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Spectroscopic Studies of Poly(ϵ -Caprolactone)/Sodium Montmorillonite Nanocomposites

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Polymer-layered silicate nanocomposites belong to a new class of hybrid materials consisting of organic-synthetic polymer matrix and inorganic filler-layered structure clay minerals. The paper presents the results of FTIR, NMR, and SAXS studies of poly(ϵ -caprolactone)/sodium montmorillonite nanocomposites. We observed a correlation between the concentration of poly(ϵ -caprolactone) in nanocomposite samples and structural changes both of the clay mineral and the intercalated polymer. Stiffening of the clay structure appears as a result of poly(ϵ -caprolactone) intercalation into a clay structure. ^{27}Al NMR studies indicated in nanocomposites two non-equivalent sites of aluminium ions, i.e. in octahedral and tetrahedral coordination, whereas in the montmorillonite clay structure the aluminium ions are located in the interlayer space too. We found also that the temperatures of structural changes and softening process of poly(ϵ -caprolactone) chains in the nanocomposites depend on the concentration of poly(ϵ -caprolactone).

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1. Introduction

Composite materials are of great interest for practical applications because they combined properties of constituent phases and can be tailored to various requirements. Among them nanocomposites are especially attractive since due to dispersions of various phases, their mechanical, thermal, and electrical properties can be improved and new high-quality compounds can be easily designed [1]. Recently, particular attention has been paid to organic matrix loaded with inorganic nanoparticles, because it exhibits much more advantageous properties than

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conventional composites. Geometric restrictions of stratiform inorganic phases can influence molecular dynamics of incorporated organic macromolecules leading thus to changes in the character of phase transitions.

Many papers have been devoted to the nature of clay minerals especially to montmorillonites ($M_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$, where M is a monovalent cation) [1–4]. The layered structure of montmorillonite is built of two-dimensional sheets of tetrahedrally coordinated silica altering with sheets of octahedrally coordinated aluminium. Each octahedral layer is placed between two tetrahedral layers forming a 2:1 phyllosilicates structure. Stacking of the layers results in the formation of a regular gap, termed gallery or interlayer space [1, 2]. As Al^{3+} ions are partially substituted by divalent Mg^{2+} cations in the octahedral sheet and Si^{4+} ions for Al^{3+} in the tetrahedral one the excess charge is compensated in the galleries by alkali or alkaline earths cations [1, 4]. Montmorillonites with monovalent interlayer cations reveal an ability to water absorption in the interlayer space leading thus to the clay swelling.

Thermostatic polymers, i.e. poly(ϵ -caprolactone), poly(ethylene oxide), poly(methyl methacrylate) and polystyrene have been used as confined components in the montmorillonite structure forming clay nanocomposites. It should be noted that poly(ϵ -caprolactone) ($\text{OH}-(\text{CH}_2)_5-\text{COO}]_n-\text{H}$) is a widely used organic material in the synthesis of nanocomposites because of its biocompatibility and biodegradability [1].

Poly(ϵ -caprolactone)-montmorillonite nanocomposites are synthesized by *in situ* intercalative polymerisation with surfactants as a catalytic agent. The catalysts increases the ability of the clay to adsorb the polymer into the interlayer space through the conversion of the hydrophilic silicate surface to an organophilic one. The conversion proceeds via an ion-exchange reaction with cationic surfactants, i.e. primary, secondary, tertiary or quaternary alkylammonium or alkylphosphonium cations [1].

2. Experimental

2.1. Materials

Synthetic sodium montmorillonite SOMASIFR[®] ME 100 (M) (CO-OP Chemical Japan) with 0.7–0.8 meq/g cation exchange capacity was used for the nanocomposite preparation. The organophilic montmorillonite (M-HTAB) was prepared using the hexadecyltrimethylammonium bromide (HTAB) provided by Aldrich. The poly(ϵ -caprolactone)/organophilic sodium montmorillonite (PCL/M-HTAB) nanocomposites were prepared by *in situ* intercalative polymerisation of Aldrich ϵ -caprolactone with the presence of different amounts of organophilic sodium montmorillonite [5]. Nanocomposite samples contained 10, 30, 50, and 64% (w/w) of M-HTAB and were labelled (PCL/M-HTAB)(90/10), (PCL/M-HTAB)(70/30), (PCL/M-HTAB)(50/50), and (PCL/M-HTAB)(36/64), respectively.

