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Preparation of highly exfoliated polyester-clay nanocomposites: process-property correlations

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ABSTRACT

A large number of polyester nanocomposite batches featuring different kinds of nanoclay surface modifiers and up to 6 wt.% nanoclay were manufactured using a solvent-based technique. Montmorillonite platelets modified with ammonium ions of different chemical architectures were examined in order to study the effect of ammonium ions on the extent of surface reactions with long chain fatty acids. The ammonium montmorillonite was first dispersed and suspended in acetone. This suspension was further esterificated with dotriacontanoic (lacceroic) acid to form high density brushes on the clay surface. This led to achieving higher basal plane spacing of the montmorillonite platelets owing to the reduction of electrostatic interactions holding them. The outcome of the surface esterification was analyzed by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The esterificated ammonium modified clays were then mixed by five different mixing strategies based on the use of a three-roll mill mixer (TRM) and/or ultrasonication (US) in order to obtain the desired polyester-nanoclay dispersion, intercalation, and exfoliation. The dispersion states of the modified nanoclay in polymer were characterized from XRD, scanning electron microscopy (SEM), and low and high magnification transmission electron microscopy (TEM). Mechanical, thermal and barrier properties of the resulting composites were experimentally characterized. The Mori-Tanaka method along with an orientation distribution function was used to verify the experimental effective stiffness of the polyester nanocomposite systems. The aspect ratio of nanoclays and their level of intercalation and/or exfoliation after mixing were also confirmed by the comparison of the experimental diffusivity results with those of Fick's diffusion model. Systems having 4 and 6 wt.% esterificated ammonium nanoclay and prepared according to a combined TRM/US mixing procedure showed optimal performance with balanced properties and processing ease, thereby showing potential for use in automotive, transportation and packaging industry.

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1. Introduction

Polymer-clay nanocomposite (PCN) is a class of materials consisting of either thermosets, thermoplastics, rubbers or co-polymers as the matrix and nanoclay as the reinforcement.^{1,2} Montmorillonite layered-silicate smectite consists of stacks of 1 nm thick aluminosilicate layers or platelets regularly spaced. Each layer consists of a central Al-octahedral sheet fused to two tetrahedral silicate sheets. Isomorphic substitutions of aluminum by magnesium in the octahedral sheet generate negative charges, which are compensated for by alkaline earth- or hydrated alkali-metal cations.^{3,4} The electrostatic and van der Waals forces holding the layers together are relatively weak in these montmorillonites and the interlayer distance varies depending on the radius of the cation present and its degree of hydration. The easy swelling of high aspect ratio platelets in water makes them suitable substrates for surface ion exchange with alkyl ammonium ions. This modifies the surface so as to make them compatible with organic polymer matrices to achieve their exfoliation.^{5,6} The exfoliation of conventional ammonium ion modified clays in polar matrices has been successfully achieved owing to positive interactions between the matrix and polar clay interlayers. On the other hand, these ammonium ion modified montmorillonites have been at best partially exfoliated or marginally intercalated when non-polar matrices, like polyethylene and polypropylene are used which is due to the absence of any interactions. The extent of exfoliation in these non-polar matrices was observed to enhance when chain density of the ammonium ion attached on the surface or the length of the alkyl chains were increased due to resulting decrease in electrostatic interactions between the clay platelets.^{7,8} But, the limit of solubility as well as steric hindrance at the surface limits the exchange of pre-formed “big” molecules on the surface. Physical adsorption of polar molecules on the surfaces of ammonium modified montmorillonites can be one way to balance the residual electrostatic forces in the platelets. However, the risk of these molecules being pulled out during heat treatment or cleaning is higher. Polarization of matrices to improve their interactions with clay interlayers has also been commonly attempted by compatibilizers, but the extent of polarization may limit the mechanical performance of the

composites.⁹⁻¹¹ Ideally, if the ammonium ions with reactive groups are exchanged first on surface and are then subsequently reacted to attach further long chains, high density brushes with long resulting alkyl chains chemically bound to the surface can be generated.¹²⁻¹⁸

PCN has recently received considerable attention, both from academia and the industry, due to their potential enhancement in physical properties such as mechanical properties (e.g., mechanical strength¹⁹, hardness²⁰, abrasion resistance²¹), thermal properties (e.g., thermal stability²², flame retardant²³, thermal conductivity²⁴), barrier properties (e.g., gas barrier²⁵, pervaporation²⁶), electro-rheological properties²⁷ and corrosion protection properties²⁸ compared to the plain polymer. The thermo-mechanical responses of polymers are favorably altered by the addition of a trace amount of nanofillers. To obtain optimal nanocomposite properties, the following four structural parameters should be maximized: (1) the particle aspect ratio, (2) particle dispersion, (3) particle packing (or alignment), and (4) polymer to particle interfacial stress transfer.²⁹⁻³³

Nanoclay particles can be used to reduce the diffusion and permeation of molecules through the polymer matrix.³⁴⁻³⁶ The type and content of clay particle, and its compatibility with the host matrix greatly influence the permeability of the membrane. Drozdov et al.³⁷ showed that the diffusivity deteriorates with higher clay content. The diffusion of molecules and its kinetics, through nanoclay-based nanocomposites were also examined by many researchers³⁸⁻⁴⁰ and a substantial decrease in moisture permeability in comparison with those of virgin polymer matrix was reported. The reduction in permeability was attributed to the extremely high aspect ratio of clay platelets, which increased the tortuosity of the diffusion path of the molecules into the nanocomposite.

The addition of clay in the polyester matrix usually leads to three different microstructures depending on the nature of the material and the method of preparation.⁴¹⁻⁴⁸ When the polyester is unable to intercalate between the silicate sheets, a phase separated composite is obtained in which the materials stay in the same range as traditional microcomposites. Intercalated structure, in which a single (or more) polymer chain intercalated between the silicate layers results in a well ordered multilayer morphology

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built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in the continuous polyester matrix, an exfoliated or delaminated structure is obtained. The intercalated and exfoliated structures are formed only when the clay is organically treated with surfactants.^{36,42}

In this study, we prepared polyester polymer-nanoclay nanocomposites in acetone by the use of esterificated ammonium modified nanoclays. Esterification with long alkyl chains led to achieving higher clay basal spacing in order to decrease the electrostatic interactions to ease the clay exfoliation in the polymer matrix system. The increase in the organic matter present on the clay surface due to esterification was characterized by FTIR and XRD. The Mori-Tanaka method and the Fick’s diffusion model were used to predict the effective stiffness and diffusivity behavior of these polyester-based nanocomposites, respectively. The following sections summarize an experimental evaluation of the polyester-nanoclay composites with details on the processing method, characterization of the nanoclay morphology and distribution, mechanical, thermal and diffusivity testing, and the optimization of the nanocomposite behavior.

2. Experimental Methods

2.1. Materials and nanocomposite preparation

The nanocomposite material was a mixture of one of the three different types of esterificated predispersed nanoclays (Cloisite® 11B, Cloisite® 15A, and Cloisite® 30B, Southern Clay Products, Louisville, USA), with different surface modifiers as listed in Table 1. A catalyst cured thermosetting polyester (RL7520, Progress Plastiques Cie, Drummondville, CAN) having a viscosity of 200 mPa.s, gel time of 75 min, tensile modulus of 3.6 GPa, and ultimate tensile strength of 80 MPa was used with NOROX® MEKP-9 (NORAC Inc., California, USA) as the catalyst. The desired amount of nanoclay (either 2, 4, or 6 wt.%) was first dispersed in acetone 99.9% and dotriacontanoic (lacceroic) acid (Sigma-Aldrich Ltd., Ontario, CAN) solution followed by 4-(dimethylamino)pyridine (DMAP) and

1 diisopropylcarbodiimide (DIC) procured from Sigma-Aldrich Ltd. (Ontario, CAN) to achieve higher
2 basal plane spacing of the montmorillonite platelets. After ultrasonication (ultrasonic cleaner 8891,
3 Cole-Parmer) at 42 kHz for 1 h, clay resuspension was done in dimethylformamide (DMF) from Sigma-
4 Aldrich Ltd. (Ontario, CAN). Then the polyester was slowly added to the solution over a stirring hot
5 plate (model SP131825, Barnstead international). The samples were further mixed by investigating five
6 different mixing strategies resulting in an array of several polyester nanocomposite experimental
7 batches listed in Table. 1.
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18 ***2.2. Esterification of ammonium modified nanoclays***

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21 For the surface esterification reactions, 0.5 g of modified clay was suspended in 5 mL of acetone.
22 The suspension was sonicated twice for 10 min while keeping cold to avoid solvent evaporation.
23 Dotriacontanoic acid (acid/clay mole ratio of 5.0) was then added to the clay followed by DMAP
24 (acid/DMAP mole ratio of 0.05). The contents were then stirred by addition of DIC (DIC/acid mole
25 ratio of 1.2) for 24 h at room temperature. The resulting thick gel was filtered to remove the unreacted
26 acid and other reagents along with the solvent-soluble urea formed during the esterification reaction.
27 The filtrate was added with ether in order to precipitate the urea formed during the reaction to confirm
28 the surface reaction. The reacted clay was resuspended in DMF followed by sonication and was filtered
29 and dried under vacuum at 90 °C.
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43 ***2.3. Nanocomposite mixing strategies and nomenclature***

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46 Figure 1 shows a schematic representation of the five mixing strategies. In strategy I, Styrene (ST,
47 $C_6H_5CH=CH_2$, Sigma-Aldrich Ltd., Ontario, CAN) and catalyst (CA) were added to the mixture and
48 then only ultrasonicated (US) for 30 min. In strategies II and III, the nanocomposite mixtures were
49 passed several times through a three-roll mixing mill (TRM, Exakt 80E, Exakt Technologies Inc.) where
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Table 1. Experimental matrix showing nanoclay specifications and specimen batch numbers according to different mixing strategies and variation in nanoclay contents.

