Production of Modified Clays and Their Use in Polypropylene-Based Nanocomposites

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ABSTRACT: The use of modified bentonite as a reinforcement in polypropylene (PP)/organoclay/maleic anhydride grafted polypropylene (MAPP) nanocomposites was investigated. The modified bentonites (organoclays) were prepared from raw (unpurified) bentonite (RB) and two quaternary ammonium salts with long alkyl tails: hexadecyl trimethyl ammonium bromide [HDA][Br] and tetrakis-decyl ammonium bromide [TKA][Br]. The ternary composites were produced by using a corotating twin screw extruder, followed by injection molding, and they exhibited microcomposite structure as observed by XRD. In order to observe the effects of purification of the bentonite, purified bentonite (PB) was obtained through sedimentation of raw bentonite, and later modified with two quaternary ammonium salts: dimethyl dioctadecylammonium chloride [DMDA][Cl] and [TKA][Br], and one quaternary phosphonium salt: tributyl hexadecyl phosphonium bromide [TBHP][Br]. Ternary nanocomposites (PP/organoclay/MAPP) with these organoclays were produced by using a corotating twin screw extruder, followed by batch mixing in an intensive batch mixer, and by injection molding. The use of [DMDA][Cl] and [TBHP][Br] resulted in nanocomposite formation, whereas the use of [TKA][Br] resulted in microcomposite formation as observed by XRD and TEM. Young's modulus of PP was increased by 30% with DMDA and 9% with TBHP. The yield strength of PP was increased by 15% with DMDA and 8.3% with TBHP. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polymer-layered silicate nanocomposites attract much attention owing to high mechanical and barrier property enhancement when a small percentage of clay is used as the filler.[1–4] The most common layered silicate used for this purpose is montmorillonite (MMT) which is beneficiated from bentonite which contains high amounts of MMT together with other clay and nonclay materials such as quartz and feldspar depending on the natural deposit. Owing to its hydrophilic nature, MMT must be modified with appropriate surfactants to make it organophilic, so that it becomes compatible with nonpolar polyolefins such as polypropylene (PP) and polyethylene (PE). Several researchers used their local bentonites as the MMT source in their studies to search for their potential to have polymer composites with improved mechanical, barrier, and thermal properties through exfoliated MMT layers.[5–8] The first agents for clay modification were amino acids which were used in polyamide-clay hybrids.[9] Quaternary ammonium and phosphonium salts are the other surfactants used in modification of MMT owing to their long alkyl chains.[10–12] The ion exchange reaction between the cations of these materials and the exchangeable cations of MMT causes insertion of alkyl chains into the clay layers, resulting in increase in the *d*-spacing of the clay.

Morphology and thermal stability of MMTs with alkyl ammonium and phosphonium ions have been studied by several researchers.[5–15] Filho et al.[5] modified bentonite with [HDA][Br], and the XRD analysis showed increase in the bentonite interlayer from 1.5 nm to 2.05 nm after modification. TGA analysis showed a decomposition temperature of ∼ 300°C confirming that this organoclay can be used in melt processing of several plastics such as PP and PE. FTIR analysis showed new absorption bands in modified bentonites, differing from the unmodified one, indicating the intercalation of salt molecules within the bentonite. Vaia et al.[10] modified MMT with quaternary ammonium salts and investigated the structure of these salts by FTIR and XRD. TGA analyses showed higher thermal stability of phosphonium ions compared to ammonium ions. Kim et al.[14] modified MMT with imidazolium- and pyridinium-based ionic liquids. It was shown that thermal stability of the

Table I. Properties of Clays

Property	Value
Raw Bentonite (RB)	
CEC (mmol/100 g of clay)[a]	67.5
Purified Bentonite (PB)	
CEC (mmol/100 g of clay)[a]	100
PGW (Nanocor)	
CEC (mmol/100 g of clay)[b]	145
Aspect ratio[b]	200-400
Specific gravity[b]	2.6

[a]Determined by Methylene Blue Method, [b]Given by the producer.

organoclay decreases as the length of the alkyl chain attached to the nitrogen increases. Their modified clays showed low dispersion in PP matrix, possibly due to their low lipophilicity.

This study is aimed to investigate the potential use of local bentonite in PP matrix as organoclay to have improved mechanical properties. For this aim, firstly unpurified (raw) bentonite was modified with two quaternary ammonium salts [HDA][Br] and [TKA][Br] and then used in the production of ternary nanocomposites of PP by twin screw extrusion. Although there have been studies[5,15] on the use of HDA cation in organoclay production and its application in PP matrix nanocomposites, TKA was not used earlier in PP nanocomposite production. In the second set of experiments, the raw bentonite was purified and then modified with two quaternary ammonium salts [DMDA][Cl] and [TKA][Br], and one phosphonium salt [TBHP] [Br]. DMDA was used in organoclay production[16,17] and in nanocomposites with PE[18,19] and PP matrices.[20] Lee et al.[20] grafted organosilane to DMDA organoclay and then used it in PP matrix. In this study, DMDA is used without grafting a silane and a detailed characterization is conducted. In

Table II. Structure of Surfactants Used in Organoclay Production

Modifier	Chemical structure of surfactants	Abb.	Types of clay	d-spacing (Å)
None	–		RB	12.0
None	–		PB	12.2
Hexadecyltrimethylammonium bromide [HDA] [Br⁻]		HDA	RB	17.8
Tetra(kis)decylammonium bromide [TKA][Br⁻]		TKA with RB & STKA with PB	RB	25.6 with RB (1.1 × CEC)
			RB	26.7 with RB (1.5 × CEC)
			PB	27.2 with PB
Dimethyldioctadecylammonium chloride [DMDA] [Cl⁻]		DMDA	PB	26.4
Tetrabutylhexadecylphosphonium bromide [TBHP] [Br⁻]		TBHP	PB	22.3
[TKA][Br⁻]		PGWTKA	PGW	28.3

the work of Manias et al.,[21] MMT was modified with DMDA and used in functionalized (styrene-based functional groups) and unfunctionalized (neat) PP to obtain nanocomposites. In the set with neat PP, DMDA was modified with semifluorinated alkyltrichlorosilane. In this study, functionalization of PP or DMDA organoclay were not needed differing from the work of Manias et al.[21] Also, TBHP organoclay was used in LLDPE matrix[19,22] but not in PP matrix nanocomposites.

