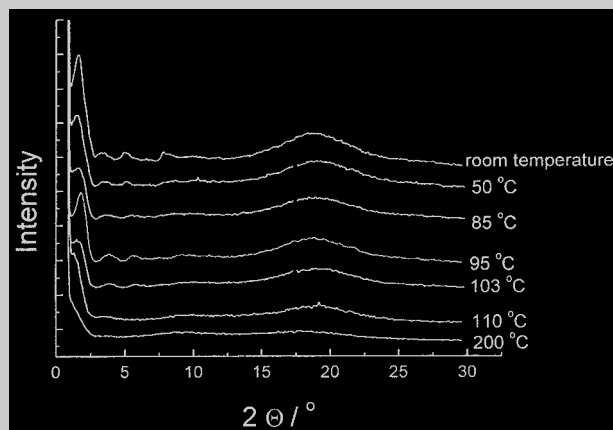


Communication: A self-assembly phenomenon in an extruded polystyrene/clay nanocomposite sample is observed during a temperature increase process. Wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and infrared dichroism techniques have been employed to investigate the self-assembly phenomenon. The results show that in the self-assembly structure the montmorillonite primary particles orient parallel, and the phenyl rings of the polystyrene align perpendicular to the primary particles, whereas no obvious orientation of the aliphatic chain was observed.



In situ WAXD patterns of the extruded polystyrene/montmorillonite pellet in the temperature range between room temperature and 200 °C

Self-assembly in a polystyrene/montmorillonite nanocomposite

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Introduction

Since the development of a nylon-6/clay nanocomposite by Toyota researchers^{1–4}, polymer layered silicate (PLS) nanocomposites are of much current interest from a wide range of scientific and practical viewpoints. Besides dramatically increasing the mechanical, thermal, and gas barrier properties^{5–8}, PLS nanocomposites exhibit a broad spectrum of unusual chemical and physical phenomena, such as highly anisotropic electrical conductivity⁹, and photoactivity¹⁰. We have recently prepared an exfoliated polystyrene/montmorillonite nanocomposite via an in situ intercalative polymerization method¹¹. A unique shear-induced ordered structure was unexpectedly observed for the extruded sample^{12–15}. Our previous studies reveal that the shear-induced ordered structure mainly results from the orientation of the clay primary particles and their local ordered microstructure, and that the phenyl rings of the polystyrene are oriented as well.

In this paper, we show a self-assembly phenomenon in the extruded polystyrene/montmorillonite nanocomposite sample during a temperature increase process. Molecular

or nanoscale self-assembly behaviors have attracted considerable attention in the fields of biological investigations¹⁶, nonlinear optical (NLO) materials¹⁷, nanoelectrochemical patterning¹⁸, block copolymers¹⁹, etc. Extensive studies on the self-assembly in PLS nanocomposites may expand the understanding of intercalation chemistry and the industrial application of PLS nanocomposites. However, few research of self-assembly phenomena in PLS nanocomposites has been reported so far. Here we report the WAXD, TEM and infrared dichroism investigations of self-assembly in an extruded polystyrene/montmorillonite nanocomposite sample.

Experimental part

Materials

Sodium montmorillonite (Swy-2 type) was kindly provided by the Source Clay Repository, Department of Geology, University of Missouri, Columbia, MO. The cation exchange capacity is 92 mequiv/100 g.

Synthesis of the exfoliated PS/clay nanocomposite

The desired amount (5 wt.-%) of cetyltrimethylammonium bromide-exchanged montmorillonite (CTAB-montmorillonite) was dispersed in styrene, then an aqueous solution of ammonium persulfate and sodium dodecylsulfate was added to form a stable water base emulsion. The emulsion was polymerized at 70 °C for 4 h in the presence of N₂. Finally, after washing several times and drying in a vacuum oven, the PS/clay nanocomposite was obtained. \bar{M}_w and \bar{M}_w/\bar{M}_n determined by gel permeation chromatography (GPC) are 3.3×10^5 and 4.3, respectively.

