



Research paper

Montmorillonite modified with lactim methyl ethers having different ring sizes



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ABSTRACT

A series of organically modified montmorillonites (organo-montmorillonites) was prepared by the method of cation exchange using hydrochlorides of lactim methyl ethers derived from cyclic amides (lactams) with varying ring size (five- to thirteen-membered). The content of the organic modifier was determined from the carbon content (elemental analysis) and using the thermogravimetric analysis. The intercalation of lactim methyl ethers into the interlayer space of the aluminosilicate was confirmed by the FTIR spectroscopy. The interlayer distance determined by the X-ray diffraction increased with increasing ring size and was correlated to the values obtained for montmorillonite intercalated by ω -aminoacids derived from lactams. Suitability of montmorillonites organophilized in this way for a preparation of nanocomposites of polyamide 6 by in situ intercalation was tested by their swelling in the ϵ -caprolactam melt. Due to the penetration of the monomer into the interlayer space of the organophilized montmorillonite, the interlayer distance further increased.

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1. Introduction

In recent years, a wide variety of modified clay minerals, especially those of smectite family, have been used to manufacture clay mineral polymer nanocomposites (Alexandre and Dubois, 2000; Bergaya et al., 2013; Kadlecová et al., 2008; Kawasumi, 2004; Kredatusová and Brožek, 2012; Lambert and Bergaya, 2013; Puffr et al., 2013). Under favourable conditions, the dispersion of individual high-aspect ratio layers has been shown to form nanocomposites, leading, even at very low filler concentrations, to dramatic improvements in mechanical properties, higher heat distortion temperature, better dimensional stability, reduced flammability, and enhanced barrier properties, as compared to the original polymer or to standard micro- or macrocomposites (Alexandre and Dubois, 2000; Paul and Robeson, 2008; Sinha Ray and Okamoto, 2003).

In a hydrophobic polymer matrix, the hydrophilic character of clay mineral hampers the exfoliation into discrete layers. This can be overcome by an organic modification of the clay minerals. The organic modification increased the distance between silicate layers and thus facilitates the penetration of the polymer chains into the interlayer space of organoclay; this led to an intercalated or exfoliated nanocomposite structure. Clay minerals, in particular, montmorillonite (Mt), were extensively used to prepare organoclays because of their interesting properties, such as high cation exchange capacity, large interlayer space swelling behaviour, large surface area and adsorption capacity. Several procedures reviewed in ref. (Bergaya and Lagaly, 2001) were

employed to modify clay minerals. Cation exchange is most convenient in the case of quaternary alkylammonium salts (Vaia et al., 1994). Usually, this is performed in an aqueous dispersion of Mt through an exchange of interlayer inorganic cations for voluminous alkylammonium cations. This process results also in an increase of the interlayer distances. It is possible to use a number of commercial products, e.g. Cloisite® (Southern Clay Product, today BYK Additives and Instrument), organophilized by amine derivatives of natural origin, containing mixtures of unequally long, both saturated and unsaturated hydrocarbon chains, possibly with various polar substituents (Fornes et al., 2002). The observed low thermal stability of ammonium surfactants represented a problem for melt compounding (with temperatures exceeding 200 °C), by which the degradation of the modifier of the clay mineral could be initiated. The difficulty with thermal stability has been overcome by the surface modification of Mt with phosphonium compound, such as *o*-xylenebis(triphenyl)phosphonium bromide (Ezquerro et al., 2015).

The first commercially produced clay polymer nanocomposites developed as automotive material by Toyota in 1985 were those of polyamide 6 (PA6) prepared by a hydrolytic polymerization of ϵ -caprolactam (CL) carried out at 240–260 °C in the presence of Mt modified by 12-aminododecanoic acid (Kojima et al., 1993; Okada and Usuki, 2006).