EXPERIMENTAL

Materials

Polypropylene EH-241 with a reported MFI of 20–28 g/min was purchased from Petkim Petrokimya Holding A.S., Izmir, Turkey. Resadiye bentonite was kindly provided by Karakaya Bentonit A.S., Turkey. As received raw bentonite was purified by sedimentation and highly pure bentonite (which is mineral MMT) was obtained for the second set of experiments. Cation exchange capacity (CEC) of the raw bentonite and purified bentonite were determined by the methylene blue (ASTM C/837-99) method[23,24] as 67.5 and 100 mmol/100 g clay respectively. Quartz, feldspar, and opal-C are present in the raw bentonite.[25] Both raw and purified bentonites were used in the production of organoclays with different modifiers. A commercial pure MMT with the brand name of PGW was purchased from Nanocor Inc., USA and used in the synthesis of one type of organoclay in order to observe the effect of degree of purification of MMT on the final properties of organoclays. Properties of the clays are given in Table I. Ammonium and phosphonium salts used in the organoclay preparation are:

- Hexadecyltrimethylammonium bromide, [HDA] [Br]
- Tetra(kis)decylammonium bromide, [TKA] [Br]
- Dimethyldioctadecylammonium chloride, [DMDA] [Cl]
- Tetrabutylhexadecylphosphonium bromide, [TBHP] [Br]

These salts were purchased from Sigma-Aldrich and their structures are given in Table II together with the type of clay used in the production of the organoclay. Organoclays are abbreviated by the cation of the modifier. Organoclay modified with [DMDA][Cl] is called DMDA. The organoclay prepared with raw bentonite and [TKA][Br] is denoted as TKA, whereas the organoclay prepared with purified bentonite and [TKA][Br] is denoted as STKA.

Organoclay Modification

In the ion exchange modification process, the concentration of the modifiers was generally taken as 1.1 x CEC of the corresponding clay except for TKA50. TKA50 was prepared with 1.5 x CEC of raw bentonite in order to observe the effect of high modifier concentration. TKA cation was also used with PGW at 1.1 x CEC in order to observe the effects of highly pure MMT usage. This resultant organoclay is denoted as PGWTKA.

In the modification of MMT, 5 wt% raw or purified bentonite was dispersed in water–ethanol (4 : 1, v/v) mixture and stirred with a stirrer for 4 h to obtain a well-dispersed mixture of clay. The mixture was heated to 80°C in a jacketed heater. 1.1 x CEC of the modifier salt was dissolved and stirred in a water-ethanol (4 : 1 v/v) mixture and poured into the bentonite dispersion.

The mixture was stirred for 24 h at 70–80°C. Then, the solution was filtered through a Buchner funnel filtration system, and the retentate was washed with 4–5 L of hot water–ethanol mixture (1 : 1, v/v) to have a bromide ion free paste. Absence of bromide ion was tested with AgNO₃. Washing was stopped when a white precipitate was not observed when a few drops of 0.1N AgNO₃ were added to the filtrate. The paste was smeared in a large glass plate and air dried overnight. Then, it was dried in a vacuum oven for 72 h at 80°C. The dried clay was ground and stored in a desiccator.

At first, modification of raw bentonite was performed with [HDA][Br] and [TKA][Br]. Then, modification of purified bentonite was performed with [DMDA][Cl], [TBHP][Br], and [TKA][Br].

PREPARATION OF POLYMER NANOCOMPOSITES

Equipment

In the production of ternary composites, a corotating twin screw extruder (Thermoprism TSE 16 TC with $L/D = 24$, screw diameter = 16 mm) and an internal intensive batch mixer manufactured by Haake Buchler Instruments, Saddle Brooke, NJ (EU-5V) with a mixing volume capacity of 300 mL were used. The batch mixer was used with roller blade type agitators, which are typically used for high intensive mixing applications such as compounding of thermoplastic and thermosetting resins with rigid fillers.

Samples for tensile testing and XRD analysis were prepared by injection molding. For injection molding, DSM Xplore, Geleen, Netherlands (micro 10 cc) ram injection molding was used. The injection pressure was 15 bars, and the melt and mold temperatures were 220 and 25°C, respectively. Hold time was 4 min 40 s for each sample.

Process Conditions

Two sets of nanocomposites, namely SET-1 and SET-2 were prepared and characterized. The samples of SET-1 were prepared by extruding twice using the organoclays HDA, TKA, TKA50, and PGWTKA produced from raw bentonite. All ternary composites formulations in this study consisted of 2 wt% of organoclay, 5 wt% of MAPP and 93 wt% of PP, and the extruded samples are abbreviated as PP/Organoclay2/MAPP5. In all the extrusion runs, a mixture of organoclay, MAPP and PP were fed to the extruder through the vibratory feeder Retsch/DR100 at a feed rate of 15–20 g/min. The temperature profile was 180°C throughout the extruder, and the screw speed was 350 rpm in both of the extrusion steps. The extrudates obtained were passed through a water bath and then pelletized. The pelletized samples were dried in a vacuum oven for 4 h at 100°C prior to the second extrusion process. The composites obtained at the end of the second extrusion were dried for 12–16 h at 100°C in a vacuum oven prior to injection molding.

The samples of SET-2 were prepared by extruding twice followed by batch mixing, using DMDA, TBHP, and STKA organoclays prepared from purified bentonite. The materials that were extruded twice were further sheared by melt mixing of samples in the intensive batch mixer/torque rheometer. Temperature and blade speed were kept at 190°C and 32 rpm,
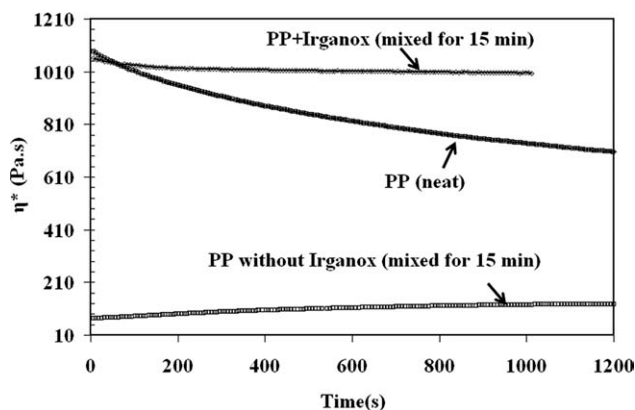
Figure 1. Time sweep test of PP with and without heat stabilizer subjected to various mixing histories.

respectively. Samples that were both extruded and batch mixed are abbreviated with an M (referring to the mixing) at the end of the sample name such as, PP/DMDA2/MAPP5-M.