Preparation of the ordered-structure samples

The pellet specimen was obtained by extruding the PS/clay nanocomposite powder at 200 ± 10 °C with a CS-183 MMX Mini Max Molder (CSI Custom Scientific Instruments, Inc., USA). It is about 1.5 mm in thickness, 20–25 mm in length and 12 mm in width. The film sample, 4 cm × 2 cm × 10 μm, was obtained by shearing the PS/clay nanocomposite or PS melt (200 ± 10 °C) between two glass slides at a shear rate magnitude of order 10^2 s⁻¹, and subsequently quenching to room temperature.

Characterization

In situ WAXD patterns were collected using a Philips PW1700 X-ray diffractometer (Cu K_α radiation). The specimen was placed horizontally, scanned at room temperature, then quickly heated to the desired temperature, and kept stable for 1.5 min, measured and then heated to a higher temperature and measured, and so on. The scanning rate in all cases was 1°/min. The temperature control was through a TTK-HC heat controller (AP PAAR Inc.) and the accuracy was 0.5 °C. TEM photographs were obtained with a HITACHI H-800 electron microscope operated at an accelerated voltage of 100 kV. All of the ultrathin sections (less than 80 nm) were microtomed by Leica Microsystems Ltd. A Perkin-Elmer System 2000 Fourier transform infrared (FTIR) spectrophotometer equipped with a Perkin-Elmer wire grid polarizer was employed to record the polarized infrared spectra.

Results and discussion

Fig. 1 shows the in situ WAXD patterns of the extruded polystyrene/montmorillonite pellet in the temperature range between room temperature and 200 °C. The four sharp diffraction peaks are due to the shear-induced ordered structure. The Bragg diffractions observed at $2\theta = 1.62, 3.22, 4.85,$ and 6.48° correspond to 001, 002, 003, and 004 reflections of the ordered structure^{12–15}. The intensities of all four diffraction peaks measured at room temperature are high, then decrease simultaneously with increasing temperature in the range between room temperature and 85 °C. Note that at 95 °C, the intensities of the four diffraction peaks characteristic of the ordered structure become rather high again. Subsequently, they decrease dramatically at 103 °C, and monotonically with

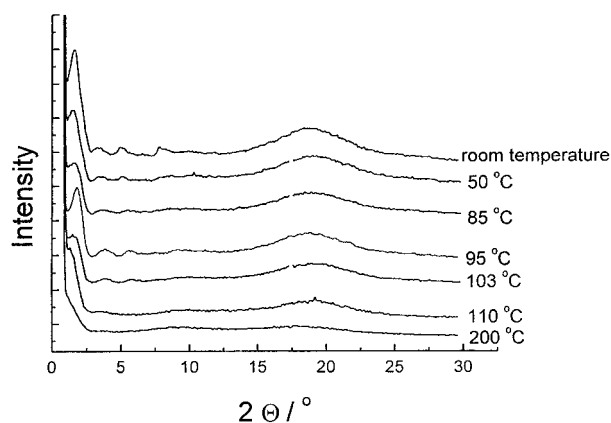


Fig. 1. In situ WAXD patterns of the extruded polystyrene/montmorillonite pellet in the temperature range between room temperature and 200 °C

temperature. Finally, no sharp diffraction peaks are discernible at 200 °C. Therefore, it may be deduced that a self-assembly phenomenon occurred during the temperature increase process in the extruded polystyrene/montmorillonite nanocomposite sample.

In order to clarify this self-assembly behavior, TEM and infrared dichroism studies were carried out. An extruded pellet and a film sample were heated under conditions similar to the above WAXD measurements, but quickly cooled down after a certain period of heating.

Fig. 2 shows TEM photographs of the extruded polystyrene/montmorillonite nanocomposite pellet before heating, and after heating at 85, 95, and 110 °C. The narrow, dark bands and the light regions represent the montmorillonite primary particles^a and polystyrene matrix, respectively. For the sample before heating, it can be seen that the montmorillonite primary particles, narrower than 50 nm, lie parallel in accordance with the shear flow direction. As for the pellet sample after heating at 85 °C, the silicate primary particles are not aligned parallel very well, and some disorder can be observed. It is interesting that for the sample after heating at 95 °C, the TEM image presents a parallel oriented structure again. This is in good agreement with the above in situ WAXD investigation, indicating that a self-assembly of clay primary particles happened around 95 °C. After heating at 110 °C, a disordered structure was observed, suggesting the damage of the self-assembled structure.

