

MORPHOLOGY AND PERFORMANCE OF UNSATURATED POLYESTER NANOCOMPOSITES MODIFIED WITH ORGANOCCLAY AND THERMOPLASTIC POLYURETHANE*

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Abstract Unsaturated polyester (UPR)/thermoplastic polyurethane (TPU)/organoclay nanocomposites were prepared by melt compounding of thermoplastic polyurethane and unsaturated polyester prepolymer, and then mixing with the hybrids of styrene monomers and organoclay at ambient temperature. The crosslinking reaction eventually occurred through the unsaturated polyester prepolymer and styrene monomer. The morphology of the composites was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results show that the impact strength of UPR/TPU/organoclay nanocomposites increases obviously; the cure shrinkage decreases markedly, the glass transition temperature is enhanced and an elastic response to the deformation is prominent at the temperature above 10°C.

Keywords: Unsaturated polyester; Thermoplastic polyurethane; Organoclay; Nanocomposites.

INTRODUCTION

Unsaturated polyester resins (UPR) are one of the most widely used thermosetting materials due to their relatively inexpensive and excellent processability as well as reasonably good oil, moisture and acid resistances and mechanical properties. However, UPR has the disadvantage of poor impact resistance and high cure shrinkage. If the properties of UPR can be further enhanced and tailored while retaining good processability, it will have value for some existing markets, and new applications can be made possible^[1, 2].

The mechanical properties of UPR can be improved by incorporating polyurethane (PU). UPR-PU interpenetrating polymer networks (IPN) have been studied by Salla and co-workers^[3] as well as other researchers^[4, 5]. During the UPR-PU IPN synthesis, the PU was formed *in situ* at ambient temperature. However, only a few studies on the unsaturated polyester-thermoplastic polyurethane (TPU) prepared by melt compounding have been found in the literature. Recent studies from our laboratory have shown that modification of unsaturated polyester with thermoplastic polyurethane has some problems such as the toughness increases while modulus and heat resistance decrease^[6].

TPU has been extensively used due to its superior physical properties and high versatility in chemical structures. TPU is a linear segmented block copolymer composed of alternating hard and soft segments. The hard segments are held together by interchain hydrogen bonds to form physical crosslinks. At melt temperatures, the hydrogen bonds break and linear primary chains are released, which can enhance the compatibility between

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TPU and UP prepolymer.

It is well known that polymer/clay nanocomposites can exhibit good mechanical properties when the polymer is intercalated between silicate layers, or the silicate layers are exfoliated by the polymer. Intercalated/exfoliated silicate layers function as nano-sized reinforcing materials. In recent years, many studies have been undertaken by researchers to find ways to apply the polymer/clay nanocomposites as industrial materials^[7–11]. However, if the clays are not dispersed uniformly or are agglomerated in the polymer, they become defects in the polymer/clay nanocomposites. The key to obtain significant property enhancements is to disperse, or exfoliate the individual silicate platelets within the polymer matrix to take advantage of their high aspect ratio and surface area.

Most methods for the preparing polymer layered silicate nanocomposites have focused on substituting long alkyl modifiers in the silicate layer to expand basal spacing. However, the expansion of basal spacing through long alkyl modifiers has been insufficient to improve the physical properties of nanocomposites because good affinity between clay surfaces and polymer chains is another key factor in enhancing physical properties^[12–16].

In our study, we used the mixture of dodecylamine and concentrated hydrochloride acid to prepare organoclay, which later was physically mixed with styrene monomers at room temperature. The results have showed that the increase in d-spacing for the styrene monomers/organoclay hybrids was from 1.94 nm to 2.36 nm^[17]. As we know, the compatibility between the styrene monomer and the unsaturated polyester is high because they both contain benzene rings^[18]. Therefore, styrene monomers can increase both the basal spacing and the favorable interaction between clay and the polymers.

UPR/TPU/organoclay nanocomposites were prepared by melt compounding of thermoplastic polyurethane and unsaturated polyester prepolymer, and then mixing with the hybrids of styrene monomers and organoclay at ambient temperature. The crosslinking reaction eventually occurred through the unsaturated polyester prepolymer and styrene monomer.

There are very few reports on UPR/TPU/organoclay nanocomposites prepared by melt compounding. The objective of this study is to explore the effect of the TPU and organoclay on the morphology and performance of UPR/TPU/organoclay nanocomposites. The impact strength, tensile strength, flexural strength, hardness and shrinkage of the nanocomposites are investigated.

