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A DSC study of the order–disorder transition of SEPS block copolymers in the block copolymer/paraffin oil/layered silicate nanocomposite gels

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Abstract

The effect of addition of layered silicate on the order–disorder transition of poly[styrene-b-(ethylene-propylene)-b-styrene] (SEPS) block copolymer in the block copolymer/paraffin oil/layered silicate nanocomposite gels was investigated by means of differential scanning calorimetry (DSC) and modulated DSC (MDSC). The addition of layered silicate has significant influences on the order–disorder transition and the phase structure of the block copolymer. With increasing layered silicate, the order–disorder transition temperature of the block copolymer decreased. The addition of layered silicate reduced the ordering level of the block copolymer. MDSC results revealed that the order–disorder transition is a glass transition-like process. A thermal event related to the ordering process, which took place in the preparation of the sample and hid in the specimen, has been revealed by MDSC first time.

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1. Introduction

Block copolymers represent an interesting class of soft polymeric materials, which are produced by covalently linking two or more contiguous linear sequences (blocks) of chemically dissimilar species [1–3]. A feature of block copolymers is that they can form a variety of self-assembled nano-scale ordered structures [3–5], which depend primarily on molecular composition, thermodynamic incompatibility of blocks, and monomer asymmetry [6]. Block copolymers have a number of unique properties resulting from their morphological features. Because of these properties block copolymers have been used in a wide range of material fields [1–4], for example, thermoplastic elastomers for impact modification, compatibilization and pressure-sensitive adhesion. Upon thermodynamic variation such as temperature, pressure and solvent concentration these microstructures can undergo thermal transformations from one ordered structure to another (order–order transition) one and from an ordered to disordered (isotropic) state (order–disorder transition) [7]. These effects occur because the systems under consideration have a small characteristic length scale owing to a connectivity of the block chains in block copolymers [1–3]. With the aim of understanding under which conditions affecting the block connectivity, the phase transition of block copolymers have been extensively studied both theoretically and experimentally over last 2 decades [1–4]. The factors that control micro-phase behaviour and govern the formation of micro-domain size are well clearly understood.

Recently, the development of new kinds of functional materials such as nano-scale templates [8], nano-structured damping and porous materials [9,10], and nanocomposites based on block copolymers has been widely investigated [11–14]. Among all the potential nanocomposite precursors, those based on layered silicate reinforcements have received considerable attention over the last few years because a relatively low level of clay can lead to significant enhancements in mechanical, thermal and barrier properties [11,12]. One has started to pay attention on the development of block copolymer–clay nanocomposites [13,14]. However, it is not clear whether such a nanofiller affects the microstructure and the order–disorder transition of the block copolymer in the nanocomposites. Although the order–disorder transition of block copolymers has been widely investigated [3,15], it is believed that the order–disorder transition in block copolymers is melting-like one revealed by DSC.

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Recent research showed that the understanding is questionable [16].

In this communication, the effect of addition of layered silicate on the order–disorder transition and phase structure of poly[styrene-b-(ethylene-propylene)-b-styrene] (SEPS) in the block copolymer/paraffin oil gels was investigated. The order–disorder transition behaviour of block copolymers was re-examined. The aim of the use of paraffin oil is to lower the order–disorder transition temperature which makes the observation of the order–disorder transition more easy by means of DSC.

2. Experimental

2.1. Materials

Poly[styrene-b-(ethylene-propylene)-b-styrene] with 30% of styrene was provided kindly by Kuraray Co. Ltd., Japan. The molecular weight of SEPS is $M_w = 76{,}500$ and $M_w/M_n = 1.3$ determined by using gel permeation chromatography. Paraffin oil was kindly provided by Idemitsu Kosan Ltd., Japan, and its molecular weight is 770. Layered silicate (clay) used in our experiments was Cloisite® 20A (C20) and Na^+-clay, purchased from Southern Clay Products (TX, USA). The modifier for organoclay C20 is dimethyl, dehydrogenered tallow ammonium.