Nanoclay type	Molecular structure	Surface modifier	Concentration	Moisture (%)	Nanoclay content (wt.%)	Batch number				
						Mixing strategy				
						I	II	III	IV	V
Cloisite® 11B	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{CH}_2 - \text{C}_6\text{H}_5 \\ \\ \text{HT} \end{array}$	2MBHT	95 meq/100g	> 4%	2	1	2	3	4	5
					4	6	7	8	9	10
					6	11	12	13	14	15
Cloisite® 15A	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	2M2HT	125 meq/100g	> 2%	2	16	17	18	19	20
					4	21	22	23	24	25
					6	26	27	28	29	30
Cloisite® 30B	$\begin{array}{c} \text{CH}_2 \text{CH}_2\text{OH} \\ \\ \text{CH}_3 - \text{N}^+ - \text{T} \\ \\ \text{CH}_2 \text{CH}_2\text{OH} \end{array}$	MT2EtOH	90 meq/100g	> 2%	2	31	32	33	34	35
					4	36	37	38	39	40
					6	41	42	43	44	45

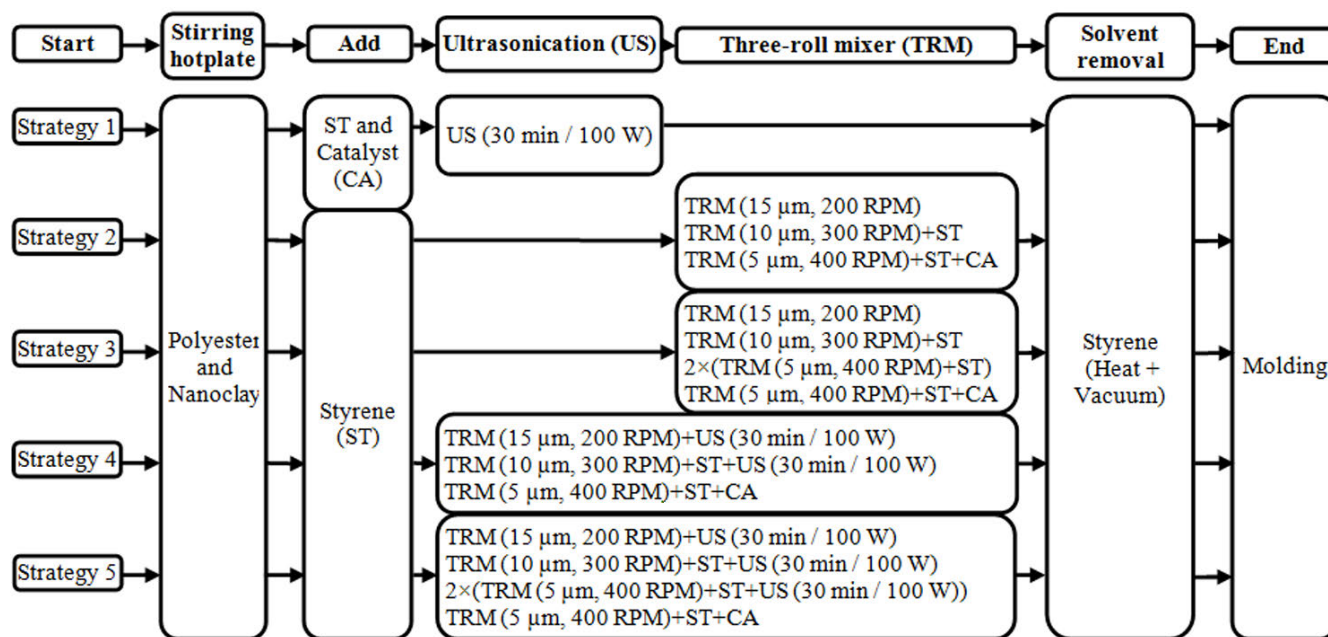


Figure 1. Processing of esterificated nanoclay reinforced polyester-based nanocomposites.

the gap between the rolls and the speed of the apron roll were adjusted at 15 μm -200 RPM, 10 μm -300 RPM and either one or three times at 5 μm -400 RPM, for three or five passes, respectively. For strategies IV and V, the same procedure and parameters as those of strategies II and III were chosen, respectively, however US was performed after each TRM process, except for the last pass. These five mixing strategies were repeated for three concentrations (2, 4, and 6 wt.%) of the three modified clays. The obtained esterificated nanoclay-polyester mixtures were then immediately degassed for ~ 30 min and poured into tensile test sample molds (ASTM D638) and placed under vacuum for ~ 6 h at room temperature for complete solvent evaporation.

The nomenclature used to describe the nanocomposite is: “A/B/C”, where “A” and “B” represent the type and the content of cloisite®, respectively. “C” refers to the selected mixing strategy number. For example, batch number 24 in Table 1 is referred to as 15A/4/IV, indicating the mixing of 100 g of resin system with 4.167 g (4 wt.%) of esterificated Cloisite® 15A nanoclay platelets according to strategy IV.

2.4. Testing and characterization

FTIR spectrums (VECTOR 22, Bruker Optics Inc.) of the surface treated nanoclays were obtained by preparing their pill shape samples in KBr. The degree of intercalation and exfoliation was analyzed based on scanning electron microscope (SEM, JEOL JSM-7600TFE), transmission electron microscope (TEM JEOL JEM-2100F) images and X-ray diffraction (XRD, X'Pert PRO Diffractometer). The interlayer separation measurements were carried out with Pro X-ray diffractometer with Cu target and Ni filter at a scanning rate of 2°/min, with CuK α radiation ($\lambda_w = 1.541 \text{ \AA}$) operating at 30 kV and 15 mA. Tensile tests were carried out using tensile test machine (MTS 810) with a 25 kN load cell at the crosshead speed of 1 mm/min (ASTM D638). A minimum of five tensile specimens were tested for each nanocomposite system. Dynamic mechanical thermal analyses (DMTA) were only performed on the specimens showing the most promising properties (i.e., specimens with batch numbers 4, 9, 14, 19, 24, 29, 34, 39 and 44 (Table 1)). The linear coefficient of thermal expansion (CTE) above and below the glass transition temperature (T_g) was obtained by thermo-mechanical analysis using a TA Instruments DMA 2980. The samples were heated from room temperature to 140 °C at a rate of 4 °C/min. The axial strain and temperature were measured throughout the test. The linear slope of the strain-temperature curve is reported as the CTE. The T_g was obtained from the intersection of the two linear portions of the strain-temperature curve. Moisture absorption testing was performed using a Cole Parmer oven that allows immersion of samples in a distilled water bath with temperature maintained at 50 °C according to ASTM D570-98. The nanocomposites samples used for moisture measurements were rectangular bars of $\sim 60 \text{ mm} \times 12 \text{ mm} \times 3 \text{ mm}$ coated with polyurethane (NEA123MB, Norland Products) on all edges to reduce edge effects and constraint the diffusion to occur mainly through the thickness of the sample. All samples were polished to ensure flat and parallel surfaces. The polished samples were placed in a vacuum oven at 80 °C for 24 h to remove residual moisture. After water immersion, the weight of the samples was measured every 8 h for the first 4 days, followed by once a day until steady state condition

was achieved. Moisture diffusivity coefficients were obtained from the moisture gain versus time plots for various polyester-based nanocomposites.

3. Results

Several nanocomposite systems (Table 1) were characterized with different mixing strategy and nanoclay type and content. Depending on the property studied, experimental results showed different levels of variation. This is to be expected, as nanocomposite materials have several sources for variation, such as multiple heterogeneities (e.g., nanoclay, styrene), processing parameters (e.g., degree of sonication, residual acetone), and their effect is different for each parameter characterized. In the following sections, the summary and observations on different properties are interpreted by considering the salient features of the average experimental data. The virgin polyester corresponds to 0% nanoclay content and is considered as the baseline material system.

3.1. *Nanoclay basal spacing enhancement by their surface treatments*

Esterification of the clay platelets to improve their exfoliation potential when sheared in non-polar polyesters, generates brushes which are not only bound ionically to the surface, but also have desired chain lengths. Quaternary ammonium ions with varying number of reactive groups can be initially exchanged to the surface and the subsequent surface reactions can help to generate varying densities of the alkyl chains on the surface. Figure 2 shows the reaction scheme of dotriacontanoic acid with dimethyl(dihydrogenatedtallow)ammonium (2M2HT) modified montmorillonite. Although the presence of carboxyl groups can lead to further enhancement of polarity in the clay interlayers, however, the attachment of long alkyl chains can impart enough non-polar character in the interlayer as well as distance separating the platelets thus reducing the interactions between them.

The evidence for the esterification of the ammonium modified clay platelets with dotriacontanoic acid comes from FTIR studies with a 2 cm^{-1} resolution in a wave-number ranging from 4000 to 400 cm^{-1}

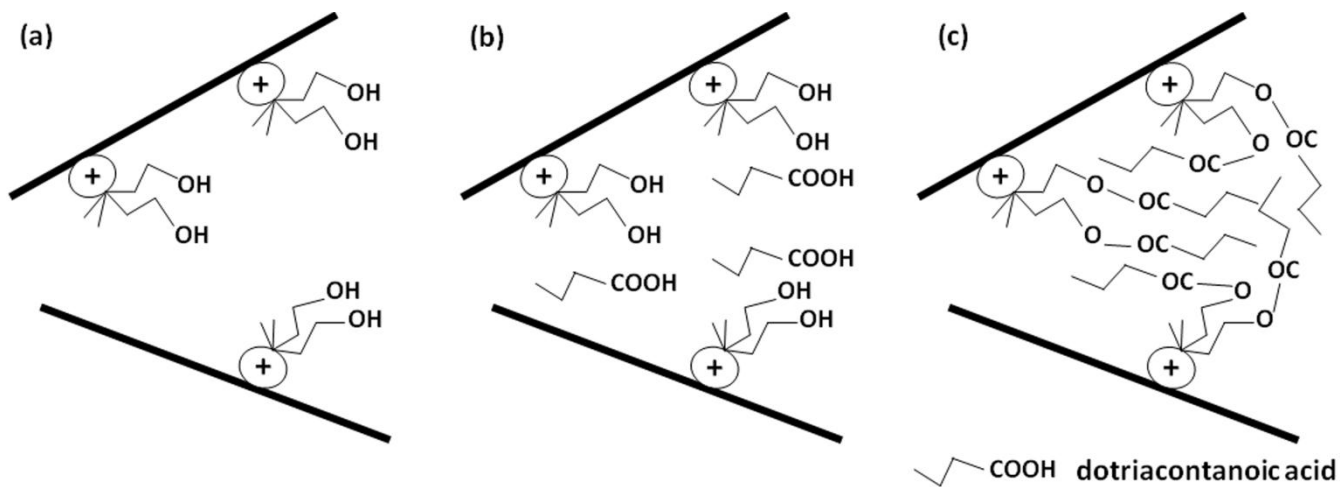


Figure 2. Schematic of surface esterification reaction of montmorillonite modified with 2M2HT with dotriacontanoic acid: (a) the ammonium modified clay platelets, (b) the addition of dotriacontanoic acid, (c) the formation of long alkyl chains.

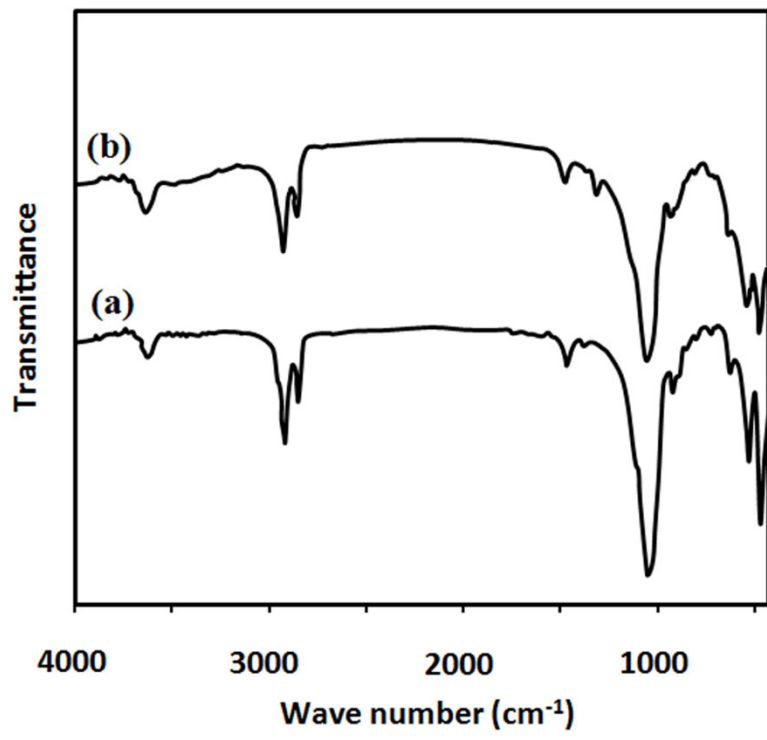


Figure 3. FTIR spectra of ammonium modified clay platelets (a) before, and (b) after esterification with dotriacontanoic acid.