Time sweep oscillatory tests were done by dynamic oscillatory rheometer (Rheometric Scientific, NJ, in conjunction with 25-mm parallel disk fixtures) in the melt state in order to observe if there is significant degradation in the PP structure with time. Figure 1 shows the complex viscosity of unprocessed (just molded) PP pellets, 15 min batch mixed PP with 1 phr of heat stabilizer Irganox®B225 (Ciba Specialty Chemicals, Japan), and PP batch mixed for 15 min without Irganox®B225. Possible degradation of PP due to chain scission can be seen from Figure 1. Polyolefins may undergo chain scission reactions leading to a decrease in molecular weight at high temperature and applied shear. However, even when chain scission occurs, under strictly controlled conditions, useful products of uniform quality can be obtained.[26] Addition of heat stabilizer Irganox®B225 provided thermal stability to PP. For this reason, Irganox®B225 was used in batch mixing of previously extruded PP composites.

CHARACTERIZATION

XRD Analysis
The XRD of bentonite samples and composites were obtained by a 100 kV Philips twin tube X-ray diffractometer (PW/1050) using CuK$_\alpha$ radiation, which generated a voltage of 40 kV and
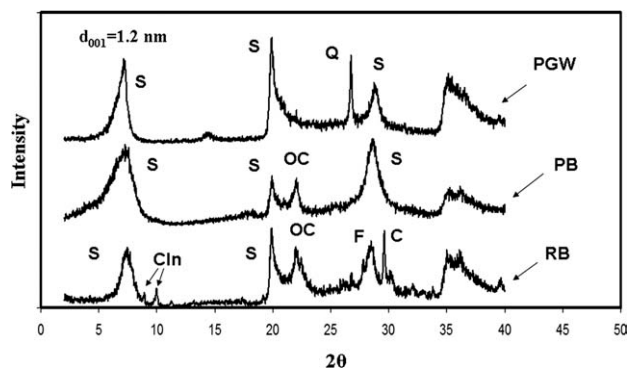

Figure 2. XRD of RB, PB, and PGW. (S, smectite; Q, quartz; C, calcite; Cln, clinptilolite; F, feldspar; OC, Opal-C).
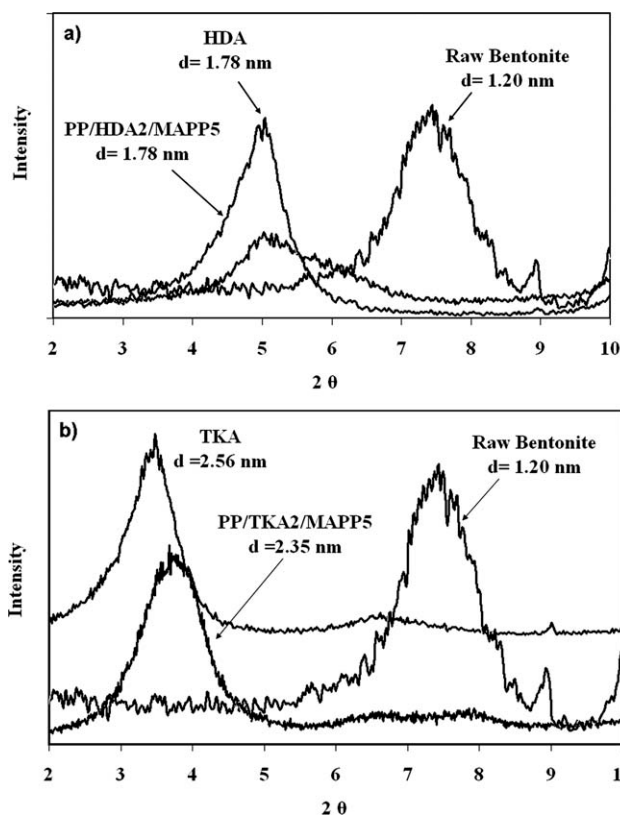

Figure 3. (a,b) XRD patterns of (a) RB, HDA, and PP/HDA2/MAPP5, (b) RB, TKA, and PP/TKA2/MAPP5.

current of 40 mA ($\lambda = 1.54A°$). The diffraction angle 2θ was scanned from 1° to 10° at a scanning rate of 1°/min and a step size of 0.01°. XRD analysis of clay samples were done in powder form. Tensile bars obtained by injection molding were used for analyzing the morphology of the nanocomposites by XRD.

Transmission Electron Microscopy
Dispersion of clay layers was analyzed by TEM using Tecnai^{TM} G2 F30 equipment produced by FEI Company that used an accelerating voltage of 300 kV. Ultra thin sections of 70 nm in thickness were cryogenically cut with a diamond knife at a temperature of −100°C. All samples were trimmed parallel to the injection molding direction.

Tensile Testing
Tensile properties were measured by Shimadzu AG-SN type machine using dog bone type of injection-molded samples. Tensile test samples were prepared according to the ISO 527-5A standard. The strain rate was 0.5 min^{-1}.

RESULTS AND DISCUSSION

XRD Analysis of Bentonite and Organoclays
The analyses of the raw and purified bentonites and commercial high purity MMT (PGW) are shown in Figure 2. Raw bentonite shows mainly the presence of smectite (S) Na$^+$MMT together with non-clay impurities such as clinoptilolite (Cln), and opal-C (OC) and feldspar (F).[23,25] XRD of purified bentonite shows that nonclay parts are reduced upon purification, and it has reflections that are similar to those of PGW. X-ray analyses,
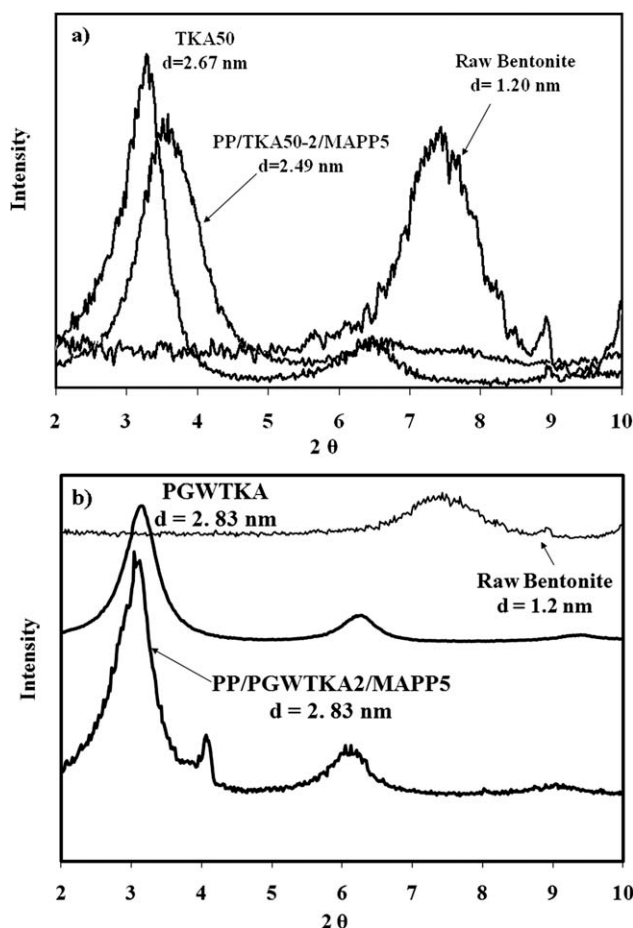
Figure 4. (a,b) XRD patterns of (a) RB, TKA50, and PP/TKA50-2/MAPP5 (b) RB, PGWTKA, and PP/PGWTKA2/MAPP5.