Fig. 3 and Tab. 1 show the infrared dichroism study of the polystyrene orientation. Some infrared absorption bands are assigned tentatively according to the previous literature²⁰, and their dichroic ratios are illustrated in

^a Throughout this paper, we use the terminology *primary particles* to describe the microstructure features of the silicate crystallites. The crystallites consist of a coherent stacking of individual silicate layers, including a compact face-to-face stacking and low-angle intergrowth of silicate monolayers.

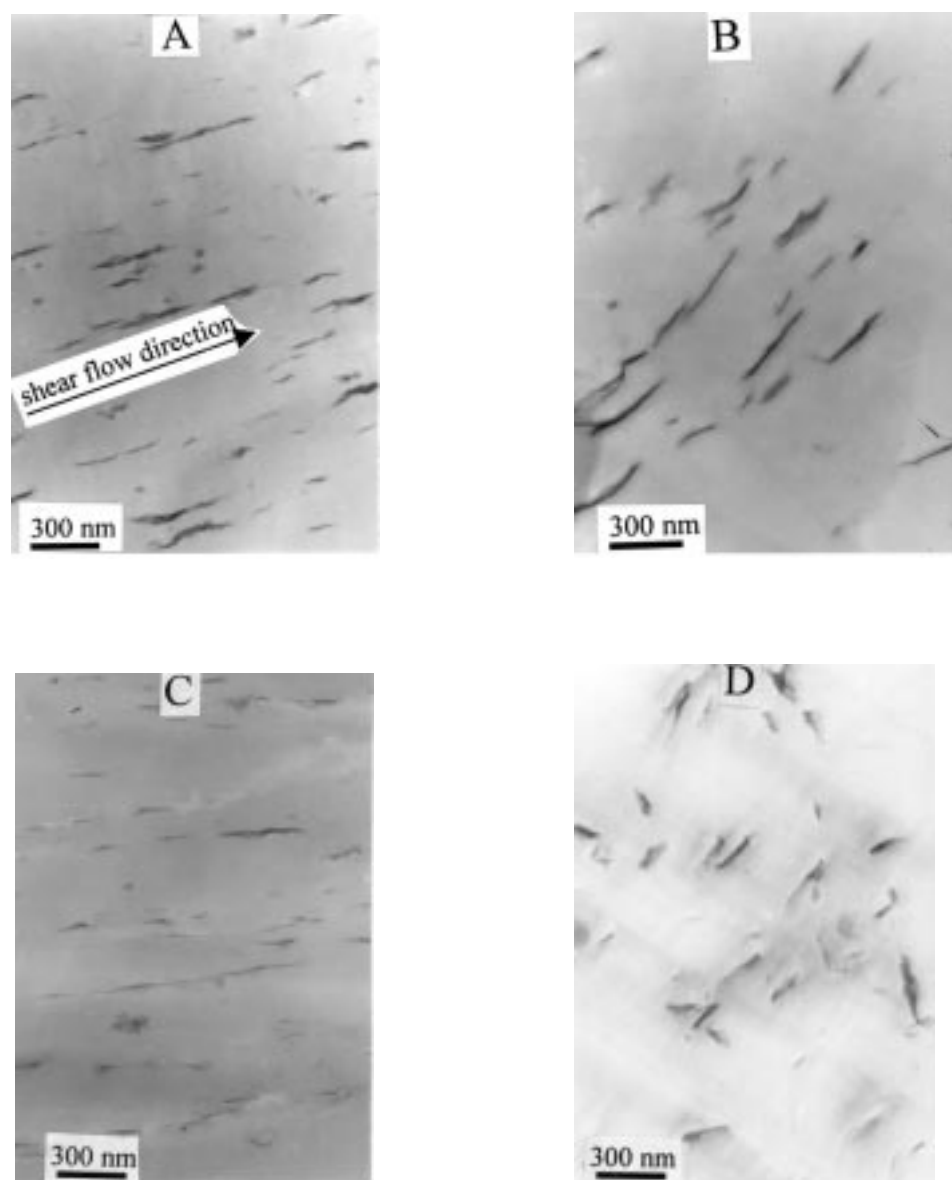


Fig. 2. Bright field TEM images of the extruded polystyrene/montmorillonite pellet under conditions similar to Fig. 1. A: room temperature, B: after heating at 85 °C, C: 95 °C, D: 110 °C