EXPERIMENTAL

Materials

Dodecylamine (DDA) (C.P. grade) was provided by Guoyao Chemical Agents Ltd.(Shanghai, China). Pristine clay (800 mesh, its cation exchange capacity = 100 mmol/100g) was supplied by Nanhai Non-Metal Mineral Co. (Guangdong, China). Concentrated hydrochloric acid (HCl) (C.P. grade) was purchased from Guangzhou Donghong Chemical Agents Factory (Guangdong, China). Unsaturated polyester prepolymer (molecular weight of about 2700 g/mol), under the trade name, LY-386, and styrene monomers were provided by Futian Chemical Agents Ltd. (Guangdong, China). Dicumyl peroxide (DCP) was supplied by Shanghai Chemical Agents Company (Shanghai, China). Thermoplastic polyurethane (molecular weight of about 39000), under the trade name, CA-1130, was purchased from Nanfei Chemical Agents Ltd. (Guangdong, China). Other reagents were used without further purification.

Preparation of Organoclay

First, 20 g of pristine clay was dispersed in distilled water with vigorous stirring, and then the mixture of 8.82 g of dodecylamine (DDA) and 4.4 mL of concentrated hydrochloride acid (HCl) was poured into the pristine clay-water solution and stirred vigorously for 4 h at 80°C. The precipitate formed were separated by filtration and washed several times with distilled water until total removal of Cl[−] ions was confirmed by AgNO₃ titration, and then dried to yield the organoclay.

Preparation of UPR/TPU/Organoclay Composites

TPU and UP prepolymer (e.g. 15 wt% respect to UPR) were heated to 190°C in an oil bath and subjected to

mechanical stirring at 250 r/min under a nitrogen atmosphere for 1 h. After the temperature was dropped to ambient temperature, the hybrids of styrene and organoclay and DCP were added and mixed for 1 h.

It was cured at press molding machine at 135°C for 7 min, and post cured at 80°C for 4 h. Tensile testing was carried out with a Tensiometer LJ-1000 (Shanghai, China) according to GB/T10654-2001. Unnotched Izod impact testing was performed according to GB/T1843-1996 with an Impact Tester UJ-4 (Tianjin, China). Flexural strength testing was performed according to GB/T14208-1993.

Hardness was measured according to GB/T4340.1-1999 with a Digital Microhardness Tester HV-1000 Vickers Durometer (Guangzhou, China).

The degree of swelling and the interlayer distance of the clay in the samples were determined by X-ray diffraction (XRD). The XRD patterns were recorded on a D/max-rB diffractometer (Japan) using Cu K α radiation at room temperature in the range of $1^\circ \leq 2\theta \leq 70^\circ$ with a scanning rate of 2 ($^\circ$)/min. Thermal properties of UPR / TPU/organoclay nanocomposites were investigated by thermogravimetric analysis (TGA), performed with NETZSCH-TG209F1 (USA) under N₂ atmosphere at the heating rate of 10 K/min. Dynamic mechanical properties of nanocomposites were measured with a DMA2980 Dynamical Mechanical Analyzer (TA Instrument, USA). The specimen size was 3 mm $\times$ 12 mm $\times$ 13 mm and the data were run in fixed frequency mode at 1 Hz, over a temperature range of 100°C to 250°C at a heating rate of 5 K/min.

The impact-fractured surfaces were examined by using a scanning electron microscope Model JSM-5910 (Germany). Before taking photomicrographs, the samples were coated with a thin layer of gold. Transmission electron microscopy (TEM) photomicrographs were obtained on a Model JEM-100CX II TEM (Japan) microscope.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 shows XRD patterns of pristine clay, organoclay and cured UPR/TPU/organoclay nanocomposite. The d-spacing of pristine clay is 1.54 nm, while that of UPR/TPU/ organoclay nanocomposite seems to be centered around 3.20 nm, with respect to 1.94 nm of the organoclay. According to conventional interpretations, this suggests some degree of polymer intercalation into the organoclay galleries.

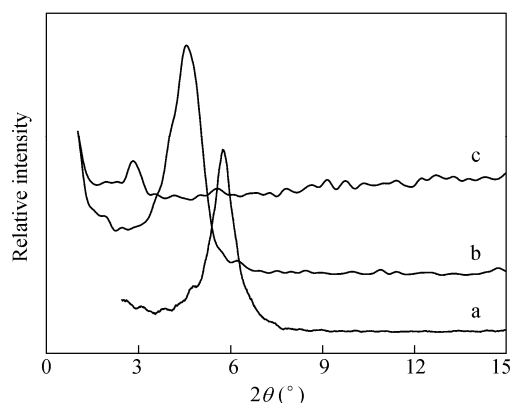


Fig. 1 XRD curves of (a) pristine clay, (b) organoclay, and (c) cured UPR filled with 15% TPU and 2% organoclay

SEM Analysis

Micrographs of the unnotched Izod fracture surface of UPR filled with different amount of TPU are shown in Fig. 2. The neat UPR sample shows smooth and fish scale-shape surface representing brittle failure in a homogenous material, as shown in Figs. 2(a). Figure 2(b) shows the fracture surface of the modified UPR with 7.5% TPU. The white lines are due to tearing of materials between two crack phases, causing a surface step. As the TPU contents increase, the smooth fracture initiation region becomes smaller while the rough secondary fracture region grows. Secondary cracks show throughout the secondary fracture region. The secondary cracks

consume more energy than the smooth initiation region. As the amount of TPU increases, large fibrils are pulled out of the secondary fracture surface.