Due to its high molar mass and high content of crystalline part, PA6 prepared by the anionic polymerization of CL has many advantages over PA6 prepared by hydrolytic polymerization. The main advantage of the fast anionic polymerization of lactams lies in the increasingly used technologies of simultaneous polymerization and molding, i.e. monomer casting and reactive injection molding (RIM). The anionic polymerization is

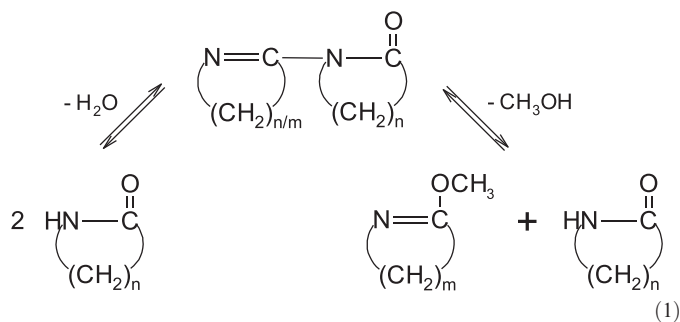
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usually carried out in the temperature range 150–180 °C, i.e. far below the melting point of the resulting PA6 (220 °C) (Kadlecová et al., 2008). Depending on the catalyst system used, duration of the process of polymerization and crystallization of polyamide phase did not exceed 0.5 h and yield of polymer was ~97%. However, due to the rapid exchange of the organic cations of organically modified Mt with the counter-cations of the ϵ -caprolactamate catalyst (e.g. Na^+ or Mg^{2+}), the anionic polymerization cannot be used for the preparation of fully exfoliated organically modified Mt/PA6 nanocomposites (Dencheva and Denchev, 2013; Kadlecová et al., 2008).

Recently, the preparation of the PA6/layered double hydroxide (LDH) nanocomposites with exfoliated structure by anionic polymerization has been reported (Lennerová et al., 2015). LDH, which is also known as hydrotalcite-like compound or anionic clay, was intercalated with taurate. The reaction of tethered amine group with polymerization activator (*N,N*-isophthaloyl-bis- ϵ -caprolactam) was associated with formation of *N*-carbamoyl- ϵ -caprolactam group anchored to LDH layer. The anionic polymerization of CL consisted in a repeated addition of the CL anion on the carbonyl of the *N*-acyllactam group. The subsequent formation of the PA6 chains resulted in a gradual disordering and exfoliation of the LDH structure.

The strategy of the Mt organophilization plays a crucial role in the preparation of Mt/PA6 nanocomposites by means of procedure mentioned above. It was reported that *N*-iminolactams derived from lactams of various ring size significantly accelerated the course of the anionic polymerization of γ -butyrolactam (or 2-pyrrolidone) and CL (Brožek et al., 1988a; Brožek et al., 1988c; Brožek et al., 1984). *N*-iminolactams could be synthesized by dehydration of lactams (the same size of both rings) (Reinisch et al., 1969) or by the reaction of lactams with lactim ethers (Glickman and Shelley, 1962), see reaction (1).



Both *N*-iminolactams and lactim ethers exist in the form of hydrochlorides. The Mt organophilization with *N*-iminolactams by cation exchange procedure could be complicated by their hydrolytic instability in water environment (Brožek et al., 1988b). On the other hand lactim ethers are stable.

In literature, no systematic study on the use the lactim ethers as organic modifiers of Mt has been carried out. In this paper we describe the modification of Mt with lactim methyl ethers derived from odd-membered lactams, i.e. γ -butyrolactam (BL), ϵ -caprolactam (CL), η -capryllactam (CLL), ι -caprinolactam (CNL) and ω -lauroactam (LL) and subsequent characterization of the products. The swelling of Mt thus modified in CL melt is also evaluated.

