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Polymer Nanocomposites from Organoclays: Structure and Properties

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Summary: Polymer nanocomposites formed from organically modified montmorillonite offer the promise of greatly improved properties over those of the matrix polymer, provided the organoclay can be dispersed, or exfoliated, into the polymer matrix to generate high aspect ratio particles. The exfoliation of organoclays in two series of ethylene-based polymers, ethylene-vinyl acetate copolymers and sodium ionomers of ethylene-methyacrylic acid copolymers, is described along with the properties of these nanocomposites.

Keywords: ethylene-vinyl acetate copolymers; nanocomposites; organoclay; sodium ionomers of ethylene-methacrylic acid copolymer

Introduction

Ammonium surfactants are usually used to modify montmorillonite clay to gain better affinity between the hydrophilic aluminosilicate clay and the organophilic polymer matrix;[1] polymers with different levels or types of polarity may require different surfactant structures to achieve the best exfoliated structure.[2–7] Even for an optimized surfactant structure, high levels of exfoliation are difficult to achieve in non-polar polyolefins due to the poor affinity of the polymer matrix for the hydrophilic silicate platelets. Considerable effort has been devoted to improving the exfoliation in these materials. Use of compatibilizers, such as maleated polypropylene or maleated polyethylene, is one of the popular choices.[8,9] Incorporation of polar comonomers like vinyl acetate [2] or methacrylic acid [10] is another attractive approach. Ionomers, such as those based on poly(ethylene-co-methacrylic acid) (EMAA), where some of the acid groups are neutralized to form metal salts, represent an extension of this approach.[6,11–13] Ethylene-vinyl acetate (EVA) copolymers have a variety of industrial applications such as cable and wire, flexible packaging, hose and tubing, photovoltaic encapsulants and footwear. They contain polar vinyl acetate and non-polar ethylene units in the polymer chain. By varying the vinyl acetate content, EVA copolymers can be tailored for applications as rubbers, thermoplastic elastomers and plastics. Recently there has been interest in improving the flammability characteristics of EVA copolymers, for their application in wire and cable jackets and insulation, by melting blending with organoclays. Ionomers formed by neutralizing EMAA copolymers to varying degrees where the cation may be sodium, zinc, etc are commercially available products that are used in various applications, and the range of possible products might be extended by forming nanocomposites. Recent studies from out laboratory on the structure and properties of nanocomposites formed from a series of EVA copolymers of varying VA contents and these organoclays and a series of sodium ionomers of vary degrees of neutralization are summarized here.[2,11]

Experimental Part

One series of ethylene-vinyl acetate copolymers with vinyl acetate contents ranging

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Table 1.
EVA Polymers used in this study.

Materials	Trade name	Supplier	wt % VA	Melt index (g/10 min)	Density (g/cm^3)	Melting temperature (°C)	Modulus[a)] (MPa)
LDPE	LF-0219-A	Novapol	0	2.3	0.918	107	142.2
EVA-9.3	Elvax® 760Q	DuPont	9.3	2.0	0.93	100	86.9
EVA-18	Elvax® 460	DuPont	18	2.5	0.941	88	35.1
EVA-28	Elvax® 265	DuPont	28	3.0	0.951	73	17.6
EVA-40	Elvax® 40L-03	DuPont	40	3.0	0.966	58	–

[a)] Modulus of these polymers were determined by the authors, while the other data reported in the above table were obtained from the manufacturers.

from 0 to 40 wt% including a comparable grade of LDPE were used in this work (see Table 1). The other series of polymers are sodium ionomers of ethylene-methacrylic acid copolymer with neutralization levels ranging from 20 to 70% along with an unneutralized EMAA copolymer (see Table 2). The organoclays used in this study are described in Table 3.

Nanocomposites were prepared by melt compounding in a Haake, co-rotating, intermeshing twin screw extruder (D = 30 mm, L/D = 10) at a screw speed of 280 rpm with a feed rate of 1000 g/h, using a barrel temperature of 170 °C for EVA compolymer based nanocomposites and 200-220 °C for Ionomer based nanocomposites as used in previous studies from this laboratory.[14] Tensile (ASTM D638) specimens were formed using an Arburg Allrounder 305-210-700 injection molding machine. All the polymer materials were dried in a vacuum oven for a minimum of 48 h prior to the compounding, while the organoclays were used as received.

TEM images were obtained using a JEOL 2010F transmission electron microscope operating under an accelerating voltage of 120 kV. Ultra-thin sections (~50 nm) were cut from the central part of the rectangular injection molded bars in the plane parallel to the flow direction under cryogenic conditions using an RMC PowerTome XL microtome. Tensile tests were performed on an Instron model 1137 machine upgraded for computerized data acquisition. Modulus values were determined using an extensometer at a crosshead speed of 0.51 cm/min. Data reported here represent an average from measurements on at least five specimens.

