Development of nanocomposites based on organically modified montmorillonite and plasticized PVC with improved barrier properties

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ABSTRACT: Montmorillonite (MMT) was organically modified with tributyl citrate (TBC). Organoclays (OMMTs) were processed with diisononyl phthalate (DINP)-plasticized polyvinyl chloride (PVC) to form polymer nanocomposites. The produced composite materials showed a contradictory change in properties to that expected of a layered silicate nanocomposite, with a decreased E-modulus and increased gas permeability compared with a material without OMMT. It was experimentally shown that the TBC modifier was extracted from the OMMT and was dispersed in the PVC/DINP matrix, whereupon the OMMT collapsed and formed micrometer-sized agglomerates. Further investigation revealed that TBC has a significant effect on the gas permeability and the E-modulus, even at low additions to a DINP-plasticized PVC. A PVC nanocomposite with the TBC acting as both the OM for MMT and as the primary plasticizer was produced. This material showed a significantly increased E-modulus as well as a decrease in gas permeability, confirming that it is possible to develop a nanocomposite based on plasticized PVC, if both the organo-modification of the MMT and the formulation of the matrix are carefully selected. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42876.

INTRODUCTION

In the area of polymer engineering, great attention has been focused on developing novel polymer nanocomposites using nanoclays. These materials exhibit unique property enhancements in relation to the virgin polymer and to conventional polymer composites. Organic modification of montmorillonite (MMT) to make the clay surface organophilic and more compatible with organic polymers is regarded as being a necessary first step to create nanocomposites. This is usually performed by ion-exchange reactions with alkylammonium or alkylphosphonium salts,[1,2] but in polyvinyl chloride (PVC), poor thermal stability during melt processing is a serious obstacle because of the decomposition of the ammonium ions into tertiary amines, which are known to catalyze the dehydrochlorination of PVC.[3,4] For this reason, we have attempted to find new types of organic species for clay modification that will allow for the preparation of organoclays (OMMTs) in the absence of quaternary ammonium salts. In our previous work, we explored the idea of using suitable chelating agents as organic modifiers (OM) rather than an ionic exchange component, that are capable of decreasing the electrostatic forces between the negatively charged flakes of MMT and the positive ions in the interlayer spacing.[5,6] In a

recent study,[6] alkyl citrates were identified as potentially suitable OM for MMT because of their good miscibility with PVC, ability to intercalate the MMT clay, and their good thermal stability.

There is much evidence that nanocomposites can be formed from OMMT and thermoplastics by melt processing. However, four main problems arise when trying to maximize the barrier properties of polymer nanocomposites. The first problem is exfoliation, which means that the clay particles, which exist as aggregates, must be broken up or exfoliated into individual layers that have a thickness close to one nanometer with lengths and widths in the order of about 400 nanometers. The aspect ratio of the particles must be such that they have a very thin cross-section, but present a large surface area in their flat dimensions, with the objective of minimizing both gas permeability and the effect of the particles on the material's clarity and colour, and improving its fire resistance. The second problem is the compatibility between the clay layers and the polymeric substrate, which means that the particles must be "functionalized" so that they will be compatible with the polymer matrix. The third problem is orientation, which means that the particles that are dispersed in the polymer must be oriented

Table I. Formulations of the PVC Compounds Processed by Extrusion and Two-Roll Milling

Component	Master batch (phr)	Dilution material (phr)	Final product with MMT (phr)	Final product without MMT (phr)
Norvinyl S6045 (S-PVC resin)	100	100	100	100
Palatinol N (DINP)	15	48	40	40
Bärostab 8807-14 (Ca/Zn)	1.5	1.5	1.5	1.5
Edenol D 81 (ESO)	1.5	1.5	1.5	1.5
Montmorillonite[a]	20	0	5	0
Tributyl citrate (OM)	10	0	2.5	0

[a] MMT-Na$^+$ was dried in a vacuum oven at 50°C for 24 h

so that the flat surface of the clay layers is aligned parallel to the surface of the material to maximize the barrier effect. The final problem is that during processing, the particles must be kept from reaggregating, which, if it occurs, would cancel the benefits of maximizing the barrier properties of polymer nanocomposites.

This article describes new developments in the organo-modification of MMT and the production of plasticized PVC/OMMT nanocomposites with improved barrier properties.