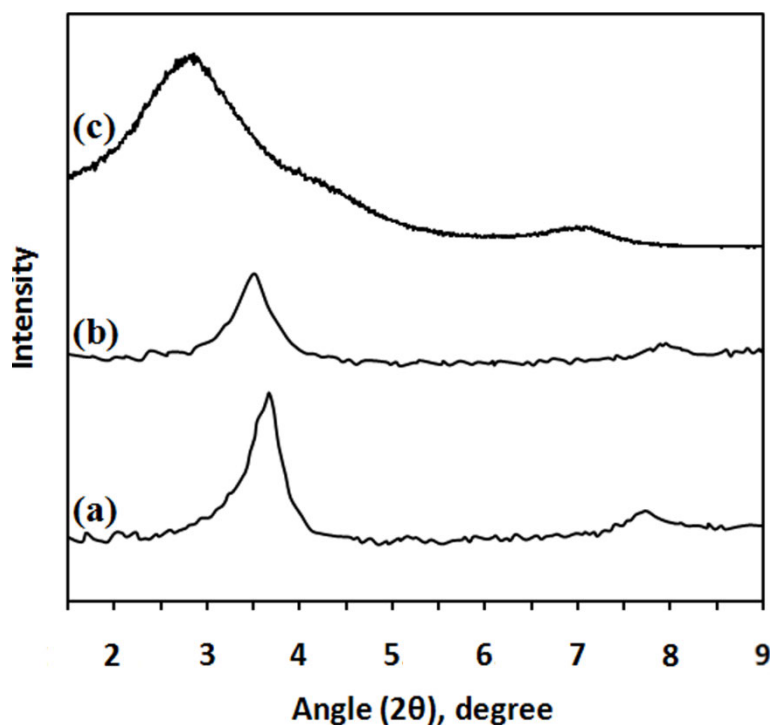


Figure 4. XRD diagrams of (a) ammonium modified clays, (b) precipitated ammonium modified clays in acetone, and (c) alkyl chain grafted ammonium modified clays.

with 20 scans. The FTIR spectrum of the ammonium modified clay platelets (curve (a) of Figure 3) displays typical --OH stretching absorbencies at 3634 cm^{-1} .⁴⁹ From 3000 to 2800 cm^{-1} , the typical CH_2 stretching band of the ammonium surfactant appears. Between 1480 and 1450 cm^{-1} , the CH_2 band for symmetric bending or scissoring mode becomes evident. CH_2 small bands are also seen from 740 to 710 cm^{-1} . The bands at 1035 , and 914 cm^{-1} can be collectively attributed to Si--O stretching vibrations.⁵⁰ The peaks at 875 and 836 cm^{-1} could be attributed to AlFeOH and AlMgOH bending vibrations, respectively.⁵¹ The spectrum of the esterificated clay platelets displays almost the same pattern as that of ammonium modified clay except for a new band of O--OC stretching at 1313 cm^{-1} , which indicates the grafting of the alkyl chains to the ammonium organic groups on the clay mineral surface.

The change of morphology of clay during each stage of processing was also monitored using XRD. The XRD diagrams of the ammonium modified clays, precipitated ammonium modified clays in acetone, as well as alkyl chain grafted ammonium modified clays are collected in Figure 4. For

1 Cloisite® 15A, a peak was observed at 3.59° (curve (a)) which was shifted to 3.50° (curve (b)) when
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3 suspended in acetone. When the clay-acetone suspension was mixed with dotriacontanoic acid, the peak
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5 was shifted to a lower peak at 2.95°. The interlayer distance (*d*-spacing) of clays inside the
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7 nanocomposites is obtained from Bragg's law:^{41,42}
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$$2d\sin\theta = n\lambda_w, \tag{1}$$

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14 where *d* is the interlayer distance of clay, λ_w is the wavelength used, *n* is the order which is equal to 1
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16 for the first order, and θ is the measured angle. Therefore, the *d*-spacing of the Cloisite® 15A is
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18 measured about 24.6 Å which is increased to 25.2 Å when suspended in acetone indicating a slightly
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20 exfoliated structure and to 29.9 Å (~ 20% improvement) for the alkyl chain grafted clays. The basal
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22 spacing increases of Cloisite® 11B and 30B, prepared with the similar surface treatment process as for
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24 Cloisite® 15A, have been depicted in Table 2.
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30 **3.2. Morphology of nanoclay inclusions by different mixing strategies**
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34 In order to compare the degree of intercalation and exfoliation, XRD patterns of 2, 4, and 6 wt.% of
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36 esterificated Cloisite® 11B-, 15A- and 30B-polyester nanocomposites prepared by stirring hotplate and
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38 five different mixing strategies were obtained. Curve (a) of Figure 5 shows the intensity data of the
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40 esterificated Cloisite® 15A-polyester nanocomposite prepared by stirring hotplate featuring a peak at
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42 2.95° derived from the basal spacing in the range between 0° and 10°. On the other hand, the
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44 nanocomposites obtained by using mixing strategies I, II, and III shifted to lower peaks at 2.64° (curve
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46 (b)), 2.21° (curve (c)), and 2.15° (curve (d)), respectively. For the nanocomposites mixed with strategies
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48 IV and V, no peaks were observed (curves (e) and (f)). Therefore, the esterificated nanoclay interlayer
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50 distance calculated from Eq. (1) was 29.9 Å, 33.4 Å, 40.0 Å, and 41.1 Å for nanocomposites prepared
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52 by stirring hotplate and mixing strategies I, II, and III, respectively. Detecting no peaks in XRD graphs
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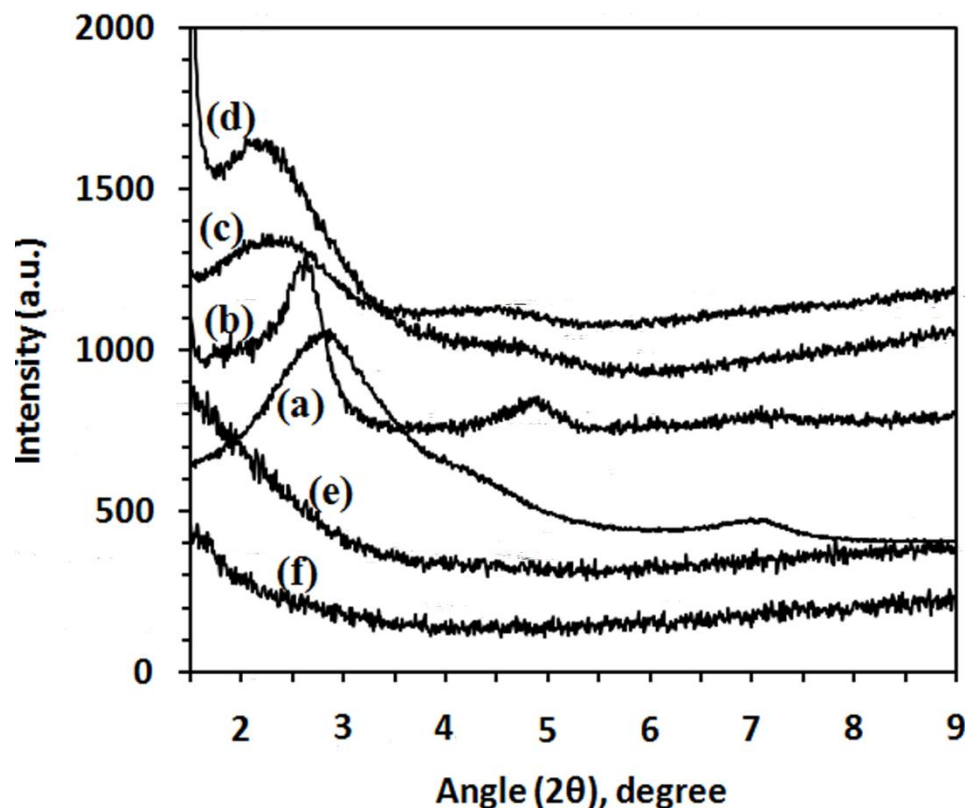


Figure 5. XRD patterns of 4 wt.% esterified Cloisite® 15A-polyester samples prepared by (a) stirring hotplate (initial mixing), (b) strategy I, (c) strategy II, (d) strategy III, (e) strategy IV, and (f) strategy V.

for nanocomposites prepared according to mixing strategies IV and V confirms the formation of well intercalated and exfoliated nanoclay structure.

Table 2 depicts the interlayer *d*-spacing of different nanocomposite systems prepared according to the different surface treatments and five mixing strategies presented here. The numbers in the parentheses show the percentages of the *d*-spacing increases in comparison to those prepared by virgin Cloisites. For esterified Cloisite® 11B- and Cloisite® 30B-polyester systems, although the interlayer *d*-spacing was increased up to 83% and 54% for nanocomposites prepared according to mixing strategy V, respectively; however none of our five mixing strategies led to a fully exfoliated structure since a peak was always observed in XRD results.

Table 2. Interlayer spacing-surface treatment and -mixing strategy correlations of different kinds of Cloisites in polyester matrix obtained from XRD measurements.