together with the increase in the CEC of the bentonite indicates that purification method applied is adequate to obtain highly pure MMT.

Organoclays prepared with both raw and purified bentonites have reflection angles shifted to the left in comparison to the pristine bentonites indicating increases in the basal spacing of the unmodified clay according to Bragg's law:

$$d = \lambda n / (2 \sin \theta)$$

All of the organoclays showed higher basal spacings compared to unmodified raw and purified bentonites. The increase in the basal spacing of the organoclays indicates that the organic modifiers had diffused between the silicate layers, and modification was effectively accomplished.

XRD and TEM of Nanocomposites in SET-1

The change in the basal spacing of the silicate layers of organoclays in the composite matrix was examined by analyzing the location of peaks in XRD with Bragg's law. While intercalated organoclay structure is assessed by the increase in the *d*-spacing, exfoliation is evaluated by the dissappearence of the peak.

Figure 3(a) shows the XRD patterns of HDA and the PP/HDA2/MAPP5 ternary nanocomposite exhibiting slight difference in

the location of the XRD peak. This indicates that the *d*-spacing of HDA was not significantly changed through compounding. The binding forces between the silicate layers and the polymer matrix are very effective in the delamination of clay layers. Absence of such an interaction may cause clay platelets to remain as tactoids without penetration of polymer chains between them. Thus, it can be inferred that under these conditions HDA is not compatible with the PP matrix.

Figure 3(b) shows the XRD patterns of TKA and its ternary composite PP/TKA2/MAPP5 showing reduced *d*-spacing of organoclay in the composite system. When structures of HDA and TKA are compared, HDA has one long (C16) tail, while TKA has four long alkyl tails (4C10) in its backbone. Kadar et al.[27] mentioned that modifiers with bulky alkyl tails may locate between the particles of clay layers and not in between the galleries which may limit the entrance of polymer chains through spacing between the silicate layers. This explanation can be valid for TKA, since the modifier has four long alkyl tails with 10 C atoms in each tail. Although one alkyl tail of HDA is more favorable, since it would not impede and limit the diffusion of polymer layers, in contrast to long alkyl tails of TKA, delamination of clay layers was also not achieved in HDA based composites. Structure, concentration, and orientation of the modifier are important factors in the delamination of silicate layers through the polymer matrix.

Figure 4(a,b) show the XRD data of organoclays TKA50 and PGWTKA and their ternary composites PP/Organoclay2/MAPP5 respectively. The amount of surfactant added to the bentonite is referred as milieequivalent ratio (MER) and it is different in TKA and TKA50, allowing comparison of different MER loadings. TKA was prepared with a surfactant concentration of 1.1xCEC, while TKA50 was prepared with a surfactant concentration of 1.5xCEC. Comparison of Figures 3(b) and 4(a) shows that addition of more surfactant during the ion exchange promoted intercalation of more cations through the clay layers and expanded the *d*-spacing of the clay to a greater extent. While TKA clay has a *d*-spacing of 2.56 nm, TKA50 clay has a *d*-spacing of 2.67 nm. Comparison of Figures 3(b) and 4(a) indicate that excess surfactant usage slightly increases the
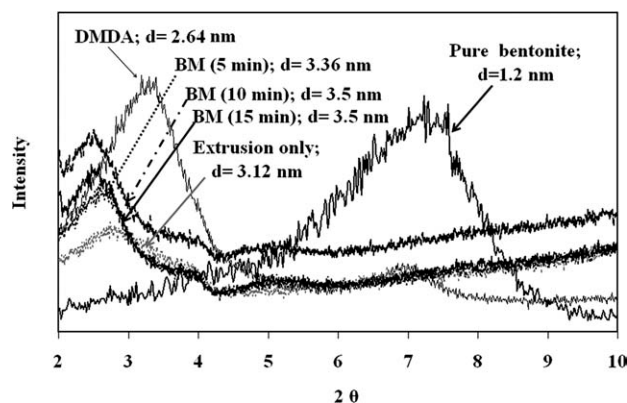

