

Formation of Polymer Nanocomposites with Various Organoclays

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ABSTRACT: The role of the type of organic modifier used with montmorillonite (MMT) on the formation of polymer/clay nanocomposites in the melt compounding process was investigated. Various organoclays including primary [12-aminolauric acid (12ALA)], secondary [dioctylamine (DOA)], tertiary [trioctylamine (TOA)], and two commercial quaternary (Cloisite 30B and 20A) MMTs were melt compounded with carefully selected polymers including polypropylene, polystyrene, styrene-acrylonitrile copolymer, poly(methyl methacrylate), poly(vinylidene fluoride), and acrylonitrile-butadiene copolymer (NBR). X-ray diffraction and transmission electron microscopy characterizations confirmed that the two quaternary ammonium organoclay (Cloisite 30B and 20A) have superior compatibility com-

pared to the primary (12ALA), secondary (DOA), and tertiary (TOA) ammonium organoclay. DOA and TOA can form polymer/clay nanocomposites only with the most polar polymer (NBR). Cloisite Na⁺ and 12ALA can not form nanocomposite with any polymers. The large organic surface area of the quaternary ammonium organoclay could be the reason of the best compatibility with polar polymers. It is estimated that long alkyl ammonium chains of organic modifier can spread over the clay surface more effectively than short alkyl chains. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1888–1896, 2005

Key words: nanocomposite; polymer organoclay; organophilicity; polarity

INTRODUCTION

Clay materials have been related to our lives in many ways from a long time ago. For example food containers and vases were made from clay and the textile industry used clay to treat fabric well before the 20th century.¹ Clay also is used in polymer compounding. With the development of polymer nanocomposites, montmorillonite (MMT) clay has become widely investigated by many scientists and researchers. Mauguin² and Pauling³ studied the structure of different clay materials with X-ray diffraction. Hofmann et al.⁴ studied the structure of MMT clay and its swelling behavior in water. The swelling of natural MMT clays was subsequently studied by Norrish⁵ with salt solutions and Barshad⁶ with diverse organic molecules. Blumstein⁷ argued that only high dipole moment monomers can swell MMT. The discovery of cation exchange reactions in clay by Smith⁸ initiated studies of the absorption of organic modified MMT clay. It was found by Jordan⁹ and Weiss¹⁰ that generally polar organic liquids were absorbed by organic modified MMT clays. These organoclays could selectively remove phenol compounds from liquid waste.¹¹

Nylon 6 MMT clay compounds later commercialized as nylon-clay hybrid was introduced by Toyota R&D Center in Japan.¹² 12-aminolauric organoclay absorbed ϵ -caprolactam monomers increasing its inter-silicate layer basal spacing. The ϵ -caprolactam monomers between silicate layers were polymerized and produced polyamide 6-clay compound, which was referred to as a nanocomposite because it appeared that silicate layers were suspended in a polymer matrix.

Many investigations have been carried out to produce polymer/clay nanocomposites with the more economic and environmentally friendly melt-compounding process. Generally, polar polymers such as polyamide 6,¹³ poly(vinyl chloride) (PVC),¹⁴ poly(methyl methacrylate) (PMMA),¹⁵ acrylonitrile-butadiene rubber (NBR),¹⁶ and styrene-acrylonitrile copolymer (SAN)¹⁷ have been melt compounded with organoclays for polymer/clay nanocomposites as witnessed by X-ray diffraction measurements of silicate layer separation and transmission electron microscopy (TEM) observations.

In our previous studies,^{18–20} we succeeded in preparing polymer nanocomposites with all commercially available chlorinated polymers (chlorinated polyethylene (PE), CR, PVC, chlorinated PVC, poly(vinylidene) chloride (PVDC) as well as poly(vinylidene fluoride) (PVDF), and vinylidene fluoride (VDF) containing fluoroelastomers. We found that

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TABLE I
List of Polymers

Material	Commercial name	T_g/T_m (°C)	Supplier
PP	8000 GK	-15/165	Equistar Chemical
PS	Styron 685D	100/—	Dow Chemical
SAN (46 mol % AN)	Lustran	108/—	Bayer
PMMA	Plexiglas	105/—	Atofina
PVDF (58 mol % F)	Solef 1008	-32/173	Solvay
NBR (33 mol % AN)	Krynac 3345C	~-35/—	Bayer

T_g = glass-transition temperature; T_m = melting temperature.

nonpolar polymers [e.g., PE, polypropylene (PP)] or natural MMT clay could not produce polymer nanocomposites. It was concluded that there are two critical factors to produce polymer/clay nanocomposite in the melt compounding process. These are the polarity of polymers and the organophilicity of organic modified MMT clay. Neither nonpolar polymers, nor natural MMT clay systems form polymer/clay nanocomposites.