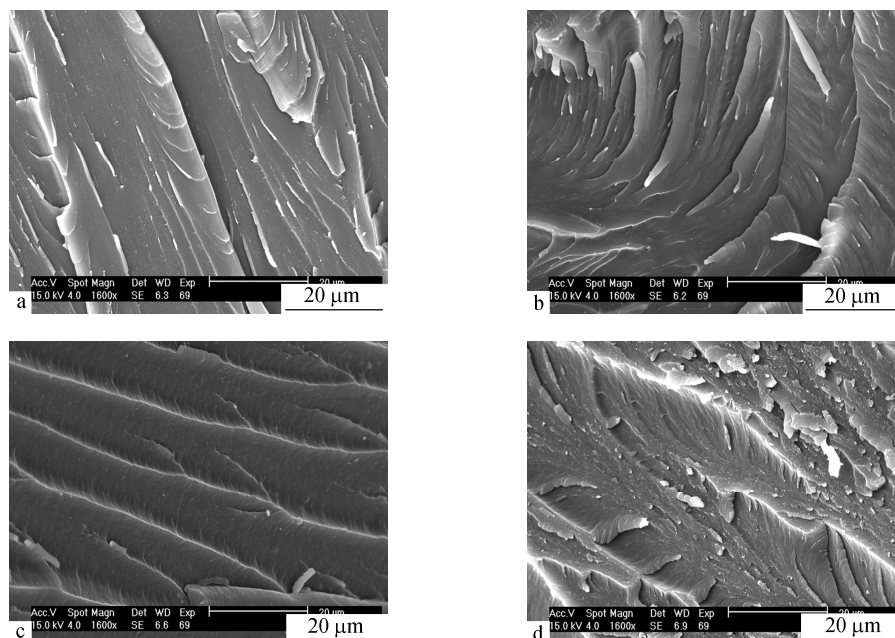


Fig. 2 SEM photographs of UPR filled with TPU: (a) 0%, (b) 7.5%, (c) 15% and (d) 22.5%

Figure 3 shows that the fracture surface of the composites filled with different amounts of organoclay. The fracture surface of a nanocomposite at 1%–3% organoclay loading exhibits very different failure mode and it looks like that of filler-modified UPR. As shown in Figs. 3(a) and 3(b), there are no distinct agglomerates observed on these micrographs. The crack bifurcation is quite evident and it is associated with the presence of very small particles that are assumed to be the dispersed clay, which may absorb larger quantity of energy upon impact force. Hence, the mechanical properties of the nanocomposites increase. When the amount of organoclay is 3%, as shown in Fig. 3(c), obvious aggregation of clay is observed. This can be attributed to the increase of contact opportunity of clay particles with increasing clay content. Moreover, many microvoids that are attributed to the pulling off of the clay particles from the polymer matrix under the stress are observed. This phenomenon indicates that the compatibility and interaction between clay and polymer phases is poor. The interphase can not transfer the stress effectively, therefore the mechanical properties decrease.

