



# Modification of montmorillonite by quaternary polyesters

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## Abstract

In this paper, we report on the preparation of organically modified montmorillonite (OMM) and its properties, using quaternary polyesters. The polyester was synthesized from *N*-methyldiethanolamine and succinic acid anhydride, converted to the quaternary polyester using benzyl bromide, and characterized by nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Quaternary polyesters with a quaternization degree of 0.25 and 0.5 were used to modify montmorillonite (MMT). The intercalation was determined by X-ray diffraction. Interlayer spacing increased with decreased MMT/polyester ratio and with increased degree of quaternization. The thermal stability of polyester bound to MMT greatly increased.

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## 1. Introduction

Polymer/clay nanocomposites have been the subject of extensive research for the last 15 years. The efficiency of clay nano filler on the mechanical and thermal properties, gas barrier, decreased flammability, etc. of the polymer depends on the intercalation or exfoliation of clay platelets within the polymer matrix [1–4].

Montmorillonite (MMT) is a layered aluminosilicate mineral most often present in clays and most often used in polymer nanocomposite preparation. The surface of MMT is hydrophilic and therefore not suitable for preparation of nanocomposites with most of commercial polymers. To ensure good intercalation the surface of MMT platelets has to be modified. There are several ways of modifying MMT but the most common method is a cation

exchange with organic ammonium salts, which differ in a number, length and structure of long chains [5]. Quaternary ammonium salts or amine hydrochlorides, having one or more long alkyl chains bound to amine, are most commonly used [6,7]. The role of the modification of MMT with ammonium salts is to increase the interlayer spacing, reduce interactions between the MMT platelets, and improve the interaction between the clay and the polymer matrix. When a proper combination of modifier and polymer is chosen, fully exfoliated nanocomposites can be obtained, otherwise only intercalation of polymer chains within the clay platelets is observed [8]. The interlayer spacing in intercalated nanocomposites also depends on the type of modifier, which strongly influences the nanocomposite's mechanical properties [9]. In our previous studies montmorillonite was modified by octadecylammonium, poly(oxypropylene)diamine, and liquid crystalline diol hydrochlorides [10–12].

Polycations have also been used as a clay modifier for decades [13,14]. Polycation-modified clay is sufficiently

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organophilic to enable hydrocarbon and other pollutants removal from industrial waste water [15,16]. They can also be used as coagulants in drinking water treatment and as catalysts [17,18].

When polycation is mixed with dispersion of clay in water the polycations are adsorbed on clay via coulombic interactions between the cationic groups on the polymer and the negatively charged clay surface. It is generally accepted that there is an instantaneous collapse of the polycation onto the clay surface and that the adsorption is essentially irreversible. The process of desorption requires simultaneous desorption of all the 'train' segments (parts of macromolecule in intimate contact with the surface) and the diffusion of the polycation away from the clay surface into the solution, which is unlikely especially when the polycation is positioned within the galleries [19]. The influence of polymer molar mass and cationicity ( $\tau$ ) has been extensively studied. It has been observed that the amount of absorbed polymer ( $Q$ ) increases with increasing molar mass when cationicity is low. However, when the molar mass is fixed and the cationicity is varied, then the  $Q$  decreases with increasing cationicity [20,21].

MMT can also be modified with cationic polyelectrolytes by the polymerization of organic ionic molecules in the presence of MMT. It has been observed that MMT dispersed in water increases the rate of polymerization of protonated 4-vinylpyridine, favors 1,6 polyelectrolyte formation, and leads to the formation of an exfoliated nanocomposite [22].

Polycation-modified clays have been extensively studied as adsorbents for organic pollutants [15,16]. To our knowledge polycation-modified MMT has not often been used as a filler in the preparation of polymer/MMT nanocomposites. The most probable reason for this is the hydrophilicity of the polycations, thus it is unlikely that they would interact with a hydrophobic polymer, leading to intercalation or exfoliation. Only copolymeric oligomers with quaternary ammonium have been used [23,24].

Polycations can be prepared from, among other methods, derivatives of diethanol amine, which have been used in the synthesis of mesogenic or liquid crystalline polyesters [25] and polyurethanes [26,27]. Polyester hydrochlorides have also been formed but no synthesis of quaternary polyesters has been reported up to the present [28].

The goal of our work is twofold. First is the synthesis of a diethanolamine-based polyester and its partial quaternization. Second is the modification of MMT with the synthesized quaternary polyesters in order to obtain organically modified MMT (OMM). These, with pendant, preferably non-quaternized polyester chains, will be further used to prepare the unsaturated polyester/MMT nanocomposites, which are under investigation. It is hypothesized that such OMM with similar chemical structures of the non-quaternized part of polyester and the unsaturated polyester could improve interactions between the resin and MMT leading to improved intercalation and improved physical and mechanical properties as compared to nano-

composites prepared with MMT modified with alkyl ammonium salts.