EXPERIMENTAL

Materials

The S-PVC resins used, Norvinyl S6045 (K-value 60) and Norvinyl S7060 (K-value 70), with appropriate stabilizers Bärostab 8807-14 (Ca/Zn) and Bärostab UBZ 777 X (Ba/Zn) and Edenol D 81 (ESO) co-stabilizer, were provided by Ineos ChlorVinyls (Porsgrunn, Norway). The MMT used in this work was Cloisite Na$^+$ (MMT-Na$^+$) containing mainly monovalent interlayer cations (Na$^+$), provided by BYK Additives GmbH. Cloisite Na$^+$ has a reported CEC = 92.6 meq/100 g[7] and a typical dry particle size = <25 μm (d_{50}) according to the supplier. The tributyl citrate (TBC) (Acros Organics) used in this work was purchased from Fisher Scientific (Schnelldorf, Germany) and was used as an OM and plasticizer. The Palatinol N (diisononyl phthalate, DINP) used was kindly provided by Ineos ChlorVinyls, and was used as a plasticizer. The solvents used in this study were tetrahydrofuran (THF) (Emsure) purchased from VWR International (Stockholm, Sweden) and deionized water produced using the purifying equipment located at the SP Technical Research Institute of Sweden in Borås.

Preparation of OMMT

The choice of OM was based on the results of an earlier study,[6] where it was shown that the type of solvent had little effect on the increase in interlayer space of the OMMTs. On the other hand, the choice of solvent influenced the morphology of the OMMTs, causing structural differences to occur. In this study, we prepared OMMTs using two solvents: H$_2$O and THF with the MMT-Na$^+$ clay mineral. The MMT was dispersed in the designated solvent using an Ultra-Turrax T 25 disperser equipped with a S25N-G25F dispersing element. The OM was then added and the dispersion, which was then stirred using a magnetic stirrer for 30 min, followed by another dispersion cycle using the Ultra-Turrax T 25 disperser. The solvent was

then removed using a rotary evaporator followed by vacuum drying at 60°C for 2 h. The dried OMMTs were ground using an IKA A10 basic mill. The MMT and OM were mixed in various proportions, with the samples being denoted as a reference code reflecting the content; e.g. OMMT 2:1 meant that the sample was mixed containing two parts by weight of MMT and one part by weight of OM.

Processing of PVC Nanocomposites

Extrusion and Two-Roll Milling. Plasticized PVC nanocomposites were processed via a master batch (MB) procedure according to the formulations shown in Table I.

Dry blends of both MB and the dilution material (DM) formulations were prepared at Ineos in Stenungsund, Sweden. The OMMTs prepared as mentioned above were added as powders to the dry blends. Processing of the PVC nanocomposites was executed using a two-step process. First, an MB containing 20 parts per hundred resin (phr) OMMT based on the inorganic MMT content was extruded in a Brabender Plasti-Corder Lab Station TSE 20/40 twin-screw extruder using a screw speed of 100 rpm, with the temperature of the heated zones (HZ) and the die being in the range from 130°C (feeding) to 160°C (die) with t_{melt} reaching approximately 162°C. The DMs were processed using the same parameters as the MBs. Both the MBs and DMs produced were pelletized to a suitable size for further processing. The final materials were then processed in a two-roll mill at 170°C for 5 min with the speed set to 30/20 rpm (Ineos, Porsgrunn). One part of the MB was processed together with three parts DM to obtain a final concentration of 5 phr OMMT based on inorganic MMT content.

Plates with dimensions 100 × 100 × 1 mm³ were pressed in a Fontijne LabEcon 300 hydraulic laboratory press at 180°C with a 3 min preheat while at the almost closed position, and then at 1 min at 250 kN. The plates were allowed to cool to 40°C while maintaining the press force.

Microcompounding. In the second study, a DSM Xplore microcompounder (15 mL) was used to produce PVC nanocomposites and reference materials via an MB process. MBs with OMMT or MMT-Na$^+$ contained a higher amount of inorganic filler than the final materials, approximately 40 phr. The different formulations of the final materials produced are shown in Table II. Dry blends were prepared using a mortar placed in a sand-filled heating jacket at approximately 110°C. The MBs and

Table II. Final Formulations of PVC Compounds Processed Using a Microcompounder via MB

Component	Formulation (phr) of the final materials and composites				
	PVC/DINP	PVC/DINP + TBC	PVC/TBC	PVC/TBC + OMMT	PVC/DINP + MMT-Na$^+$
NORVINYL S7060 (S-PVC resin)	100	100	100	100	100
Bärostab UBZ 777 X (Ba/Zn)	4	4	4	4	4
Palatinol N (DINP)	40	40	–	–	40
Tributyl citrate (TBC)[a]	–	2.5	40	40	–
Montmorillonite[b]	–	–	–	10	10

[a] Total amount of TBC, i.e. both as plasticizer and as OM.
[b] MMT-Na$^+$ were dried in a vacuum oven at 50°C for 24 h.

DMs were processed for 5 min at 170°C and 50 rpm, while the final products were microcompounded for 5 min at 180°C and 100 rpm.

Plates with dimensions $100 \times 100 \times 1$ mm^3 were pressed in a Fontijne LabEcon 300 hydraulic laboratory press at 185°C with a 3 min preheat while at the almost closed position, and then for 1 min at 250 kN. The plates were then allowed to cool to 40°C while maintaining the press force.

