

The Structure and Dynamic Properties of Thermoplastic Polyurethane Elastomer/Hindered Phenol Hybrids

Daling Xiao,¹ Xiuying Zhao,¹ Yiping Feng,² Ping Xiang,¹ Liqun Zhang,^{1,2} Weimin Wang³

¹The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China

²The Key Laboratory for Nano-Materials, China Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

³Department of Chemistry, College of Staten Island, City University of New York Graduate Center, New York 10016

Received 1 June 2009; accepted 14 November 2009

DOI 10.1002/app.31828

Published online 7 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The organic hybrids of thermoplastic polyurethane (TPU)/hindered phenol (AO-80) were prepared through melt blending, which was followed by hot and cold pressing procedure. The microstructure and dynamic mechanical properties of the hybrids were systematically investigated through SEM, DSC, XRD, FTIR, DMA and a tensile tester. The experimental results indicated that AO-80 was completely dissolved in the matrix. The glass transition of the soft segments of TPU was found to shift to higher temperature with the amount of AO-80 increasing, whereas the glass transition of the hard segments exhibited nearly no evident change, indicating that AO-80 was selectively located in the soft region of TPU and the formation of the strong intermolecular interactions (hydrogen

bonding) between AO-80 and the soft region of TPU. With the increase of AO-80 in the hybrids, the $\tan\delta$ peak gradually shifted to higher temperatures and the maximal $\tan\delta$ value increased from 0.4 to 1.6. Meanwhile, the glass transition temperature ranges broadened and the TA value increased greatly with the more content of AO-80. Because of the decrease of the hard segments amount in the hybrids, the tensile stress of these hybrids decreased, but still maintained at a high level. The hybrids were expected to have potential applications as high performance damping materials combined with good mechanical properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2143–2150, 2010

Key words: TPU; hindered phenol; hybrids; damping

INTRODUCTION

Damping materials are widely used in the auto industry, building, precious machines and some other areas. The special viscoelasticity of polymers can transform sound and vibration energy into heat,^{1,2} and make them suitable candidate for applying as damping materials. Polyurethane (PU) is one of the earliest and the strongest damping materials to be studied.³ In the past years, PU materials were mainly synthesized into IPN (interpenetrating polymer network) damping materials.^{4–6} It was reported that the binary and ternary PU IPN damping materials had good damping properties, wide glass transition range, high loss factor ($\tan\delta$ value) and so on.^{7–10} However, the preparation process of IPN is rela-

tively complicated. Moreover, the cost of preparing PU IPN materials is high and further processing is difficult, which limits the application of PU IPN materials.

In recent years, a great of effort has been devoted to developing organic hybrid damping materials with the high damping factor.¹¹ A hindered phenol of 3,9-bis[1,1-dimethyl-2- β -(3-tertbutyl-4-hydroxy-5-methylphenyl) propionyloxy] ethyl]-2,4,8,10-tetraoxaspiro-[5,5]-undecane (AO-80) was used as the functional additives in the hybrids. Figure 1 displays the chemical structures of AO-80, which shows the one with many hydroxyl groups and ester groups. Wu and his coworkers blended chlorinated polyethylene (CPE) and acrylic rubbers (ACM) with AO-80 to prepare damping materials.^{12–14} Such hybrids exhibited two distinct relaxation transitions: (1) the glass transition associated with CPE in the matrix, and (2) the hydrogen bonding dissociation associated with AO-80 in the particles. Compared with the neat CPE, the hybrids possessed a much higher dynamic mechanical loss property. Zhao et al.¹⁵ and Xiang et al.¹⁶ succeeded in developing NBR/AO-80 cross-linked composites, with the max $\tan\delta$ value approaching 3.2 and the glass transition temperature (T_g) range also broadening markedly. The static

Correspondence to: L. Zhang (zhanglq@mail.buct.edu.cn).

Contract grant sponsor: The Outstanding Young Scientists Foundation of the National Natural Science Foundation (NSF) of China; contract grant number: 50725310.

Contract grant sponsor: The NSF of China; contract grant number: 50973007.

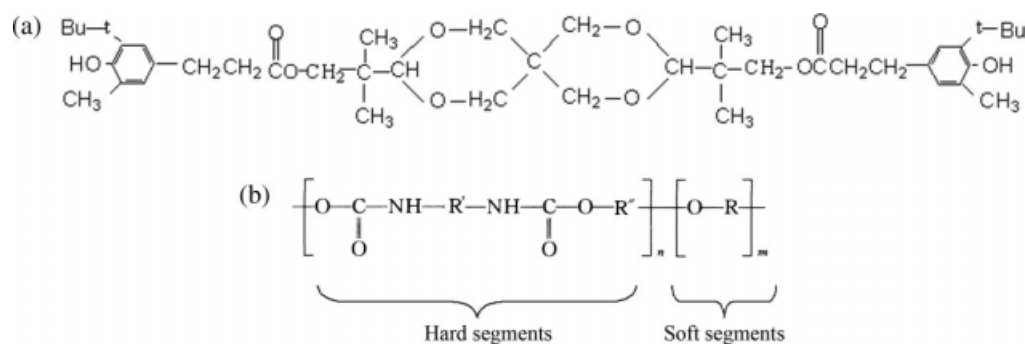


Figure 1 Chemical structure of AO-80 (a) and structure schematic of TPU macromolecule (b) R, R' and R'' represent alkyl group or aromatic group, respectively.