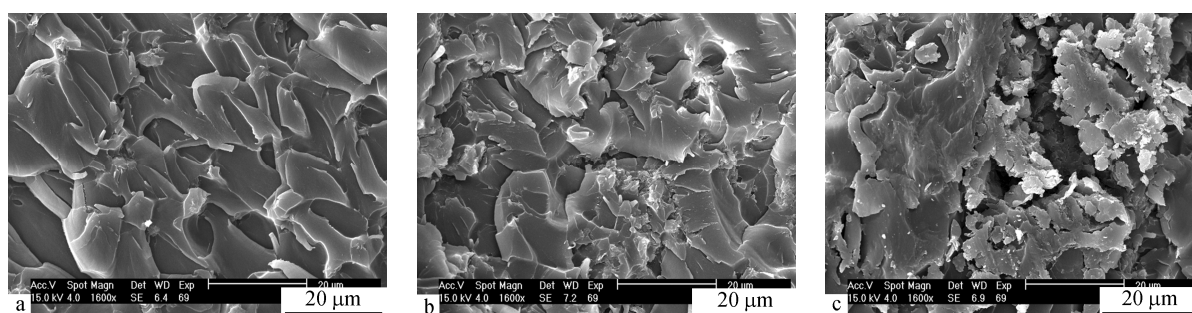


Fig. 3 SEM photographs of UPR filled with organoclay: (a) 1%, (b) 2%, (c) 3%

When the UPR is modified with both TPU and organoclay, at low organoclay loading, the fracture surfaces show both features of fracture surfaces described above (Figs. 2 and 3). However, the crack bifurcations are smaller. It indicates that the toughening by TPU dominates the toughness of these materials at lower organoclay loading. On increasing organoclay loading to 2%, the fracture surfaces exhibit a finer three dimensional appearance, as shown in Fig. 4(b). The cracks bifurcate, creating multiple fracture surfaces and causing greater energy dissipation. It indicates that the addition of both TPU and organoclay can increase the toughness of the composites markedly.

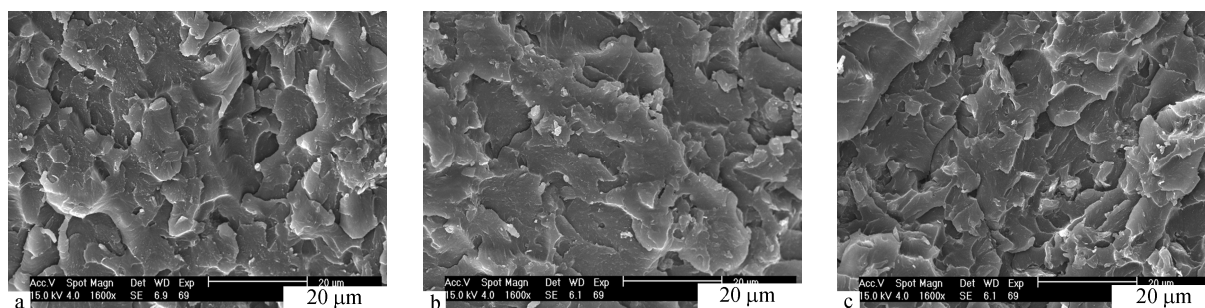


Fig. 4 SEM photographs of UPR/TPU/organoclay nanocomposites: (a) 15% TPU, 1% organoclay, (b) 15% TPU, 2% organoclay and (c) 15% TPU, 3% organoclay

It seems that the TPU phase in the nanocomposites has the role of dispersing crazes and stopping the spread of crazes, while clay particles induce crazes due to shearing, the larger fine crazes in the nanocomposites can absorb more impact energy, therefore the mechanical properties increase.

TEM Analysis

Figure 5 shows the TEM micrographs for UPR with different contents of TPU. It is clear that TPU domain sizes increase with the increase of TPU content. When TPU is 7.5%, the diameter of TPU phase in the UPR matrix is about 100 nm, the interphases are blurred. With increase of the TPU content, the morphology of the particles become irregular and the sizes increase. The TPU domains act as crack stoppers and improve the impact strength^[14–22].

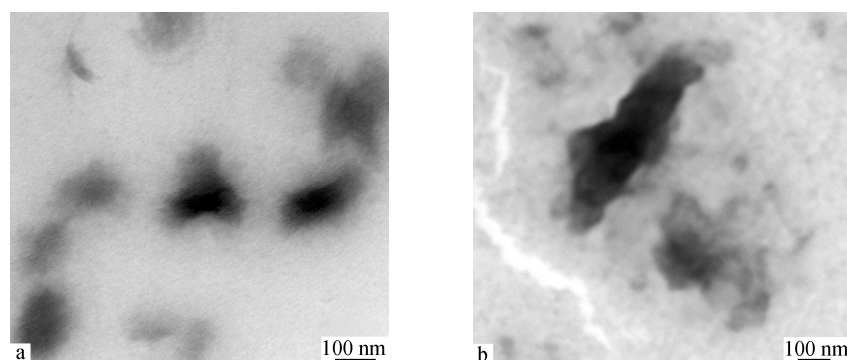


Fig. 5 TEM photographs of UPR filled with TPU: (a) 7.5%, (b) 15%

The TEM images in Fig. 6 display individual silicate layers apparent as dark lines. The dispersion of the silicate layers is regular with the intercalated structure.