In this study, we explore a variety of organic modified MMTs to understand the contribution of the organophilicity of organoclay on the formation of the polymer/clay nanocomposite.

EXPERIMENTAL

Materials

Polymers were carefully selected in terms of their level of polarity. These include PP, polystyrene (PS), SAN (acrylonitrile (AN) 30 wt %, 46 mol %), PMMA, PVDF, and NBR (AN 32.5 wt %, 33 mol %) (Table I).

Southern Clay Co. supplied MMT clays (Cloisite Na, Cloisite 30B, Cloisite 20A). Cloisite Na⁺ is sodium containing natural MMT. Cloisite 30B is an organic treated MMT with methyl tallow bis-2-hydroxyethyl quaternary ammonium.

Cloisite 20A is also an organic treated MMT with dimethyl dihydrogenated tallow quaternary ammonium. In addition to the three commercially available MMT (Cloisite Na, 20A, 30B), three more organic modified MMT were synthesized by a cation exchange process. A primary alkyl ammonium, 12-aminolauric acid (12ALA), a secondary alkyl ammonium, dioctylamine (DOA), and a tertiary alkyl ammonium, trioctylamine (TOA) were cation exchanged with Cloisite Na⁺ MMT to produce 12ALA, DOA, and TOA organoclays. Table II summarizes these organoclays.

Synthesis of organoclay

Sodium MMT (Cloisite Na⁺) was dispersed in distilled water with a magnetic stirrer. To obtain a very well dispersed clay solution, the clay dispersion time

was about 24 h at room temperature. This procedure was adopted from Gieseking.²¹

0.01 mol of 12ALA was mixed with 0.01 mol of hydrochloric acid (HCl) in distilled water. A temperature of 70–80°C was used to accelerate the ammonium salt reaction.

The resulting clear solution was poured into the clay and water mixture slowly. The final mixture was vigorously mixed in a blender for more than 10 min. To saturate the cation exchange capacity (92 mequiv/100 g) of Cloisite Na MMT 110% of the required alkyl ammonium salts for full cation replacement was added. The mixing time was about 5 h until the solution become transparent. Subsequently we filtered and washed the organoclay with water/ethanol (0.4/0.6 in volume). The wet clay cake was dried in a vacuum oven at 80°C overnight (12 h). It was then ground to get powder. This procedure was adopted from Usuki et al.²²

Because of the poor solubility of TOA and DOA in water, ethanol and a water mixture of ethanol and water (1:1 in volume) were used, respectively to make TOA and DOA ammonium salts with hydrochloric acid (HCl). Again 0.01 mol of DOA and TOA mixtures were mixed for 5 h. These were subsequently mixed with clay as described above.

A Soxhlet extraction process with ethanol for 24 h was used to eliminate any excess organic molecules between the silicate layers. The final organoclay possessed a single X-ray diffraction basal spacing peak (Fig. 1) distinguished from and at a lower than Na⁺ MMT.

Mixing

Thermoplastic polymers such as PP, PS, SAN, PMMA, and PVDF were melt compounded with organoclays at 180°C and 100 rpm rotor speed for 5 min mixing time in a Brabender internal mixer. NBR because of concerns over the stability of the butadiene units was mixed with the organoclays at 90°C and 50 rpm rotor speed for 5 min.

TABLE II
Organic Modifiers

Clay	Organic modifier	MW of organic ammonium salt (g/mol)
Cloisite Na ⁺	No organic modifier	—
12ALA	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_{11}\text{COOH} \\ \\ \text{H} \end{array}$	216.3
DOA	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{(CH}_2\text{)}_7\text{CH}_3 \end{array}$	242.5
TOA	$\begin{array}{c} \text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{(CH}_2\text{)}_7\text{CH}_3 \end{array}$	354.7
Cloisite 30B	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3-\text{N}^+-\text{T} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	404.8
Cloisite 20A	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}_3-\text{N}^+-\text{HT} \\ \diagup \\ \text{HT} \end{array}$	551.6

T = ~65% C₁₈, ~30% C₁₆, and ~5% C₁₄; HT = ~65% C₁₈, ~30% C₁₆, and ~5% C₁₄.