Cloisite®	Virgin	Precipitated in acetone	Alkyl chain grafted	Strategy I	Strategy II	Strategy III	Strategy IV	Strategy V
15A	24.6	25.2 (+2%)	29.9 (+22%)	33.4 (+36%)	40.0 (+63%)	41.1 (+67%)	---	---
11B	16.3	16.5 (+1%)	18.4 (+13%)	19.4 (+19%)	22.7 (+39%)	23.9 (+47%)	27.3 (+67%)	29.8 (+83%)
30B	16.7	17.0 (+2%)	18.5 (+11%)	21.3 (+28%)	22.5 (+35%)	23.6 (+41%)	25.2 (+51%)	25.7 (+54%)

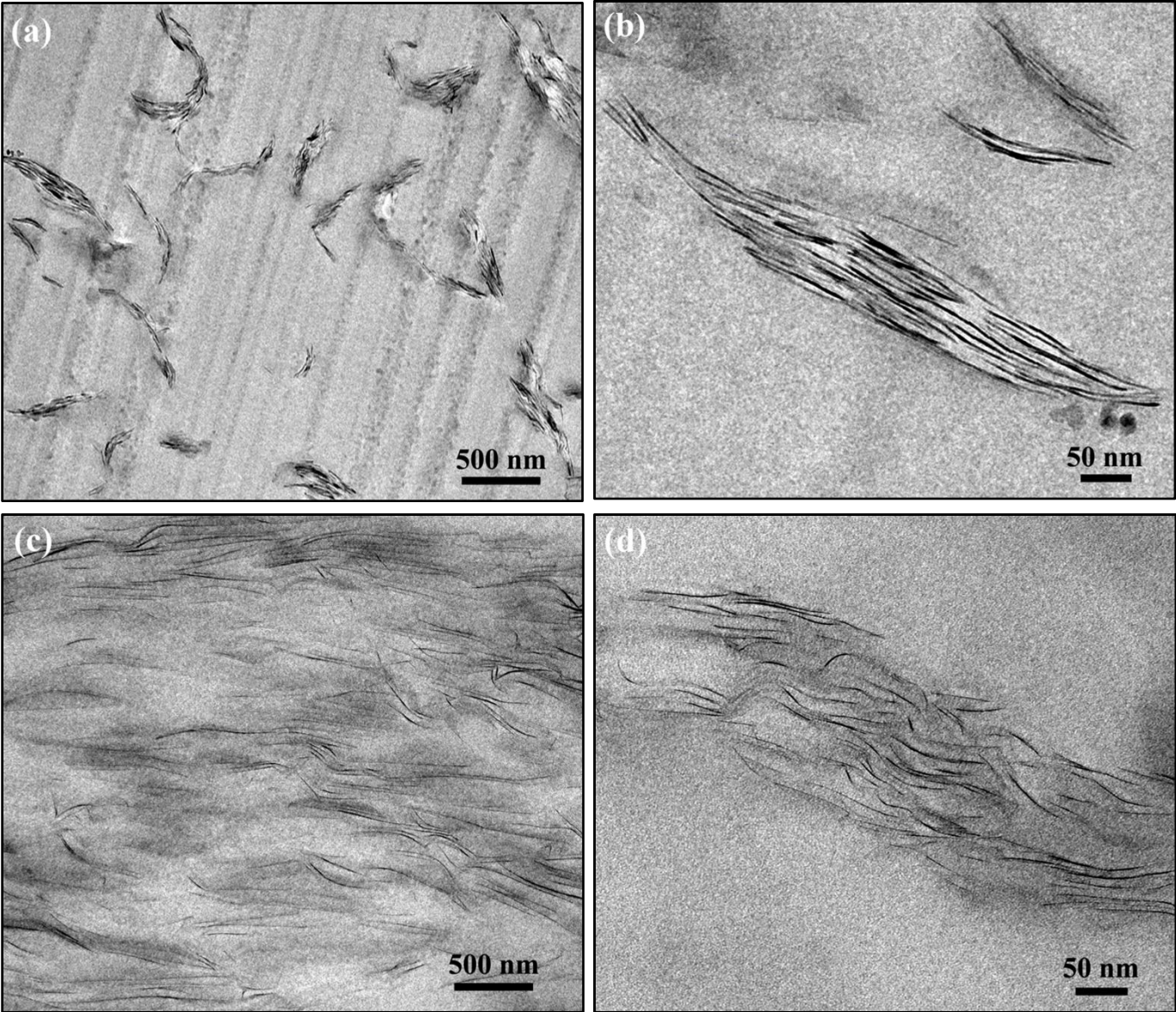


Figure 6. Low and high magnification TEM micrographs of 4 wt.% esterificated Cloisite® 15A-polyester samples prepared according to (a,b) mixing strategy II, and (c,d) mixing strategy IV.

Figure 6 shows the representative TEM images of 4 wt.% esterificated Cloisite® 15A-polyester samples prepared by mixing strategy II (a,b), and strategy IV (c,d). The bright region represents the matrix portion and the dark lines represent the clay nanolayers. The nanoclay aggregates in Figure 6a show that the exfoliation of the clay nanolayers has not been uniformly reached throughout the polyester. The corresponding higher magnification image (Figure 6b) shows the existence of intercalated nanoclay structure inside the matrix. However, the esterificated nanoclay-polyester samples prepared according to mixing strategy IV, show a more uniform dispersion (Figure 6c) of exfoliated (Figure 6d) nanoclay which is in agreement with the results obtained from XRD patterns.

3.3. Mechanical properties

3.3.1 Tensile Modulus

The measured tensile modulus obtained from the initial slope of the stress-strain curve for virgin polyester and polyester-based nanocomposites made with different mixing strategies and clay contents are provided in Figure 7. The results have been averaged over five repetitions for each nanocomposite system and the error bars were calculated based on the 95% confidence interval. The dashed horizontal line corresponds to the virgin polyester data. The stiffness values obtained from the tensile tests revealed a decrease of the tensile modulus due to the addition of nanoclay for the samples prepared using strategies I, II, and III while an increase for those prepared by strategy IV and V. The nanocomposites having 4 wt.% of esterificated nanoclay content showed a stiffness increase of 53%. The effect of nanoclay content on stiffness of samples prepared by strategy IV was almost the same or even better than those provided by strategy V and hence limited improvement was observed by increasing the number of TRM passes over three.

Figure 8 shows the tensile modulus values of different polyester- esterificated nanoclay systems obtained using mixing strategy IV. A significant enhancement in tensile modulus was observed for

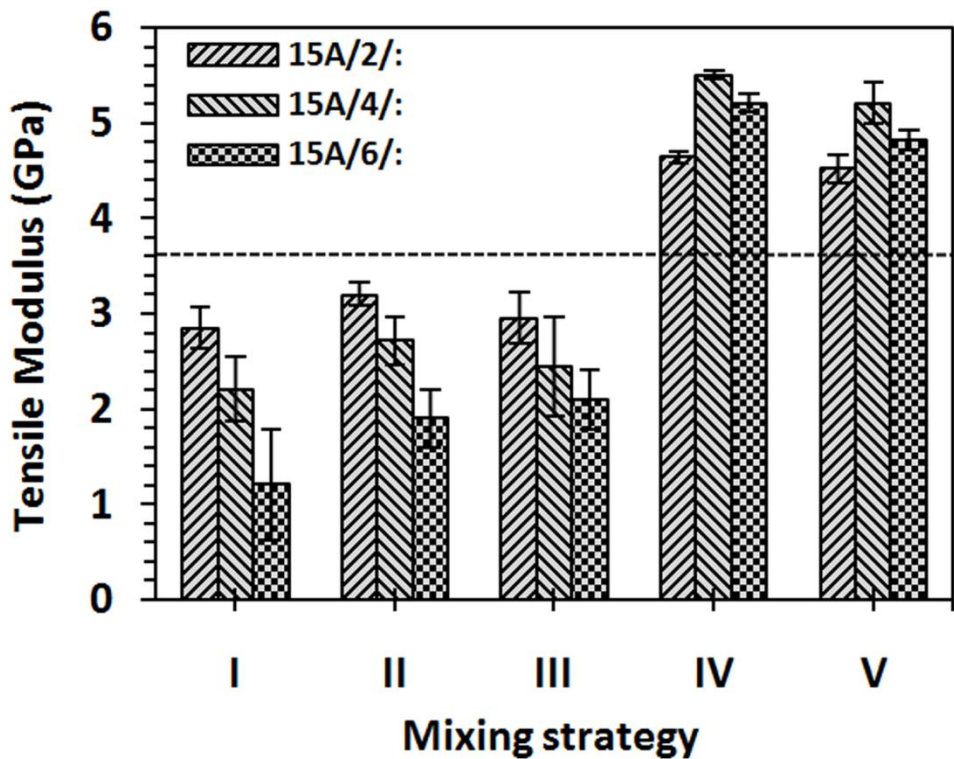


Figure 7. Experimental tensile modulus of polyester-based esterified Cloisite® 15A systems

featuring different esterified nanoclay content and mixing strategy. Dotted horizontal line represents the baseline value of the virgin polyester.

esterified nanoclays having 2M2HT as surface modifier (Cloisite® 15A). The samples prepared with esterified Cloisite® 30B showed a decrease of ~ 42% in modulus. This detrimental effect is probably due to the formation of phase separated nanoclay aggregates as confirmed from SEM and TEM images (not shown).

To demonstrate the effects of the degree of nanoclay dispersion in the improvement of the nanocomposite mechanical properties, the fracture surfaces of several polyester-esterified nanoclay systems were qualitatively analyzed. The roughness of the fracture surface has generally been associated to fracture properties and fracture energy release rates.^{52,53} A smooth fracture surface is attributed to brittle failures and rougher fracture surfaces are attributed to tougher materials.⁵³ Figure 9a shows the

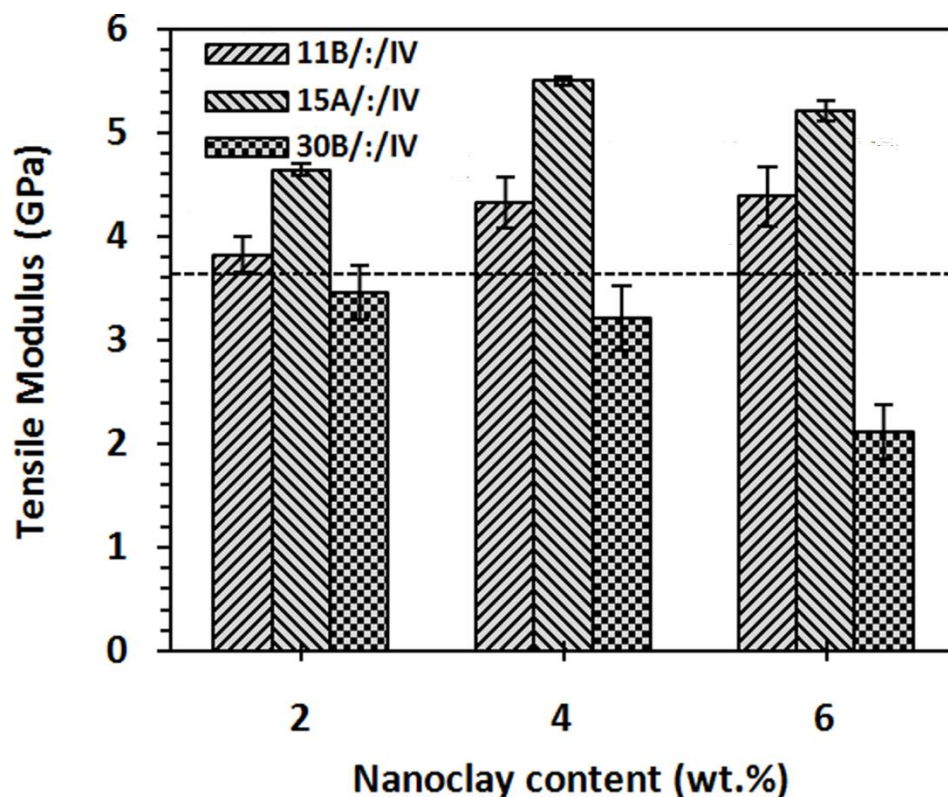


Figure 8. Experimental tensile modulus of polyester-based esterificated nanoclay systems having different nanoclay type and content. Dotted horizontal line represents the baseline value of the virgin polyester.

