile of 150/175/200/190°C for the first, second, third, and die zone, respectively, at 40 rpm. The extrudate was pelletized.

The clay concentration in the MB is 20% by wt. The final PP-nanocomposites were prepared at the clay concentration of 3% by wt, using the above prepared MB diluted with PP in the twin screw extruder (ZSK-30, Werner Pfeiderer, Stuttgart, Germany) at 80 RPM. The extrudate were quenched, pelletized, and dried, and MFI was measured. These pellets were injection molded as per ASTM D 638 specifications in an injection molding machine (Windsor, India) in the form of dumbbell and bar specimens.

XRD

Powder samples were scanned on a Bruker X-ray powder diffractometer (model: D-8 Advance) at room temperature. Copper k-alpha radiation with a nickel filter was used. Tube voltage of 40 kV and current of 30 mA were used. The samples were scanned in the two theta ranges of 1.5 to 60 degrees, with a step width

TABLE II
Results of X-Ray Diffraction Analysis on Clays

S. no.	Sample	FWHM (2-theta) deg.	Interlayer spacing (Å)	Crystallite Width* (Å)	Number of layers in tactoid
1	Cloisite 20 A	1.192	31.8	73	>5
2	Bentonite	1.712	15.1	49	>3
3	Bentonite [exfoliated]	2.929	14.0	28	2

* Crystallinity is generally always proportional to Crystallite size. Thus, crystallinity in the above samples follows the pattern: Cloisite > bentonite > exfoliated bentonite.

TABLE III
Internal Surface Areas of Clays and Minerals*

Filler	Surface Area (m ² /g)
Cloisite 15A	17
Cloisite 20A	20
Bentonite	77
Exfoliated bentonite	126
Silica powder	1–2
Kaolin	7
Fumed Silica	150–200
Talc	7
Calcium silicate	2.6
Diatomaceous earth	1–3.5

* Surface areas of last 6 entries are included from literature to highlight surface areas of bentonite clay.

of 0.02 degree and step time of 0.75 s. Crystallite size measurements were made from full width at half maximum (FWHM) of the corresponding peak using the Scherer equation.¹⁹ These were corrected for instrumental half widths. The number of layers in a clay tactoid was calculated by dividing the crystallite width by 14, which is the distance between adjacent platelets.

Internal surface area

Determination of the surface area was carried out by the BET method.²⁰

RESULTS

X-ray diffraction

In nanocomposite research, X-ray diffraction is used to determine the degree of exfoliation from the peak height and peak position measurements of organoclays in the polymer matrix. As the organoclay is dispersed through the polymer, it is forced to delaminate, increasing the distance between the silicate layers. This process is termed intercalation and results in

greater distance between the silicate layers. The distance of separation is represented as a change in peak width and positioning of the peak from that of the pure organoclay on an XRD diagram. The nano-structure of the nanocomposites was investigated by wide angle X-ray diffractometry (WAXD).

Normalized X-ray diffractograms of raw, intercalated, and exfoliated clays are compared in Figure 1. Various parameters calculated from these are compared in Table II. XRD results given in Table II show a two-fold increase in interlayer spacing of Cloisite 20A over that of raw clay, thus confirming that it is intercalated. The number of platelets in exfoliated bentonite is only two (which may mean an average range of 1 to 3 platelets). Present data justify the use of the term “partially self-exfoliated” for raw bentonite. This is evidence of delamination existing in BNT by a natural process or that caused by the presence of impurities. Raw bentonite has almost equal interlayer spacing to the exfoliated one and has a crystallite size of 49 Å, which is less than the corresponding value of 73 Å for Cloisite. The crystallinity of Cloisite is vastly greater than BNT, as shown by a much greater peak intensity and sharpness of peak width. (Also see footnote under Table II.)

Figure 1 shows normalized X-ray diffractograms of Cloisite 20A, BNT, and exfoliated BNT.²⁰ There is a very high difference, both in peak height and peak position, between XRD traces of Cloisite and BNT. The higher interlayer spacing of Cloisite indicates only the occurrence of intercalation in it. There is a further flattening and slight peak shift of exfoliated BNT with respect to the other two peaks.