Extraction Experiments of OMMTs in DINP
Experiments to investigate if TBC could be extracted from OMMT into DINP were performed. MMT-Na$^+$, dried in vacuum oven at 70°C for 68 h, was modified with TBC in THF to form samples with different proportions between MMT-Na$^+$ and TBC (2:1, 4:1, and 8:1). After the modification procedure, the solvent was evaporated and the OMMTs were ground before testing and analysis. In the extraction experiments, 100 mL of DINP was heated in an oil bath and 5 g of the OMMT with proportions of 2:1 were added at 172°C, which were then dispersed for 5 min at 4000 rpm in the heated DINP using an Ultra-Turrax T 25 disperser equipped with a S 25 N – 25 F dispersion tool. After 5 min the temperature reached 180°C, and the OMMT/DINP suspension was centrifuged in a Hettich Universal 1200 centrifuge for 15 min at 80% speed before the precipitate was analyzed using wide-angle X-ray diffraction analysis (WAXD). This experiment was also repeated at room temperature (23°C).

Wide-Angle X-ray Diffraction Analysis
The organically modified clay minerals were analyzed using WAXD. A shift to lower theta angles by the OMMTs compared with nonmodified clay minerals indicated that the interlayer space had increased. The WAXD analysis was performed using a Bruker D8 Advance X-ray diffractometer employing CrKα radiation with a wavelength of $\lambda = 0.22897$ nm. Scanning was performed in the range $2\theta = 2.5$–$15.0°$ at intervals of 0.05° and a step time of 10 s. Bragg's equation ($\lambda = 2d \sin\theta$, where λ is the wavelength of the X-ray radiation in the diffraction experiment, d is the spacing between the diffraction lattice planes, and θ is the measured diffraction angle or glancing angle) was used to calculate the corresponding d spacings for the 2θ values of the peaks. The OMMTs were analyzed as powders.

Samples from the OMMT/DINP extraction experiments and from the material with the TBC acting as both the OM for MMT and as the primary plasticizer were analyzed using a Rigaku Miniflex 600 X-ray diffractometer using CuKα radiation with a wavelength of $\lambda = 0.15418$ nm. Scanning was performed in the range $2\theta = 2.0$–$12.0°$ with in steps of 0.02° and a scan speed of 2°/min. Bragg's equation was used for the calculations, as described above.

High-Resolution Scanning Electron Microscopy
In the characterization of polymer/clay nanocomposites, High-resolution scanning electron microscopy is a useful tool that can be used to evaluate not only the dispersion and distribution of fillers but also the structural properties and the compatibility between the different components.

Test samples were immersed in liquid nitrogen and cryogenically fractured. The cross-sections were sputter-coated with a 10–15 nm thick Au/Pd layer before analysis. A Zeiss Supra 40VP field emission scanning electron microscope (FE-SEM) equipped with a high-efficiency in-lens detector was used in high vacuum mode for the surface analysis of the samples.

Mechanical Tests
Mechanical testing was performed based on the ISO 527-2 standard using 5A-type 1 mm-thick samples, a preload of 2 N, and a speed of 50 mm/min. The test method deviated from the standard method as an initial slower speed (1 mm/min) was applied up to a strain of 2% to obtain values of the elastic modulus (E).

Determination of Hardness
Measurement of the hardness of the samples was performed using a Bareiss Digitest hardness tester equipped with an IRHD M (microtest) measuring unit. Test samples with a thickness of 1 mm were placed in two layers and the hardness was measured for 30 s at three locations. The results were presented as average values.

Gas Permeability Analysis
A Lyssy L100-5000 manometric gas permeability tester was used to evaluate the barrier properties of the developed PVC nanocomposites. The test method was based on the change in pressure on gas transmission through the sample. The equipment was calibrated using a PET calibration film with known gas

Table III. Results from Mechanical Tests, Gas Permeability, Hardness Measurements, and Vicat Softening Temperature