Results

Properly prepared TEM images always offer the most direct visualization of the dispersion of the clay particles in nanocomposites. TEM images for nanocomposites formed from various organoclays (nominally 5 wt% MMT) and based on LDPE and two kinds of EVA copolymer matrices, in which the % VA contents are 9.3 and 28 respectively, are shown in

Table 2.
Ionomer Polymers used in this study*.

Polymers	Trade name	Type of counter ion	Acid content (wt%)	Melt index (g/10 min)	Neutralization (%)	Ion (wt%)
EMAA	Nucrel® 925	–	15	25	0	0
Ionomer 1	Experimental	Na	15	47.7	20	0.80
Ionomer 2	Experimental	Na	15	24.9	30	1.20
Ionomer 3	Experimental	Na	15	12.6	40	1.60
Ionomer 4	Experimental	Na	15	5.93	50	2.00
Ionomer 5	Experimental	Na	15	2.29	60	2.40
Ionomer 6	Experimental	Na	15	0.98	70	2.74

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Table 3.
Organoclays used in this study.

Organoclay designation	Commercial designation	Surfactant chemical structure
$M_2(HT)_2$	Cloisite 20A	Dimethylbis(hydrogenated-tallow) ammonium montmorillonite
$M_3(HT)_1$	SCPX 1137	Trimethyl hydrogenated-tallow ammonium montmorillonite
$(HE)_2M_1T_1$	Cloisite 30B	bis(2-hydroxy-ethyl)methyl tallow ammonium montmorillonite
$B_1M_2(HT)_1$	Cloisite 10A	dimethyl, benzyl, hydrogenatedtallow, quaternary ammonium

Figure 1. Clearly, the clay stacks in nanocomposites with 28% VA EVA copolymer are much smaller and thinner, in other words, more exfoliated. The nanocomposite with the $M_2(HT)_2$ organoclay is always the most exfoliated one no matter what is the VA content in the matrix polymer, and the others with $M_3(HT)_1$ or