## 2. Experimental

### 2.1. Materials

The clay Sokolac was provided by Glinara Kutina, Croatia. Succinic anhydride, *N*-methyldiethanolamine, benzyl bromide and acetone (Aldrich) were used as received.

### 2.2. Polymerization

Thirty grams of succinic anhydride and *N*-methyldiethanolamine (MDEA) were mixed in a molar ratio 1:1.03. The mixture was flushed with nitrogen and heated to 150 °C for 2 h. The temperature was then raised to 180 °C. After 1 h a vacuum was applied and the pressure was set to 25 mbar. The reaction proceeded under vacuum for 3 h. The polyester was then cooled to room temperature and analysed.

### 2.3. Synthesis of quaternary polyesters

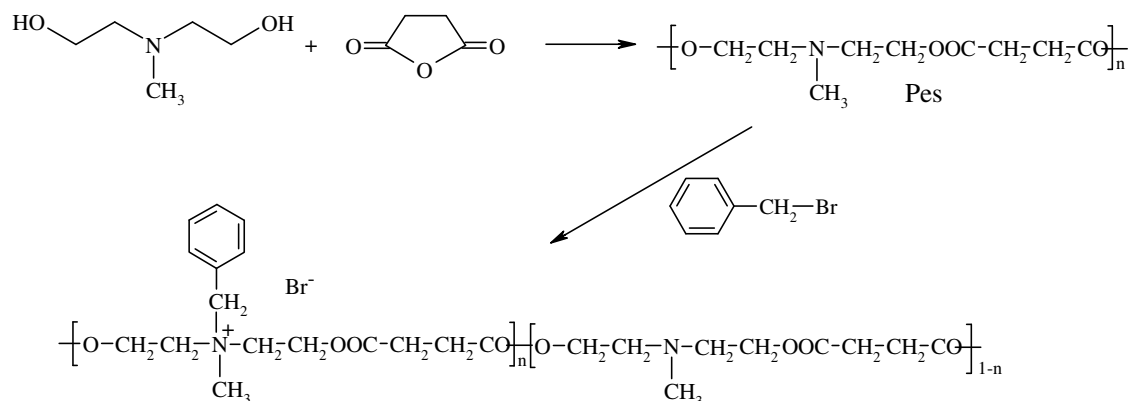
Polyester (25 g) was dissolved in a mixture of 25 g ethanol and 25 g of acetone, mixed with a magnetic stirrer and heated to reflux. Benzyl bromide (BB) was added in a molar ratio polyester (nitrogen): BB = 1:0.25 (Pes A) or 1:0.5 (Pes B) with a syringe through a rubber septum. The reaction proceeded for 4 h and the disappearance of BB was followed by thin layer chromatography (TLC). The solvents were removed on a rotatory evaporator, the polyesters were then dried in vacuum at 90 °C and analysed. The reactions are depicted in Scheme 1.

### 2.4. MMT preparation and modification

Montmorillonite clay was purified by sedimentation and converted to a Na-montmorillonite (Na-MMT) form with a diluted NaCl aqueous solution. The cation exchange capacity (CEC) was determined by ammonium acetate method to be 84 meq/100 g. To modify Na-montmorillonite, stoichiometric (1:1; were labeled A1 and B1) and non-stoichiometric amounts (1:1.5; A2 or B2; 1:0.5 A3 or B3) of the resins A or B, calculated from the CEC, were used. Cation exchange proceeded in a mixture of water and ethanol (50/50). These suspensions were stirred using a magnetic stirrer for 24 h at 75 °C. The solid phases of ion-exchanged montmorillonite were separated by centrifugation. The separated solid phases were then washed four times using distilled water and finally air-dried at 40 °C for 1 day.

### 2.5. Characterization

X-ray diffraction measurements (XRD) were performed using a Philips PW 1830 X-ray diffractometer with Cu K $\alpha$



Scheme 1. Polyesterification of *N*-methyl diethanolamine with succinic acid (Pes) and quaternization of the polyester with benzyl bromide;  $n = 0.25$  (Pes A),  $n = 0.5$  (Pes B).

radiation ( $\lambda = 0.154$  nm) and vertical geometry, operated at 40 kV and 30 mA. Diffraction measurements were conducted within the range of  $5$ – $10^\circ$ , at a scanning rate of  $0.02^\circ$ .

Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer thermobalance TGS-2. Samples of about 15 mg were heated from room temperature to  $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in a synthetic air flow of  $150\text{ cm}^3/\text{min}$ . Nuclear magnetic resonance  $^1\text{H}$  NMR spectra were recorded at  $25^\circ\text{C}$  on a Varian Unity Inova-300 spectrometer using  $\text{CDCl}_3$  as the solvent and TMS as the internal standard.

Average molar masses and molar mass distributions were determined by Size exclusion chromatography combined with multi-angle light scattering (SEC-MALS) using a Hewlett Packard pump series 1100 coupled to a Dawn Heleos laser photometer (658 nm) and to an Optilab rEX refractometer. An AM Polymer Standards column with AM GPC gel with a particle size of  $5\ \mu\text{m}$  was used.  $0.05\ \text{M}\ \text{CF}_3\text{COONa}/\text{THF}$  was used as an eluent with a flow rate of  $1\text{ cm}^3/\text{min}$ .

Thermal properties were determined using a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC). The samples were heated twice and subsequently cooled over a temperature range from  $-10$  to  $150^\circ\text{C}$ . Heating and cooling rates were  $10^\circ\text{C}/\text{min}$ .

The quantity of Br in quaternary polyesters and modified MMT was determined by ionic chromatography (IC).

### 3. Results

The polyester synthesized from MDEA and succinic acid anhydride is of light brown color. The molar mass of the polyester is  $M_n = 11.000 \pm 300$ , with a polydispersity index 1.45. The structure of polyester and quaternary polyesters was confirmed by NMR spectroscopy.

The  $^1\text{H}$  NMR spectrum of the polyester shows the following characteristic signals: 4.07 ppm (t, 4H,  $\text{CH}_2$  groups of succinic acid), 2.4–2.7 ppm (m, overlapped with

$\text{DMSO}_{d6}$ ,  $\text{CH}_2$  groups of MDEA), 2.24 ppm (s, 3H,  $\text{CH}_3$  group of MDEA). There are some small signals at 3.0–3.6 ppm, which belong to the  $-\text{CH}_2-\text{OH}$  end groups or side products. The small broad signal at 5.2 ppm belongs to  $-\text{OH}$  end groups, while there was no signal for the  $-\text{COOH}$  end groups in the region near 10 ppm. The NMR spectra of the quaternary polyesters are much more complex and were assigned with the help of 2D proton NMR and a model compound prepared from *N*-methyl diethanolamine and acetic anhydride: 7.5–7.7 ppm (m, aromatic protons of benzyl), 4.70 ppm (s,  $\text{CH}_2$  group of benzyl), 4.55 ppm (t,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{O}$ ), 3.9 ppm (t,  $\text{CH}_2$  groups of succinic acid), 3.8–3.6 (m,  $\text{N}-\text{CH}_2-$ ), 3.01 ppm (s,  $\text{N}-\text{CH}_3$ ).

The quantity of bromine determined by IC shows good agreement with calculated values (Table 1).

Polyester and both quaternary polyesters are viscous liquids at room temperature. On cooling they exhibit a glass transition ( $T_g$ ). The glass transition temperature is the lowest for the non-quaternized polyester and increases with the degree of quaternization from  $-41^\circ\text{C}$  (Pes) to  $15^\circ\text{C}$  (Pes B) (Table 2). Benzyl bromide when bound to Pes reduces the flexibility of the polymer chain due to high polarity of ionic quaternary groups formed and steric interactions introduced with its size [29].

The cation exchange in MMT by quaternary polyesters was proved by XRD. Fig. 1 shows the comparison of XRD spectra of Na-MMT and MMT modified with Pes B in a different MMT/Pes B ratio. Similar diffractograms to those shown in Fig. 1 were obtained with Pes A.

Diffraction maximum for Na-MMT is located at  $2\theta = 6.97^\circ$  which is equivalent to basal spacing  $d_{001}$  of 1.30 nm (calculated according to the Bragg equation). By

Table 1  
Quantity of bromine ions in quaternary polyesters

Polyester	Quantity of $\text{Br}^-$	
	Determined (%)	Calculated (%)
Pes A	$8.6 \pm 0.2$	8.2
Pes B	$13.2 \pm 0.1$	13.9

