

Synthesis and Characterization of Poly(urethane-benzoxazine)/Clay Nanocomposites

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Introduction

Since the development of nylon 6/clay nanocomposite by the group of Toyota Central R&D Lab Inc [1-2], polymer-clay hybrid nanocomposites have been drawing more and more attention as a class of the most rapidly developing state-of-the-art materials. Due to the homogeneous dispersion of layered clay at nanometer scale, the polymer-clay interactions are maximized, affording dramatic improvements in the mechanical properties, barrier properties and thermal stability even at very low clay loading. Recently, we reported a synthesis of poly(urethane-benzoxazine) films from PU prepolymer and benzoxazine monomers, aiming at the improvement of the thermal stability of PU [3-4]. It was shown that the cure of the benzoxazine was limited in the presence of PU, due to the decomposition of PU at ca. 200°C. The poly(urethane-benzoxazine) films based on a monofunctional benzoxazine monomer **Pa** have little improvement on the thermal stability, which is due to the incomplete cure of **Pa**. From our studies on polybenzoxazine-clay nanocomposites, we knew that curing temperature of benzoxazine was lowered remarkably in the presence of organophilic montmorillonite (OMMT) [5]. In the light of this knowledge, we prepared poly(urethane-benzoxazine)/clay hybrid nanocomposites (PU/**Pa**-OMMT) from a copolymer based on PU prepolymer and **Pa**, and studied the effect of clay on the preparation and thermomechanical properties of poly(urethane-benzoxazine).

Experimental

PU prepolymer was prepared from 2,4-tolylene diisocyanate and polyethyleneadipate polyol in 2:1 molar ratio, and **Pa** was kindly supplied by Shikoku Corporation (Fig. 1). OMMT used in this study was prepared by a cation-exchange reaction using dodecyl ammonium chloride, according to the reported methods [2]. PU/**Pa**-OMMTs were prepared by a solvent method as follows: 0.81 g of 5 wt% OMMT suspension (40.7 mg of

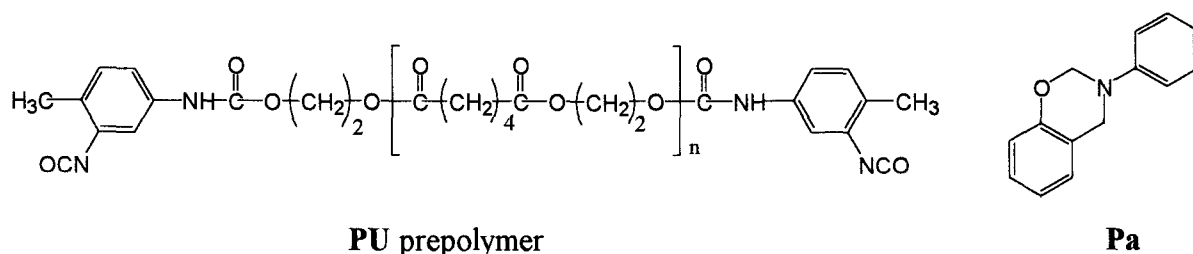


Fig. 1. Structure of PU prepolymer and **Pa**

OMMT) in DMAc was mixed with 2.012 g (9.52 mmol) of **Pa** and 2.013 g (2.03 mmol) of **PU** prepolymer. After stirring continuously for 2 h, the transparent homogenous solutions were cast on glass plates, and dried at 60°C for 18 h in an air-blowing oven. The cast films were then thermally treated at 100°C, 150°C, 170°C and 190°C for 1 h each. We also prepared the corresponding pristine poly-(urethane-benzoxazine) films for comparison.