Characterization of the compounds

A Bruker X-ray machine with a wavelength of 1.5422 Å was used. Powder diffraction patterns were prepared for thermoplastic compounds. Elastomer compounds were sliced to make thin specimens for X-ray diffraction.

A transmission electron microscope (TECNAI-12) operated at 120 kV was used for taking images of the specimens. Ultrathin sectioning was performed with a Reichert Ultracut sectioning system. The elastomer compounds were sectioned at -100°C in liquid nitrogen.

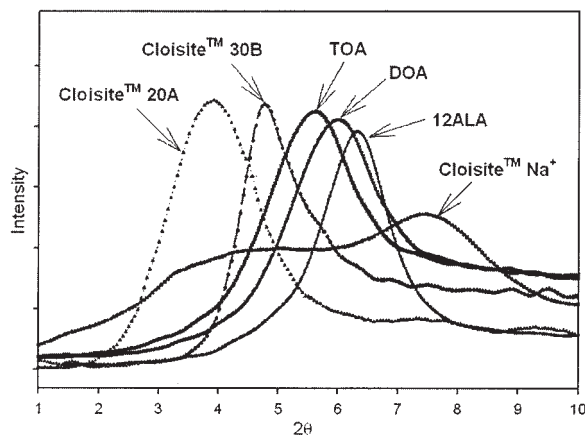


Figure 1 WAXS of MMT clays.

RESULTS

Characteristics of the organoclays

Wide-angle X-ray scattering (WAXS) measurements for the clay materials are shown in Figure 1. The increased basal spacing of TOA, DOA, and 12ALA organoclays as compared to the initial Cloisite Na⁺ clay (*d*-spacing = 11.7 Å) indicates that the organic modifiers came to reside between silicate layers. The tertiary (TOA), secondary (DOA), and primary (12ALA) organoclays have *d*-spacings of 15.8, 14.8, and 14.0 Å, respectively. The quaternary commercial organoclays, Cloisite 20A and 30B have *d*-spacings of 24.2 and 18.5 Å in that order (Table II).

Thermogravimetric analysis (TGA) in nitrogen (N₂) gas was used to confirm the presence organic mole-

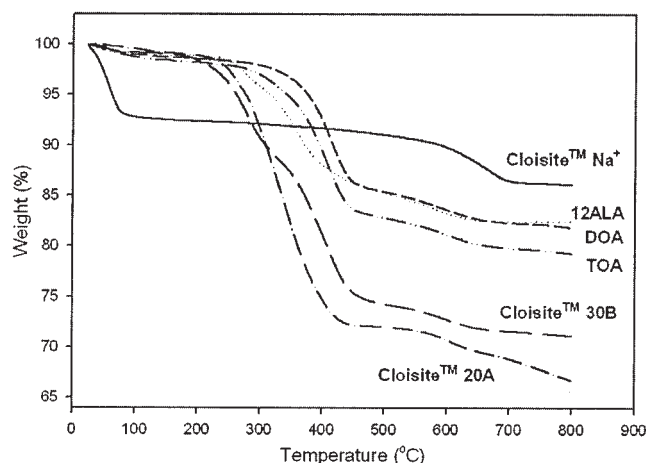


Figure 2 TGA of MMT clays.

cles in the MMT clays (Fig. 2). Cloisite Na⁺ showed about 14% weight loss at 800°C. 12ALA and DOA showed about 18% weight loss. 12ALA thermally degraded before 300°C and DOA did around 400°C. TOA exhibited about 20% weight loss by 800°C. Cloisite 30B and 20A had 29 and 32% weight loss, respectively (Table III).

Compatibility of polymer and clay systems

We examined the polymer–organoclay compounds that we prepared as to whether the intersilicate layer spacing increased on WAXS measurements and their appearance in TEM characterizations.

Figure 3 shows WAXS indicating the primary alkyl ammonium cation exchanged clay (12ALA) did not absorb any polymer. WAXS shown in Figures 4 and 5 represents the secondary alkyl ammonium (DOA) and the tertiary alkyl ammonium (TOA) clay could forms nanocomposite only with the NBR copolymer.