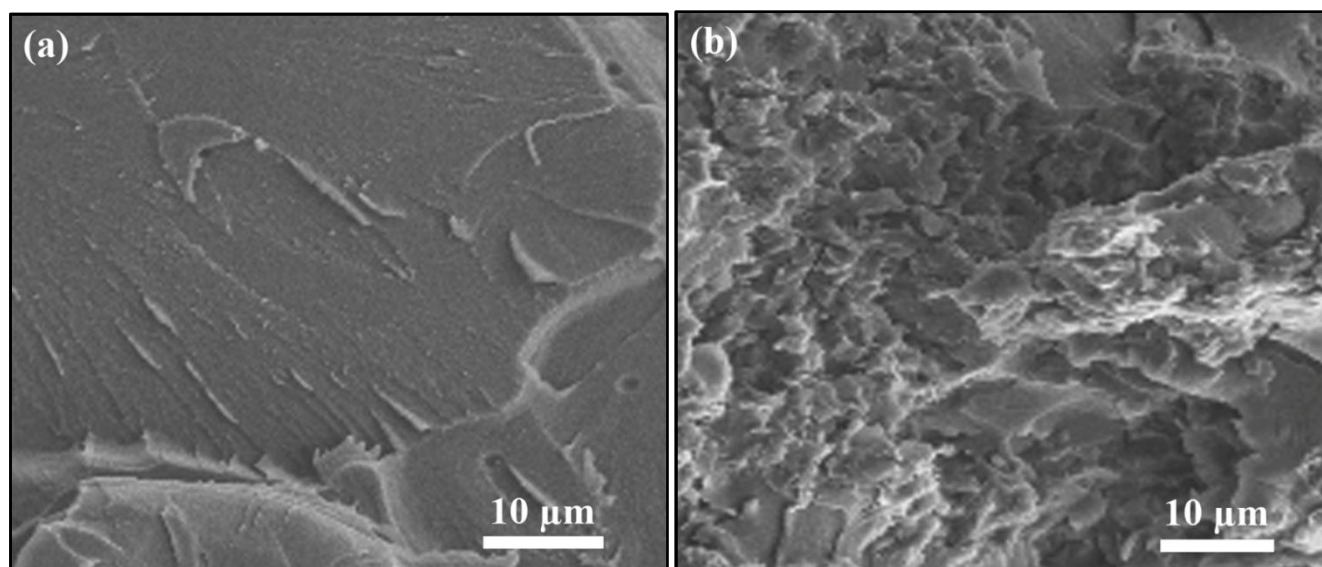


Figure 9. SEM images showing tensile fracture surface morphologies for the 4 wt.% esterificated Cloisite® 15A-polyester nanocomposites prepared according to (a) strategy II, and (b) strategy IV.

SEM images of the relatively smooth tensile fracture surface of the 4 wt.% esterificated Cloisite® 15A-polyester nanocomposites prepared according to strategy II. However, for the same system prepared according to strategy IV, significantly rougher fracture surfaces can be observed (Figure 9b), which proves the better dispersion of clay particles in the polyester matrix.

3.3.1.1 Modeling the effective stiffness

According to our XRD experiments, esterificated Cloisite® 15A particles prepared according to strategy IV seem to be well exfoliated in the polyester matrix. However, an indirect verification of the degree of exfoliation can be obtained using an effective medium theory. The idea is that no matter which theoretical model is chosen, it is necessary to make some assumptions about the degree of exfoliation. So the comparison between the experimentally determined Young's modulus with the theoretical predictions will indirectly give information about the degree of exfoliation. The Mori-Tanaka method⁵⁴ along with an orientation distribution function⁵⁵ was used to predict the effective stiffness of the polyester-based nanoclay nanocomposites. The effective Mori-Tanaka stiffness, $\mathbf{k}^{(MT)}$, of a two-phase material can be expressed as

$$\mathbf{k}^{(MT)} = \mathbf{k}_1 + f_2\{(\mathbf{k}_2 - \mathbf{k}_1)\mathbf{T}\}[\mathbf{f}_2\mathbf{I} + \mathbf{f}_2\{\mathbf{T}\}]^{-1}, \quad (2)$$

where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the fourth order stiffness tensors of the polyester matrix and the nanoclay particles, respectively. The volume fraction of the particles are denoted as f_2 . $\mathbf{I}$ is the fourth order identity tensor and $\mathbf{T}$ is the Wu tensor⁵⁶ and is given as

$$\mathbf{T} = [\mathbf{I} + \mathbf{S}\mathbf{k}_1^{-1}(\mathbf{k}_2 - \mathbf{k}_1)]^{-1}, \quad (3)$$

where $\mathbf{S}$ is the fourth order Eshelby tensor depending only on the aspect ratios of the particles and the properties of the matrix material. $[\]^{-1}$ denotes the inverse and the curly brackets denotes averaging over

all possible orientations. Using the orientation function from⁵⁴, the effective stiffness, $\langle k_{ijkl} \rangle$, of a two-phase material with particle orientation distribution function, $g(\theta, \varphi, \beta)$, is

$$\langle k_{ijkl} \rangle = \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} g(\theta, \varphi, \beta) a_{ip} a_{jq} a_{kr} a_{ls} k_{pqrs} \sin(\theta) d\theta d\varphi d\beta, \quad (4)$$

where $g(\theta, \varphi, \beta)$, is given as

$$g(\theta, \varphi, \beta) = \frac{\sin(\theta)^{2P-1} \cos(\theta)^{2Q-1}}{\int_{\theta_a}^{\theta_b} \sin(\theta)^{2P-1} \cos(\theta)^{2Q-1} d\theta}, \quad (5)$$

where θ_a and θ_b are the lower and upper limits of θ being present in the distribution and $0 \leq \theta_a$, $\theta_b \leq \pi$ and $P \geq \frac{1}{2}$, $Q \geq \frac{1}{2}$ and finally a_{ij} is a function of the Euler angles (θ, φ, β) defined in Appendix A.

The relevant measured modulus and Poisson's ratio of polyester RL7520 are $E_{\text{RL7520}} = 3.6$ GPa and $\nu_{\text{RL7520}} = 0.33$. The similar data for the nanoclay particles are taken from.^{57,58} In fact the nanoclay particles are transversely isotropic, but wang et al.,^{57,58} compared the predicted effective stiffness when assuming isotropic and transversely isotropic particles, respectively and found the difference to be negligible. Thus, for simplicity the particles are considered to be isotropic with $E_{\text{nanoclay}} = 107$ GPa and $\nu_{\text{nanoclay}} = 0.30$. The aspect ratios, i.e. length to thickness ratios, of the nanoclay particles given by the material supplier are in the range of 70-150, as it was also confirmed from TEM images, meaning that the nanoclay particles are of platelet shape. In the following an aspect ratio equal to 100 is chosen since the difference in effective stiffness of the two limits is less than 10% for the volume fractions considered in this work. The effective Young's modulus for polyester-based nanoclay nanocomposites with Mori-Tanaka random particle orientation (E^{MT}) is compared to the experimental values (E^{EXP}), the Voigt upper (E^U) and Reuss lower (E^L) bounds. The values obtained are shown in Table 3.

Table 3. Effective Young’s modulus for polyester-based nanoclay nanocomposites with random particle orientation. E^L , E^{EXP} , E^{MT} and E^U are the Reuss lower bound, experimentally measured, Mori-Tanaka and Voigt upper bound values, respectively. The numbers in the parentheses show the percentages of the stiffness improvements in comparison to those of virgin polyester.

Effective stiffness	Nanoclay content (wt.%)		
	2	4	6
E^L (GPa)	3.67 (+2%)	3.74 (+4%)	3.82 (+6%)
E^{EXP} (GPa)	4.64 (+29%)	5.50 (+53%)	5.21 (+45%)
E^{MT} (GPa)	5.04 (+40%)	6.44 (+79%)	7.85 (+118%)
E^U (GPa)	5.65 (+57%)	7.74 (+115%)	9.79 (+172%)

As it can be seen from Table 3, the experimental values for 2 and 4 wt.% esterificated Cloisite® 15A are relatively close to that calculated with Mori-Tanaka model, which directly suggests that the nanoclay particles are relatively exfoliated, since that is the basic assumption in the modeling. The reason for the difference between the theoretical and the experimental results may be due to surface bonding effects which are not incorporated into the model in its present formulation. For higher volume fractions (e.g., 6 wt.%) the experimental values decrease and become much smaller than the theoretical predictions. This is most likely due to agglomeration of the particles and as a consequence the stiffness of the particles is not exploited to their full potential, thus not significantly increasing the effective stiffness of the composite. This has also been observed by⁵⁹⁻⁶¹ where the Young’s modulus decreased for volume fractions above 2-3%.

3.3.2 Ultimate tensile strength

Figure 10 shows the ultimate tensile strength (UTS) results which are generally decreasing with the addition of esterificated nanoclay. However, adding 2 and 4 wt.% of esterificated Cloisite® 15A leads

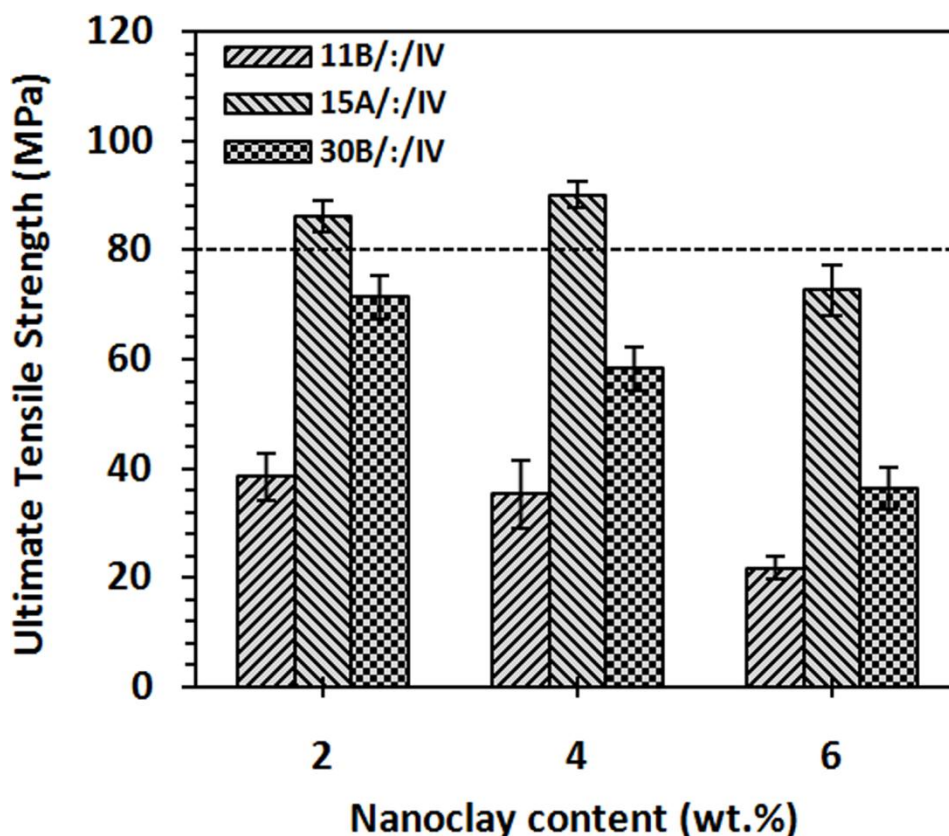
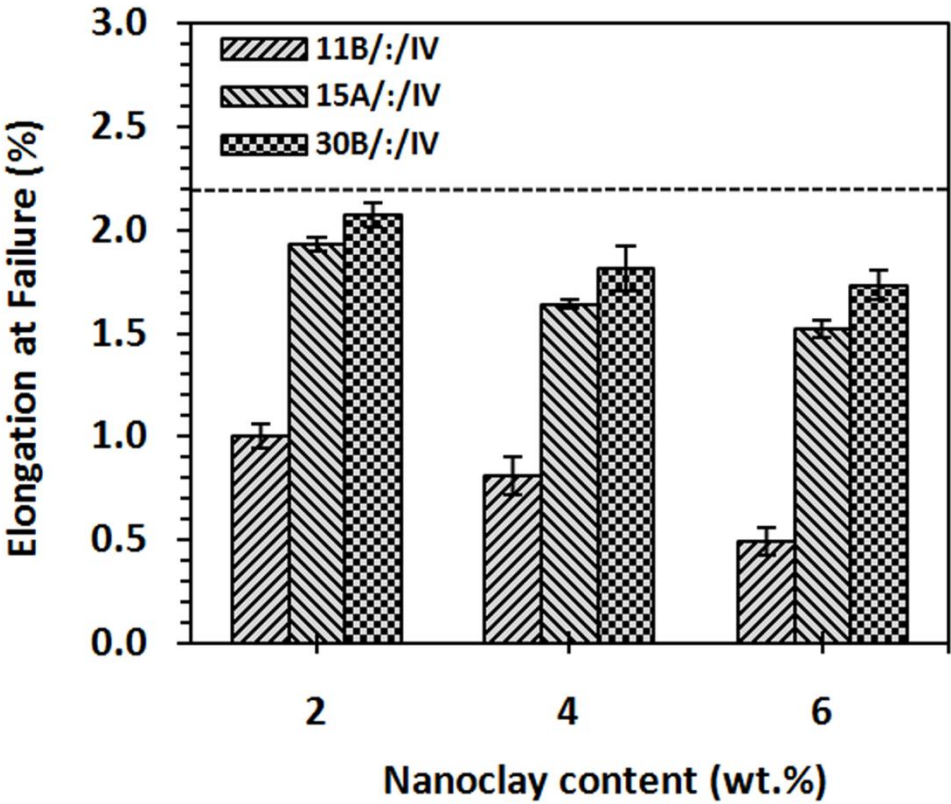