Material	E-modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Gas permeability (mL/m^2 day) Oxygen	Nitrogen	Hardness IRHD (M)	VST (°C)
Materials processed by extrusion (MB) and two-roll milling							
PVC S6045 + 40 phr DINP	20.2 (1.0)	21.8 (0.3)	273.8 (10.3)	118	27	90.2 (0.2)	56.8 (0.2)
PVC S6045 + 40 phr DINP + 5 phr Na$^+$MMT/TBC/H$_2$O^a	17.0 (0.5) Δ −16%	18.1 (0.5) Δ −17%	210.9 (13.7) Δ −23%	141 Δ +19%	–	87.4 (0.4) Δ −3.1%	57.7 (0.3) Δ +1.6%
PVC S6045 + 40 phr DINP + 5 phr Na$^+$MMT/TBC/THF^a	14.5 (1.3) Δ −28%	18.8 (0.3) Δ −14%	245.8 (9.6) Δ −10%	133 Δ +13%	32 Δ +19%	86.6 (0.5) Δ −4.0%	58.3 (0.2) Δ +2.6%
Materials processed by micro compounding (via MB)							
PVC S7060 + 40 phr DINP	25.1 (1.4)	26.1 (1.4)	295.8 (17.3)	144	–	93.2 (0.2)	59.2 (0.1)
PVC S7060 + 40 phr TBC	13.5 (0.5) Δ −46%	24.9 (0.6) Δ −1%	281.6 (9.0) Δ −5%	192 Δ +33%	–	85.6 (0.6) Δ −8.2%	58.6 (0.5) Δ −1.0%
PVC S7060 + 40 phr DINP + 2.5 phr TBC	17.8 (1.2) Δ −29%	24.9 (1.3) Δ −1%	302.2 (18.8) Δ +2%	162 Δ +13%	–	90.7 (0.8) Δ −2.7%	59.5 (0.2) Δ +0.5%
PVC S7060 + 40 phr DINP + 10 phr MMT-Na+	36.4 (2.9) Δ +45%	22.4 (0.5) Δ −14%	231.4 (9.6) Δ −22%	144 Δ ±0%	–	94.3 (0.7) Δ +1.2%	65.2 (0.5) Δ +10%
PVC S7060 + 35 phr TBC + 10 phr OMMT^b	18.0 (0.9) Δ +33%^{c}	20.1 (0.7) Δ −19%^{c}	242.5 (19.2) Δ −14%^{c}	150 Δ −22%^{c}	–	89.7 (0.6) Δ +4.8%^{c}	65.4 (0.4) Δ +12%^{c}

Standard deviations are shown in brackets
[a] Based on inorganic MMT content, i.e. 5 phr MMT + 2.5 phr TBC.
[b] Based on inorganic MMT content, i.e. 10 phr MMT + 5 phr TBC.
[c] Compared with "PVC S7060 + 40 phr TBC".

permeation values and possible leakage was detected using an aluminium foil. The temperature was kept at 23°C using an external cooling thermostat. Results are presented as the mean value of two samples alternately operated in separate chambers of the instrument.

Thermogravimetric Analysis

A thermogravimetric analyzer (Mettler Toledo TGA/DSC1 STAR^e system) was used to monitor the mass loss of the samples at different temperatures. All the samples were analyzed in an inert (N$_2$) atmosphere in the temperature range 30–550°C using a heating rate of 10°C/min. There were at least two replicates for each sample.

Vicat Softening Temperature

Vicat temperatures were determined using a Ceast HV3 HDT Vicat thermomechanical tester. The tests were performed according to the ISO 306 (A50) standard with a medium- to high-temperature silicone oil used as the heating medium.

RESULTS AND DISCUSSION

For true nanocomposites, the clay mineral must be exfoliated and the nanolayers uniformly dispersed in the polymer matrix. Once exfoliation has been achieved, an improvement in properties can be expected, such as enhanced barrier properties and an increase in the elastic modulus among other properties. The enhanced barrier characteristics occur because the impermeable clay layers create a tortuous pathway for a permeant to transverse the nanocomposite. The use of organo-modified clays as precursors for nanocomposite formation is commonly utilized in various polymer systems, including epoxies, polyurethanes, polyimides, nitrile rubber, polyesters, polypropylene, polystyrene, and polysiloxanes.[8] Organic modification of clays not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the interlayer distance in the clays.

Effect of OMMT in DINP-Plasticized PVC

We have shown in a previous study[6] that TBC is an excellent OM for MMT. Consequently, we have manufactured a material composed of DINP-plasticized PVC and TBC-modified MMT using a two-step melt process. The OMMTs used here were MMT-Na$^+$ modified with TBC in two different solvents. These showed d-spacing values of ∼1.9 nm (THF) and ∼2.0 nm (H$_2$O).

The ensuing characterization of the composite materials revealed unexpected results, with a lower E-modulus (up to −28%) and a higher oxygen permeability (up to 19%) compared with the corresponding material without OMMT, as shown in Table III.

The only compositional difference between the material without OMMT and the composite materials (besides MMT) was an additional amount of 2.5 phr of TBC. Thus, the effect of 2.5 phr TBC on the properties of the DINP-plasticized PVC was investigated further.