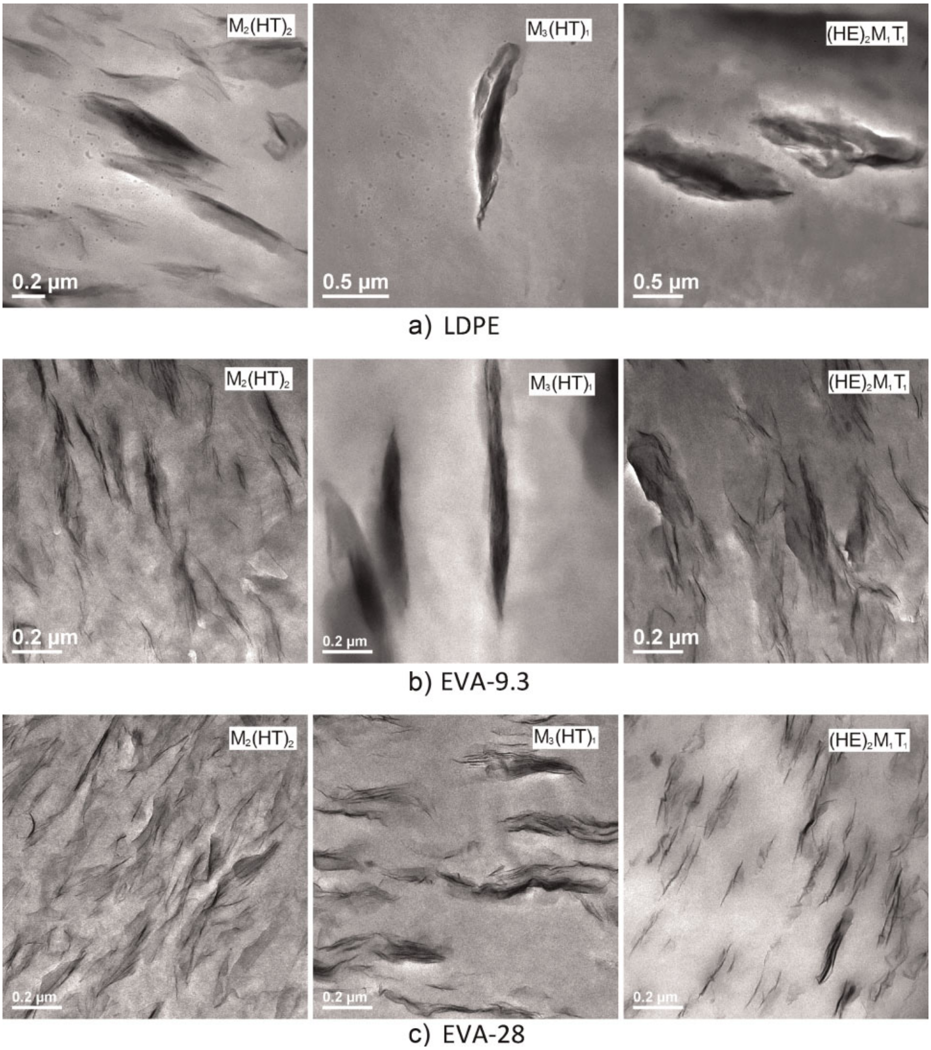

Figure 1.
Effect of %VA on the morphology of nanocomposites formed from various organoclays. Reproduced with permission of Elsevier.[2]

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$(HE)_2MT_1$ organoclays have bigger stacks of clay platelets.

Figure 2 compares the morphology of the nanocomposites formed from the $M_2(HT)_2$ organoclay and different ionomers with various degrees of neutralization of acid groups (0, 30, 70%). The montmorillonite content in all cases is nominally 5 wt% as well. Morphologies consisting of combinations of individual platelets and intercalated stacks of platelets can be observed in all the nanocomposites, indicating fair, but not complete, exfoliation of the organoclays. It appears that there are more thinner and smaller particles in nanocomposites based on ionomers with higher degrees of neutralization of the acid groups. In the mean time, it is obvious that the nanocomposites formed from the $M_2(HT)_2$ organoclay always have the best clay exfoliation.

To have a quantitative and more convincing assessment of the level of organoclay

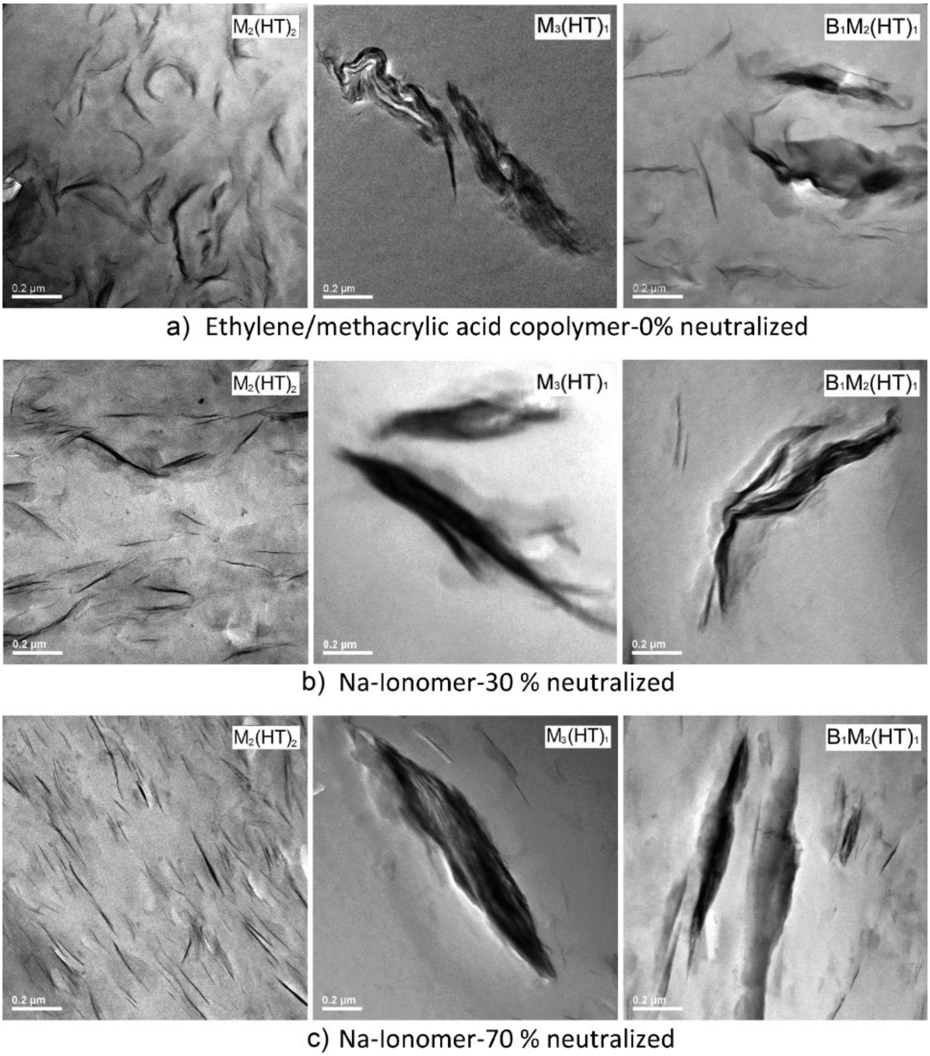

Figure 2.
Effect of degree of acid groups neutralization on the morphology of nanocomposites formed from various organoclays. Partially reproduced with the permission of American Chemical Society.[11]

