

Note

STRESS-INDUCED CRYSTALLIZATION OF POLYURETHANE/MONTMORILLONITE NANOCOMPOSITE*

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Abstract Exfoliated polyurethane/montmorillonite nanocomposites with both high elongation at break and high tensile strength were studied by dynamic-infrared spectroscopy (dynamic-IR). The results show that crystallization induced by additional stress is impeded by the nano-layered organo montmorillonite.

Keywords PU/montmorillonite nanocomposite, Dynamic-IR, Crystallization

INTRODUCTION

Polymer/clay composites have been developed rapidly to the point where we can expect to apply this knowledge and derive maximum benefit from nano-layer dispersal and reinforcement^[1–3]. Recently polyurethane (PU)/montmorillonite nanocomposites with good mechanical properties, and especially high elongation at break, have been prepared in our group^[4, 5]. This paper presents our studies on the PU/montmorillonite nanocomposites by means of dynamic-IR for probing changes of the structure under stretching deformation. This would be helpful for understanding the molecular mechanism of the unusual mechanical properties of the material.

EXPERIMENTAL

Preparation of the Nanocomposites

Pure PU was produced by a one-step method in which 4,4-diphenylmethane diisocyanate (MDI) and polytetramethylene glycol (PTMG) in a molar ratio of 2:1 were directly mixed in *N,N*-dimethylformamide (DMF), and then the solution was heated to 80°C for 2.5 h. Subsequently, the solution was cooled to 40°C and propylenediamine was added followed by vigorous stirring for 1 h to complete the reaction. The molar ratio of propylenediamine and PTMG was 1:1. Detailed preparation of PU/montmorillonite nanocomposite was reported elsewhere^[4, 5].

Dynamic-IR

The dynamic-IR measurement was performed using a Bruker Equinox 55 spectrometer equipped with a wire-grid polarizer and MCT detector. Spectrum resolution is 4 cm⁻¹ and every spectrum is averaged with 32 scans.

RESULTS AND DISCUSSION

In Fig. 1, the infrared band at 3301 cm⁻¹ is attributed to the hydrogen-bonded N—H stretching of the polyurethane. The 1731 cm⁻¹ band is assigned to the free carbonyl, and the 1710 cm⁻¹ band is associated with the hydrogen-bonded carbonyls. It is clear that the bands for distinctive functional groups of the pristine PU and its

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nanocomposites are identical, confirming that the chemical structures of PU are not altered by the presence of silicate layers^[6]. According to the assignment of IR bands in the PU spectrum studied by Seymour *et al.*^[7], the degree of hard segment linking hard segment or silicate layers (degree of phase separation, DPS) and the degree of hard segment linking soft segment (degree of phase mixing, DPM) can be obtained easily^[8]. The values of carbonyl hydrogen bonding, DPS and DPM for pure PU and its nanocomposites are given in Table 1. The degree of hydrogen bonding of carbonyl groups and the resultant DPS increase in the presence of a small amount of silicate layers. This phenomenon shows that more C=O functional groups are bonded with the hydroxyl groups on the surface of silicate layers. The hard-segment-rich domains are dispersed in a soft-segment-rich matrix^[9], acting as the physical tie points as well as the reinforcing filler. As DPS increaseds, the tie points decrease allowing increase in chain slippage and disentanglement. The elongation at break of PU/montmorillonite nanocomposites is improved.

Table 1. The carbonyl hydrogen bond index (A_{1710}/A_{1731}), the degree of phase separation (DPS) and the degree of phase mixing (DPM) in pure PU and PU/montmorillonite nanocomposites

	Organoclay content (wt%)	A_{1710}/A_{1731}	DPS (%)	DPM (%)
Pure PU	0	0.579	36.67	63.33
Nanocomposite 1	2.0	0.653	39.50	60.50
Nanocomposite 2	3.6	0.745	42.69	57.31

Table 2. Strain-induced crystallization of PU/montmorillonite nanocomposites and pure PU

	Organoclay content (wt%)	Onset strain of strain-induced crystallization (%)
Pure PU	0	300
Nanocomposite 1	2.0	500
Nanocomposite 2	3.6	600

Table 3. Mechanical properties of PU/montmorillonite nanocomposites and pure PU

	Organoclay content (wt%)	Elongation at break (%)	Tensile strength (MPa)
Pure PU	0	600	15.91
Nanocomposite 1	2.0	1700	28.37
Nanocomposite 2	3.6	1560	36.45

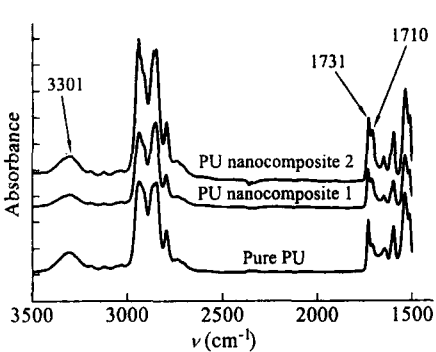


Fig. 1 The FT-IR spectra of pure PU and its nanocomposites

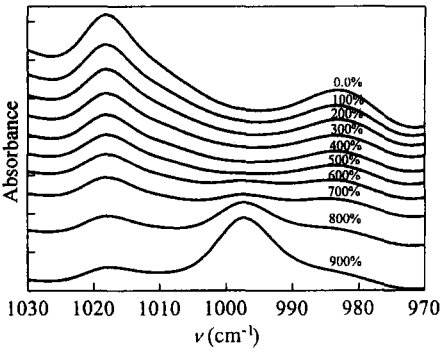


Fig. 2 The dynamic-IR spectra of nanocomposite 1 between 1030–970 cm^{-1}
Montmorillonite content: 2.0 wt%

As shown in Fig. 2, when the specimens were stretched, the strain-induced crystallization of soft segments gradually showed a characteristic band at 997 cm^{-1} ^[10]. This characteristic band appeared at 150%–180% low

elongation in pure PU^[11]. The existence of organo-montmorillonite shifts the onset of crystallization to higher strain. Here the values for the onset of crystallization of the soft segments are given in Table 2. The results illustrate that the strain-induced crystallization of the soft segments is impeded greatly by the organically modified montmorillonite. If extensive crystallization induced by stress take place, some micro-domains in these materials have to sustain the most stress supplied finally leading to the cleavage of the material. The nano-scale montmorillonite does have an inhibition effect on the orientation and crystallization of soft segments subjected to external strain, and prevent them effectively from the regular arrangement among macromolecular chains. The soft segment can be more elongated under an additional stress field. The PU/montmorillonite nanocomposites will give both good elongation behaviors and tensile strengths, as listed in Table 3.

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