2.2. Methods

2.2.1. FTIR

PCL/M-HTAB powders were dispersed in KBr (2 mg of sample for 200 mg of KBr) for infrared spectroscopy studies. FTIR spectra of the pellets were recorded with BRUKER IFS 66/s spectrometer in the temperature range from 203 to 253 K. The experiments were performed with the resolution of 1 cm^{-1} and 256 scans in the $4000\text{--}400\text{ cm}^{-1}$ spectral range.

2.2.2. SAXS/WAXS

Structural parameters of both sodium montmorillonite and filled nanocomposites were measured using a small and wide angle X-ray scattering technique (SAXS/WAXS) at room temperature as reported previously [5]. Temperature variation of the interlamellar distance in the nanocomposites [5] was used for comparison with the FTIR data.

2.2.3. NMR

Solid-state magic angle spinning NMR spectra were recorded using a BRUKER DMX 400 MHz (9.4 T) spectrometer operating at the frequencies of 104.3 and 105.8 MHz for ^{27}Al and ^{23}Na , respectively. The samples were placed in zirconium rotors, 4 mm in diameter, and spun at 14.5 kHz. The measurements for ^{27}Al and ^{23}Na nuclei were performed at room temperature. The NMR spectra were collected by applying a single short RF pulse to the first channel and a CW-decoupling for ^1H protons during the acquisition period to the second channel (dipolar decoupling — DD). The width of the RF pulse was much shorter than that of the $\pi/2$ pulse in order to observe the central transition only. The $\pi/4$ RF pulse of duration of $1.0\ \mu\text{s}$ was used for ^{27}Al , whereas for ^{23}Na the $\pi/5$ RF pulse was generated for a period of $0.7\ \mu\text{s}$. The repetition time was set as 1 s for the both nuclei.

3. Results and discussion

FTIR study was performed to detect structural differences between the pure sodium montmorillonite, the one modified by HTAB and the other intercalated by poly(ϵ -caprolactone). Characteristic Si–O–Si stretching vibration band of the montmorillonite occurs at $\sim 1006\text{ cm}^{-1}$, whereas in the spectra of the nanocomposites the band appears at $\sim 1020\text{ cm}^{-1}$ at room temperature (Fig. 1). The difference can be interpreted as a stiffening of the clay structure. It should be observed, however, that in the spectrum of the HTAB-modified montmorillonite the bands are shifted by a few cm^{-1} toward higher wave numbers in comparison with that of pure montmorillonite (Fig. 1). Figure 2 shows room temperature IR spectra for sodium montmorillonite (M), HTAB-modified montmorillonite (M-HTAB) and the poly(ϵ -caprolactone)/organophilic montmorillonite (PCL/M-HTAB) nanocomposite; the respective bands are given in the Table. The bands characteristic of the clay

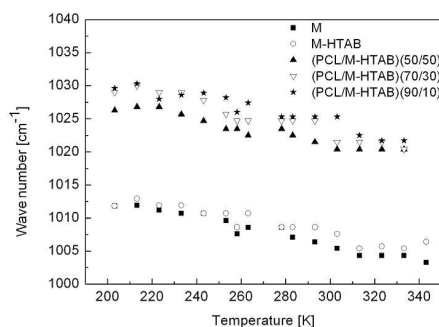


Fig. 1. Temperature dependence of the wave number of Si–O–Si band in montmorillonite and modifications induced by HTAB and PCL.

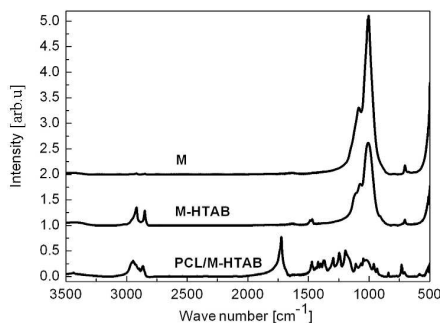


Fig. 2. IR spectra of sodium montmorillonite (M), HTAB-modified montmorillonite (M-HTAB), and the poly(ϵ -caprolactone)/organophilic montmorillonite (PCL/M-HTAB)(90/10) nanocomposite at room temperature.