Figure 10. Experimental UTS values of polyester-based nanoclay systems having different esterificated nanoclay type and content. Dotted horizontal line represents the baseline value of the virgin polyester.

to 9% and 13% improvement in UTS, respectively. For 15A/6/IV system, the UTS reduces by 25% in comparison with 15A/4/IV which is believed to be attributed to the stiffening effect of adding further nanoclay leading to more brittle nanocomposites systems.

3.3.3 Elongation at break

The elongation at break is reported in Figure 11. The ductility of the nanocomposites is generally reduced with increasing the nanoclay content. Significant differences in failure elongations were observed for 30B/IV systems (: is a notation representing all the nanoclay contents tested) in comparison with those of 11B/IV and 15A/IV. For 15A/IV systems, ~ 31% more deterioration in failure strains was observed in comparison to that of 30B/IV which can be attributed to the higher aspect ratio of Cloisite® 15A after mixing, measured from TEM images (not shown).



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Figure 11. Experimental tensile test elongations at break of polyester-based esterificated nanoclay systems having different nanoclay type and content. Dotted horizontal line represents the baseline value of the virgin polyester.

3.4. Thermal properties

The CTE above and below T_g are provided in Figure 12 for the specimens prepared according to strategy IV (i.e., batch numbers 4, 9, 14, 19, 24, 29, 34, 39 and 44 in Table 1). The variation of T_g for nanocomposites with varying nanoclay type and content is also shown in Figure 13. For structural applications the CTE above T_g is not of much importance as by this point the load carrying capacity is considerably reduced. As a result, only discussions on CTE results below T_g are presented. Nonetheless, CTE values below and above T_g follow similar trends and thus the observations noted here are also valid for CTE values above T_g .

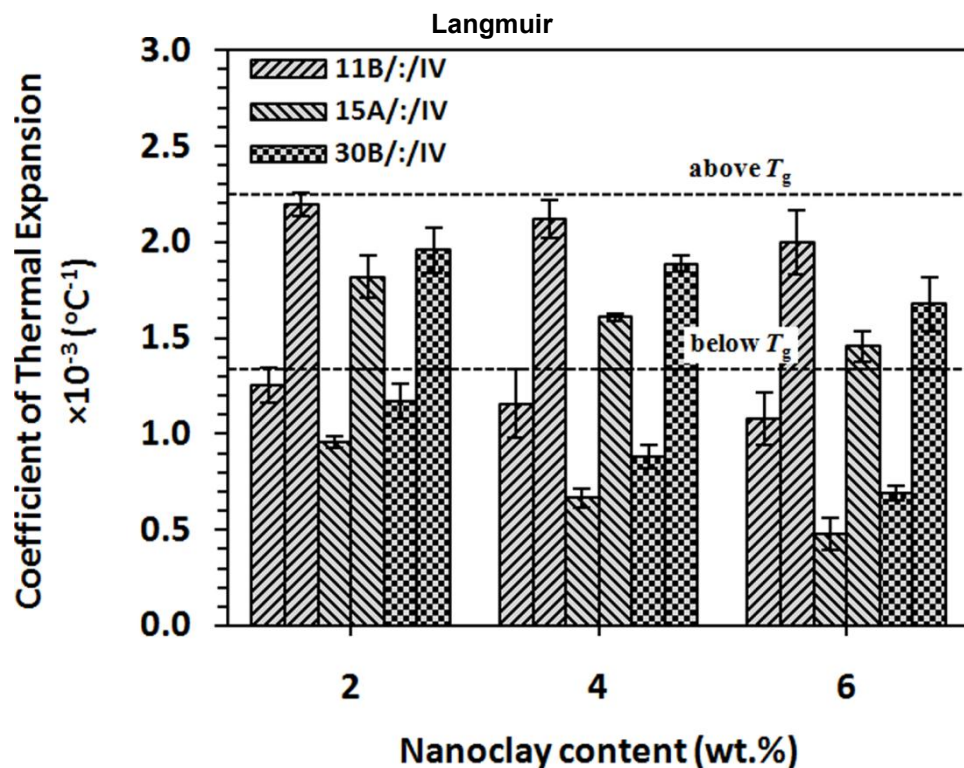


Figure 12. Variation of CTE below (left column) and above (right column) T_g of polyester-based nanoclay systems having different esterified nanoclay type and content. Dotted horizontal line represents the baseline values of CTE below and above T_g of the virgin

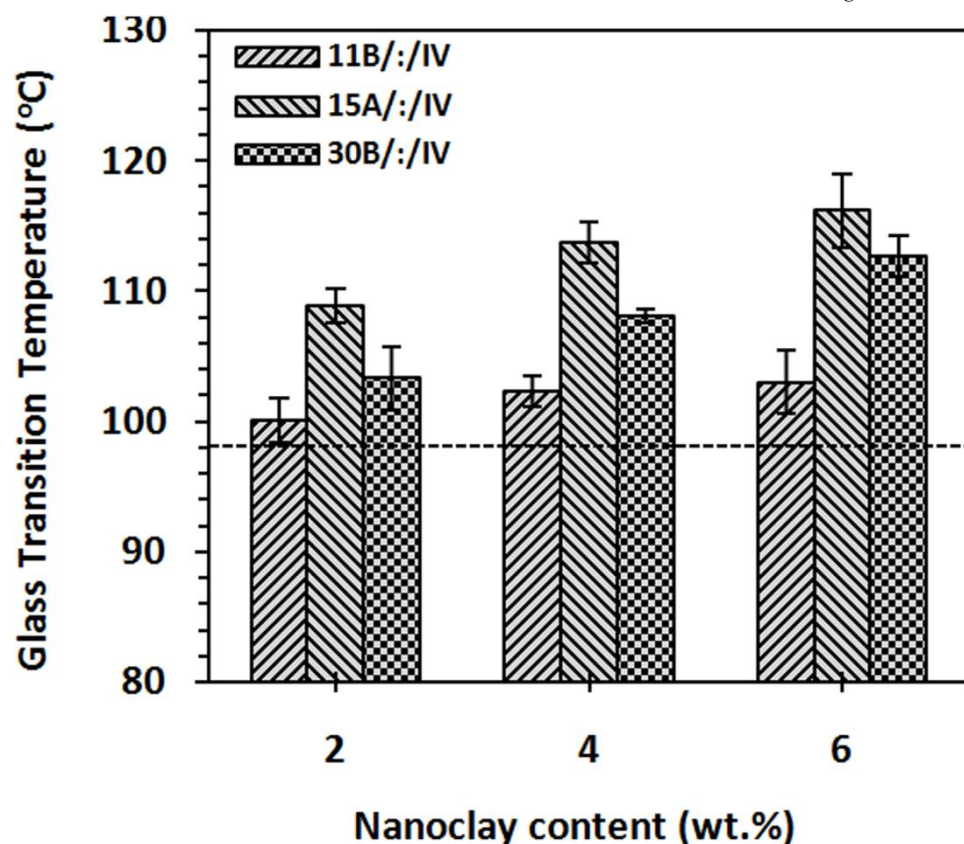


Figure 13. Variation of glass transition temperature (T_g) of polyester-based nanoclay systems having different esterified nanoclay type and content. Dotted horizontal line represents the baseline value of the virgin polyester.

The addition of nanoclay generally decreased the CTE of the polyester-based nanocomposite compared to that of plain resin. In general, the thermal properties (CTE and T_g) due to nanoclay addition were better than the corresponding neat resin values, specially for 15A/4/IV and 15A/6/IV systems with an improvement of up to 16 °C and 18 °C in T_g , respectively.

3.5. Moisture absorption

The moisture diffusivity coefficient D ,³⁹ was used as the parameter to assess the effect of nanoclay type and content and was computed from the initial slope of the moisture gain M_t/M_∞ versus time ($\sqrt{t}/d$) based on Fick's law:⁶²

$$D = \frac{\pi}{16} \left(\frac{M_t/M_\infty}{\sqrt{t}/d} \right)^2, \quad (6)$$

where M_t is the mass gain at any time t , M_∞ is the maximum mass gain at equilibrium/steady state, and d is the thickness of the specimen.

The diffusivity coefficient of all polyester-based nanocomposites obtained using the mixing strategy IV has been summarized in Figure 14. As for the thermal properties, esterificated nanoclay addition increased the barrier properties (i.e., reduced diffusivity). Overall, noticeable decrease in diffusivity of up to 370% was observed in 15A/4/IV and 15A/6/IV systems.

