ELSEVIER

Polymer 43 (2002) 1017–1020

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Polymer/layered clay nanocomposites: 2 polyurethane nanocomposites

K.J. Yao[a], M. Song[a,*], D.J. Hourston[a], D.Z. Luo[b]

[a]Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK
[b]Hyperlast Ltd, Birch Vale, Derbyshire SK22 1BR, UK

Received 24 September 2001; accepted 25 September 2001

Abstract

A kind of novel polyurethane/Na$^+$-montmorillonite nanocomposites has been synthesised using modified 4,4′-di-phenymethylate diisocyanate (M-MDI), modified polyether polyol (MPP) and Na$^+$-montmorillonite (layered clay). Here, MPP was used as a swelling agent to treat the layered clay. Experimental results indicated that with increasing the amount of layered clay, the strength and strain-at-break increased. The storage modulus below the glass transition temperature of the soft segments in the polyurethane was increased by more than 350%. With increased loading of layered clay, the thermal conductivity decreased slightly rather than increased. This finding will provide valuable information for polyurethane industry. © 2001 Published by Elsevier Science Ltd.

Keywords: Polyurethane; Nanocomposites; Clay

1. Introduction

In recent years, the investigation of organic–inorganic nanocomposites has become a very important field [1–4], since such materials exhibit unexpected synergistical properties derived from two components. One of the most promising composites systems is a hybrid based on organic polymers and inorganic clay minerals consisting of layered silicates.

The polyurethanes are an important and very versatile class of polymer materials. With desirable properties, such as its high abrasion resistance, tear strength, excellent shock absorption, flexibility and elasticity. However, there also exist some disadvantages, for example, thermal stability and barrier properties. To overcome the disadvantages, research on novel polyurethane/Na$^+$-montmorillonite nanocomposites is being developed in our group.

In this communication, we report our initial results on polyurethane/Na$^+$-montmorillonite nanocomposites.

2. Experimental

2.1. Materials

Modified 4,4′-di-phenylmethylate diisocyanate (M-MDI) (HYPERLAST 200/65-2875046), an amber liquid and modified polyether polyol (MPP) (HYPERLAST 200/65-2851045), a colourless liquid were kindly provided by Hyperlast in the United Kingdom. The viscosity and density of M-MDI are 150cps and 1.22 g cm^{-3} at 25°C, respectively. The viscosity and density of MPP are 1500cps and 1.03 g cm^{-3} at 25°C, respectively. Na$^+$-montmorillonite (layered clay) — PGW was obtained from Nanocor in USA.

2.2. Preparation of polyurethane/layered clay nanocomposites

Different amounts of layered clay were mixed with 100 ml of MPP, and stirred at 50°C for 72 h. The mixture of MPP and layered clay was blended with a known amount of M-MDI and stirred for 30 s at 20°C. The mixture was moulded in an O-ring mould. Curing was conducted at 78°C for 168 h, after which an elastic film was obtained.

2.3. Characterisation

X-ray diffraction experiment were performed on film samples on a Bruker X-ray diffractometer (AXS D8 Advance) using K_α ($\lambda = 0.54$ nm) radiation. Samples were scanned at a rate 0.24 °/min from ca. 1 to 25° in 2θ.

Mechanical tests were preformed according to the relevant ASTM standards. Tensile strength was measured using an Instron Material Tester (UK) at room temperature. All the reported result was the average of at least five measurements for tensile determinations.

---

* Corresponding author. Tel.: +44-1509-223-160; fax: +44-1509-223-949.
E-mail address: m.song@lboro.ac.uk (M. Song).