Results and discussion

1. Preparation of **PU/Pa-OMMT** nanocomposite films

The formation of the exfoliated nanocomposite structures of **PU/Pa-OMMT** was confirmed by XRD, from the disappearance of the peak due to the basal diffraction of the layer-structured clay found in both **MMT** and **OMMT** (Fig.2). DSC showed that the exothermic peak due to the cure of **Pa** in **PU/Pa-OMMT** lowered remarkably compared with the pristine **PU/Pa**. For example, in the presence of 3% **OMMT**, the curing temperature of **PU/Pa** lowered by ca. 60°C for the onset, and 20°C for the max, as compared with the pristine one. The exothermic peak on DSC disappeared after curing at 190°C for 1 h as shown in Fig. 3. Therefore, **OMMT** has an outstanding catalytic effect on the ring-opening polymerization of **Pa**, as illustrated in Fig. 4. All the obtained films of **PU/Pa-OMMT** were deep yellow, transparent, and insoluble in THF, DMF and NMP.

2. Mechanical properties of **PU/Pa-OMMT** nanocomposite films

The tensile properties for some **PU/Pa-OMMT** films are listed in Table 1. As the content of **OMMT** increases, both tensile strength and modulus of **PU/Pa-OMMT** films

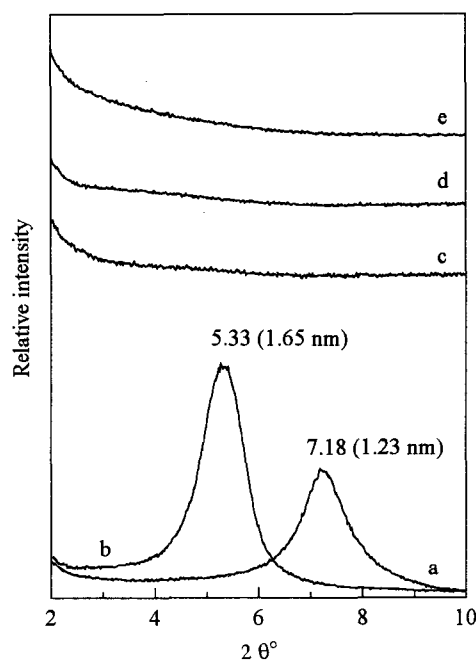


Fig. 2. XRD patterns of (a) MMT, (b) OMMT and PU/Pa=50/50 with OMMT loading: (c) 1%, (d) 3% and (e) 5%.

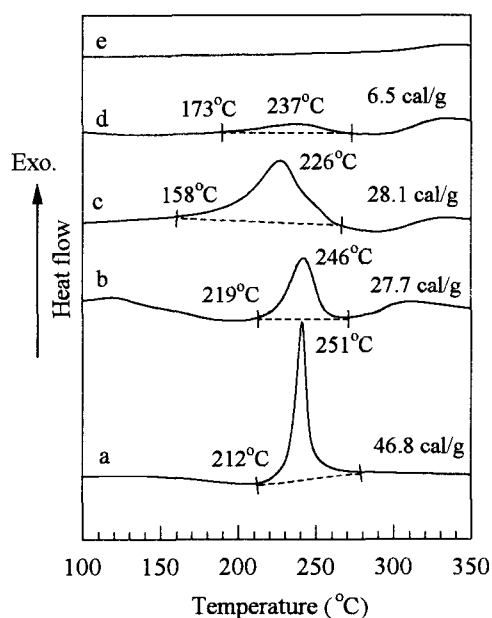


Fig. 3. DSC thermograms of (a) **Pa**, (b) **PU/Pa=50/50**, and **PU/Pa(50/50)** with 3% **OMMT** of (c) before cure and cured at (d) 150°C and (e) 190°C.