mechanical properties of NBR with AO-80 were greatly improved correspondingly. The high dynamic mechanical loss property was attributed to the strong intermolecular interactions between the AO-80 and the matrix, as such interactions would enhance the intermolecular friction and result in a large consumption of energy during dynamic deformations.

The aim of this study was to prepare, characterize, and evaluate TPU/AO-80 hybrids with high damping performance. Thermoplastic polyurethane (TPU) is such an important type of polyurethane, which contains lots of polar groups such as ester groups, ether groups and imino groups in its main chain (Fig. 1 displays the structural representation of TPU). The polar groups of TPU could provide possibilities for the formation of hydrogen bonding with the functional groups of hindered phenol. Hence, the addition of AO-80 in TPU hybrids could improve the dynamic performance of TPU for damping application. The organic hybrids of TPU/AO-80 were prepared through melt blending. The microscopic structure and dynamic mechanical properties of the hybrids were systematically investigated by SEM, DSC, XRD, FTIR, and DMA. Some interesting phenomena were found. Especially, it was observed that AO-80 only formed molecular interaction with the soft segments and selectively dispersed in the soft regions of TPU. In addition, as expected, these hybrids displayed excellent comprehensive performance and had potential applications as high performance damping materials coupled with good mechanical properties.

EXPERIMENTAL

Materials

The TPU (Desmopan DP9380A) used in this research was provided by Germany Bayer Co., AO-80 (ADK ATAB AO-80), in the form of crystalline powder, was provided by Asahi Denka Co., (Tokyo, Japan). All materials were used without further purification.

Sample preparation

TPU/AO-80 hybrids were prepared by using the following procedure and conditions: (1) The as-received TPU was dried in the cabinet dryer at 110°C for 2 h. (2) Then the dried TPU was kneaded on a two roll mill at 150°C for 3 min. After that, AO-80 powder were added with the TPU/AO-80 mass ratios of 100/0, 100/10, 100/30, 100/50, 100/70, and 100/100, respectively. These mixtures were then kneaded on the two roll mill at 150°C for 5 min to prepare TPU/AO-80 hybrids. (3) To get the samples for characterizations, the hybrids were molten for 3 min, hot-pressed at 170°C for 10 min under the pressure of 15 MPa, and then cool-pressed at room temperature for 15 min under the pressure of 15 MPa.

Characterization

Scanning electronic microscope (SEM) images were taken from the representative fracture surfaces of TPU/AO-80 hybrid, using a XL-30 field emission SEM made by FEI Company. The SEM specimens were prepared by brittle fracturing the hybrid in liquid nitrogen.

X-ray diffraction (XRD) data were acquired from a Rigaku D/Max 2500VBZt/PC X-ray diffractometer made by Rigaku Corporation in Japan. The XRD data were recorded in the scattering angle range of 3–90°.

Differential scanning calorimeter (DSC) measurements were performed on the DSC 204F1 calorimeter made by NETZSCH Co. (Germany). The DSC curves were recorded from –100 to 150°C with an increasing temperature rate of 10°C/min.

The FTIR spectra were obtained by scanning the specimens in the wavenumber range from 400 to 4,000 cm⁻¹ with the resolution of 2 cm⁻¹ for 128 times. By using the Attenuated Total Reflection (ATR) technique, the FTIR spectra of AO-80 were obtained from the pressed ultrathin disk specimen made of AO-80 and potassium bromide (KBr), whereas the spectra of TPU hybrids were obtained

from the film specimens with the thickness approximately 1mm.

Dynamic viscoelasticity measurements were carried out on a Dynamic Mechanical Analyzer (DMA VA3000) made by 01dB-METRAVIB Co., in France. The specimen dimensions were 20mm long, 6mm wide, and around 1mm in thickness. The temperature dependence of the loss factor $\tan\delta$ was measured in the range from -90 to 150°C with the frequency of 1 Hz and the heating rate of $3^\circ\text{C}/\text{min}$. The frequency dependence of the $\tan\delta$ was performed at different temperatures, ranging from -40 to 60°C . In this temperature range, isothermal tests were run on the specimens by increasing the temperature stepwise by 5°C . Before to measurement, the specimens were equilibrated for 5 min at each temperature and then tested from 1 to 200 Hz.