Tab. 1. Infrared band assignment and dichroic ratio (D) of the polystyrene/montmorillonite nanocomposite film specimens before and after heating

Frequency cm^{-1}	Intensity ^{a)}	Tentative assignment	Dichroic ratio (D) ^{b)}		
			a	b	c
2923	s	$\nu_{\text{as}}(\text{CH}_2)$, CH_2 asymmetric stretching	1.05	1.06	0.99
2851	ms	$\nu_{\text{s}}(\text{CH}_2)$, CH_2 symmetric stretching	1.01	1.04	0.99
760	vs	$\nu_{10\text{B}}$, CH out-of-plane bending of phenyl ring	0.66	1.14	1.01
700	vs	ν_{11} , CH out-of-plane bending of phenyl ring	0.86	1.14	0.97
542	s	ν_4 , out-of-plane deformation of phenyl ring	0.85	1.15	1.02

^{a)} s: strong; vs: very strong; ms: medium strong.

^{b)} a: before heating, b: after heating at 95 °C, c: after heating at 110 °C.

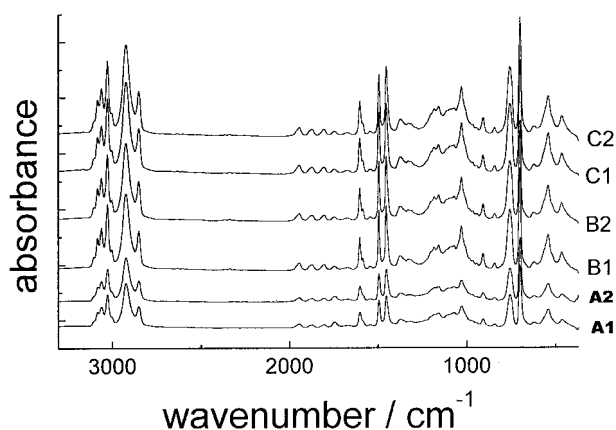


Fig. 3. FTIR spectra of the extruded polystyrene/montmorillonite sample under conditions similar to Fig. 1. A: room temperature (1) parallel polarization and (2) perpendicular polarization; B: after heating at 95 °C (1) parallel polarization and (2) perpendicular polarization; C: after heating at 110 °C (1) parallel polarization and (2) perpendicular polarization

Tab. 1. The dichroic ratios of the CH₂ asymmetric stretching ($\nu_{as}(\text{CH}_2)$) and symmetric stretching ($\nu_s(\text{CH}_2)$) of all the specimens are essentially equal to unity, indicating that little orientation occurs for the aliphatic chain of the polystyrene before and after heating. With respect to phenyl rings, it is complex. For the film specimen, the phenyl rings lie parallel to the shear flow direction and the montmorillonite primary particles. This is because the dichroic ratios of the phenyl ring out-of-plane vibration modes, ν_{10B} , ν_{11} , and ν_4 , are obviously lower than unity, and each of the out-of-plane vibration bands has a transition moment perpendicular to the phenyl ring plane. As for the film specimen after heating at 95 °C, the dichroic ratios of ν_{10B} , ν_{11} , and ν_4 are larger than unity, revealing that the phenyl rings lie perpendicular to the montmorillonite primary particles. However, no apparent orientation was measured for the specimen after heating at 110 °C.

The fact that the polystyrene phenyl ring changes from parallel to perpendicular orientation with respect to the silicate primary particle, and then becomes disordered may be explained as follows. In the extruded sample, the parallel orientation is induced by shear flow and fixed by adjacent inorganic planar oriented silicate layers. With increasing temperature the phenyl rings obtain a certain degree of mobility. They prefer face-to-face orientation, i. e., perpendicular to silicate layers, due to the interaction among the phenyl rings. When the temperature is high enough, near the glass transition temperature ($T_g = 103^\circ\text{C}$, determined by DSC) of the nanocomposite, the mobilities of both aliphatic chain and phenyl ring of the

polystyrene are strong, resulting in a disordered orientation of the phenyl ring.

In summary, we have demonstrated that a self-assembly in an extruded polystyrene/montmorillonite nanocomposite happened during a temperature increase process. In the self-assembled structure, the montmorillonite primary particles align parallel and the phenyl rings lie perpendicular to the montmorillonite primary particles.

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