were assigned according to the spectral data presented earlier [6–8, 10] and those of PCL according to data published in [9, 10]. It should be observed that the degree of hydration of the samples studied was rather low since the band at 1620–1630 cm^{-1} , related to the H–O–H deformation, and the bands in the range of 3350–3700 cm^{-1} assigned to the water contained in the interlayer space, are very weak. Additional bands at 1470 cm^{-1} and 1488 cm^{-1} observed in the spectrum of the HTAB-modified montmorillonite we assigned to the stretching vibrations of the C–C bonds of HTAB, whereas the band at $\sim 1120 \text{ cm}^{-1}$ may be related to CH_2 vibrations of the surfactant [10]. The number of IR bands in the spectra of the composites increases considerably as a result of PCL addition (Table). Several bands in the range of 770–960 cm^{-1} were tentatively assigned to a deformation of O–H groups linked to the interlayer cations, as it has been proposed earlier [8].

Particular attention has been paid to the doublet at 725 cm^{-1} and 730 cm^{-1} usually assigned to the CH_2 rocking vibrations and we studied its temperature dependence in details. Figure 3 shows the CH_2 bands of poly(ϵ -caprolactone) in the spectrum of (PCL/M-HTAB)(90/10) nanocomposite at various temperatures.

TABLE

Characteristic IR bands of PCL/M-HTAB nanocomposites.

Assignments	Frequency maxima [cm ⁻¹]			
	M	M-HTAB	(PCL/M-HTAB) (9010)	PCL [7, 8]
Si-O-Al ³⁺	705 (w)	706 (w)	709 (w)	
ρ (CH ₂) long chains			726 (m)	730
			732 (m)	
			772 (m)	
			840 (m)	
			934 (m)	
			961 (m)	
ν (Si-O-Si)	1006 (vs)	1006 (vs)	1021 (m)	
ν (C-O-C)			1047 (m)	
ν (Si-O-Si)	1085 (sh)	1074 (sh)	1067 (sh)	
ω (CH ₂)		1121 (m)	1109 (m)	
ν_s (OC-O)			1196 (m)	1190
ν_{as} (C-O-C)			1246 (m)	1240
ν_{cr} (C-O), ν_{cr} (C-C)			1296 (m)	1297
ρ (CH ₂)			1369 (m)	1369
δ (CH)			1376 (m)	1380
			1400 (m)	
δ (CH ₂ , CH ₃)			1415 (m)	
				1420
δ (CH ₂ , CH ₃)			1420 (m)	
δ (CH ₂)			1438 (s)	1450
ν (C-C)		1470 (m)	1471 (m)	
		1488 (m)	1477 (m)	
ν (C=O)			1724 (s)	1727, 1740
organic	2849 (vw)	2849 (m)	2850 (sh)	
impurities	2917 (vw)	2918 (m)	2924 (sh)	
ν_s (CH ₂)			2864 (m)	2865
			2894 (sh)	
ν_{as} (CH ₂)			2946 (m)	2949
ν (CH ₂)			2956 (sh)	3000-2800

Abbreviations: vs — very strong, s — strong, m — medium, w — weak, vw — very weak, sh — shoulder.

The two bands of the doublet become closer at higher temperatures and merge into a single band on melting. The temperature variation of the positions of the CH₂ bands of PCL in the spectrum of nanocomposite is presented in Fig. 4. We

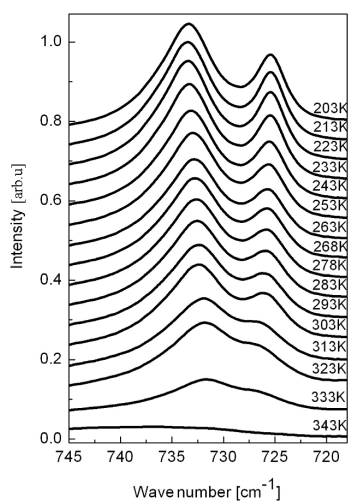


Fig. 3. CH₂ bands in (PCL/M-HTAB)(90/10) nanocomposite at various temperatures.