Figure 5. XRD patterns of PB, DMDA, "extruded only" ternary composite PP/DMDA2/MAPP5, and "extruded+batch mixed : (BM) ternary composites" that are batch mixed for various time intervals.
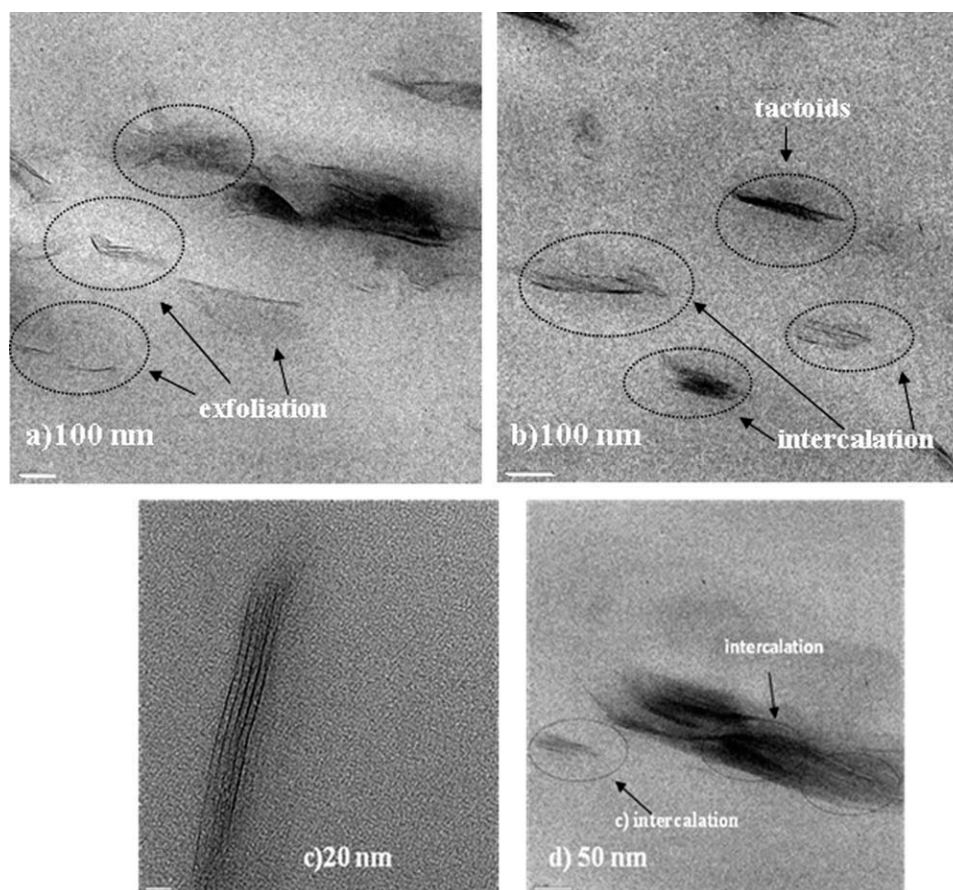
Figure 6. TEM micrographs of PP/DMDA2/MAPP5-M.

d-spacing in TKA-based composites. Figure 4(b) indicates that *d*-spacing of PGWTKA did not change in PP matrix indicating the difficulty of diffusion of polymer chains through the crowded TKA layers.

XRD and TEM Analysis of Nanocomposites in SET-2

Figure 5 shows the XRD diffractograms of DMDA and its ternary composite, PP/DMDA2/MAPP5, prepared by "extrusion only", and the composite, PP/DMDA2/MAPP5-M, prepared by extruding twice followed by batch mixing for various time intervals indicated on the figure. During the batch mixing, samples were taken from the melt at different time intervals (5, 10, and 15 min) in order to observe the effects of applying more shear to the composite system. Samples taken were analyzed by XRD to determine the optimum mixing time for the composite system which would produce the highest *d*-spacing according to XRD. Figure 5 shows that the peak of DMDA is at a *d*-spacing of 2.64 nm, whereas "extruded only" composite shows a peak at a *d*-spacing of 3.12 nm. In contrast to the samples prepared in SET-1, intercalation was achieved by "extrusion only" in SET-2 when DMDA clay was used. The observed higher level of intercalation may be explained by the high chemical attraction between the matrix and the surfactant of DMDA which has two long alkyl tails. Chemical attraction and affinity between the organoclay surfaces and polymer matrix is a key factor in achieving delamination and separation of clay layers through

the matrix. As it can be seen in Figure 5, further mixing in the batch mixer for 10–15 min shifted the clay peak further to the left with respect to 5 min of mixing. While the DMDA clay peak is at a *d*-spacing of 2.64 nm, the *d*-spacing of DMDA clay in the matrix increased from 3.36 to 3.50 nm after mixing for 5 and 10–15 min respectively. Totally, 32% increase in the *d*-spacing was achieved after 10–15 min batch mixing of the extruded
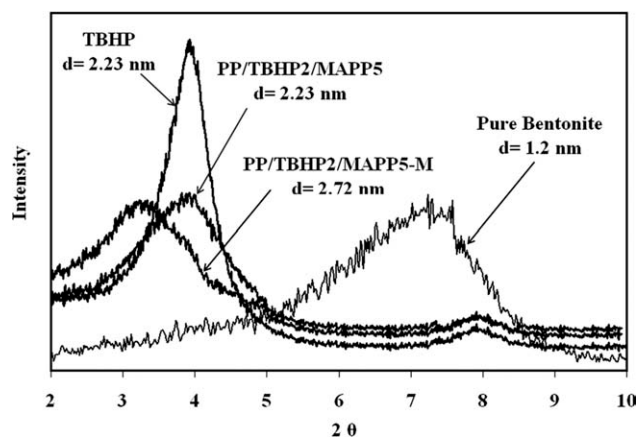

Figure 7. XRD patterns of PB, TBHP, "extruded only" ternary composite PP/TBHP2/MAPP5, and "extruded+batch mixed" ternary composite PP/TBHP2/MAPP5-M.
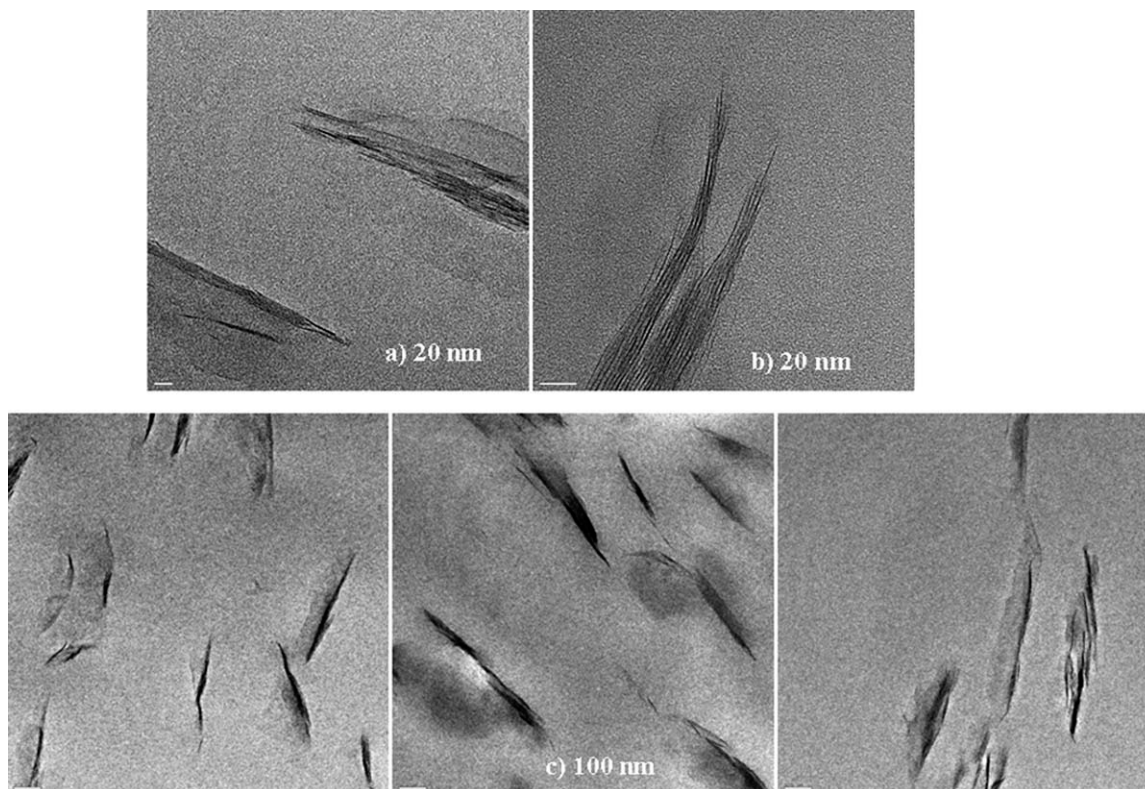
Figure 8. TEM micrographs of PP/TBHP2/MAPP5-M.