Table 2  
Thermal properties of polyester and partially quaternized polyesters

	Pes	Pes A	Pes B
$T_g$ (°C)	$-41 \pm 1$	$-24 \pm 1$	$15 \pm 1$

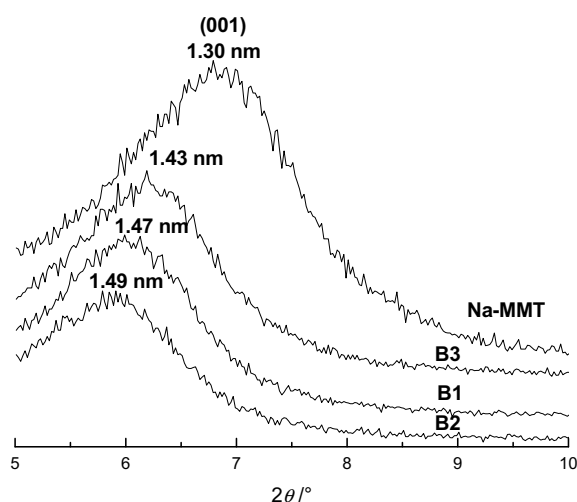


Fig. 1. XRD patterns of montmorillonite, Na-MMT, and organically modified montmorillonite with Pes B: B1, B2 and B3.

subtracting the thickness of the silicate layer of montmorillonite, which equals 0.96 nm, the layer distance ( $\Delta d$ ) of 0.34 nm was calculated. In Table 3 the basal spacing values and the layer distances for all investigated systems are summarized. As expected, the smallest interlayer spacing and therefore the lowest intercalation was observed when a less than stoichiometric ratio (1:0.5) was used, and the highest when a more than stoichiometric ratio was used (1:1.5).

The decomposition behavior of all samples was examined by TGA analysis as shown in Fig. 2. In Table 4 the mass loss associated with different temperature ranges and events are summarized. The mass loss below 200 °C is assigned to the loss of water residing between montmorillonite crystallites. [30] In comparison to the unmodified montmorillonites, the OMMTs are characterized by lower mass loss in the mentioned temperature range, indicating that OMMTs are less hydrophilic than Na-MMT. Although an OMMT is conventionally considered hydro-

Table 3  
Basal spacing and layer distance of OMM prepared with Pes A and Pes B at different MMT/quaternary polyester ratios

Sample name	Ratio MMT/Pes	Basal spacing $d_{001}$ (nm)	Layer distance $\Delta d$ (nm)	Weight loss (%)
Na-MMT		1.30	0.34	
A3	1: 0.5	1.40	0.44	18.4
A1	1: 1	1.41	0.45	19.6
A2	1: 1.5	1.47	0.51	20.1
B3	1: 0.5	1.43	0.47	19.9
B1	1: 1	1.47	0.51	22.5
B2	1: 1.5	1.49	0.53	24.3

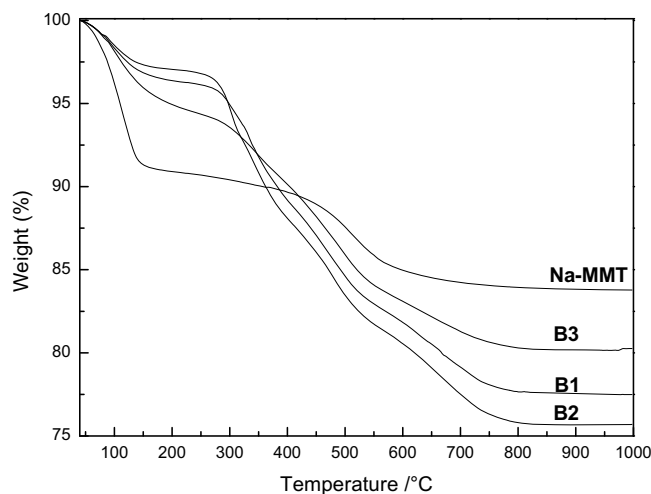


Fig. 2. TGA curves for montmorillonite, Na-MMT, and organically modified montmorillonite with resin B: B1, B2 and B3.

Table 4  
Results of weight loss during decomposition of investigated samples

Sample	Total weight loss (40–1000 °C) (%)	Water (<200 °C) (%)	Polyester (%)
MMT	16.2	9.1	–
A3 (1:0.5)	18.4	6.6	4.9
A1 (1:1)	19.6	4.7	8.1
A2 (1:1.5)	20.1	4.0	9.3
B3 (1:0.5)	19.9	5.1	8.1
B1 (1:1)	22.5	3.6	12.3
B2 (1:1.5)	24.3	3.0	14.9

