



Research paper

Properties of epoxy and unsaturated polyester nanocomposites with polycation modified montmorillonites



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ABSTRACT

Polyesters (P) based on N-alkyldiethanolamines (alkyl being octyl, ODEA; dodecyl, DDEA; or hexadecyl, HDEA) and succinic acid anhydride were synthesized and transferred to polyester hydrochlorides (P-HCl) by the addition of HCl. They were used for modification of mineral montmorillonite (Mt). It was assumed that one part of the P-HCl molecule exchanged sodium cations from the interlayer spaces, while the other part was subsequently unprotonated with water. This part of the macromolecule should be better miscible with polymers of similar polarity, such as unsaturated polyesters (UP) and epoxides (E), than quaternary ammonium salts. Molar ratio Mt:P:HCl was 1:3:3 or 1:3:1.5 in accordance with Mt cation exchange capacity. The d-values of Mt, modified with polyesters P-ODEA, P-DDEA and P-HDEA, were 1.80 nm, 3.65 nm, and 4.12 nm, respectively, and they were independent of HCl ratio.

Unsaturated polyester and epoxy resin nanocomposites with 1%, 3%, and 5% of modified Mt were prepared and characterized by dynamic mechanical analysis (DMA), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). The storage modulus increases with the increasing Mt content, and it decreases with the length of alkyl side chain in modifying polyester, indicating a plasticizing effect of the long alkyl chain, which is supported also by the decrease of glass transition temperatures. The thermal stability of the clay polymer nanocomposites (CPN) is the same as that of the neat resin for unsaturated polyester and deteriorates for epoxy nanocomposites.

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1. Introduction

Clay/polymer nanocomposites (CPN) have attracted great interest from academic and industrial researchers, since by adding a small amount of clay (3–5%) they frequently obtain improvements in many properties compared to neat polymers, including increased strength, moduli, and thermal stability and decreased thermal expansion coefficient as well as reduced gas permeability (Alexandre and Dubois, 2000; Ray and Okamoto, 2003).

The surface of the Mt layers is hydrophilic and therefore has to be modified to ensure good interaction with mostly hydrophobic conventional polymers. The most common method of Mt modification is a cation exchange with organic ammonium salts containing different numbers, lengths and structures of organic chains (Bergaya and Lagaly, 2001).

Beside cations, polycations have also been used for Mt modification. Mt can be modified by polycations using two synthetic approaches: by

cation exchange (Mabire et al., 1984) or by polymerization of monomeric ionic molecules in the presence of Mt (Fournaris et al., 2001). Polycation modified clay minerals have been extensively studied as catalysts (Breen and Watson, 1998a; Adams and McCabe, 2006) or adsorbents for organic pollutants (Breen and Watson, 1998b; Churchman, 2002; Churchman et al., 2006), while the possibility of their use for CPN preparation has not been extensively studied. Intercalated CPN have been prepared from pristine Mt and copolymers of methyl methacrylate with a quaternary ammonium salt having an acrylic group and a subsequent cation exchange in acetonitrile (Biasci et al., 1994). In other experiments, mostly oligomers (Costache et al., 2006) or amine terminated polymers were used for clay modification and CPN preparation (Hoffmann et al., 2000; Wang et al., 2003; Zhang et al., 2008). Burmistr et al. (2005) reported the preparation of CPN based on Mt modified with polymeric quaternary ammonium salt. A strong increase in tensile strength, impact strength and thermal stability were observed in polyamide 6 and polystyrene.

Polycations can be prepared as polyester hydrochlorides (P-HCl) from polyesters based on alkyl derivatives of diethanolamine ((R-N-C₂H₄OH)₂ ADEA). It was observed that P-HCl can easily be transformed

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to polyester by the simple extraction of HCl with water and vice versa (Huskić and Žigon, 2003; Šebenik et al., 2012).

The purpose of this study was to use polyester hydrochlorides for modification of Mt and subsequent CPN preparation. It was assumed that one part of the P-HCl molecule exchanged sodium cations from the interlayer spaces, while the other part was subsequently unprotonated with water. This part of the macromolecule should be better miscible with polymers of similar polarity, such as unsaturated polyesters (UP) and epoxides (E), than quaternary ammonium salts. Better miscibility would lead to enhanced intercalation and consequently improved physical and mechanical properties of CPN. The effect of polymers' side chain length, cation exchange ratio and amount of organoclays on the morphology and mechanical and thermal properties was determined.

2. Experimental

2.1. Materials

The pristine montmorillonite (Mt) Nanofil 757, cation exchange capacity ((CEC) = 85 meq/100 g) was donated by Rockwood clay additives GmbH, Germany. Other chemicals were obtained from Aldrich and used as received.

The synthesis of N-alkyl diethanolamines (alkyl being octyl, ODEA; dodecyl, DDEA; or hexadecyl, HDEA) and polyesters P-ODEA, P-DDEA, and P-HDEA is described elsewhere (Šebenik et al., 2012). The molecular structure of polyesters and polyester hydrochlorides is presented in Scheme 1.