First, we compared the gas permeability of DINP- and TBC-plasticized PVC (40 phr plasticizer) and found a 33% higher gas permeability in the TBC-plasticized PVC along with a 46% lower E-modulus. Furthermore, we found that addition of 2.5 phr TBC to 40 phr DINP-plasticized PVC resulted in a 13% increase in gas permeability and a 29% decrease in the E-modulus, which is
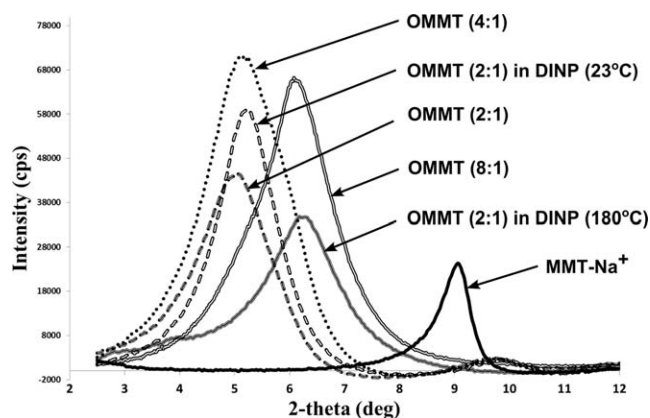
Figure 1. WAXD pattern of OMMTs with various concentrations of OM and of OMMTs dispersed in DINP.

almost the same change in properties as in the DINP-plasticized PVC containing TBC-modified MMT. This result indicates that the OM leaves the OMMT and is dispersed in the DINP/PVC matrix.

The DINP-plasticized PVC with 10 phr MMT-Na$^+$ showed no change in gas permeability, indicating that a nonmodified filler does not contribute to improved barrier properties. The same results have been reported in several studies, e.g. Zheng and Gilbert[9] concluded that PVC nanocomposites cannot be prepared using Cloisite Na$^+$ and melt compounding. However, the E-modulus was higher for this material compared with the material where no MMT-Na$^+$ was added.

Determination of the hardness [IRHD (M)] was performed as a complement to the measurements on the elastic modulus. As can be seen in Table III, the results show the same tendency as the observed mechanical properties.

We interpret these results as follows. The compatibility between TBC and DINP is better than between TBC and MMT, as was predicted by the Hansen solubility parameter (HSP).[6] In other words, the chelating effect of the alkyl citrate ester is too mild,

and consequently during melt processing of DINP-plasticized PVC with TBC-modified MMT, the TBC leaves the MMT, which collapses and reaggregates, and so does not significantly influence the final material properties, while TBC alone causes the changes in properties. To further support our interpretation, a series of extraction experiments was then performed.

Extraction Experiments

To investigate the tendency of TBC to leave MMT in the presence of DINP, a series of experiments were performed. TBC-modified MMT was dispersed in DINP at room temperature and at 180°C for 5 min. The results were evaluated by measuring the d-spacing, where a decrease in the d-spacing was attributed to the depletion of TBC from the interlayer space.

In Figure 1, the results from a WAXD analysis of OMMTs from the extraction experiments are presented. The unmodified MMT-Na$^+$ showed a d-spacing of 0.98 nm, where upon modification with TBC in THF it increased to about 1.7 nm for both the OMMT 2:1 and OMMT 4:1. At a MMT-Na$^+$/TBC proportion of 8:1, the d-spacing of the OMMT increased to only 1.4 nm, almost 20% lower than the other two OMMTs. This indicates that less OM had intercalated into the interlayer spaces of the MMT-Na$^+$. It can also be seen in Figure 1 that when OMMT (2:1) had dispersed in DINP at 180°C, the d-spacing decreased significantly. This is a clear indication that TBC had been removed from the OMMTs in the systems containing DINP at the temperature used in extrusion and two-roll milling. At room temperature, a similar effect was not observed within the timeframe of the experiments.

Effect of OMMT in TBC-Plasticized PVC

If our interpretation was correct, then the problem of reaggregation of the TBC-modified OMMT should disappear if we used TBC as plasticizer instead of DINP. In Table III, the results of using TBC-modified MMT in TBC-plasticized PVC are shown.

The results did indeed confirm our hypothesis, showing a significant increase in E-modulus and a significant decrease in the oxygen permeability (Table III).
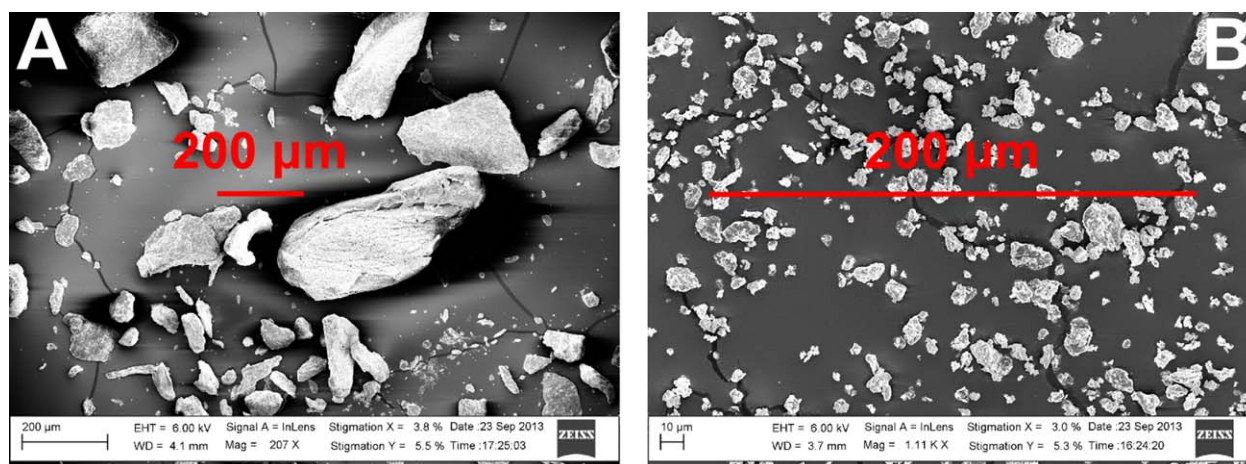