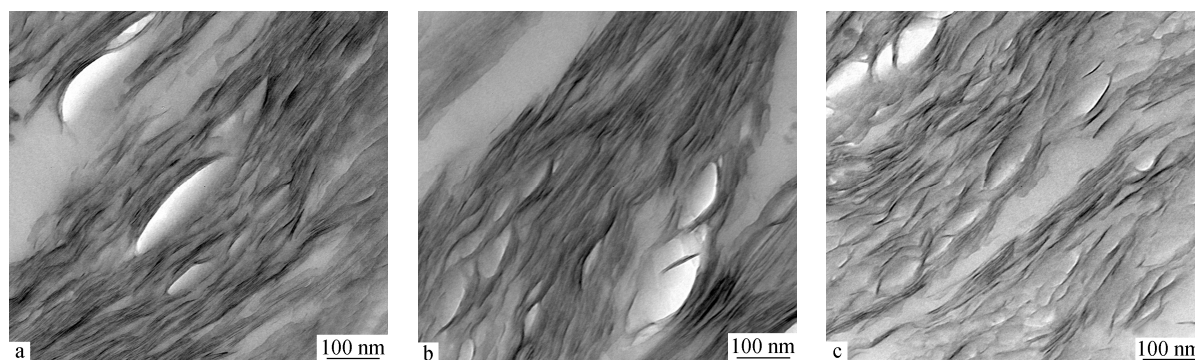


Fig. 6 TEM photographs of UPR filled with organoclay: (a) 1%, (b) 2%, (c) 3%

Figure 7 shows the UPR/TPU/organoclay nanocomposites. Adding organoclay to the nanocomposites causes a reduction of the TPU particle size. This suggests that the organoclay suppresses the coalescence and agglomeration of TPU particles. It also appears to contribute to an improvement of the interfacial adhesion between the phases^[19].

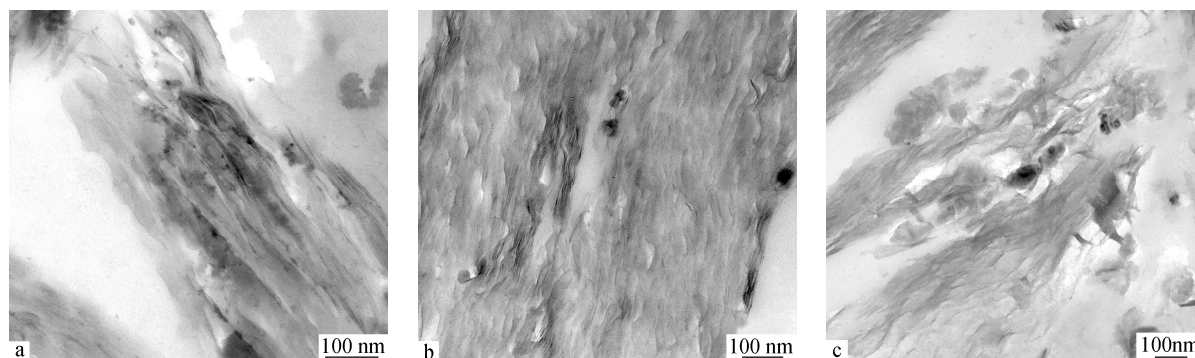


Fig. 7 TEM photographs of UPR/TPU/organoclay nanocomposites: (a) 15% TPU, 1% organoclay, (b) 15% TPU, 2% organoclay and (c) 15% TPU, 3% organoclay

Thermal Degradation

The results of thermogravimetric analysis (TGA) of the UPR/TPU/organoclay nanocomposites are listed in Table 1. For UPR with 2% organoclay, the onset temperature of degradation is significantly enhanced^[20, 21]. This can be explained by the strong interaction between the copolymer chains and the organoclay layers in the nanocomposite, hence preventing the decomposition. This increase in the thermal stability can be attributed to the high thermal stability of clay and to the interactions between the clay particles and the polymer matrix. The maximum mass loss (MML) decreased from 96.4 to 82.3 as the clay content increases from 0% to 2%. This enhancement of char formation is ascribed to the high heat resistance of clay^[22]. The results show that the thermal stability of the UPR/TPU/organoclay nanocomposite is higher than that of neat UPR.

Table 1. TGA results for the thermal degradation of UPR/TPU/organoclay nanocomposites

Samples	T_{onset}^* (°C)	$T_{0.5}^{**}$ (°C)	MML (%)
Pristine UPR	202.5	378.2	96.4
TPU/organoclay (15/0)	235.0	379.9	92.9
TPU/organoclay (0/2)	257.0	386.9	82.3
TPU/organoclay (15/2)	250.0	383.5	88.1

* The onset point as 5 wt% weight loss; ** The mid-weight point as 50 wt% weight loss