Table 1 Tensile properties of PU/Pa-OMMT films

Film composition		E (MPa)	σ (MPa)	Elongation (%)	Remark
PU/Pa (wt ratio)	OMMT (wt%)				
20/80	0	238	34.2	8	Plastics
	1	623	52.6	9	Plastics
	3	934	83.2	5	Plastics
50/50	0	9.8	9.6	203	Elastomer
	1	278	14.8	35	Plastics
	5	587	45.1	23	Plastics
80/20	0	5.7	3.7	343	Elastomer
	1	8.6	5.0	309	Elastomer
	5	19.0	12.9	173	Elastomer
	10	217	29.3	27	Plastics

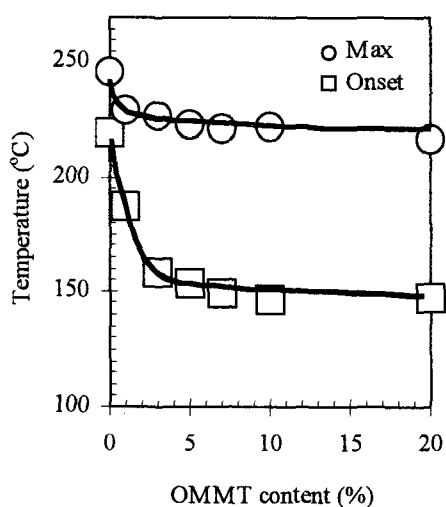


Fig. 4. The effect of OMMT content on the cure temperature of PU/Pa

increase, and the elongation at break decreases. The films have the characteristics of either plastics or elastomers depending on the ratio of PU/Pa. It was observed that in the case

of PU/Pa = 50/50, the nanocomposite films became plastic, while the pristine films were elastomer characteristics. As the OMMT loading up to 10%, all the films became plastics.

The viscoelastic properties of PU/Pa-OMMT elastomer films were shown in Fig. 5. All of the nanocomposite films also have only one Tg, and it shifted to high temperature as the content of OMMT increases (Fig. 6).