Figure 2. Representative SEM images showing the size distribution of dried and ground OMMTs: (A) MMT-Na$^+$/TBC/H$_2$O and (B) MMT-Na$^+$/TBC/THF. The difference in magnification is highlighted by the length of the scale bar. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
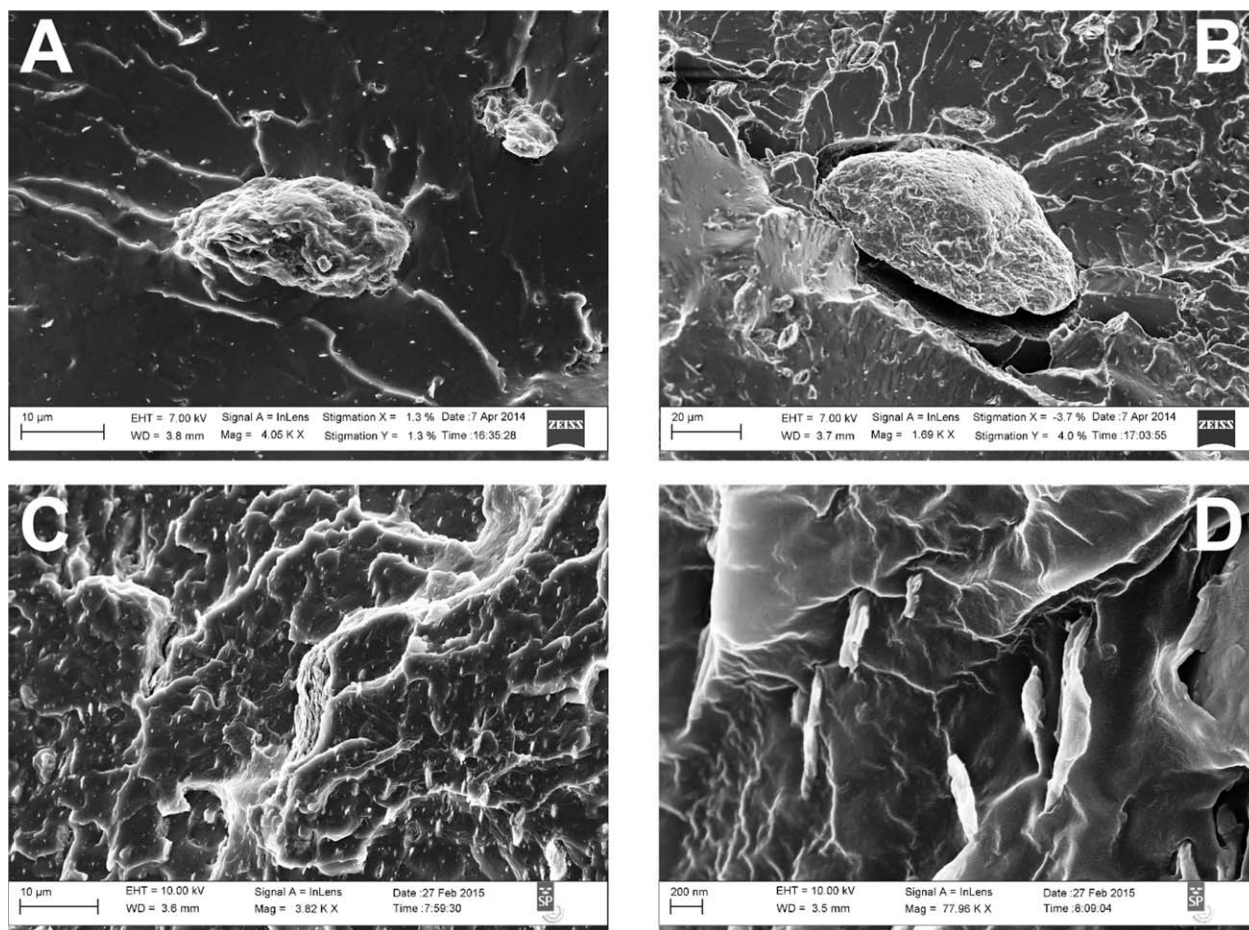
Figure 3. SEM micrographs of: (A) PVC S6045/DINP/OMMT (5 phr MMT-Na$^+$/TBC/THF); (B) PVC S6045/DINP/OMMT (5 phr MMT-Na$^+$/TBC/H$_2$O); and (C) and (D) PVC S7060/TBC/OMMT (10 phr MMT-Na$^+$/TBC/THF). Note the difference in magnification.