A diffusion model of intercalated nanoclays inside a polymer matrix was previously developed by Liu et al.,⁶³ by using a Fickian numerical model³⁹ and assuming that the nanoclays have been randomly oriented and uniformly dispersed inside the polymer as;

$$D^* = \frac{1}{\left(1 + \frac{2\zeta f_c}{3\pi n}\right)^2}, \quad (7)$$

where D^* is diffusivity ratio, i.e. diffusivity of nanocomposite to that of virgin polyester; ζ , f_c are the

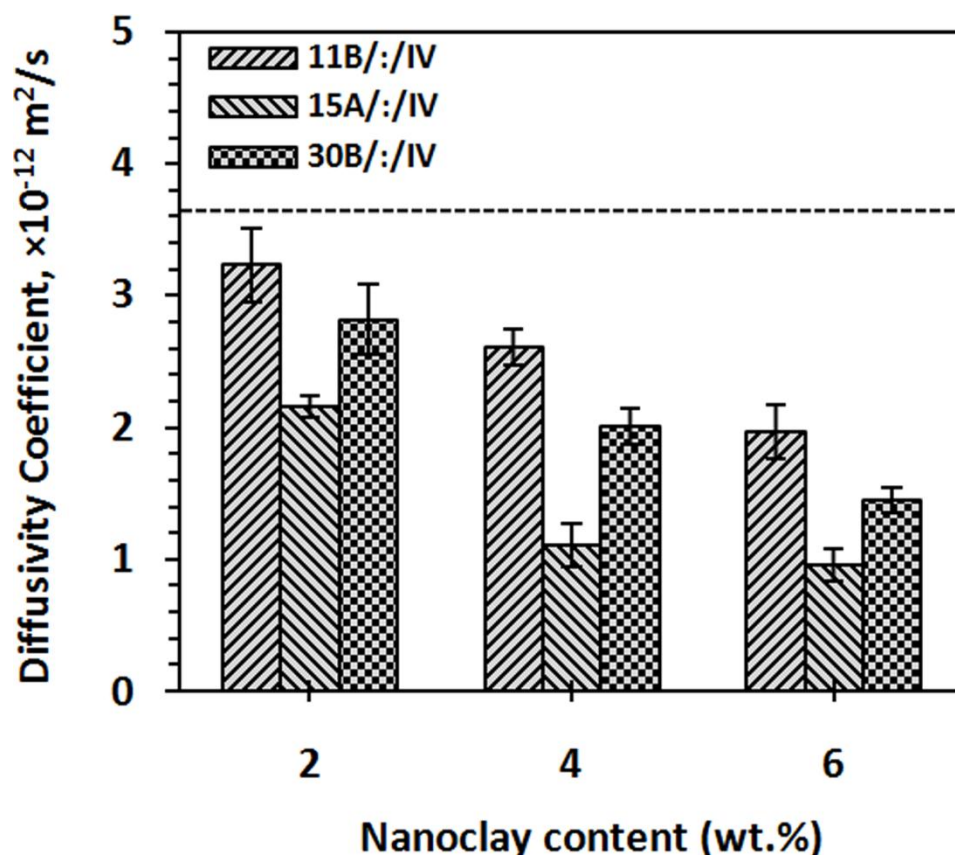


Figure 14. Experimental diffusivity coefficients of polyester-based nanoclay systems having different esterificated nanoclay type and content. Dotted horizontal line represents the baseline value of the virgin polyester.

aspect ratio and volume fraction of the nanoclays inside the matrix, respectively. n is the number of clay platelets in each agglomerate. Based on equation (7), D^* in nanoclay nanocomposites decreases with increasing the clay loading and the aspect ratio, while an increase should be expected when clay agglomerates inside the polymer matrix include higher number of platelets.

Curves based on the Fickian diffusivity model for intercalated nanocomposites have been plotted in Figure 15. As it can be seen, the experimental diffusivity values for esterificated Cloisite® 15A polyester-based nanocomposites prepared according to mixing strategy IV fall between the model prediction curves for nanoclays having either 1 or 2 clay platelets in agglomerates which confirms the fully exfoliated nanoclay structure as it was also observed from TEM images (Figure 6c-d). The

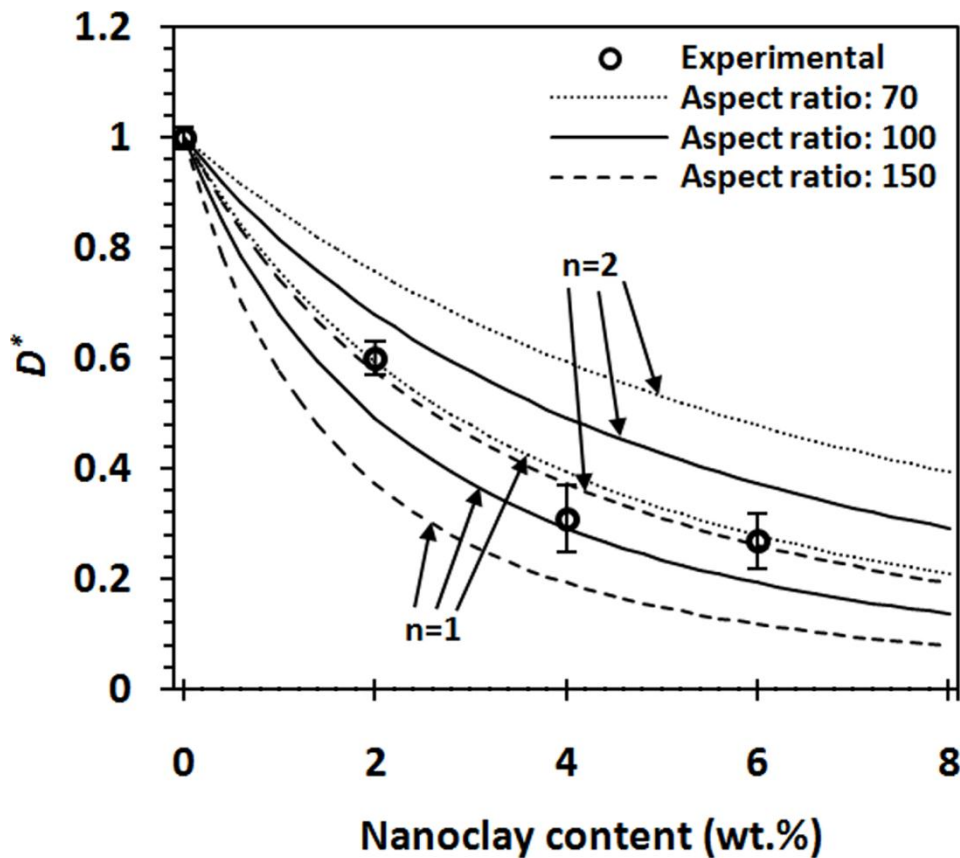


Figure 15. Diffusivity ratio (D^*) obtained by mixing strategy IV for esterificated Cloisite® 15A-polyester systems versus clay content, at 50 °C.

comparison among the experimental diffusivity measurements and those of theoretical estimations suggests a value between 100-150 for the aspect ratio of the nanoclays after performing several times three-roll mixing and ultrasonication. This is in the same aspect ratio range of nanoclays before mixing with polyester matrix suggesting the fact that during the mixing process no breakage in nanoclay structure occurred.

4. General Discussion

The experimental characterization of our different polyester-based nanoclay nanocomposites revealed that the combination of nanoclay type, surface treatment, content, and mixing strategies resulted in producing materials having superior, similar, or even inferior mechanical, thermal, and barrier properties in comparison with those of the virgin polyester matrix.

4.1. Surface treatment analysis

Clay platelets modified with ammonium ions carrying hydroxyl groups were surface reacted with long chain fatty acids in order to achieve enhancement in their basal plane spacing so as to achieve their shear induced exfoliation in the polymer matrices. The extent of surface reaction enhanced with increasing the amount of excess acid used for the reaction which subsequently increased the basal plane spacing. The XRD analysis showed an increase of the d -spacing of the Cloisite® 15A from 24.6 Å to 25.2 Å when suspended in acetone and to 29.9 Å for the alkyl chain grafted clays indicating a slightly exfoliated structure. The initial higher basal plane spacing of the surface treated clay platelets led to better swelling of the montmorillonite resulting in the enhancement of the basal plane spacing. FTIR diagram revealed the ionically bonding of high density brushes to the clay surface when the initial modification was optimal to generate higher extents of surface reaction.

4.2. Physical behavior characterization

The maximum stiffness for all nanocomposite systems were obtained when combined TRM and US were used (strategies IV and V). Strategies I, II, and III, generally led to a decrease in modulus up to 39% for 15A/4/I while an increase of 53% for 15A/4/IV. Moreover, the tensile modulus did not even follow similar trends for different types and contents of esterificated nanoclay. For example, a continuous increase in modulus was observed for 11B/IV systems by increasing the esterificated nanoclay content, while an inverse behavior for 30B/IV systems. On the other hand for 15A/IV, the maximum modulus was obtained when 4 wt.% esterificated nanoclay was added.

The tensile tests also revealed an overall reduction in ductility and strength due to the addition of nanoclay. The increase in strength up to 13% was only observed when 2 and 4 wt.% esterificated Cloisite® 15A was mixed according to strategy IV. The strength of 15A/IV systems decreased with an increase in the nanoclay content over 4 wt.% (i.e., 8% strength loss for 15A/6/IV system). A reduction of 55% in strength for 11B/4/IV in comparison to the gain of 13% for 15A/4/IV is attributed to the type

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of the surface modifiers used, suggesting esterificated Cloisite® 15A as a more suitable reinforcement for this type of the polyester-based nanocomposites. The reduced UTS values in 11B/IV and 30B/IV systems are believed to be due to the weaker nanoclay-polyester interface and consequently the creation of the nanoclay aggregates in the polyester matrix, which promotes microcrack formation and leads to the formation of nanocomposites having lower tensile strength and ductility. While there is no general consensus on this point of view, computational studies by Haq et al.⁶⁴ have shown evidence to this mechanism.

The CTE and the moisture diffusivity also showed a noticeable improvement of up to 270% and 370% for 15A/6/IV system which is due to choosing the right type and amount of esterificated nanoclay and mixing strategy. The addition of higher contents of esterificated nanoclay into polyester system generally resulted in nanocomposites with inferior thermal and barrier properties. The improvements in barrier properties could be explained by considering the physical aspects of the diffusion. During the diffusion process, the clay platelets act as impervious barriers to permeant molecules, thereby forcing a tortuous diffusion path that improves moisture barrier property. The use of a similar analogy for the CTE suggests that the expansion of the polymer network due to heat is higher than the restraining action provided by the nanoclay, which results in the nanoclay platelets moving along with the polymer under temperature expansion and consequently a decrease in CTE values which is considered as improvement in the thermal properties.

Although our experimental results showed that improvements in mechanical, thermal and barrier properties are possible for polyester-based esterificated nanoclay nanocomposites, the material composition that yields the best gain for a given property is different. Thus, when multiple properties are of interest, optimized material compositions that balance the improvements and detriments of the polyester system are needed.