Internal surface areas (Table III) give a picture complementary but in reverse order to that given by XRD traces as shown in Table II. The surface areas of Cloisite, BNT, and exfoliated BNT are 20, 77, and 126, respectively. This internal surface can be generated by the rising extent of exfoliation over and above that existing in BNT. Expected benefits from nanocomposites include improvement in modulus, flexural

TABLE IV
Results on Mechanical Properties of PP - Clay Nanocomposite (ASTM Test Specimens), Temperature: Ambient

Test	Neat PPHP	PP+MB-Raw BNT (3%)	% increase with respect to PP	PP+MB-Raw BNT (1.5%)	PP+MAPP (10%) +Raw BNT (3%)
MFI [g/10min]	11.32	11.51	1.68	11.28	13.27
HDT [°C], @18.2 Kgf	58.0	61.0	5.17	60.0	56.5
I.S. [kg.cm/cm]	2.70	2.46	-8.90	3.09	2.96
T.S. at Yield [kg/cm ²]	358.0	392.0	9.50	396.0	352.0
T.M. [kg/cm ²]	11200.0	11652.0	4.04	10656.5	10386.8
F.S. [kg/cm ²]	336.0	398.4	18.60	360.2	340.0
F.M. [kg/cm ²]	12766.0	16210.0	26.98	14320.0	13830.0

Results reported based on average values of six specimens.

PPHP: polypropylene homopolymer; I. S: notched Izod impact strength (6 mm thickness); MFI: melt flow index; HDT: heat deflection temperature; T. S: tensile strength; T. M: tensile modulus; FS: flexural strength; FM: flexural modulus; MAPP: maleated polypropylene; Master batch (MB)-raw BNT: master batch of raw bentonite clay.

TABLE V
Mechanical Properties of PP-Bentonite Nanocomposites (ASTM Specs)

Sample detail	Tensile strength (kg/cm ²) at yield	Elongation (%) at yield	Tensile modulus (kg/cm ²)	Flexural strength (kg/cm ²)	Flexural modulus (kg/cm ²)	HDT@ 18.2 kg f (°C)	Izod impact strength, notched, kg.cm/cm
PP (12MFI)	358	7.8	11200	336	12766	58	2.7
*1	392	6.7	11652	398	16210	61	2.46
**2	401	8.0	14000	430	15550	NA	2.4

Under single and double extrusions *1 = PP+MB-RAW BNT CLAY(3%) (single extrusion) specimen injection molded. **2 = PP+MB-RAW BNT CLAY(3%) (double extrusion) specimen injection molded.

strength, heat distortion temperature, barrier properties, and other benefits, and, unlike typical mineral reinforced systems, they are without the conventional trade-offs in impact and clarity.

Mechanical properties

Various mechanical properties of PP-BNT nanocomposites, with and without compatibilizer, are compared in Table IV at BNT concentrations of 1.5 and 3%. The BNT(3%)-PP nanocomposite shows increase in all its properties (except impact strength) over neat PP. The increase is substantial in flexural modulus (26.98%), flexural strength (18.6%), and tensile strength at yield (9.5%). Such an increase in the above properties cannot be caused by the nucleation effect of BNT on PP alone, but can be explained by low crystallinity and crystallite size. The nanocomposite status is given to PP-BNT because of using only 1.5–3% BNT. Use of 10% MA-g-PP in the PP-BNT(3%) nanocomposite (Table IV) upsets these property gains.

Effect of double extrusion on mechanical properties

Repeat extrusion of the PP-bentonite formulation gave further encouraging enhancement in properties, both in comparison with PP as well as in comparison with once-extruded PP-BNT (Table V). Compared to PP, double-extruded PP-BNT shows 25%, 28%, and 22%

gains in tensile modulus, flexural strength, and flexural modulus, respectively. When compared to once-extruded material, the notable increase of > 20% takes place in double-extruded material. Increase in flexural strength was 10%. Even with addition of 1.5% raw bentonite clay to neat PP, thermal stability of the resultant PP nanocomposite is enhanced (Table VI).