The quaternary alkyl ammonium clays (Cloisite 30B and 20A) produced nanocomposite with styrene SAN, PMMA, PVDF, and NBR, as shown in Figure 6. The PS could form nanocomposite with Cloisite 20A clay, but not with 30B clay.

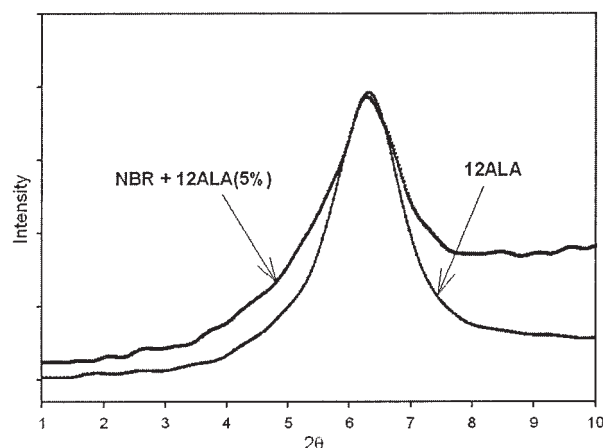


Figure 3 WAXS of 12ALA and NBR/12ALA compounds.

TEM pictures of PVC/20A, PVDF/30B, PS/20A, and SAN/20A compounds are shown in Figures 7 and 8. The silicate layers are separated in nanometer scale. These results are summarized in Table IV.

DISCUSSION

TGA and the amounts of the organic modifiers

Na⁺ MMT lost about 7 wt % by 100°C presumably due to unbound H₂O. By 800°C, it lost another 5% probably due to chemically bound H₂O.

We now seek to interpret the weight losses of the organoclays in the TGA experiments. The molecular weights (MWs) of 12ALA, DOA, TOA, Cloisite 30B and 20A organic modifiers are shown in Table V together with their TGA weight loss.

The Cloisite Na⁺ clay has, according to Southern Clay, cation exchange capacity = 92 mequiv/100 g clay. Because of the extraction process, it can be estimated that 12ALA, DOA, and TOA organoclays have 92 mequiv for 100 g of clay. According to Southern Clay Cloisite 30B and 20A have 90 and 95 mequiv organic modifier per 100 g of clay. These are equivalent to the amounts listed in Table VI.

There is a discrepancy between TGA weight loss and the predicted organic modifier content with the

TABLE III
Clay Characteristics

Clay	d_{001} (Å)	Weight loss in TGA to 800°C (%)	Comment
Cloisite Na ⁺	11.7	14	Weight loss was presumably mostly water
12ALA	14.0	18	Weight loss was probably mostly organic molecules
DOA	14.8	18	Weight loss was probably mostly organic molecules
TOA	15.8	20	Weight loss was probably mostly organic molecules
Cloisite 30B	18.5	29	Weight loss was probably mostly organic molecules
Cloisite 20A	24.2	32	Weight loss was probably mostly organic molecules

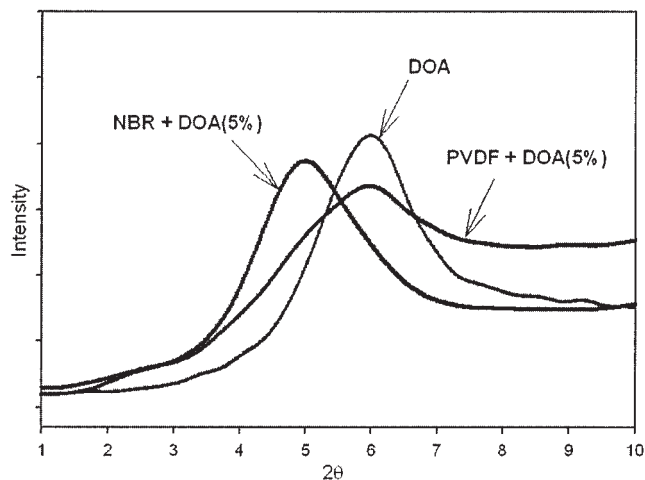


Figure 4 WAXS of DOA, PVDF/DOA, and NBR/DOA compounds.

TGA values being too low as shown in Tables V and VI. This discrepancy is about 10% for 12ALA, 20% for DOA, 30% for TOA, 20% for Cloisite 30B, 40% for Cloisite 20A organoclays. Presumably 5% or so of the TGA weight loss is due to H_2O loss making the discrepancy larger.