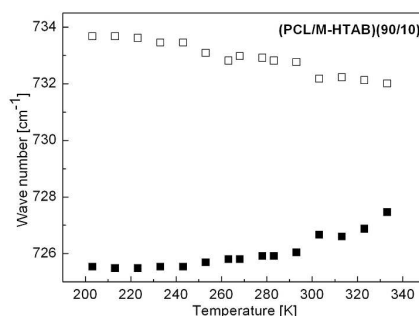


Fig. 4. Temperature dependence of positions of the CH₂ bands in (PCL/M-HTAB)(90/10) nanocomposite.

observed also a decrease in the band intensities at higher temperatures. Figure 5 shows temperature changes in the maximum band intensity for all (PCL/M-HTAB) nanocomposites. One can distinguish two processes characterised by different dI/dT slopes. In low temperature range the temperature dependence of the intensities I of the bands at $\sim 725 \text{ cm}^{-1}$ and $\sim 730 \text{ cm}^{-1}$ can be related to structural changes, whereas at high temperatures to a softening process of poly(ϵ -caprolactone) chains in the interlayer space. The temperatures of the transitions depend on the concentration of poly(ϵ -caprolactone) in the nanocomposites and vary from $\sim 290 \text{ K}$ for the nanocomposite of the smallest concentration of the polymer to 305 K for the (PCL/M-HTAB)(90/10) nanocomposite.

As the structural changes observed in IR studies it should be related to structure parameters measured by XRD, Fig. 5 presents also the results of SAXS/WAXS studies of the nanocomposites [5]. The basal spacing 0.93 nm of sodium mont-

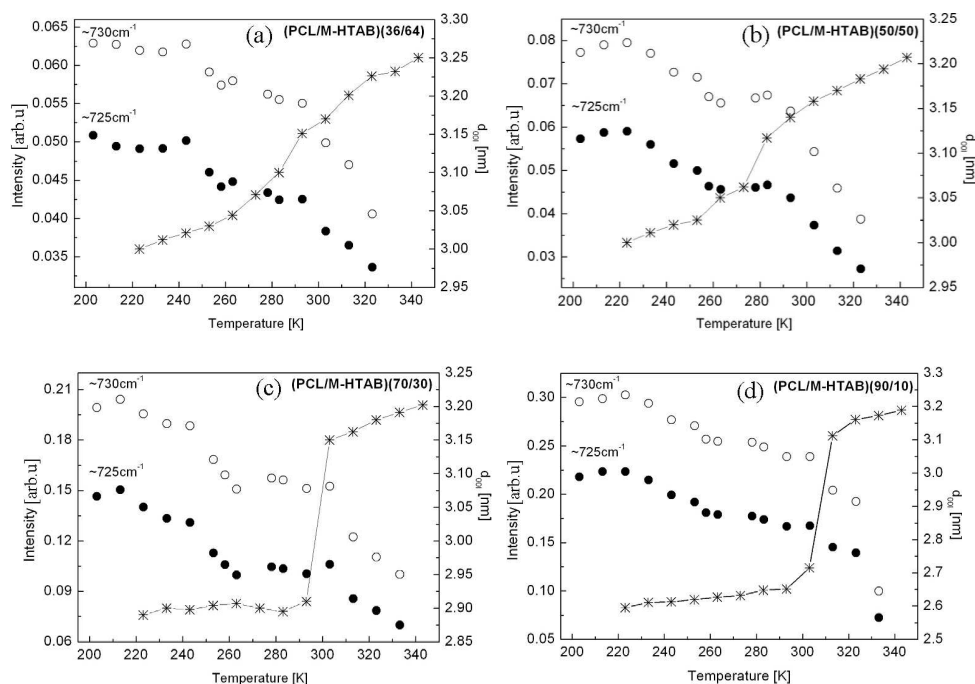


Fig. 5. Temperature changes in the maximum intensity of the CH₂ bands (○, ●) and *d*-spacing (*) in (a) (PCL/M-HTAB)(36/64), (b) (PCL/M-HTAB)(50/50), (c) (PCL/M-HTAB)(70/30), and (d) (PCL/M-HTAB)(90/10) nanocomposites.

morillonite increases after modification by HTAB to 1.96 nm. The incorporation of montmorillonite modified with HTAB into poly(ϵ -caprolactone) matrix results in a further increase in *d*-spacing. The interlamellar distances (d_{001}) varied from about 2.63 nm (PCL/M-HTAB)(90/10) to 3.07 nm for PCL/M-HTAB 36/64 at room temperature. It is visible that the results of FTIR experiments are in good agreement with those of the SAXS studies.