samples. After this finding, the samples obtained by extrusion were further mixed for 15 min in the batch mixer in the other ternary systems. In the work of Lee et al., 2006,[20] organosilane grafted DMDA showed % 31 increase in *d*-spacing in the PP matrix. Results of this study indicate that intercalated PP nanocomposites can be achieved without silane grafting. The general conclusion in the polymer layered silicate nanocomposites (PLSN) is that, besides the chemical affinity, sufficiently long residence time is necessary to intercalate or exfoliate the organoclays in the polymer matrix. Applying further shear in the batch mixer following extrusion resulted in fracture of the clay particles into smaller aggregates and the sample exhibited delamination.[28,29]

Although XRD is a widely used technique in polymer–clay nanocomposites, it is a problematical issue in the literature to decide upon the degree of the distribution of the silicate layers or any structural inhomogeneity in nanocomposites by XRD alone.[30] Morgan and Gilman[31] explained the inadequacy of XRD alone to characterize the state of dispersion of the clay layers and stated that XRD should be used in conjunction with TEM. Figure 6 shows the TEM micrographs of the sample PP/DMDA2/MAPP5-M (after extrusion twice, followed by 15 min of batch mixing) at different magnifications. Figure 6(a–d) show stacked clay layers as darker lines, while intercalated and few exfoliated regions are also observed, indicating a mixed morphology. Figure 6(c) clearly exhibits intercalated layers.

Figure 7 shows the XRD diffractogram of TBHP and its ternary composite, PP/TBHP2/MAPP5, prepared by "extrusion only", and the composite, PP/TBHP2/MAPP5-M, prepared by extrusion twice followed by 15 min of batch mixing. Original TBHP

clay and "extruded only" composites have peaks at the same *d*-spacing of 2.23 nm. Stoeffler et al.[22] modified MMT with TBHP and the resultant organoclay had a *d*-spacing of 2.19 nm which is slightly lower than one obtained in this study. The samples with TBHP do not exhibit intercalation upon "extrusion only," since the *d*-spacing of the TBHP and the composite are the same. Additional 15 min of mixing in batch mixer resulted in a shift of the XRD peak to smaller angles and in increase in the *d*-spacing of the TBHP to 2.72 nm indicating 22% increase. In another study using LLDPE/elastomer matrix,[22] TBHP organoclay *d*-spacing was increased just by 2.3%, while in this study the increase is 22% in the PP matrix. TBHP organoclay exhibits
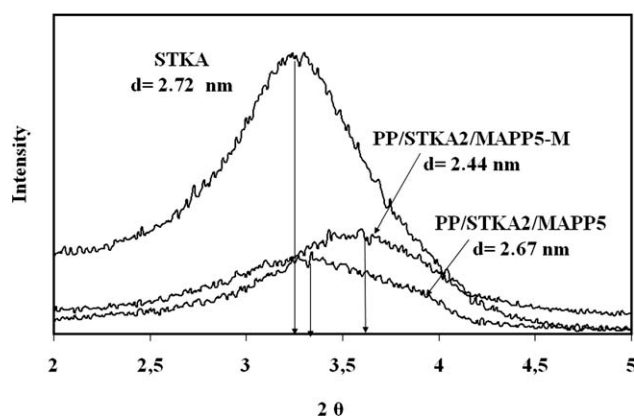

Figure 9. XRD patterns of STKA, "extruded only" ternary composite PP/STKA2/MAPP5, and "extruded+batch mixed" ternary composite PP/STKA2/MAPP5-M.

Table III. DSC Results of PP and İts Composites

	T_m (°C)	PP wt%	ΔH (J/g)	X_c (%)
PP	167.2	100	85.42	40.87
PP-M	166.8	100	90.17	43.14
PP/TKA2/MAPP5	167.2	93	86.41	44.46
PP/TKA50–2/MAPP5	165.9	93	83.06	42.73
PP/PGWTKA2/MAPP5	166.2	93	80.45	41.39
PP/DMDA2/MAPP5	165.9	93	84.70	43.58
PP/DMDA2/MAPP5-M	164.8	93	84.69	43.57
PP/TBHP2/MAPP5	165.8	93	83.51	42.97
PP/TBHP2/MAPP5-M	165.7	93	86.49	44.50
PP/STKA2/MAPP5	166.8	93	83.82	43.12
PP/STKA2/MAPP5-M	165.9	93	85.29	43.88

intercalated and partially exfoliated single layers that are shown in the TEM image (Figure 8).