Xie et al.²³ have argued that the TGA weight loss includes water or gases, organic molecules, clay dehydration reactions, and residual organic carbonaceous residue. If we consider these entities, TGA weight loss might be larger than the predicted organic modifier content. However, as Xie et al. also argued, the organic molecules that are trapped between silicate layers undergo further chemical and thermal reactions. These reactions might produce crosslinked organic residues, which are not removed.

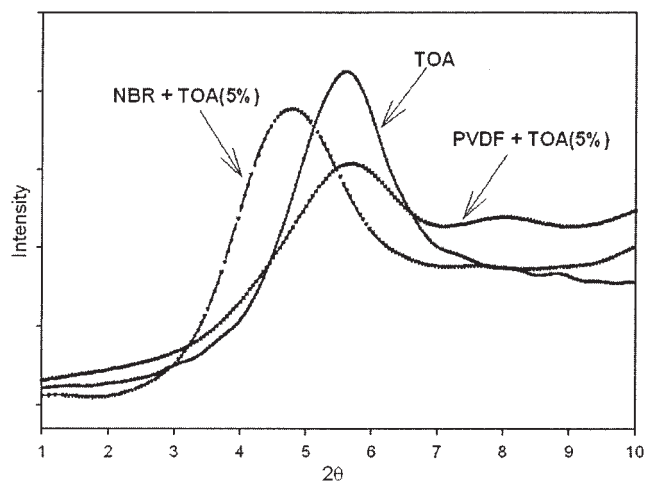


Figure 5 WAXS of TOA, PVDF/TOA, and NBR/TOA compounds.

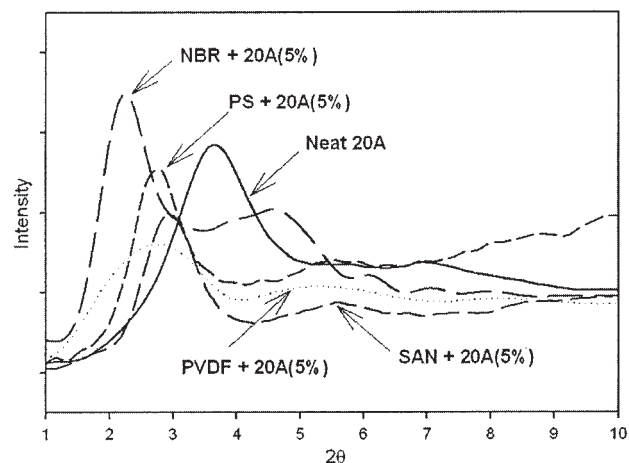


Figure 6 WAXS of PS/20A, SAN/20A, PVDF/20A, and NBR/20A compounds.

Organic coating area on the clay surface

We can estimate that the organic surface area of organic modified MMT clays.

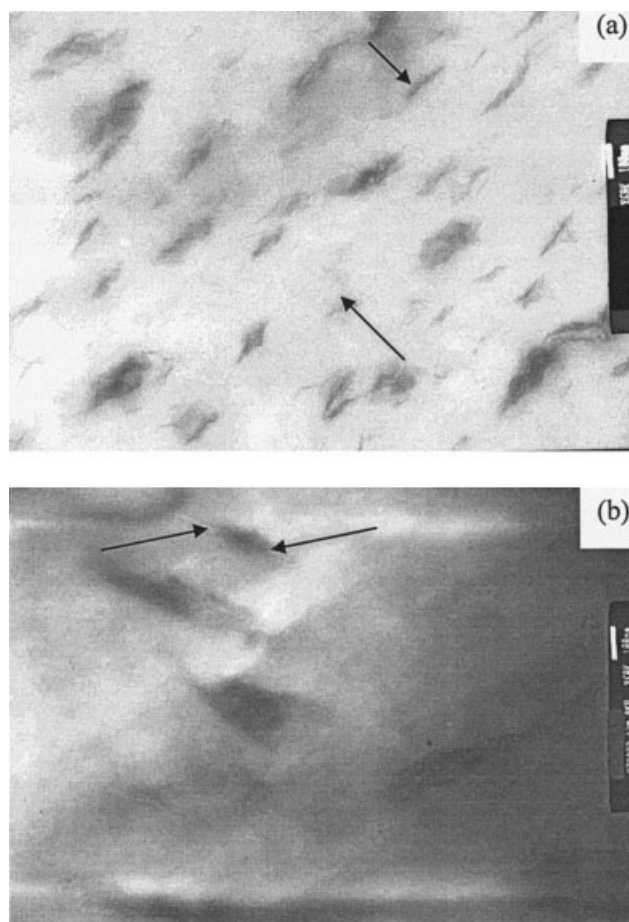


Figure 7 TEM pictures of (a) PVC/20A and (b) PVDF/30B compounds.