exfoliation, the TEM images obtained for each nanocomposites were subjected to particle analysis using the method described elsewhere[2] and the results are compared in Figure 3 (a) and (b). The aspect ratio of the EVA nanocomposites based on the same type of organoclay increases with the % VA of matrix EVA copolymer. Among these nanocomposites, those based on the $M_2(HT)_2$ organoclay always have larger aspect ratio, indicating better exfoliation of the organoclay.

In the case of the sodium ionomer based nanocomposites, the exfoliation of the $M_2(HT)_2$ organoclay progressively improved as the neutralization level of the sodium ionomers was increased. Figure 3 (b) shows the increase in particle density and the aspect ratios as the degree of neutralization of the metharylic acid groups increases.

For pure EVA copolymers, as the VA content increases, on one hand the affinity of the base polymers for organoclay improves, but on the other hand the modulus of the pure EVA polymers decreases dramatically due to the loss of crystallinity by incorporating acetate units in the polyethylene main chain and it is useful to examine the moduli of the nanocomposites, E, normalized by the modulus of the pure EVA copolymer, E_m, versus the montemorillonite content as shown in Figure 4 (a). As expected, increasing the degree of exfoliation usually leads to improved reinforcement. With the clay exfoliation improved with the increase of the VA content of the matrix polymer, the relative modulus of these nanocomposites increases as well in general. The addition of MMT compensates for loss of

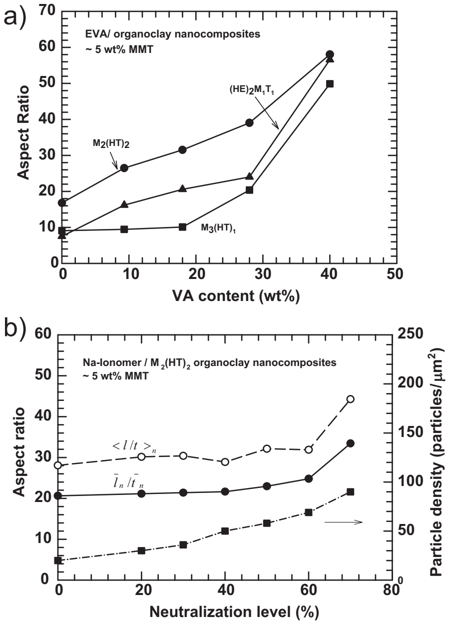

Figure 3.

Clay particle analyses of TEM images for nanocomposites containing ~ 5 wt% MMT. (a) Aspect ratio of clay particles from TEM images for EVA nanocomposites. Reproduced with permission of Elsevier.[2] (b) Effect of % of neutralization of the acid groups in ionomer on particle aspect ratios and density. Reproduced with the permission of American Chemical Society.[11]

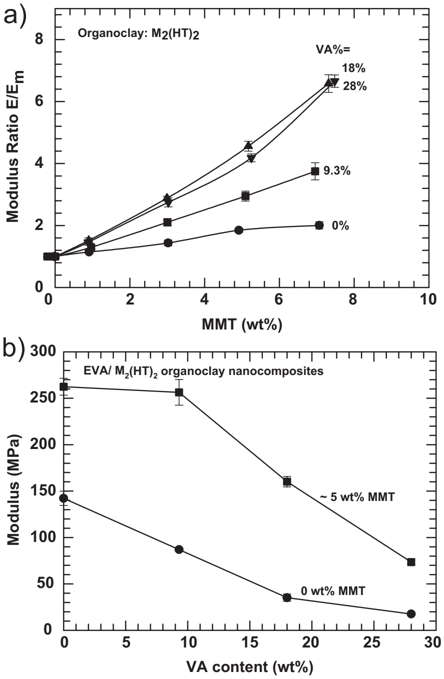

Figure 4.

Tensile moduli of EVA nanocomposites. (a) Comparison on relative moduli of nanocomposites from various EVA copolymers, E_m = the modulus of each VA indicated EVA with no MMT. Reproduced with permission of Elsevier.[2] (b) Effect of adding organoclay on the moduli of various EVA copolymers and their nanocomposites.