Figure 9 shows STKA and its ternary composites PP/STKA2/MAPP5 prepared by "extrusion only" as well as PP/STKA2/MAPP5-M prepared by extrusion followed by 15 min of batch mixing. A comparison of TKA clay in Figure 3(b), PGWTKA clay in Figure 4(b) and STKA clay in Figure 9 shows the importance of purification in increasing the d-spacing of the organoclay powder. The TKA clay obtained from raw bentonite has a d-spacing of 2.56 nm in Figure 3(b), the highly pure PGWTKA clay has a d-spacing of 2.83 nm in Figure 4(b), and the STKA clay obtained from purified bentonite has a d-spacing of 2.72 nm (Figure 9). However, all the three organoclays exhibit no intercalation by "extrusion only". The STKA clay has a peak at a d-spacing of 2.72 nm, whereas its "extruded only" composite in Figure 9 has a peak at a d-spacing of 2.67 nm revealing the incompatibility of the TKA cation with PP. PP/STKA2/MAPP5-M composite shows a peak at $d = 2.44$ nm indicating a decrease in the d-spacing as the material was further processed by mixing, in contrast to the results of SET-2 with DMDA and TBHP.

The degree of delamination of clay layers depends on the compatibility between the particle and matrix, the d-spacing of the

organoclay,[32] processing conditions, and applied shear during the processing.[29,33–35] Various processing conditions were applied for the processing of the PP-STKA-MAPP system. However, intercalation was not achieved. Thus, chemical incompatibility of the TKA cation with PP is thought to be the main cause of microcomposite formation in the PP-STKA-MAPP system. During melt blending of clay into a polymer, organoclay layers slide apart from each other. Clay layer delamination can be increased by diffusion of polymer chains into the spacing between the clay layers.[34] As shearing reduces the size of the tactoids or the size of the intercalated stacks, more delamination occurs in the case of high adhesion and compatibility between the clay layers and matrix.[36] Induced and increased specific energy input increases as exfoliation takes place which also increases the elasticity and shear viscosity of the sample.[37] In the exfoliation process, shear intensity is necessary to initiate the dispersion by shearing particles apart into tactoids or intercalates. In addition, long residence time is essential to allow polymer chains to enter the clay galleries and peel the platelets apart[38]. In this study, as residence time increased through batch mixing, DMDA and TBHP showed more delamination in the PP matrix.
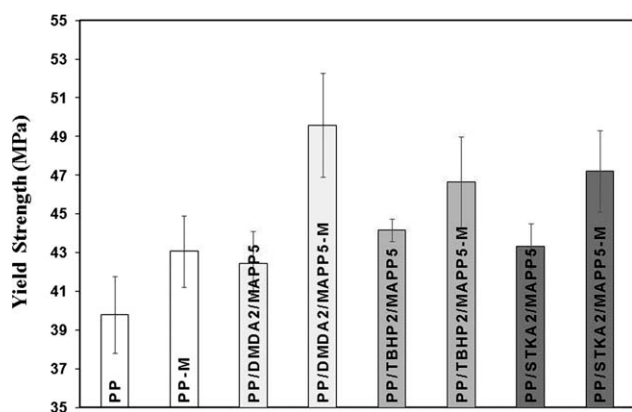

Figure 10. Effect of organoclay type on the yield strength of PP, PP-M, PP/Organoclay2/MAPP5, and PP/Organoclay2/MAPP5-M composites prepared in SET-2.
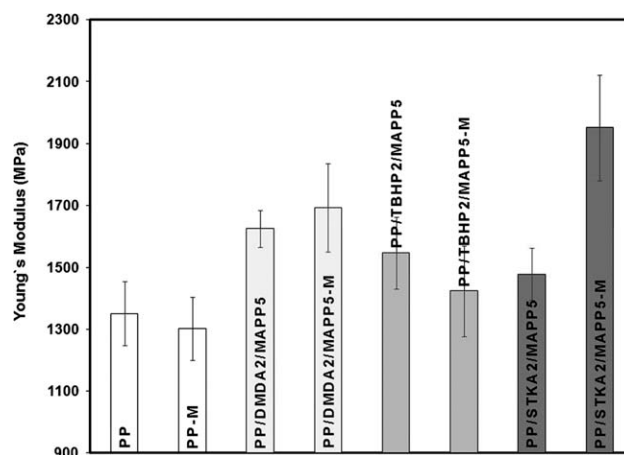

Figure 11. Effect of organoclay type on the Young's modulus of PP, PP-M, PP/Organoclay2/MAPP5, and PP/Organoclay2/MAPP5-M composites prepared in SET-2.

DSC Analysis of Nanocomposites

Table III shows the DSC results of the samples prepared in SET-1 and SET-2. Ternary composites of PP/organoclay2/MAPP5 samples show slight increase in crystallinity owing to the nucleation effect of the clay. Melting temperatures of the ternary composites decrease slightly probably due to the impurity effect of MAPP on PP, similar to "freezing point depression".

Mechanical Tests on Nanocomposites

Figures 10 and 11 show that the yield strength and the Young's modulus of PP and PP-M increased by nanocomposite formation regardless of the type organoclay used. Lopez et al.[39] gives Young's modulus and tensile strength of their PP as 1828 MPa and 34.3 MPa (PP in this study has an modulus of 1302 MPa and yield strength of 43 MPa, respectively). In their study, ternary composite consisting of organoclay from bentonite with octadecylammonium/MAPP/PP was prepared with an organoclay content of 3 and 9 wt% of MAPP. Young's modulus and tensile strength of these composites showed 11% and 7% increase respectively compared with those of pure PP. In another study,[40] tensile modulus and tensile strength of PP are given as 1078 and 29.2 MPa, respectively. In that study, ternary composites prepared with 2% of organoclay (ethanolamine modifier)/MAPP/PP has 13% higher modulus and 8.5% higher tensile strength compared with those of neat PP. Tiwari and Paul[41] used different grades of PP and produced nanocomposites with ethylene-*co*-octene elastomer (30%), MAPP (compatibilizer) and organoclay. In their study, blends of PP (MFI = 24 g/10 min, yield stress = 28 MPa), elastomer, and MAPP showed a yield strength of 20 MPa. The yield strength increased to approximately 22 MPa with 3 wt% of organoclay addition, indicating a 10% increase. Tensile modulus of the same composite set increased from 1000 MPa to about 1170 MPa with 3% organoclay addition indicating 17% increase. In this study, ternary composite of PP/DMDA2/MAPP5-M showed 30% and 15% increase in modulus and yield strength respectively compared with those of PP.