DMA Analysis

Plots of $\tan\delta$, storage modulus and loss modulus as a function of temperature for UPR/TPU/organoclay nanocomposites are shown in Figs. 8–10. It is seen from Fig. 8, the introduction of soft TPU results in the decrease of storage modulus of the composites, but storage modulus of the composites increase markedly by incorporation of organoclay^[23–25]. At 20°C, E' of the nanocomposite with 2% organoclay is about 1000 MPa higher than that of neat UPR. The significant enhancement of storage modulus indicates that organoclay has a strong effect on the elastic properties of neat UPR and can be attributed to the fine dispersion of silicate clay that restricts the plastic deformation of polymer chains under loading as well as the good interfacial adhesion between the polymer matrix and the clay particles^[26]. It is clear that the TPU and organoclay have important effects on the storage modulus. On the other hand, above 10°C, E' of the UPR/TPU/organoclay nanocomposite is higher than that of the UPR/organoclay nanocomposite, indicating that an elastic response to the deformation is prominent in the presence of both TPU and organoclay when the material becomes soft.

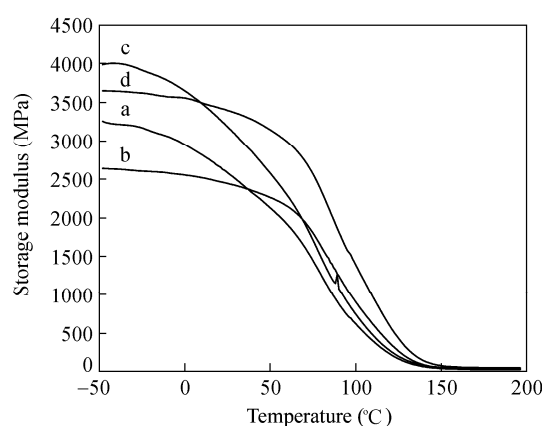


Fig. 8 Storage modulus of UPR/TPU/organoclay nanocomposites: (a) neat UPR, (b) 15% TPU, (c) 2% organoclay and (d) 15% TPU, 2% organoclay

Figure 9 shows loss modulus of UPR/TPU/organoclay nanocomposites. Above room temperature, the enhancement of E'' is significant in the UPR with 2% organoclay (Fig. 9c). It is seen that organoclay has obvious effect on the movement of molecules.

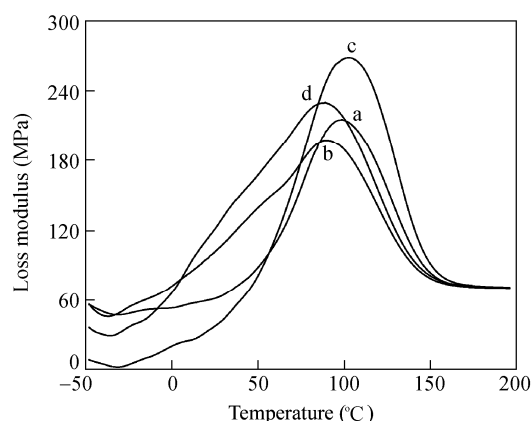


Fig. 9 Loss modulus of UPR/TPU/organoclay nanocomposites: (a) neat UPR, (b) 15% TPU, (c) 2% organoclay and (d) 15% TPU, 2% organoclay

Figure 10 shows the $\tan\delta$ of UPR/TPU/organoclay nanocomposites. The composite with TPU has lower T_g s due to the presence of TPU with soft chains (Fig. 10b), but the T_g increases with 2% organoclay loading

(Fig. 10c). This increase in T_g can be attributed to the strong interaction between the polymer and layered silicate surfaces because of the nanometer size, which restricts segmental motion near the organic-inorganic interface^[27].

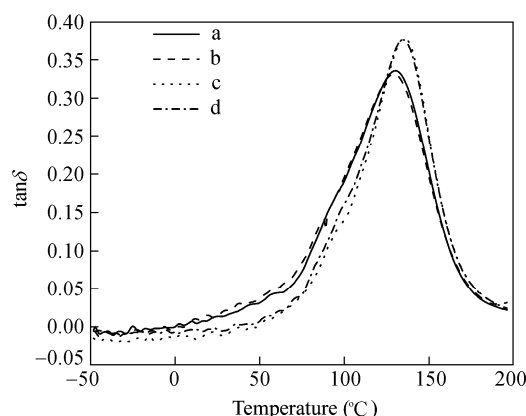


Fig. 10 $\tan\delta$ values of UPR/TPU/organoclay nanocomposites: (a) neat UPR, (b) 15% TPU, (c) 2% organoclay and (d) 15% TPU, 2% organoclay

The UPR/TPU/organoclay nanocomposite (Fig. 10d) has nearly the same T_g value as UPR/orgnaoclay nanocomposite (Fig. 10c). The interaction between polymer chains and organoclay layers may prevent the segmental motion of the macromolecules, leading to the increase of T_g ^[28, 29].