PII: S0032-3861(01)00650-4

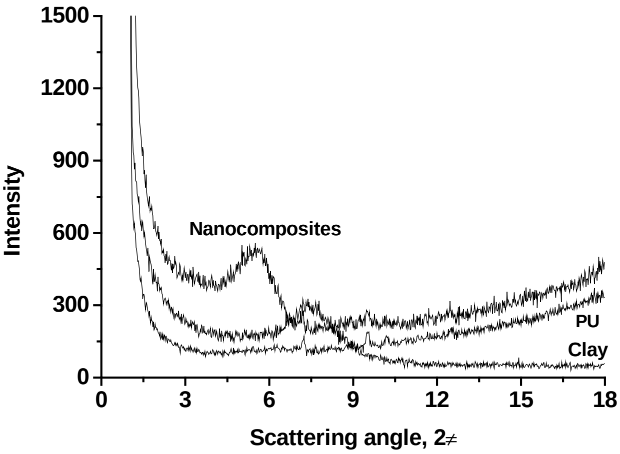

Fig. 1. The wide angle X-ray diffraction patterns of the polyurethane (PU)/layered clay nanocomposites: (a) pure PU, (2) pure clay and (3) 21.5% of clay. The d-spacing shifts to a higher value for the intercalated sample as the gallery example to receive the intercalating polymer.

Dynamical mechanical thermal analysis (DMTA) measurements were carried out on a model 2980 DMA Dynamic Mechanical Analyser (TA Instruments) (USA) in the tension mode using rectangular samples for the polyurethane/layered clay nanocomposite samples. A frequency of 10 Hz, a static force of 0.1N and amplitude of 5.0 μm were used. The temperature ramp was 3.0°C/min and the scanning range from −120 to 180°C.

The measurement of thermal conductivity was performed using a modulated differential scanning calorimeter (TA Instruments 2920 calorimeter) according to ASTM E1952-98 standard method [5]. An oscillation amplitude of 0.5°C and an oscillation period of 80 s were used. An oscillation amplitude of 1°C and oscillation period of 60 s with a heating rate of 3°C/min were used for the study of the glass transition behaviour of the soft segment in the polyurethane/layered clay nanocomposites.

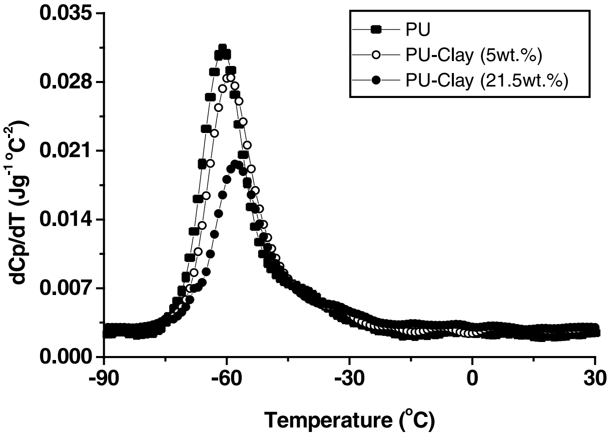

Fig. 2. dC_p/dT signals vs. temperature for PU/layered clay nanocomposites with different weight fractions of layered clay.

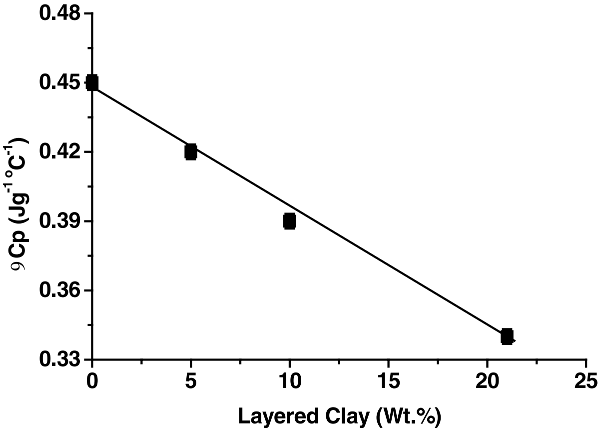

Fig. 3. ΔC_p value vs. weight fraction of layered clay.

3. Result and discussion

The X-ray diffraction patterns of the layered clay, the pure PU and PU/layered clay (21.5 wt%) nanocomposites are presented in Fig. 1. The pure PU exhibits an amorphous halo at 20° in 2θ. The gallery spacing of the layered clay is 1.1 nm. The gallery spacing of the layered clay in the composite increases to 1.6 nm for the PU/layered (21.5%) nanocomposites. This indicates that the PU chains were intercalated between the layered of clay [1].