2. Experimental

2.1. Materials

γ -Butyrolactam (BASF), ϵ -caprolactam (DSM), η -capryllactam (BASF), ι -caprinolactam (Fluka AG) and ω -lauroactam (Atofina) were used as obtained. Cloisite Na^+ (Southern Clay Product) was used as Na-montmorillonite, with cation exchange capacity (CEC) = 1.0 mmol/g. Benzene (Penta) was distilled, dried over Na and distilled

again (b.p. 79 °C, water content was 60 ppm); dimethyl sulphate p.a. (Sigma-Aldrich) was used as obtained.

2.2. Preparation of lactim methyl ethers

γ -Butyrolactim methyl ether (BLME), ϵ -caprolactim methyl ether (CLME) and η -capryllactim methyl ether (CLLME) were prepared by reaction of dimethyl sulphate with BL (Petersen and Tietze, 1957), CL (Benson and Cairns, 1948; Petersen and Tietze, 1957) and CLL (Petersen and Tietze, 1957), respectively. To a stirred solution of 50 g lactam in 160 cm³ benzene, kept at 60–70 °C, dimethyl sulphate (DMS) was added dropwise from a dropping funnel during 2 h, to get equimolar ratio with respect to lactam. Then the reaction mixture was kept boiling for 6 h. 70 g potassium carbonate was added to the reaction mixture cooled to 5 °C and 100 cm³ distilled water was added dropwise during 1 h to the suspension thus formed. The upper (organic) layer was separated and dried for 24 h over freshly annealed potassium carbonate. The product was separated from benzene by a distillation under reduced pressure using the Vigreux column, see Table 1.

ι -Caprinolactim methyl ether (CNLME) and ω -lauroactim methyl ether (LLME) were prepared from CNL or LL, respectively, using dimethyl sulphate according to (Lüssi, 1973). 10 g CNL or 34 g LL was introduced to a reaction flask, and then 15 or 43 g DMS, respectively (a twofold mole excess with respect to lactam), was added dropwise during 15 min under stirring by a magnetic stirrer at the bath temperature of 70 °C. After DMS had been added, the temperature of the bath was increased to 80 °C. After 4 h of keeping this temperature, the originally heterogeneous mixture turned clear. To the reaction mixture, cooled to room temperature, 15 or 43 cm³ benzene, and then 7 or 24 g sodium hydroxide dissolved in 25 or 72 cm³ water, respectively, was added. The organic layer was transferred to a distillation flask and the product obtained by a distillation under reduced pressure (Table 1).

2.3. Cation exchange of montmorillonite

The intercalation of lactim methyl ethers (LME) was carried out according to procedure described in (Usuki et al., 1993b). BLME, CLME and CLLME were dosed into 30 cm³ of HPLC water and hydrochloric acid (1 mol/dm³) was added to adjust pH at a value of ~5. Solution of LME hydrochloride was slowly added in a twofold molar excess with respect to exchange capacity to the dispersion of Mt (2 g Mt in 75 cm³ of HPLC water) effectively stirred at 25 °C. After 2 h, the precipitated intercalate was filtered, washed with HPLC water and redispersed in HPLC water. The washing procedure was repeated until no chloride anions were detected in washing water. The intercalate was dried at room temperature, first under atmospheric pressure and then under vacuum. Finally the product was dried at 70 °C/13 Pa for 6 h following slight grinding to particle size < 0.2 mm.

The process of intercalation with CNLME and LLME was the same as above, but both preparations of hydrochlorides of CNLME or LLME solutions and dispersions of Mt were carried out at 80 °C.

Table 1
Preparation of lactim methyl ethers and their characterization.

LME	Yield (%)	b.p.	Found			Calculated		
			C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
BLME	24	35 °C/1.6 kPa	63.46	8.03	17.14	63.08	7.88	18.40
CLME	41	35 °C/13 Pa	65.04	10.72	10.86	66.14	10.20	11.02
CLLME	75	62 °C/20 Pa	69.23	10.76	9.37	69.63	11.04	9.02
CNLME	15	–/13 Pa	72.60	12.25	7.64	72.13	11.47	7.65
LLME	10	80 °C/13 Pa	74.30	12.61	6.63	73.93	11.84	6.64

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