Mechanical Properties

Table 2 shows the properties of UPR/TPU/organoclay nanocomposites. The results show that the impact strength increases greatly while the other mechanical properties decreased with the corporation of TPU. For the composites without organoclay, when 15% TPU is added, the tensile strength, flexural strength and Vickers hardness decrease by 13.1%, 18.6% and 42.8%, respectively due to the increased flexibility caused by uncross-linked TPU content^[30, 31]. Some of these problems can be solved by adding organoclay^[32].

Table 2. Properties of UPR/TPU/organoclay composites

Samples	Impact strength (kJ/m ²)	Tensile strength (MPa)	Flexural strength (MPa)	Vickers hardness (degree)	Cure shrinkage (%)
Pristine UPR	0.74	36.7	61.7	332	4.46
TPU/organoclay (0/1)	0.78	37.6	64.89	352	4.16
TPU/organoclay (0/2)	0.89	38.6	79.2	376	3.56
TPU/organoclay (0/3)	0.75	36.3	65.2	394	2.66
TPU/organoclay (7.5/0)	0.90	35.4	54.4	275	4.01
TPU/organoclay (7.5/1)	1.10	36.0	60.7	282	3.51
TPU/organoclay (7.5/2)	1.80	37.1	78.5	288	3.11
TPU/organoclay (7.5/3)	1.20	35.5	61.5	295	2.56
TPU/organoclay (15/0)	1.52	31.9	50.2	190	3.53
TPU/organoclay (15/1)	1.79	34.6	55.24	201	3.21
TPU/organoclay (15/2)	2.29	36.0	74.4	215	2.79
TPU/organoclay (15/3)	1.55	34.2	56.95	218	2.13

In the UPR/TPU/organoclay nanocomposites containing 2% organoclay and 15% TPU, the impact strength shows more than 200% increase with respect to neat unsaturated polyester resin, and tensile strength reaches the maximum. It is believed that up to 2% organoclay loading, the organoclay is well intercalated in the polymer matrix. The clay platelets possess an extremely high aspect ratio^[33, 34], and thus act as reinforcing elements, assuming a good filler-matrix interaction^[35]. Increasing organoclay content to 3% in the nanocomposites

decreases the tensile strength. This is attributed to agglomeration of clay and thus clay-polymer surface interactions decrease. This agglomeration leads to a reduction in the tensile strength.

Usually, the flexural strength of the composites depends on the ratio of filler modulus to matrix materials modulus^[35, 36]. Since organoclay has a higher modulus than the polymeric matrix, the flexural strength increases with low clay contents. However, the flexural strength gradually decreases as the amount of the low modulus, flexible phase increases.

It is seen in Table 2 that Vickers hardness increases in the experimental range. The agglomerates of organoclay have little effect on the Vickers hardness of the composites. On one hand, the molecular chains are confined and stiffness is increased due to the incorporation of organoclay and the intercalation effect of the polymers. On the other hand, clay itself can play the reinforcement role as inorganic filler. Therefore, Vickers hardness increases with increasing the amount of organoclay. The cure shrinkage of the composites decreases obviously with introduction of TPU and organoclay. Because TPU and UPR are not completely compatible, some of TPU separate from UPR and become dispersed phases which have heat expansion properties to compensate the shrinkage of the UPR continuous phase.

The enhancement of mechanical properties is directly attributed to the reinforcement by the finely dispersed silicate layers^[37] and to the strong interactions between matrix and silicate layers *via* the formation of hydrogen bonding^[38, 39].

CONCLUSIONS

Unsaturated polyester (UPR)/thermoplastic polyurethane (TPU)/organoclay nanocomposites were prepared by melt compounding of thermoplastic polyurethane and unsaturated polyester prepolymer, and then mixing with the hybrids of styrene monomers and organoclay at ambient temperature. For the UPR/TPU/organoclay nanocomposites containing 15% TPU and 2% organoclay, the impact strength increases by 3 times, the shrinkage reduces markedly, while other properties have little decrease.