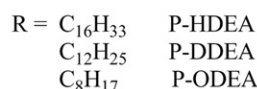
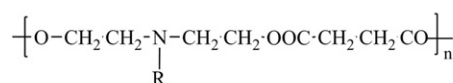
All chemicals needed for synthesis were purchased at Sigma-Aldrich and used as received.

The epoxy resin for infusion L 1100 (epoxy equivalent = 192) and the amine-based curing agent EPH 294 were products of R&G Faserverbundwerkstoffe GmbH, Waldenbuch, Germany. Unsaturated polyester, Colpoly 7201, was a product of Helios, Domžale, Slovenia. It is based on orthophthalic acid and propylene glycol with 40% of styrene.

2.2. Mt modification

Mt was modified by polyester hydrochloride by cation exchange using two molar ratios of Mt:P:HCl, 1:3:1.5 and 1:3:3 (quantity of P in mmol of nitrogen atoms) and HCl is defined according to Mt CEC as follows.

5 g of Mt (4.25 mmol cations) and 130 ml of demineralized water have been mixed together at 60 °C for 3 h. Polyester hydrochloride (P-X-HCl; X = H, D, or O for hexadecyl, dodecyl, and octyl) has been prepared by dissolving polyester (12.75 mmol nitrogen atoms) in 100 ml of HCl_(aq) (6.38 or 12.75 mmol HCl) at 60 °C. P-X-HCl was added to Mt and mixed by using a magnetic stirrer for 21 h at 70 °C. Then the product was filtered and washed several times with demineralised water until there was no reaction of AgNO₃ with chlorine ions. After drying at 60 °C to constant mass, the modified Mt was milled to a particle size of less than 50 μm. Mt modified by polyesters P-HDEA, P-DDEA and P-ODEA and a lower amount of HCl were designated as H1.5, D1.5 and O1.5 respectively (ratio Mt:P:HCl = 1:3:1.5) and Mt with a higher amount of HCl (ratio Mt:P:HCl = 1:3:3) as H3 (P-HDEA), D3 (P-DDEA) and O3 (P-ODEA), respectively (ratio Mt:P:HCl = 1:3:3).



2.3. Extraction of modified Mt

To determine the quantity of unbound polyester, the modified Mt were extracted with acetone by Soxhlet extraction for 24 h, with 6 cycles per hour.

2.4. CPN preparation

Unsaturated polyester (UP) and epoxy resin (E) nanocomposites with 1%, 3% and 5% of modified Mt (H1.5, D1.5, O1.5, H3, D3 and O3) were prepared as described below. CPN were designated according to the modified Mt used (for example H1.5/UP and H1.5/E). Neat unsaturated polyester and neat epoxy were prepared in the same manner as CPN, except for the first mixing part. CPN were also prepared with extracted, modified Mt (H1.5e, D1.5e, O1.5e, H3e, D3e and O3e), but aggregates could have been observed by eyes. Therefore, the samples were characterized only by XRD.

2.5. Mt-UP nanocomposite preparation

0.1 g, 0.3 g or 0.5 g of modified Mt and 10 g of UP were mixed at room temperature by using a magnetic stirrer for 24 h and during that time it was 3 times sonicated for 10 min. After 24 h of mixing, 0.05 g of benzoyl peroxide was added and mixed for another 3.5 h. Then the mixture was poured into a glass model (10 × 10 × 0.17 cm) coated with anti-sticking agent and transferred to an oven heated to 90 °C for 20 h.

2.6. Mt-E nanocomposite preparation

0.08 g, 0.24 g or 0.4 g of modified Mt and 2 g of hardener were mixed at room temperature by using a magnetic stirrer for 3.5 h and during that time it was 3 times sonicated for 10 min. Then 6 g of epoxy resin was added and mixed for another hour. The mixture was stirred under reduced pressure (100 mbar) for 10 min to remove air bubbles, poured into a glass model and transferred to an oven heated to 90 °C for 20 h.

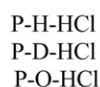
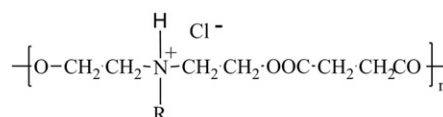
2.7. Characterization

¹H NMR spectra were recorded by using a Varian Unity Inova 300 spectrometer in CDCl₃ at 25 °C, with an acquisition time of 5 s, a delay time of 5 s, and 100 scans.

The XRD experiments were performed on an X-ray powder diffractometer PANalytical X'Pert PRO MPD (CuKα₁ radiation = 1.5406 Å) in 0.033° steps from 1.0 to 35° (in 2θ). The basal spacing was calculated according to Bragg's law.

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC1. The samples of ~15 mg were heated from 40 °C to 1000 °C at a heating rate of 10 °C/min in a nitrogen flow of 50 ml/min.

Viscoelastic properties and glass transition temperature were determined by a TA Q800 dynamic mechanical analyzer (DMA) using dual cantilever. Rectangular samples (55 × 10 × 1.7 mm) were heated from 25 °C to 120 °C at a heating rate of 2 °C/min, amplitude of 15 μm and frequency of 1 Hz.



Scheme 1. The molecular structure of polyesters P-ODEA, P-DDEA and P-HDEA and their hydrochlorides P-O-HCl, P-D-HCl and P-H-HCl.

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