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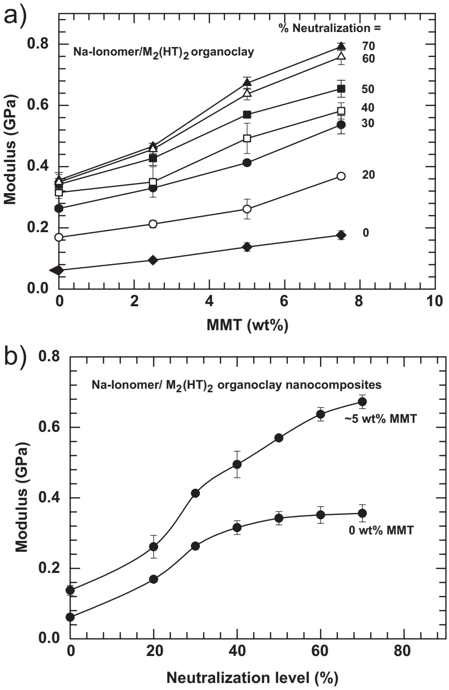

Figure 5.
Tensile moduli of Ionomer nanocomposites. (a) Effect of neutralization levels of the acid groups on the moduli of nanocomposites formed from various sodium ionomers. Reproduced with permission of Elsevier.[11] (b) Effect of adding organoclay on the moduli of various sodium ionomers and their nanocomposites.

crystallinity as %VA increases and makes the decreasing trend less progressive as shown in Figure 4 (b).

The moduli of neat sodium ionomers with various neutralization levels and their nanocomposites are compared in Figure 5 (a) and (b). The addition of the organoclay produces significant improvements in stiffness in all cases, and better exfoliation at the elevated neutralization level leads to a greater reinforcing effect as one intuitively expects.

Conclusion

Morphology and mechanical properties of the EVA copolymer and EMAA-based ionomer nanocomposites are presented and discussed to obtain insights about the effect of the VA concentration and degree of neutralization of acid groups on the organoclay exfoliation. Nanocomposites based on EVA copolymers show improved exfoliation of organoclay with increased % VA. It seems that the ionic units on the polymer chain provide a more favorable interaction between the polymer matrix and the organoclay compared to acid units and, thus, lead to better dispersion of the clay particles. Various organoclays were involved in this study, and it appears that the two tail organoclay is generally preferred to form better exfoliated structure in these polyolefins or modified polyolefins based nanocomposites. Among the organoclays involved, nanocomposites based on the $M_2(HT)_2$ organoclay always lead to better exfoliation than those based on $M_3(HT)_1$, $B_1M_2(HT)_1$, or $(HE)_2M_1T_1$ organoclays within the range of % VA or degree of neutralization of the acid groups examined. In general, the morphology and the mechanical properties of these nanocomposites formed are consistent with each other. Increased exfoliation leads to better reinforcement of the nanocomposite materials.

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[1] S. Pavlidou, C. D. Papaspyrides, *Progress in Polymer Science* **2008**, *33*, 1119.
[2] L. Cui, X. Ma, D. R. Paul, *Polymer* **2007**, *48*, 6325.
[3] F. Chavarria, D. R. Paul, *Polymer* **2006**, *47*, 7760.
[4] T. D. Fornes, P. J. Yoon, D. L. Hunter, H. Keskkula, D. R. Paul, *Polymer* **2002**, *43*, 5915.
[5] T. D. Fornes, D. L. Hunter, D. R. Paul, *Macromolecules* **2004**, *37*, 1793.
[6] R. K. Shah, D. L. Hunter, D. R. Paul, *Polymer* **2005**, *46*, 2646.
[7] S. Hotta, D. R. Paul, *Polymer* **2004**, *45*, 7639.
[8] L. Cui, D. R. Paul, *Polymer* **2007**, *48*, 1632.

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[9] M. Zanetti, G. Camino, R. Thomann, R. Mulhaupt, *Polymer* **2001**, *42*, 4501.

[10] R. K. Shah, D. H. Kim, D. R. Paul, *Polymer* **2007**, *48*, 1047.

[11] L. Cui, C. Troeltzsch, P. J. Yoon, D. R. Paul, *Macromolecules* **2009**, *42*, 2599.

[12] R. K. Shah, D. R. Paul, *Macromolecules* **2006**, *39*, 3327.

[13] Y. J. Yoo, R. K. Shah, D. R. Paul, *Polymer* **2007**, *48*, 4867.

[14] T. D. Fornes, P. J. Yoon, H. Keskkula, D. R. Paul, *Polymer* **2001**, *42*, 9929.

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