Tensile tests of the TPU/AO-80 hybrids were conducted according to ASTM standard (D412; Dumb-bell-shaped), and the specimens were tested on a LRX Plus Tensile Tester made by Lloyd instruments, in UK.

RESULTS AND DISCUSSION

Morphology of TPU/AO-80 hybrids

Figure 2 shows the SEM photographs of the fracture surfaces of TPU/AO-80(100/50) hybrids. The fracture surface was very smooth, and no any particles corresponding to micro or nano dispersion of AO-80 were observed. In TEM micrographs (not shown here), a homogeneous structure with no dispersed particles was observed. These phenomenon just indicated the favorable compatibility between AO-80 and TPU, and implied that small molecules such as AO-80 might disperse in TPU at the molecular level. Subsequent XRD, DSC and DMA results will further support this viewpoint. Generally, good dispersion of mixtures comes from the thermodynamic driving force. Beside this, the strong shear stress associated with high temperature (higher than the melting point of AO-80), and the mechanical kneading process could significantly promote fine dispersion of AO-80 molecules in the TPU matrix.

Crystallization and glass transition of TPU/AO-80 hybrids

Figure 3 shows the DSC traces of the as received AO-80, quenched AO-80, neat TPU, TPU/AO-80 hybrids, respectively. As shown in Figure 3(a), the as-received AO-80 powder was crystallized and the melting temperature was around 122.5°C . After the as-received AO-80 was heated to 160°C and quickly quenched to the room temperature, the amorphous AO-80 with the T_g about 40.9°C was obtained.

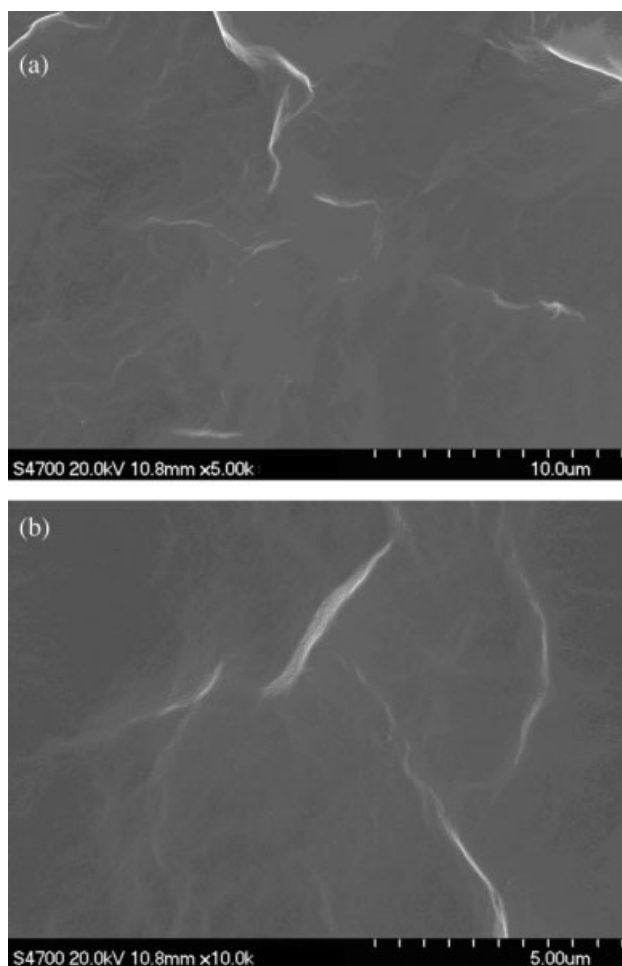


Figure 2 SEM photograph of fracture surface of TPU/AO-80 (100/50) hybrids.

As shown in Figure 3(b), the as-received TPU had two glass transition temperatures at around -50.5°C and 47.0°C , respectively, corresponding to the glass transition of soft segments (termed as $T_{g,s}$) and hard segments (termed as $T_{g,h}$) in the TPU. Since the ratio of hard region in TPU is lower than soft region and hard region contains ordered parts and disordered part, the glass transition reflected by disordered part of the hard region is not strong and sometimes not easy to be observed. Compared with the as-received TPU, TPU/AO-80 hybrids showed two glass transition temperatures, corresponding to the $T_{g,s}$ and $T_{g,h}$ of the TPU. However, the $T_{g,s}$ of TPU/AO-80 hybrids shifted from -50.5 to 0.8°C along with the content of AO-80 increased from 0 phr to 100 phr (parts per hundred of rubber by weight). Interestingly, the $T_{g,h}$ of TPU/AO-80 hybrids just had 2 or 3°C change as AO-80 increased. Moreover, the DSC curves of the hybrids did not show either the melting peak or glass transition peak of AO-80. All these phenomena suggested that AO-80 were dispersed in TPU at a molecular level through melt blending, and