An increase in yield strength and modulus due to decreased elongation ability takes place by clay incorporation, because inorganic particles cannot be strained by external stresses, but
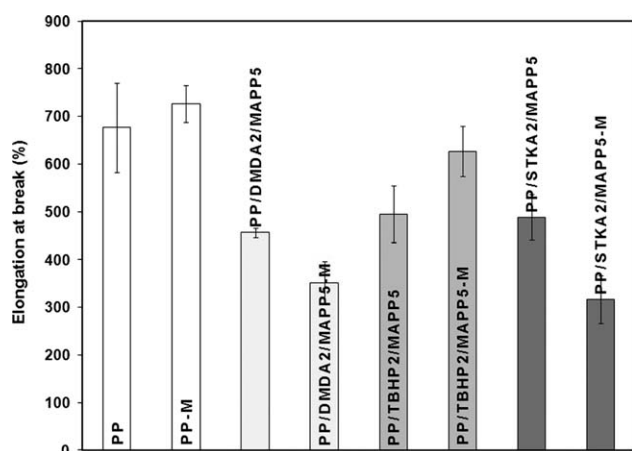

Figure 12. Effect of organoclay type on the elongation at break of PP, PP-M, PP/Organoclay2/MAPP5, and PP/Organoclay2/MAPP5-M composites prepared in SET-2.
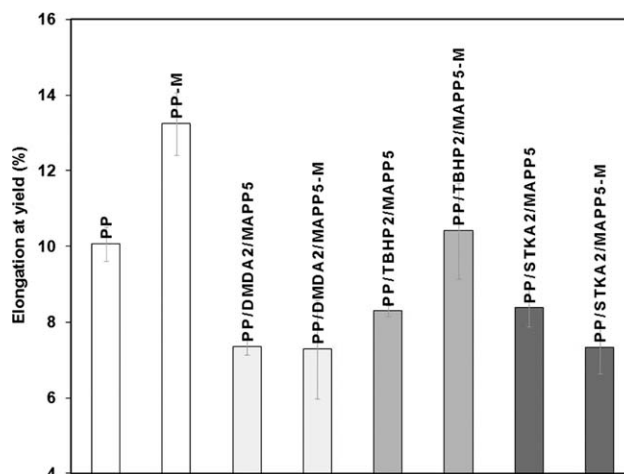

Figure 13. Effect of organoclay type on the elongation at yield of PP, PP-M, PP/Organoclay2/MAPP5, and PP/Organoclay2/MAPP5-M composites prepared in SET-2.

behave as stress concentrators in the matrix during the straining process.[42] In all the ternary nanocomposites, the yield strength increased after more shear was applied by melt mixing owing to the increased organoclay dispersion. Intercalation increases the ratio of surface area to volume of silicate layers which in turn increases polymer-filler contact area giving rise to higher yield strength.

However, the elongation at yield and break values (Figures 12 and 13) of PP and PP-M are higher than those of the nanocomposites. In classical analysis of the effect of fillers on elongation, it is thought that the extension is due to the matrix, and the filler cannot extend as much, leading to smaller elongations at yield and break. It should also be noted that the elongation at break is sensitive to the adhesion between the phases.

Effect of Organoclay Type on Mechanical Properties

Composites prepared with DMDA "by extruding twice followed by batch mixing process" show higher yield strength (Figure 10) compared with the one prepared with TBHP using the same procedure. XRD analysis of the nanocomposites prepared with DMDA indicate intercalation of clay layers, while TEM analysis show that partially intercalated clay layers, few exfoliated layers, and tactoids are present in the system. The same conclusions can be drawn for TBHP. On the basis of the TEM results, even more ordered layers are observed in the system with TBHP compared with the one with DMDA. When structure of DMDA and TBHP cations are compared, DMDA has two long alkyl tails with C18 in each of them and two short methyl groups (2C) in two tails, whereas TBHP has one long alkyl tail with C16 atoms and three medium length alkyl tails with (C4) in each of them. As previously mentioned, it gets harder for the surfactant molecules to enter between the clay layers as the number of long alkyl tails of the surfactant increases. Higher number of long alkyl tails results in sheltering of the polymer–organoclay interactions and generation of a more hydrocarbon-like environment.[43] Comparison of Figures 5 and 7 indicates that DMDA organoclay gets dispersed in the matrix even without the aid of batch mixing, whereas the TBHP organoclay

cannot. Thus, the nanocomposite PP/DMDA2/MAPP5-M exhibits higher yield strength than the nanocomposite PP/TBHP2/MAPP5-M does.

The composite PP/STKA2/MAPP5-M produced with STKA clay shows higher Young's modulus compared with the nanocomposites of PP/DMDA2/MAPP5-M and PP/TBHP2/MAPP5-M (Figure 11). The modulus is not only affected by the interaction and the surface area between the matrix and organoclay, but it also strongly depends on the alignment of the organoclay layers in the direction of testing. STKA with lower level of intercalation and exfoliation in comparison to the other two organoclays would exhibit higher degree of alignment in the direction of injection molding which is also the direction of tensile testing. Young's modulus of the composite of PP/STKA2/MAPP5-M points to the importance of orientation of clay layers during injection molding.

CONCLUSIONS

Effects of different alkyl groups were investigated through the formation of organoclays and nanocomposites by employing XRD, TEM, and mechanical testing. Potential use of local bentonite in nanocomposite production was verified. Sensitivity of clay dispersion to the processing conditions was confirmed. Increased duration of shear applied by batch mixing on previously extruded materials significantly affected the properties of composites as confirmed by XRD and mechanical testing.

TKA with 40 C atoms (4Cx10) in its backbone sheltered the possible entry of polymer segments through the clay layers. In addition, bulky alkyl groups of TKA cation may have increased the interaction energy of the clay and intercalants resulting in relatively less organophilic organoclay. Comparison of TKA and TKA50 showed that use of excess surfactant during modification process is unnecessary, since composites prepared from both of them displayed microcomposite structures as shown by XRD. Organobentonite prepared with PGW, which is a commercial pure MMT, also showed microcomposite formation. It can be pointed out that TKA is not a suitable cation for preparation of PP-organoclay nanocomposites.

Results indicated the sensitivity of clay dispersion to the processing conditions as well as to the chemical affinity between the filler and polymer matrix. XRD and TEM analysis showed increased interlayer spacing through "extrusion followed by batch mixing" with organoclays DMDA and TBHP, whereas STKA did not show a dispersed structure. Ternary composite of PP/DMDA2/MAPP5-M showed 30 and 15% increase in modulus and yield strength respectively compared with those of PP. The study indicated that DMDA and TBHP are suitable in obtaining intercalated nanocomposites with the PP/MAPP matrix.

ACKNOWLEDGMENTS

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