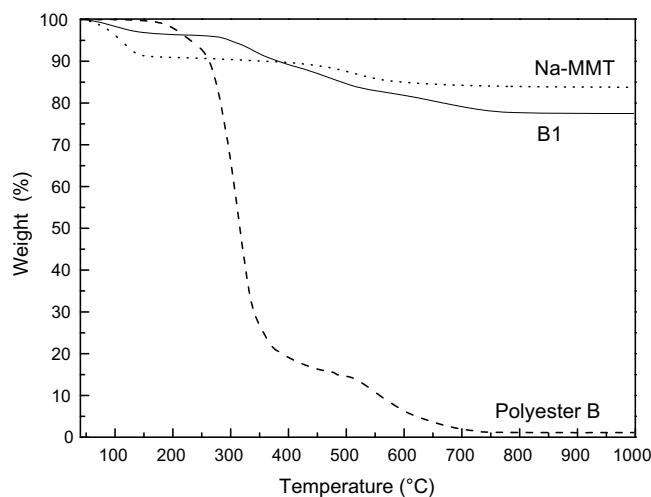


Fig. 3. A comparison of the decomposition of a quaternary polyester, before and after the incorporation into MMT.

phobic water absorption still occurs on the exterior of the aggregates and along the hydrophilic layer edges and depends on environmental conditions, such as relative humidity. [31] In this instance, approximately 3–5 wt% water is contained in the OMMTs. Between 400 and

700 °C, dehydroxylation of the aluminosilicate occurs. [31] In general, all of the OMMTs decompose in similar fashion. At temperature between 260 and 550 °C, the organic constituent (polyester) in the OMMT decomposes. TGA analysis was performed on both neat polyesters as well. The decomposition of polyester B, Na-MMT and MMT modified with polyester B is compared in Fig. 3.

TGA analysis also showed an increase in thermal stability of polyester resin when bound to MMT. Decomposition of polyester B starts at approx. 150 °C, while the decomposition of polyester A starts at approx. 175 °C. Above 300 °C resin A decomposes faster and quantitatively (100%) while resin B decomposes up to 99%. When the resin is intercalated between MMT sheets the degradation starts at approx. 260 °C, which is 100 °C higher than the pure resin. Similar results were observed in MMT modified with alkyl-imidazolium salts. The enhancement in the thermal stability of imidazolium compounds after being intercalated into montmorillonite showed the dramatic increase in the thermal stability of dimethyl hexadecyl-imidazolium-intercalated montmorillonite as compared to the dimethyl hexadecyl-imidazolium chloride and bromide salts, which may be due to the removal of the halide effect [32].

#### 4. Discussion

Partially quaternized polyesters were successfully used for MMT modification which was confirmed by XRD. The interlayer spacing increased with modification. Increased interlayer spacing can lead to improved intercalation in the preparation of nanocomposites, which usually leads to improved properties as compared to pure polymers or classical composites. On the other hand, modification of Na-MMT is performed in order to reduce the hydrophilicity of Na-MMT, which leads to increased interaction with non-polar polymers. This goal can not be reached if an excess of polycation (which is hydrophilic) is used. We can assume that excess of ionic parts of the macromolecule may reduce the compatibility with non-polar polymers, leading to pore intercalation of polymers during the nanocomposite preparation. Since the quaternary nitrogen atoms are randomly distributed on the macromolecular chain there is a possibility that a part of the molecule is bound to MMT and that there are other quaternary atoms still free. This would be unwanted since quaternary atoms increases hydrophilicity of modified MMT. Therefore, the quantity of bromine atoms was determined for samples A2 and B2. It appears that the quantity of bromine is less than the detection limit of the method (0.1 mg/g), which means that most, if not all macromolecules are bound by all quaternary centers to the MMT.

Increasing interlayer spacing with a decreased Na-MMT/polyester ratio and with increased quaternization (resin B compared to resin A) indicates an increased quantity of bound polyester onto the MMT platelets, which was

confirmed by TGA. The quantity of bound resin A under the same conditions is less than resin B. Even when the interlayer spacing is the same (B1, A2) the quantity of resin A is smaller. Assuming that the number of exchanged cations is the same, this can be explained by the lower molar mass of resin A due to the smaller number of bulky benzyl groups.

#### 5. Conclusions

The polyester was synthesized from methyl diethanolamine and succinic anhydride and transformed to a quaternary polyester using benzyl bromide. The degree of quaternization was 25 and 50 molar percent. All polyesters are amorphous with a glass transition temperature that increases with increasing benzyl bromide content. Quaternary polyesters were successfully used for MMT modification performed in a water/ethanol mixture. Stoichiometric and non-stoichiometric amounts of the quaternary polyester calculated from the CEC, were used. Interlayer spacing increased with decreased MMT/polyester ratio and with increased quaternization. The thermal stability of the polyester resin when intercalated between MMT sheets is greatly increased.

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