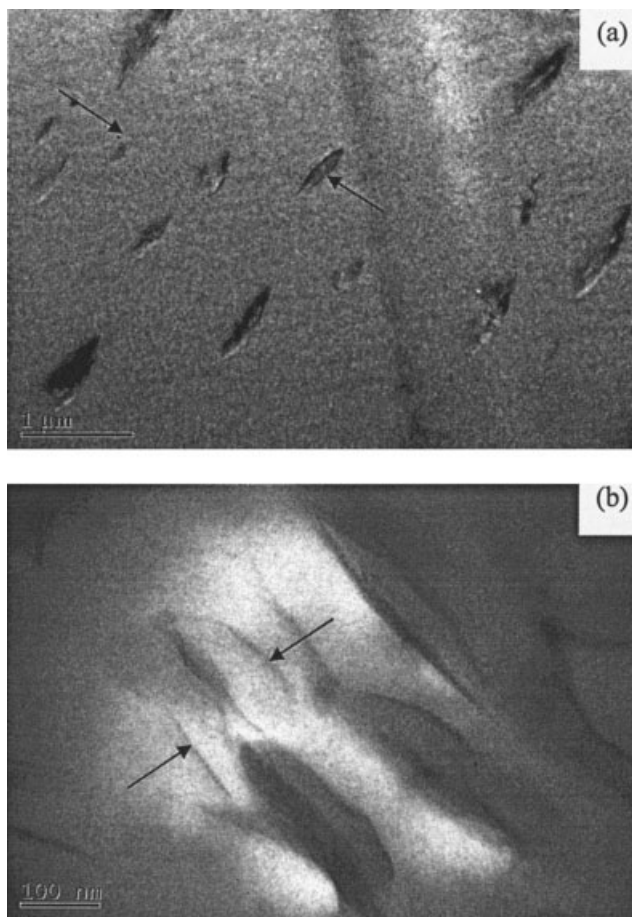


Figure 8 TEM pictures of (a) PS/20A and (b) SAN/20A compounds.

First consider the original clay; Cloisite Na⁺ has a surface area of 800 m²/g from Southern Clay Company.

The surface area of the primary alkyl ammonium organic molecules may be estimated by simple calculation. An individual 12-aminolauric ammonium molecule has a cross sectional around 78.8 Å^{29,22} with a length of 19.7 Å and a diameter of 4.0 Å. If the clay is completely exchanged with 12ALA molecule (92 mequiv/100 g), the surface area of 12ALA molecule is

4.4 X10²³ Å²/100 g or 440 m²/g. This is about 50% of total surface area of the MMT clay may be covered by self-assembled 12ALA molecules.

DOA has two C8 chains. Approximately each C8 chain is 8.82 Å in length. Two C8 chains have about 70.4 Å², which can cover about 50% of clay surface. TOA has three C8 chains, which can cover about 70% of clay surface.

Cloisite 30B has one tallow containing about 65% of C₁₈, 30% of C₁₆, and 5% of C₁₄ and two ethanol molecules. Each tallow could have 20.4 Å and ethanol has 5 Å in length. All organic molecules in Cloisite 30B presumably cover about 70% of the clay surface. Cloisite 20A, which have two hydrogenated tallow could cover 120% of clay surface (Table VII).

Except the primary alkyl ammonium molecules, which presumably have linear conformations over the silicate surface, we cannot estimate the exact conformation of the secondary, tertiary, and quaternary ammonium organic molecules between silicate layers. From our calculation the ideal surface area of TOA molecules was similar to that of Cloisite 30B organoclay. The long C18, C16, and C14 alkyl chains of Cloisite 30B might spread over the silicate surface more effectively and the TOA not.

In addition, from the TGA, Cloisite 30B showed larger weight loss than TOA between 200 and 500 deg. C temperature ranges even the expected content of organic molecules are similar. This indicated that Cloisite 30B contains additional organic molecules. Morgan and Harris²⁴ argued that the commercial organoclays like Cloisite 30B contain more organic modifiers than their cation exchange capacity because the producer may use only water to wash out extra organic molecules.