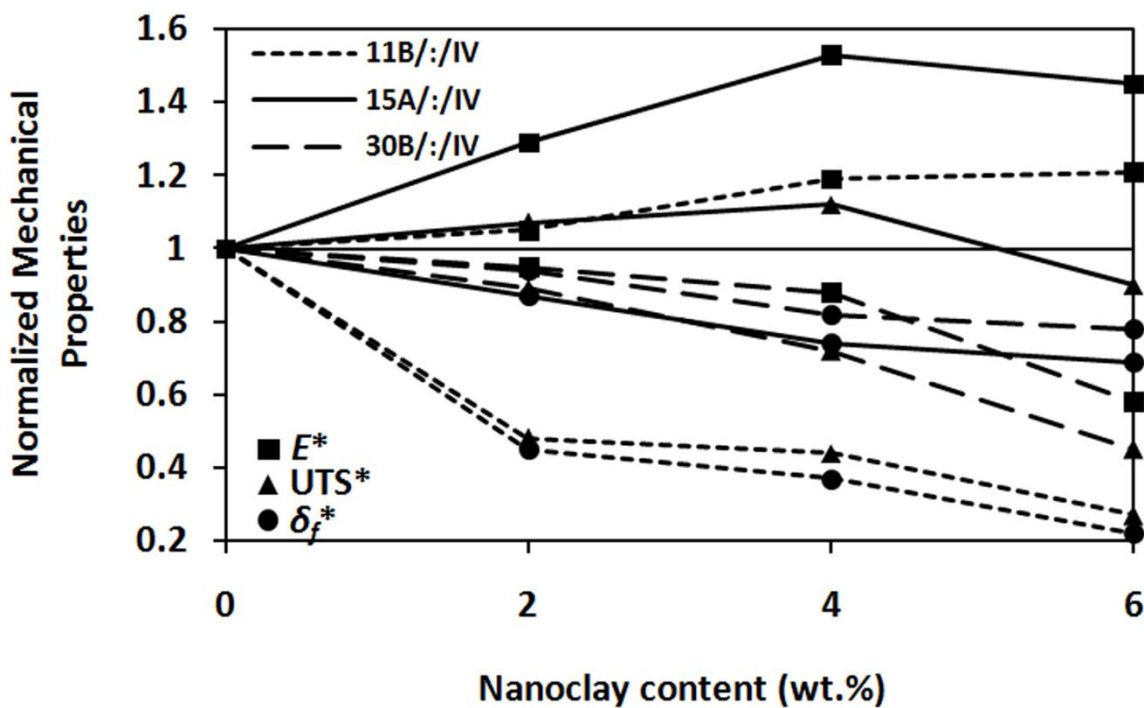


Figure 16. Normalized mechanical properties and identification of optimized material constituents.

Notation * shows the normalized property of the polyester-based nanocomposite relative to that of the virgin polyester.

4.3. Performance limits and optimized material design

Detailed experimental characterization of polyester-based esterified nanoclay nanocomposites with up to 6 wt.% of different types of esterified nanoclay allows obtaining performance limits of the resulting properties. Optimal material combinations that result in a balance of multiple properties, along with ease in processing are thus identified. According to the results obtained in this paper, esterified nanoclay reinforcement of more than 4 wt.% has generally little or sometimes negative effect on the mechanical properties of the nanocomposites. However, the thermal and barrier properties are continuously improving with the addition of esterified nanoclay up to 6 wt.%, ranking the samples having 6 wt.% of esterified nanoclay (:/6/IV) as the optimal designs.

Figures 16 and 17 show a comparison of mechanical properties such as stiffness (modulus, E),

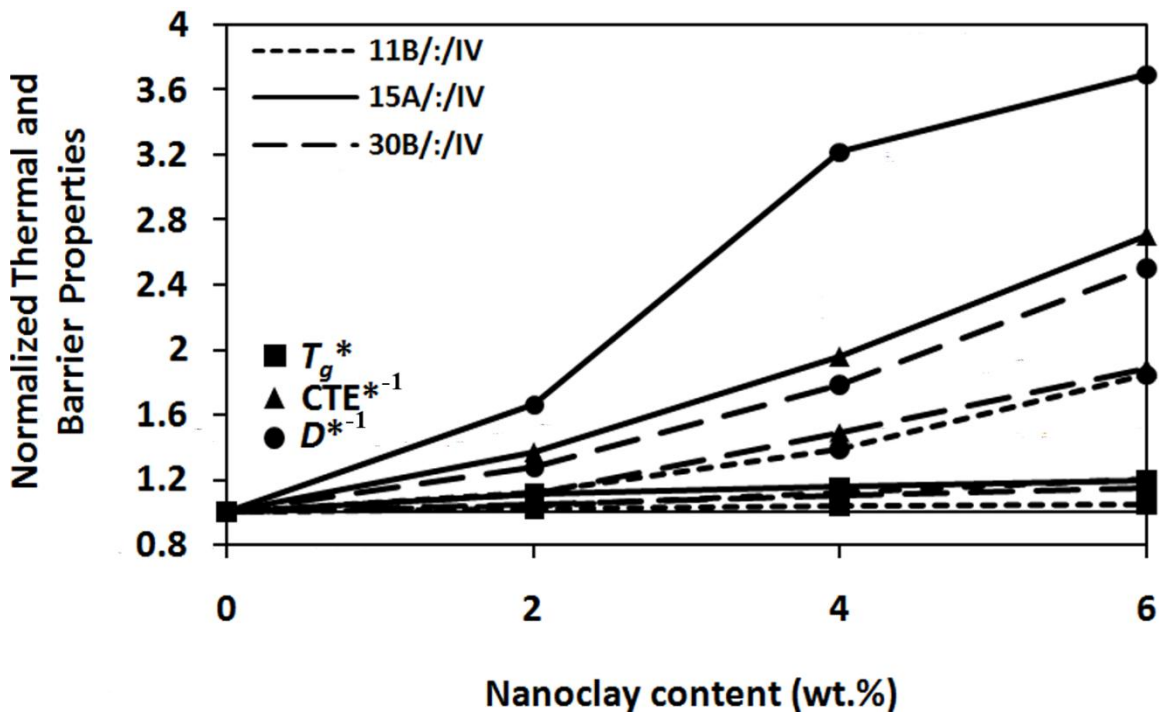


Figure 17. Normalized thermal and barrier properties and identification of optimized material

constituents. Notation * shows the normalized property of the polyester-based nanocomposite relative to that of the virgin polyester.

strength (UTS) and ductility (elongation at failure, δ_f), and thermal and barrier properties namely thermal stability (glass transition temperature, T_g ; coefficient of thermal expansion, CTE) and diffusivity (diffusivity coefficient, D). Notation * shows the normalized property of the polyester-based nanocomposite relative to that of the virgin polyester for mechanical properties and glass transition temperature. For the coefficient of thermal expansion and diffusivity, CTE^* and D^* are inversed resulting in values greater than unity to show improvements in all properties. The general trend for the values of stiffness and ductility confirms that the addition of esterificated nanoclay improves stiffness for 15A/IV and 11B/IV while reducing its ductility; however, in case of 30B/IV both stiffness and ductility decrease. It should be noted that the area of interest in Figures 16 and 17 is subjective and can be determined based on the target properties and the material application. If properties strictly better than the baseline polyester are desired, constituent concentrations that satisfy such requirements can thus be selected. Generally, when multiple opposing parameters are considered, material constituents

that reveal good balance without significant compromise on other properties are sought. Overall, 15A/4/IV and 15A/6/IV systems were identified as optimized material compositions as they show promise in their processing ease and balanced properties.

5. Conclusion

Results from this study indicate that various nanoclay types, surface treatments and contents can be mixed with polyesters in different ways to produce polyester-based nanocomposites with desired mechanical, thermal and barrier properties. This study aimed at finding an optimum mixing strategy of the proposed surface reacted nanoclays with polyesters based on the three-roll mill mixing, the ultrasonication, or a combination of both. It was shown that depending on the nanoclay type, surface treatment and mixing strategy, the addition of nanoclay into nanocomposites may improve mechanical (stiffness and strength) parameters and transient (thermal and moisture diffusion) properties; however it generally adds to their brittleness which could not be favorable. The efficiency of the nanoclay addition depends on many factors including the chemistry of the surface modifiers and their treatments, the mixing strategy selected, the nanoclay content and their level of dispersion. An extended experimental test matrix (up to 6 wt.% of three different kind of nanoclay along with five mixing strategies) with detailed characterization of mechanical and transient properties allowed obtaining the performance limits of these nanocomposite materials. Including ease of processing along with the resulting balanced or enhanced properties, polyester-based nanocomposites reinforced with 4 and 6 wt.% esterificated Cloisite® 15A were identified as optimal designs.

XRD analyses and TEM observations suggested the formation of exfoliated structures in 15A/2,4/IV systems. The Mori-Tanaka method was used to predict the effective stiffness of the 15A/2,4/IV nanocomposite systems which were in close agreement with those of the experimental values. Water diffusion behavior of polyester-nanoclay systems was found to follow very closely the Fickian behavior at 50 °C. As esterificated nanoclay was mixed into polyester according to strategy IV,

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diffusivity was improved about 370% at 6 wt.% clay loading. The model for diffusivity for 15A/2,4/IV predicted the platelets to contain either 1 or 2 sheets of clay (i.e., exfoliated structure) and this agreed well with TEM observations.

For 15A/4/IV system, the tensile modulus and strength were increased by 53% and 13% compared to those of virgin polyester. The maximum improvement in CTE and moisture diffusivity of 270% and 370% were obtained for 15A/6/IV system, respectively. Overall, the balanced behavior of the showcased polyester-based esterificated nanoclay nanocomposites shows promise for high-performance materials in automotive, transportation and packaging industry.

Acknowledgement

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Appendix A: a_{ij} coefficients as a function of the Euler angles

$$a_{11} = \cos(\theta)\cos(\varphi)\cos(\beta) - \sin(\varphi)\sin(\beta),$$

$$a_{12} = -\cos(\theta)\cos(\varphi)\sin(\beta) - \sin(\varphi)\cos(\beta),$$

$$a_{13} = \sin(\theta)\cos(\varphi),$$

$$a_{21} = \cos(\theta)\sin(\varphi)\cos(\beta) + \cos(\varphi)\sin(\beta),$$

$$a_{22} = \cos(\theta)\sin(\varphi)\sin(\beta) + \cos(\varphi)\cos(\beta),$$

$$a_{23} = \sin(\theta)\sin(\varphi),$$

$$a_{31} = -\sin(\theta)\cos(\beta),$$

$$a_{32} = \sin(\theta)\sin(\beta),$$

$$a_{33} = \cos(\theta).$$

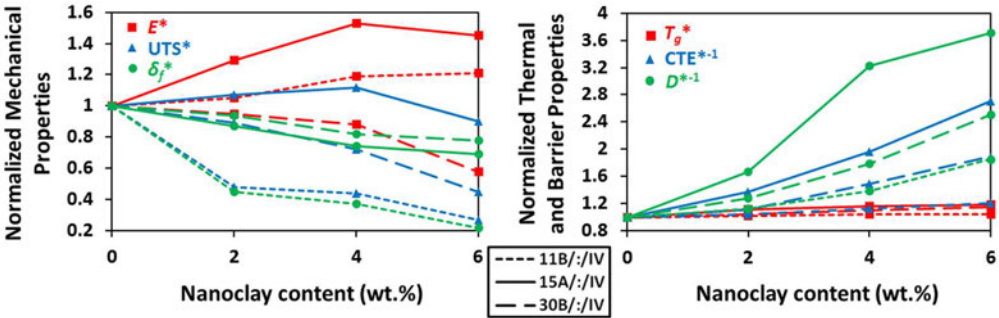
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Performance limits and optimized polyester-clay nanocomposite design

442x158mm (300 x 300 DPI)