Fig. 2 shows the differential of heat capacity signal, dC_p/dT, vs. temperature for PU/layered clay nanocomposites with different amounts of layered clay. By increasing the weight fraction of layered clay, the peak area of dC_p/dT signal vs. temperature decreased. The peak area of a dC_p/dT vs. temperature is equal to the increment of heat capacity, ΔC_p, at the glass transition temperature [6]. By increasing the weight fraction of layered clay, the value of ΔC_p decreases (see Fig. 3), indicating some MPP chains were intercalated between the layers in the clay. The glass transition of that part of MPP intercalated between the layers in the clay does not occur because these chains were confined strongly. By using a simple method [7], one can estimate the weight fraction, ω, of MPP chain intercalated between the layers in the clay

$$\omega = 1 - \Delta C_p(\text{MPP in nanocomposites})/\Delta C_p(\text{MPP in pure PU}) \quad (1)$$

For example, the values of ΔC_p for the PU/layered clay (21.5 wt%) and the pure PU were found to be 0.34 and 0.45 J g^{-1} °C^{-1}, respectively. According to Eq. (1), ω was found to be 24%. This means that 24% of MPP was intercalated between the layers in the clay.

Tensile — extension curves for the pure PU and the PU/layered clay (21.5%) nanocomposites are shown in Fig. 4. Data of tensile strength and strain-at-break vs

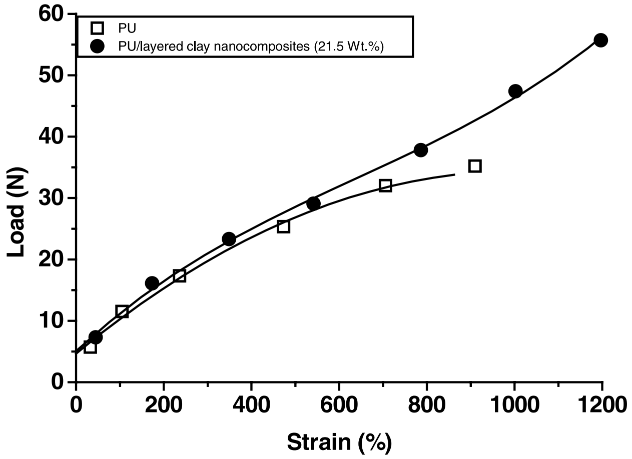

Fig. 4. Force-extension curves for the pure PU and nanocomposites (clay 21.5%).

Table 1
Tensile strength and strain-at-break vs. the loading of layered clay

Weight fraction of the clay (%)	Tensile strength (MPa)	Strain-at-break (%)
0	5.9	950
5	6.2	1020
10	6.5	1065
21.5	8.3	1160

the loading of layered clay are shown in Table 1. The layered clay result in a significant increase in strength and strain-at-break. At a loading of 21.5 wt% layered clay, the strength is increased by more than 44% and the strain-at-break is increased by more than 20%. It is believed that the improved elasticity may be attributed in part to the plasticising effect [8] of gallery onium ions, which contribute to dangling chain formation in the matrix.