Consequently the actual organic molecule surface area of Cloisite 30B could be larger than that of TOA.

The quaternary ammonium ions coat completely and more the silicate surfaces. The primary and secondary amines cover only a modest fraction of the surface.

TABLE IV
Formation of Nanocomposites from the Polymer and Organoclays

Polymer	ε'	Organoclay					
		Na ⁺	12-ALA	DOA	TOA	30B	20A
PP	2.25	No	No	No	No	No	No
PS	2.8	No	No	No	No	No	Yes
SAN (46 mol % AN)	3.1	No	No	No	No	Yes	Yes
PMMA	3.6	No	No	No	No	Yes	Yes
PVDF	8.4	No	No	No	No	Yes	Yes
NBR (33 mol % AN)	13	No	No	Yes	Yes	Yes	Yes

ε' = dielectric constant.

TABLE V
Estimated Amounts of Amine Molecules in Organoclays Based on Weight Loss

Organoclay	Weight loss (%)	MW of organic ammonium salt (g/mol)	Organic modifiers (g/10 g of clay) based on TGA weight loss
12ALA	18	216.3	1.75
DOA	18	242.5	1.81
TOA	20	354.7	2.07
Cloisite 30B	29	404.8	2.89
Cloisite 20A	32	551.6	3.33

Volumetric inclusion of organic amine compounds and an increase in d_{001}

The amount of organic modifiers absorbed by MMT clay might be determined by d -spacing increase of silicate layers. As Jordan⁹ indicated the thickness of silicate layer should be 9.7 Å. Cloisite Na⁺ (d -spacing = 11.7 Å) include sodium cation inside.

12ALA (d -spacing = 14.0 Å) showed 4.3 Å increase. DOA (d -spacing = 14.8 Å) relative to the cited 9.7 Å and TOA (d -spacing = 15.8 Å) exhibited 5.1 and 6.1 Å increases, respectively. Cloisite 30B (d -spacing = 18.5 Å) and Cloisite 20A (d -spacing = 24.2 Å) have 8.8 and 14.5 Å d -spacing increase. These are summarized in Table VII.

If we consider each amine to have the same mean density (e.g., 1.0 g/cm³) inside the silicate gallery, the relative volumes of amines would be as their MWs in Table II. This indicates the greatest volume for the Cloisite 20A, and TOA and Cloisite 30B to be similar.

From the TGA and d -spacing increase comparison Cloisite 20A would be the most organophilic organoclay containing dimethyl dihydrogenated tallow quaternary ammonium hydrogenated tallow. The next would be Cloisite 30B including methyl tallow bis-2-hydroxyethyl quaternary ammonium organic molecule. The tertiary (TOA), secondary (DOA), finally primary (12ALA) organoclay would be followed consecutively.

The calculated surface area and volume increase would indicate Cloisite 30B and TOA should be more similar.

The reasons for the superior performance of the Cloisite 30B is probably related to its organic amine

being tetrafunctional ($R_2R_2'N^+Cl^-$) with long alkyl chains rather than trifunctional ($HR_3N^+Cl^-$) with relatively short alkyl chains.

Cloisite 30B has polar ethanol end groups of organic modifiers but 20A has only saturated alkyl groups. Presumably the organic modifier of 30B organoclay is more polar than that of 20A organoclay. However, the contribution of the polar organic modifier of 30B on the formation of polymer/clay nanocomposites seems to be minor compared to that of the polarity of amine compounds.

Polarity of the polymers

The relative value of dielectric constant allows us to order our polymers as to increase of polarity as PP, PS, SAN, PMMA, PVDF, and NBR.

Generally polar polymers appear more favorable to form polymer/clay nanocomposite for example SAN, PMMA, PVDF, NBR polymer do so with both Cloisite organic modified MMT clays. Any polymer and clay combination, which includes nonpolar polymer (PP) could not produce nanocomposite.

Only the most polar polymer, NBR, dielectric constant = 13, can produce polymer/clay nanocomposite with the secondary alkyl ammonium (DOA), the tertiary alkyl ammonium clay (TOA), and the quaternary alkyl ammonium (Cloisite 20A and 30B) MMT clays.