REFERENCES

- 1 Huang, Y.J. and Jiang, W.C., *Polymer*, 1998, 39: 6631
- 2 Li, W. and Lee, L.J., *Polymer*, 2000, 41: 697
- 3 Ramis, X., Cadenato, A., Morancho, J.M. and Salla, J. M., *Polymer*, 2001, 42: 9469
- 4 Valette, L. and Hsu, C.P., *Polymer*, 1999, 40: 2059
- 5 Ajithkumar, S., Patel, N.K. and Kansara, S.S., *Eur. Polym. J.*, 2000, 36: 2387
- 6 Zhang, X.Y., Thesis, South China University of Technology, 2008
- 7 Park, J.H. and Jana, S.C., *Macromolecules*, 2003, 36: 2758
- 8 Kojima, Y.A., Kawasumi, U.M., Okada, A., Kurauchi, T. and Kamigaito, O.J., *Polym. Sci.*, 1993, 31: 1755
- 9 Lee, K., Nam, J.H., Lee, J.H., Lee, Y., Cho, S.M., Jung, C.H., Choi, H.G., Chang, Y.Y., Kwon, Y.U. and Nam, J.D., *Electrochem. Commun.*, 2005, 7(1): 113
- 10 Liu, A., Xie, T. and Yang, G., *Macromol. Chem. Phys.*, 2006, 207: 701
- 11 Tjong, S.C. and Bao, S.P., *J. Polym. Sci. B*, 2004, 42: 2878
- 12 You, C.J. and Jia, D.M., *Chinese J. Polym. Sci.*, 2003, 21(4): 443
- 13 You, C.J., Jia, D.M., Zheng, Z.Y., Ding, K., Xi, S., Mo, H.L. and Zhang, Y.H., *Chinese J. Polym. Sci.*, 2003, 21(5): 551
- 14 You, C.J., Xu, J.G., Xi, S., Duan, X.X., Shen, J. and Jia, D.M., *Chinese J. Polym. Sci.*, 2005, 23(5): 471
- 15 Pearson, A.R. and Yee, F.A., *J. Matter Sci.*, 1991, 26: 2838
- 16 You, C.J. and Jia, D.M., 2004, *Chinese Pat.*, ZL 200410015450.4
- 17 Xu, J.G., Thesis, South China University of Technology, 2006
- 18 Lin, S.P., Shen, J.H., Lee, Y.J., Liao, K.H., Yeh, J.T., Chang, F.C. and Hsieh, K.H., *Compos. Sci. Technol.*,

- 2008, 68: 709
- 19 Mahmood, M.Z. and Musa, R.K., *Polym. Eng. Sci.*, 2004, 44: 1152
 - 20 Yano, K., Usuki, A., Okada, A., Kurauchi, T. and Kamigaito, O., *J. Polym. Sci. Part A: Polym. Chem.*, 1993, 31: 2493
 - 21 Ward, W.J., Gaines, G.L., Alger, M.M. and Stanley, T.J., *Membrane Science*, 1991, 55: 173
 - 22 Wen, J. and Wikes, G.L., *Chem. Mater.*, 1996, 8: 1667
 - 23 Hasegawa, M., Okamoto, H., Kato, M. and Usuki, A., *J. Appl. Polym. Sci.*, 2000, 78: 1918
 - 24 Nam, P.H., Maiti, P., Okamoto, M., Kotaka, T., Hasegawa, N. and Usuki, A., *Polymer*, 2001, 42: 9633
 - 25 Liu, X. and Whu, Q., *Polymer*, 2001, 42: 1001
 - 26 Oh, T.K., Mervat, H., Charles, B. and Hassan, E.S., *J. Appl. Polym. Sci.*, 2006, 100: 3465
 - 27 Agag, T., Kogs, T. and Takeichi, T., *Polymer*, 2001, 42: 3399
 - 28 Zhang, Z., Zhang, L., Li, Y. and Xu, H., *Polymer*, 2005, 46: 129
 - 29 Zhang, Z., Zhang, L. and Li, Y., *Macromol. Mater. Eng.*, 2005, 290: 430
 - 30 Wu, S., *Polym. Eng. Sci.*, 1990, 30: 105
 - 31 Wu, S., *Polymer*, 1985, 26: 855
 - 32 Perrin-Sarazin, F., Ton-That, M.T., Bureau, M.N. and Denault, J., *Polymer*, 2005, 46: 11624
 - 33 Park, S.J., Seo, D. and Lee, J.R., *J. Colloid Interface Sci.*, 2002, 251: 160
 - 34 Wu, Q., Liu, X. and Berglund, L.A., *Polymer*, 2002, 43: 2445
 - 35 Ma, J., Xu, J., Ren, J.H., Yu, Z.Z. and Mai, Y.W., *Polymer*, 2003, 44: 4619
 - 36 Nieksen, L. and Landel, R., "Mechanical properties of polymers and composites," 2nd ed, Marcel Dekker, New York, 1994
 - 37 Wang, Z. and Pinnavaia, T.J., *Chem. Mater.*, 1998, 10: 3769
 - 38 Ray, S.S. and Okamoto, M., *Prog. Polym. Sci.*, 2003, 28: 1539
 - 39 Kawasumi, M., *J. Polym. Sci. Part A: Polym. Chem.*, 2004, 42: 819