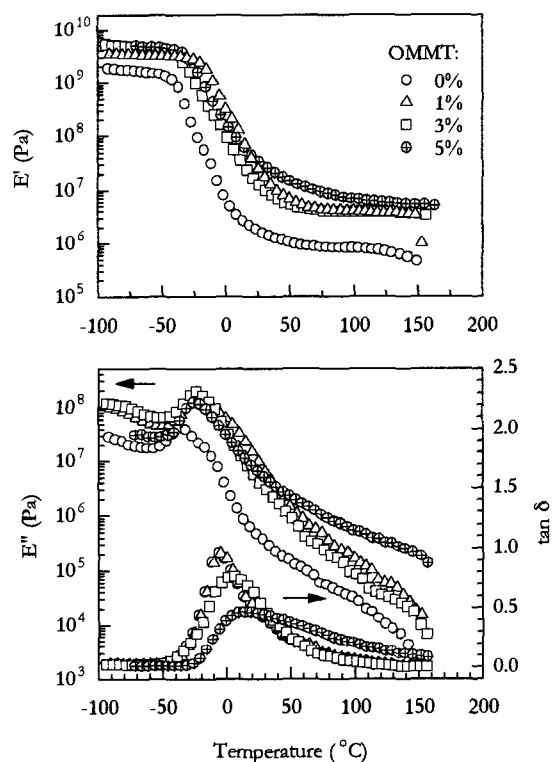


Fig. 5. Viscoelastic properties of PU/Pa=80/20 with various OMMT loadings

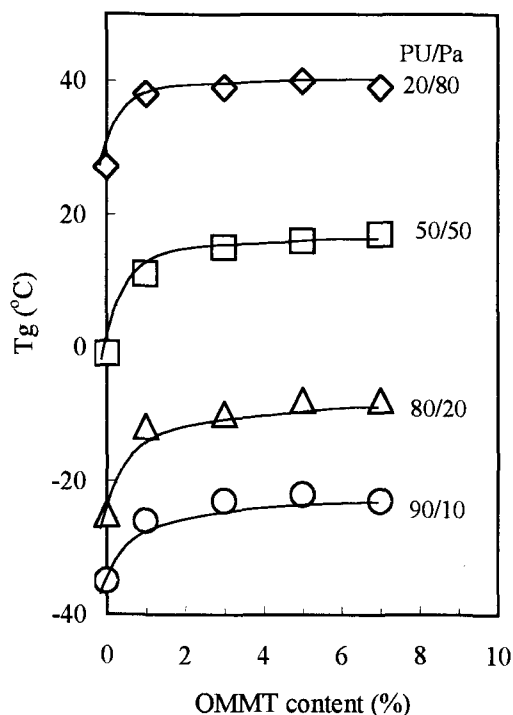


Fig. 6. Effect of OMMT on Tgs of PU/Pa

3. Thermal stability of PU/Pa-OMMT nanocomposite films

The thermal properties of PU/Pa-OMMT were investigated by TGA. Fig. 7 shows the results and Fig. 8 illustrates the effect of OMMT on the thermal decomposition temperature of PU/Pa. It is clear that the thermal stability of PU/Pa was enhanced remarkably by the addition of OMMT even with small amount of OMMT.

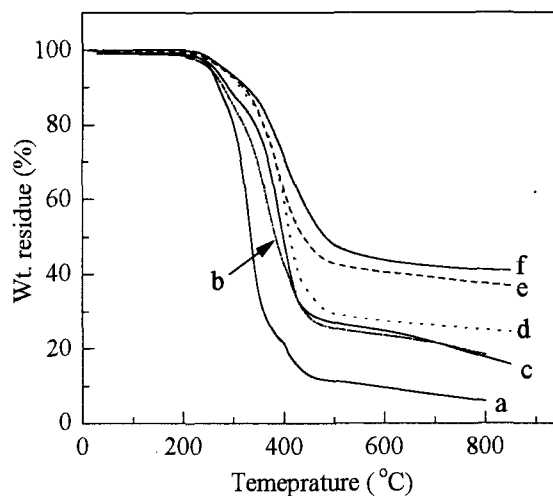


Fig. 7. TGA of the pristine PU/Pa of (a) 90/10, (b) 20/80; and PU/Pa-OMMT with 1% OMMT in the ratios of (c) 90/10, (d) 80/20, (e) 50/50 and (f) 20/80.

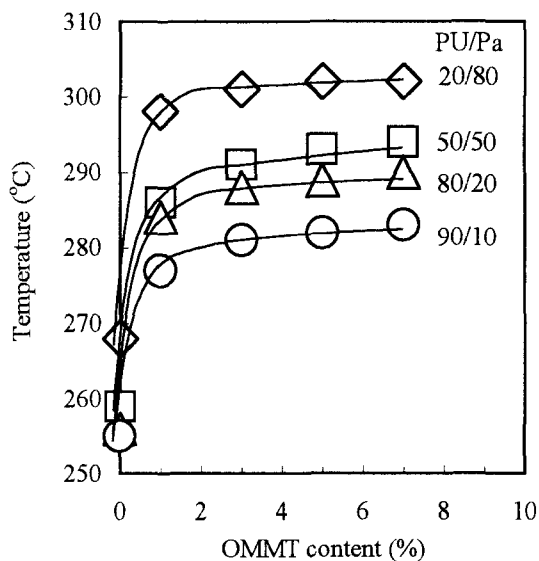


Fig. 8. Effect of OMMT on the Decomposition temperature of PU/Pa.

References

- [1] Okada A, Fukushima Y, Kawasumi A, Inagaki S, Usuki A, Sugiyama S, Kurauchi T, and Kamikaito O, *US Patent*, 4,739,007 (1988).
- [2] Okada A, Kawasumi A, Usuki A, Kojima Y, Kurauchi T and Kamikaito O, *Mater. Res. Soc. Proc.*, **171**, 45 (1990).
- [3] Takeichi T, Guo Y, and Agag T, *J Polym. Sci., Part A: Polym. Chem.*, **38**, 4165 (2000).
- [4] Takeichi T and Guo Y, *Polym. J.*, **33**, 437 (2001).
- [5] Agag T and Takeichi T, *Polymer*, **41**, 7083 (2000).