SEM Images

SEM was used to study the morphology of the OMMTs and their dispersion and exfoliation in different formulations of the melt processed plasticized PVC samples.

If the MMT samples were allowed to swell in H$_2$O, then they formed a self-standing film when the solvent evaporated, as has been reported in the literature.[10,11] Our organic modification procedure showed the same behavior of the clay mineral when H$_2$O is used as the solvent. After evaporation of the water and drying the OMMTs, the samples were ground to form a (free-flowing) powder. The result after grinding is shown in Figure 2(A), and as can be seen, a considerable number of particles had sizes of several hundred microns. When THF was used as the solvent, we observed different results. After drying the OMMT, they still formed a free-flowing powder that was easy to grind into particles having a smaller size with an apparent narrow size distribution when analyzed using SEM [Figure 2(B)].

Figure 3(A,B) show SEM images of the final products of PVC S6045/40 phr DINP processed via MB: (A) MMT-Na$^+$ modified with TBC in THF and (B) MMT-Na$^+$ modified with TBC in H$_2$O. All the developed materials containing OMMT revealed a considerable number of agglomerates with compact and elliptical structures. Only a minor extent of exfoliated OMMT or OMMT tactoids was observed. In general, OMMTs modified in THF showed smaller agglomerates than OMMTs modified in H$_2$O, similar to the observations made with the OMMT samples shown in Figure 2. These images, along with the results from the gas permeability tests, mechanical tests, and the extraction experiments indicate that the OMMT, when processed into the
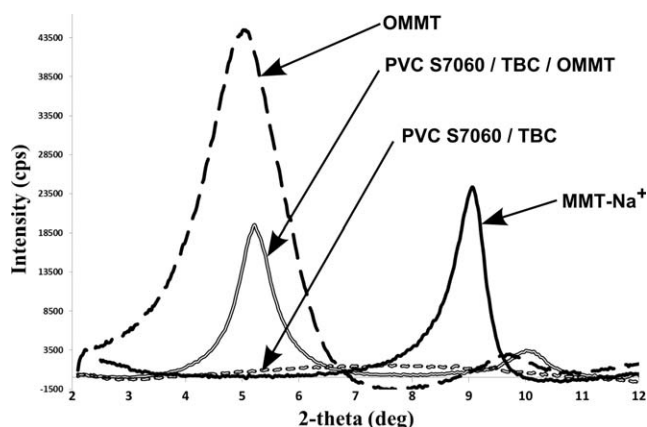

Figure 4. WAXD pattern of materials with TBC acting as both the OM for MMT and as the primary plasticizer.

Table IV. Results of TGA Measurements on MMT-Na$^+$ and OMMT Samples with Different OM Content

Material	Step 1		Step 2		Step 3	
	Temp (°C)	Mass loss (%)	Temp (°C)	Mass loss (%)	Temp (°C)	Mass loss (%)
MMT-Na$^{+a,b}$	<100	0.7	–	–	–	–
OMMT (2 : 1)^{a,c}	<100	1.0	∼ 250	21.1	∼ 320	11.3
OMMT (4 : 1)^{a,c}	<100	1.7	∼ 240	7.7	∼ 310	11.7
OMMT (8 : 1)^{a,c}	<100	3.4	–	–	∼ 280	10.4
TBC	–	–	∼ 290	100	–	–

[a] MMT-Na$^+$ was dried in a vacuum oven at 70°C for 68 h before modification.
[b] Unconditioned.
[c] Conditioned at 23°C and 50% RH for 72 h.

plasticized PVC, to a great extent collapses as the OM is dispersed in the PVC/DINP matrix.