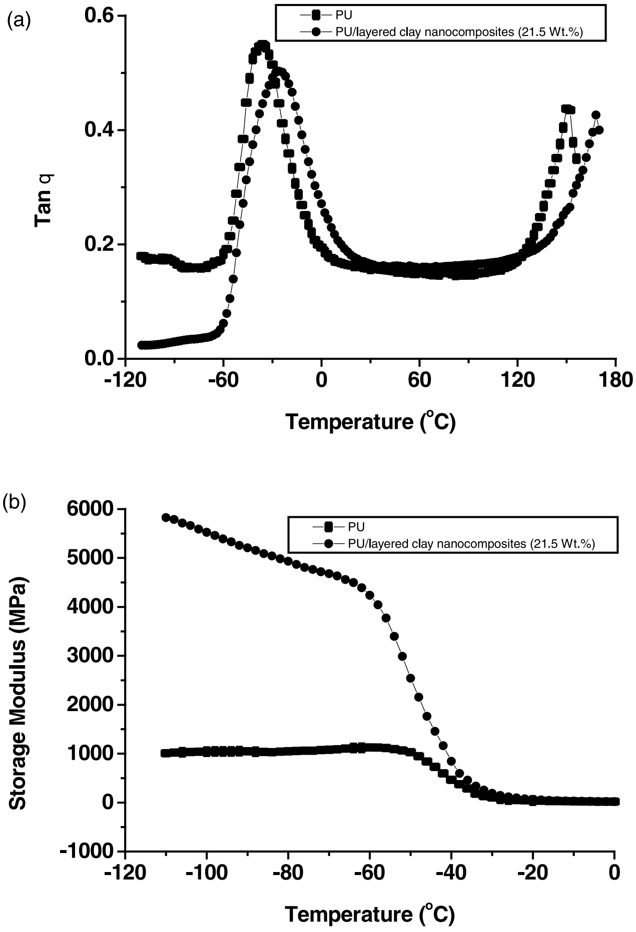

Fig. 5. (a) Tan δ vs temperature and (b) storage modulus vs. temperature for the pure PU and the nanocomposites (clay 21.5%).

Tan δ and storage modulus against temperature are shown in Fig. 5(a) and (b). The tan δ peak was slightly broadened which may result from the motion of polymers at the clay–polymer matrix interface [8]. By increasing the loading of layered clay, the glass transition temperature of soft segments shifted to high temperature, which was also confirmed by MDSC results (see Fig. 2). The storage modulus below the glass transition temperature is dramatically increased by more than 350%.

Fig. 6 shows the relationship between thermal conductivity and the loading of layered clay. By increasing the weight fraction of layered clay, the thermal conductivity decreased slightly rather than increased. Polyurethane being an excellent isothermal material has been used widely in refrigeration, the construction and petroleum industries. It is very important to reduce the thermal conductivity of polyurethane. It is believed that this finding, i.e. increasing the loading of layered clay in the nanocomposites does not result in an increase of thermal conductivity, should provide valuable information for the polyurethane industry.

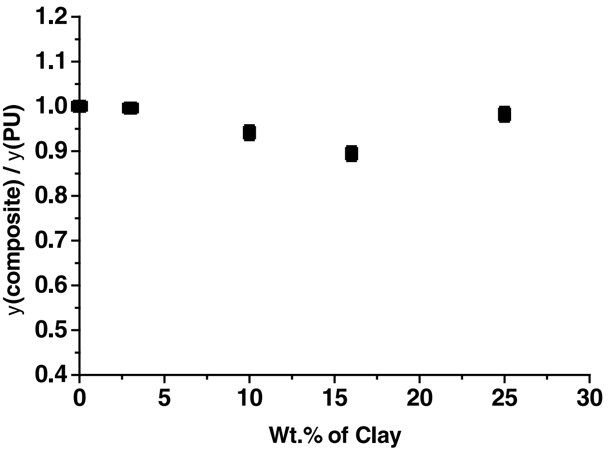

Fig. 6. Thermal conductivity vs. weight fraction of layered clay.

4. Conclusions

A kind of novel polyurethane/layered clay nanocomposites has been developed using modified 4,4′-di-phenylmethylane diisocyanate (M-MDI), MPP and Na^+-montmorillonite (layered clay). Layered clay has an important influence on thermal and mechanical properties of polyurethane. By increasing the amount of layered clay, the strength and stain-at-break increased. Storage modulus below the glass transition temperature of soft segments in the polyurethane was increased by more than 350%. Thermal conductivity decreased slightly with an increase in the loading of layered clay-a finding that will provide valuable information for the polyurethane industry.

References

[1] Giannelis EP, Krishnamoorti R, Manias E. Adv Polym Sci 1999;138: 108, also see references within.
[2] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. J Polym Sci Polym Chem 1993;31:2493.
[3] Ogawa M, Uroda K. Bull Chem Soc Jpn 1997;70:2593.
[4] Yano K, Usuki A, Okada A. J Polym Sci Polym Chem 1997;35:2289.
[5] ASTM, E1952-98: Standard test method for thermal conductivity and thermal diffusivity by modulated temperature differential scanning calorimetry.
[6] Song M, Hammiche A, Pollock HM, Hourston DJ, Reading M. Polymer 1995;36:3313.
[7] Song M, Hourston DJ, Pollock HM, Schafer FU, Hammiche A. Thermochim Acta 1997;304/305:335.
[8] Wang Z, Pinnavaia TJ. Chem Mater 1998;12:3769.