2.2. Sample preparation

The blends of SEPS and C20, and of SEPS and Na+-clay with different weight fraction (0, 0.5, 1, 3 and 5%) were prepared by a solution method, respectively. Toluene was used as a solvent. The ratio of polymer component to toluene was about 10 wt.%. The solutions of SEPS/clay/toluene were stirred (400 rpm) at room temperature for 24 h. Mixtures of SEPS/clay/toluene and paraffin oil with different contents (80%, 70%, 60% and 50%) were prepared. The mixtures were stirred at room temperature for 36 h. After that, the mixture was cast on to a PET film, and the solvent was gradually evaporated for 2 days at room temperature. The films obtained were finally dried in vacuum over at 80 °C for at least 3 days.

2.3. Wide angle X-ray diffraction (WAXD)

X-ray diffraction experiments were performed on film samples on a Bruker X-ray diffractometer (AXS D8 Advance) using Kα ($\lambda = 0.154$ nm) radiation. Samples were scanned at a rate $0.24^\circ\ \mathrm{min}^{-1}$ from about 1° to 20° in 2θ.

2.4. Differential scanning calorimetry and modulated differential scanning calorimetry

Differential scanning calorimetry (DSC) and modulated DSC (MDSC) were used in this research for the measurement of the order–disorder transition temperature. A TA Instrument DSC 2920 calorimeter was employed. All measurements were run in nitrogen atmosphere and temperature ramp was set at 10 °C/min for DSC measurements. For MDSC measurements, oscillation amplitude of ±1.0 °C, oscillation period of 60 s and a heating rate of 3 °C/min were used. The calorimeter was calibrated with a standard method [see the operator's manual of TA DSC 2920 Differential Scanning Calorimeter] including baseline, temperature and cell constant calibrations.

2.5. Small angle X-ray scattering

The phase structure of SEPS/oil and SEPS/oil/clay nanocomposite gels were determined by means of small angle X-ray scattering (SAXS) using a the Kratky Compact Small Angle System with a stationary-anode copper-target X-ray tube (wavelength 0.1542 nm) at room temperature. The fine-focus X-ray generator was operated at 45 kV and 40 mA. The measured intensity was desmeared and corrected for background scattering and photoelectric absorption in the samples.

3. Results and discussions

3.1. Effect of the addition of layered silicate on the order–disorder transition of SPES block copolymer in SEPS/paraffin oil/clay nanocomposite gels

Normally, WAXD is used to identify intercalated structure [17]. The intercalation of the polymer chains usually increase the interlayer spacing, in comparison with the spacing of the clay used, leading to a shift of the diffraction peak towards the lower angle values.

Fig. 1A and B shows WAXD patterns for pure clay and SEPS nanocomposite gels (5% clay content) for the two kinds of clays, Na^+-clay and C20, respectively. The obvious shift of peak position to lower value of the nanocomposite (for Na+-clay system, from 7.4° to 5.5°; for C20 system, from 3.8° to 2.3°) suggests that an intercalated nanocomposite gels was obtained. The two peaks shown in Fig. 1B are first and second order ones. Beside, it can be seen that the change of the peak positions for the Na^+-clay nanocomposite was smaller than that of C20 nanocomposite showing that the compatibility of C20 with SEPS is higher than that of Na^+-clay with SEPS.

Thermal measurements [18] are able to identify a heat of fusion at the order–disorder transition temperature (T_{ODT}). Fig. 2 shows the plots of the heat flow versus temperature for SEPS/oil gels. The results indicate that the order–disorder transition is likely to be a melting transition of semi-crystalline polymers. It is obvious that T_{ODT} depends on the polymer/oil concentration. The higher the concentration of the block copolymer, the higher the T_{ODT} was. The reason for this is that the addition of paraffinic oil in the gel swells the block copolymer and increases free volume, which result in the decrease of the T_{ODT}. The effects of composition of paraffinic oil on T_{ODT} in SEPS/oil gels have been intensively investigated in our group [19] and will not be discussed here. However, it must indicate that these transition peaks became weak in second heating runs.

Fig. 3 shows heat flow versus temperature for SEPS/oil/Na^+-clay (0.5 wt.%) nanocomposite gels. In comparison between

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