Figure 3(C,D) show images of a formulation comprising PVC S7060, OMMT, and TBC, where TBC acted as both the primary plasticizer and as the OM. The PVC nanocomposite was processed via MB in the microcompounder. The result was a larger number of small MMT particles, i.e., exfoliated layers and small tactoids. The agglomerates of OMMT in the material exhibited an elongated form, with a less compact structure and better separation between the layers. These images, together with the decrease in gas permeability of the material, indicate that the OMMT had been exfoliated, creating a physical barrier for the gas molecules. WAXD analysis of this material shows peaks at positions similar to the pristine OMMT (Figure 4) which points to the fact that there are intercalated clay particles that are not fully exfoliated. The material without OMMT showed no peak within the range of the analyzed theta angles. Morgan and Gilman[12] combined WAXD with transmission electron microscope (TEM) and concluded that results from WAXD analyses alone cannot be used to sufficiently describe the nanoscale dispersion of the clay particles. The absence of a peak in the WAXD pattern does not necessarily prove that the OMMT is fully exfoliated, instead the results are influenced by factors such as the order of the clay mineral and the concentration. Likewise, a peak from a composite material in the pattern similar to the pristine OMMTs or only slightly shifted towards lower theta angles does not imply that the material is a conventional micro composite. Instead, a combination with other techniques such as TEM, or as used in this study HR-SEM, can provide information for a more correct characterization of the material's morphology.

Thermogravimetric Analysis
Thermogravimetric analysis (TGA) was used to study the distribution of OM between clay surface and the interlayer space and its effect on moisture uptake using OMMT samples with different OM content. OMMT samples with different proportions of MMT : OM were produced, as described previously. After evaporation of the solvent (THF), the OMMT samples were conditioned at 23°C and 50% RH for 72 h. Table IV shows that the moisture uptake, i.e. mass loss at temperatures below 100°C in the thermograms, is the highest for the OMMT with the lowest concentration of OM (8:1). The moisture content was 3.4% for

OMMT 8:1, while OMMT 2:1 showed a mass loss below 100°C of 1.0%, which is close to dried MMT-Na$^+$. This means that no additional moisture was absorbed during conditioning, which we believe is because of the excess OM that protects the clay particles from moisture absorption.

In addition, it can be seen that the lowest concentration of OM exhibits a single mass loss step of OM, while for OMMT 2:1 and 4:1 samples there were two mass loss steps of OM. This has been discussed in previous works[5,6] and that the first mass loss step is interpreted as a desorption of the OM molecules from the surface of the clay mineral particles, and the second step is the loss of OM molecules trapped in the interlayer spaces of the MMT from a chelate effect. The single mass loss step of OM in OMMT 8:1 reveals that there was no excess OM that covered the surface of the clay particles. Instead, the lower *d*-spacing of OMMT 8:1 indicated a deficiency in OM molecules in the interlayer spaces compared with OMMT 4:1 and OMMT 2:1. Therefore, the high moisture uptake of OMMT 8:1 is explained by the absence of OM on the surface of the clay particles, leaving them unprotected toward moisture exposure.

Vicat Softening Temperature
The Vicat softening temperature (VST) is defined as the temperature at which a needle with a 1 mm^2 flat nose penetrates the sample to a depth of 1 mm: the tests are performed under constant load and a uniform rate of increase in temperature. This is an important property when selecting materials for specific applications where dimensional stability at elevated temperatures is required. In Table III, the VST of different PVC materials is summarized. It can be seen that the VST can be increased by 7°C by the addition of 10 phr OMMT to TBC-plasticized PVC.

CONCLUSIONS

In this article, we have investigated differences in particle morphology between organo-modification using THF and H$_2$O and the nanoscale dispersion of the OMMTs in plasticized PVC. Using SEM, we have shown that OMMTs modified in THF form much smaller agglomerates than OMMTs modified in H$_2$O.

In addition, in a previous study, we have reported that TBC is an excellent OM for MMT. Consequently, we have manufactured a material composed of DINP-plasticized PVC and TBC-modified

MMT. Contrary to our expectations, the composite material showed an almost 30% decrease in the E-modulus and a 13% increase in oxygen permeability compared with the material without any OMMT. As the only difference between these materials is an additional 2.5 phr of TBC (apart from MMT), we investigated the effect of TBC alone. The results show the same magnitude of changes in the properties. Thus, our interpretation of the achieved results is as follows.

The compatibility between TBC and DINP is much better than between TBC and MMT, while the chelating effect of TBC is evidently too weak to prevent the OM from migrating out of the interlayer spaces of the MMT and into the PVC/DINP matrix. Consequently, during the melt processing of DINP-plasticized PVC and TBC-modified MMT, the TBC leaves the MMT, which then reaggregates, and as a consequence, makes no significant contribution to the material properties. This hypothesis has been confirmed by extraction experiments.

The compatibility problem disappeared when we used TBC-modified MMT in PVC plasticized with TBC instead of DINP. As a result, we achieved a significant increase in the E-modulus and a significant decrease in the oxygen permeability. SEM analyses in combination with WAXD patterns showed that our material have a mixed morphology, that is a nanocomposite with a combination of regions of intercalated and exfoliated nanostructures. Our results have indeed confirmed that it is possible to develop a nanocomposite based on plasticized PVC, if both the organo-modification of the MMT and the formulation of the matrix are carefully selected. With a further optimization of the dry-blend preparations and the processing parameters, a higher degree of exfoliation is likely to be reached using our approach.

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