Figure 6 shows NMR fully decoupled-spectra of ²⁷Al that provide the information about the environment of the aluminium ions in montmorillonite and nanocomposite structures. For pure montmorillonite we observed two asymmetric lines of the ²⁷Al nuclei. The line at about 0 ppm is related to the octahedral coordination of the aluminium ions, whereas the line at ~ 50 ppm indicates that some of the ²⁷Al ions are present in the tetrahedral environment [11, 12]. These coordinations appear as a consequence of isomorphic ions substitution within the layers. After the clay structure modification the intensity of ~ 50 ppm line decreases in comparison with that of the ~ 0 ppm line whose intensity does not change. It seems that after polymer intercalation the aluminium ions are washed out from the interlayer space and only a part (~ 20%) of tetrahedrally-coordinated Al-ions remain in the clay structure.

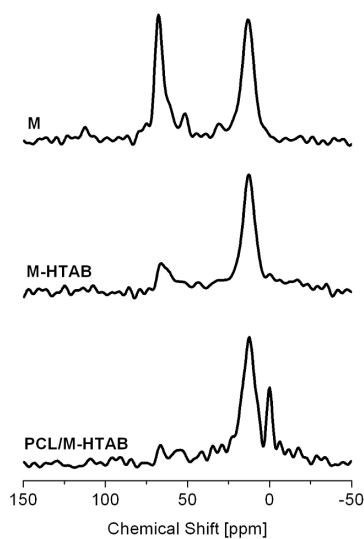


Fig. 6. ^{27}Al NMR spectra of sodium montmorillonite (M), HTAB-modified montmorillonite (M-HTAB) and the poly(ϵ -caprolactone)/organophilic montmorillonite (PCL/M-HTAB) nanocomposite.

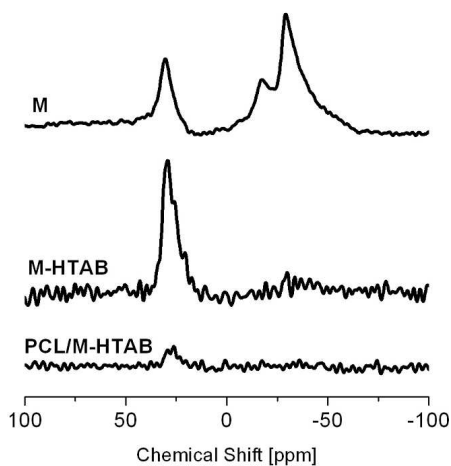


Fig. 7. ^{23}Na NMR spectra of sodium montmorillonite (M), HTAB-modified montmorillonite (M-HTAB) and the poly(ϵ -caprolactone)/organophilic montmorillonite (PCL/M-HTAB) nanocomposite.

^{23}Na NMR spectroscopy studies also reveal the existence of two types of sodium ions in the interlayer space — two asymmetric lines at ~ 30 ppm and a broader line in the range from -15 to -50 ppm. The line at ~ 30 ppm we relate to sodium ions located near the clay basal planes and the broader line with the ions in the gallery. Figure 7 shows ^{23}Na NMR lines for pure sodium montmorillonite

as well as montmorillonite modified by HTAB and PCL. It can be seen that the modification results in an increase in number of sodium ions in the basal planes of the clay and in reduction of the Na concentration in the gallery.

4. Conclusions

The aim of our studies was to determine the temperature range of the stability of the PCL/M-HTAB nanocomposites. Intercalation of the layered clay mineral by a thermostatic polymer causes in changes of the mechanical and thermal properties of the polymer. To characterize the thermal behaviour of the nanocomposite we proceeded to study temperature variation of the CH₂ group dynamics of the polymer in poly(ϵ -caprolactone)/montmorillonite nanocomposites and the results were compared with the SAXS/WAXS data. Modification of the structure of the montmorillonite was investigated by NMR spectroscopy and IR studies of the Si–O–Si vibrations.

The results can be summarized as follows:

1. (PCL/M-HTAB)(90/10) nanocomposite are stable in the temperature range from ~ 200 to ~ 300 K and the softening temperature of the nanocomposite becomes shifted downward with increasing concentration of the filler (Fig. 5).
2. PCL affects the tetrahedral coordinated Si-ions of the montmorillonite in the nanocomposite. The band at ~ 1010 cm⁻¹, ascribed to Si–O–Si vibrations, is shifted toward higher wave numbers due to the intercalation (Fig. 1).
3. Intercalation of the clay by the poly(ϵ -caprolactone) reduces considerably the number of tetrahedrally coordinated Al-ions in the clay structure (Fig. 6). The ion-exchange process forced by the surfactant (HTAB) removes Na-ions from the interlayer space of the clay (Fig. 7).

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