It might be expected that the flow behavior of polymeric materials might effect the formation of polymer nanocomposite. Organoclays absorb both low-molecular-weight compounds (with viscosity $\eta = 10^{-3}$ Pa s)

TABLE VI
Amount of Modifiers in Organoclays

Organoclay	Cation-exchange capacity (medium/100 g of clay)	MW of organic ammonium salt (g/mol)	Predicted amount (g) organic modifier in 10 g of clay
2ALA	~92	216.3	1.99
DOA	~92	242.5	2.23
TOA	~92	354.7	3.26
Cloisite 30B	90	404.8	3.64
Cloisite 20A	95	551.6	5.24

TABLE VII
Organic Surface Area of Organoclays

Clay	Organic modifier	d_{001} (Å)	Δd (Å)	Organic surface area (%)
12ALA	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_{11}\text{COOH} \\ \\ \text{H} \end{array}$	14.0	4.3	50
DOA	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{(CH}_2\text{)}_7\text{CH}_3 \end{array}$	14.8	5.1	50
TOA	$\begin{array}{c} \text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{(CH}_2\text{)}_7\text{CH}_3 \end{array}$	15.8	6.1	70
Cloisite 30B	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3-\text{N}^+-\text{T} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	18.5	8.8	70
Cloisite 20A	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{N}^+-\text{HT} \\ \\ \text{HT} \end{array}$	24.2	14.5	120

T = ~65% C₁₈, ~30% C₁₆, and ~5% C₁₄; HT = ~65% C₁₈, ~30% C₁₆, and ~5% C₁₄.
 $\Delta d = d_{001}$ of organoclay - thickness of silicate layer (= 9.7 Å).

TABLE VIII
Viscosity of the Polymers

Thermoplastic	Melt flow rate (g/10 min)	Test method (ASTMD 1238)
PE	1	190°C/2.16 kg
PP	5	230°C/2.16 kg
PS	1.5	200°C/5.0 kg
P(E-CTFE)	10	235°C/2.16 kg
PVDF	8	230°C/2.16 kg
SAN	8	230°C/3.8 kg
PMMA	2.8	230°C/3.8 kg
Elastomer	Mooney viscosity	Test method (ASTMD 1646)
BR	40	
CR	45	
NBR	46	ML(1+ 4)100°C
HNBR	70	
P(VDF-HFP)	22	
P(VDF-HFP-TFE)	65	ML(1+10)121°C

P(E-CTFE), poly(ethylene-chlorotrifluoroethylene); BR, polybutadiene; HNBR, hydrogenated NBR (acrylonitrile butadiene rubber); P(VDF-HFP), poly(vinylidene-hexafluoropropylene); P(VDF-HFP-TFE), poly(vinylidene-hexafluoropropylene-tetrafluoroethylene).

and polymer melts/elastomers with zero shear viscosities of 10×10^3 to 50×10^3 Pa s under mixing conditions. The thermoplastics in our studies have melt indices of 1.0 to 5.0, which are equivalent to viscosities of order 10,000 Pa s and the elastomers with Mooney viscosities of 50 to 70 are closer to 50,000 Pa s. If we compare the shear viscosity of the studied polymers (Table VIII), the highest viscosity was found in NBR. However, NBR forms nanocomposites in clays with the broadest range of organic amine types. It also has the highest dielectric constant. The much lower viscosity polyolefins cannot form nanocomposites at all. We must conclude that viscosity does not play a strong role within the ranges studied.

In summary we see that the key role in achieving polymer intercalation into MMT organoclays is the quality of organic amine coating coupled with the polarity of polymers. By quality we mean largely the extent.

CONCLUSIONS

Five different organoclays including primary (12ALA), secondary (DOA), tertiary (TOA), quaternary (Cloisite 30B and 20A) were melt compounded

with a range of polymeric materials (PP, PS, SAN, PMMA, PVDF, NBR) with different level of polarity to understand the effect of various organoclays on the formation of polymer/clay nanocomposite.

The primary, secondary, and tertiary ammonium organoclays showed relatively poor compatibility with the polymers compared to the two quaternary ammonium organoclays. Only the highest polarity polymer (NBR) can form nanocomposite with secondary and tertiary ammonium organoclays.

It was suggested that the large organic surface area created by long alkyl chains of quaternary ammonium could be the major reason of superior compatibility of the quaternary ammonium organoclays with polar polymers. In addition, polymer chains can penetrate more easily between the large basal spacing silicate layers of the quaternary ammonium organoclay than that of the primary, secondary, and tertiary ammonium organoclays.

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