TGA and DSC Analysis

TGA and DSC results of PP-BNT nanocomposites are shown in Tables VI and VII, respectively. TGA results (Table VI) show maximum thermal stability gains in PP-BNT(1.5%) and minimum thermal stability for PP-BNT(3%)-10% PP-g-MAH. DSC results (Table VII) show a good nucleating effect of (3%) bentonite on crystallization of PP ($\Delta(T_m - T_c) = 7.5^\circ\text{C}$). Nanoscale clay platelets act as nucleating agents in the heterogeneous crystallization process (Table VII). It can be concluded that montmorillonite in BNT acts as the nucleus of PP and changes the crystalline behavior of this polymer matrix. Impurities present in BNT do not interfere with the rise in mechanical properties as such, but their removal may increase crystallinity, thereby decreasing exfoliation. As the 2-D lattice spacing increases due to intercalation of macromolecules, X-ray peaks reach progressively lower 2-theta. When exfoliation occurs, the lattice is destroyed and the X-ray peak vanishes.

TABLE VI
Results of TGA Analysis

Sample no.	Sample description	IDT (°C)	FDT (°C)	Temperature at 50 % wt loss (°C)	Residue (%)
1	Neat PP	354.5	413.9	380.9	0.04
2	PP+MB-Raw BNT (3%)	335.0	395.0	365.3	2.18*
3	PP+MB-Raw BNT (1.5%)	356.0	465.0	440.4	1.33*
4	PP+ Raw BNT (3%)+MAPP (10%)	334.8	390.5	364.3	2.61*

IDT: Initial decomposition temp.

FDT: Final decomposition temp.

* Reduction in rated values gives lower value of % residue due to loss of water from BNT.

TABLE VII
Results of DSC Analysis

Sample no	Sample description	T _m (°C)	T _c (°C)	Δ (T _m – T _c) (°C)
1	Neat PP	170.36	117.80	52.56
2	PP+MB-Raw BNT (3%)	167.23	122.16	45.07
3	PP+MB Raw BNT (1.5%)	172.24	122.79	49.45
4	PP+ Raw BNT (3%) +MAPP(10%)	169.11	120.91	48.20

T_m: Crystalline melting temp.

T_c: Crystalline solidification temperature.

DISCUSSION

Clay is abundant and clays other than BNT, such as hectorite, kaolinite, illite, vermiculite, and other characterized and uncharacterized clays, will rule the roost in the future. This article points out ways of enabling mass production of industrial nanocomposites, which, in turn, will provide society with low-cost high-tech appliances and automotives for mass transportation; make air, sea, and space travel much cheaper; conserve plastics by recycling; save energy; and protect our environment, thus giving a boost to clay materials science.

Compared to conventional composites, polymer layered-silicate (PLS) nanocomposites have maximized polymer-clay interactions since the clay is dispersed on a nanometer scale. This results in lighter materials with higher modulus and strength, making them desirable for some applications, such as exterior automobile parts.

The following are required to produce the intensity of surface interactions to exfoliate and disperse the clay platelets in the polypropylene matrix:

The primary difference between conventional composites and nanocomposites is the nanoscale dimensions and interfacial area in the latter.

The use of the word “nanocomposite” for raw clay/PP composites can be justified by use of 3% and lower concentrations, which causes an improvement, particularly notable in flexural and tensile properties. “Filler effect” can’t exist at such a low concentration.

CONCLUSIONS

1. Bentonite [3%] is an efficient nucleating agent for PP.
2. Bentonite [3%] causes an enhancement of mechanical properties of PP, even without use of a compatibilizer.
3. Double-extrusion of a PP-bentonite formulation further boosts properties, notably the tensile modulus.

4. XRD data indicate that raw BNT is partially exfoliated, probably due to impurities present in BNT along with the MMT fraction [75–95%].
5. Use of the term “nanocomposite” is justified for describing PP-BNT.

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