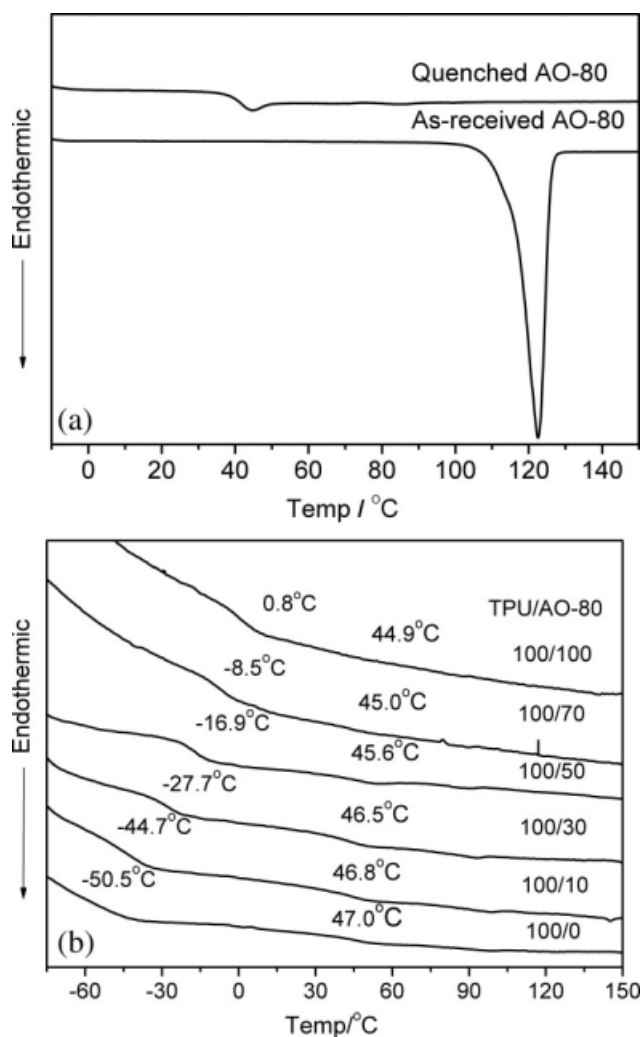


Figure 3 DSC curves of (a) neat AO-80 and (b) TPU/AO-80 hybrids.

TPU/AO-80 hybrids were successfully prepared as expected. Moreover, it was demonstrated that AO-80 molecules formed strong intermolecular interactions with TPU, especially with the soft segments of TPU. The strong intermolecular interactions greatly restricted the motion of soft segments and evidently increased the T_g s of TPU. Since the volume fraction of whole soft region in TPU increased with the incorporation of AO-80, the hard segments possibly became more active owing to the chemical connection between soft segments and hard segments, which further resulted in a slight decrease of T_g . Another result was that the glass transition of soft segments became more and more apparent because of the expansion of soft region, whereas the glass transition of hard segments became more difficult to be observed.

Figure 4 shows the X-ray diffraction (XRD) traces of the neat TPU and TPU/AO-80(100/50) hybrid, as

well as the XRD traces of AO-80 (both as-received and quenched). The as-received and quenched AO-80 displayed typical crystalline and amorphous characteristics, respectively. The XRD trace of the TPU/AO-80(100/50) was similar to that of pure TPU and quenched AO-80, indicating that AO-80 in the hybrid was amorphous. Overall, the XRD results were consistent with the DSC results, and further supported the above results.

Figure 5 shows the FTIR spectra of the quenched AO-80, TPU and the TPU/AO-80 hybrids. The spectrum of the quenched AO-80 indicated a significant absorption at 3494 cm^{-1} , which is assigned to O—H vibration affected by OH—OH interactions (hydrogen-bonded) between AO-80 molecules.¹⁵ For the TPU/AO-80 (100/30) and TPU/AO-80(100/70) hybrids, the infrared band of O—H groups clearly appeared at 3460 cm^{-1} . Moreover, compared with the pure TPU, the C—O—C band shifted from 1080 cm^{-1} to 1085 cm^{-1} . However, the -NH groups of the hard segments at 3323 cm^{-1} was unchanged when AO-80 added in the hybrids. All these could be attributed to the formation of intramolecular hydrogen bonding between —OH groups of AO-80 and —C—O—C— groups of segments of TPU. Furthermore, we also observed that the wave number of (OH—O, 3460 cm^{-1}) hydrogen bond was lower than that of (OH—OH, 3494 cm^{-1}) hydrogen bond of quenched AO-80, indicating that the bond energy of the former was stronger than the latter. These FTIR results were consistent with SEM, XRD, and DSC. More importantly, FTIR experiments provided possible interactions existed in the hybrids and explained why AO-80 selectively dissolved in soft regions of TPU.

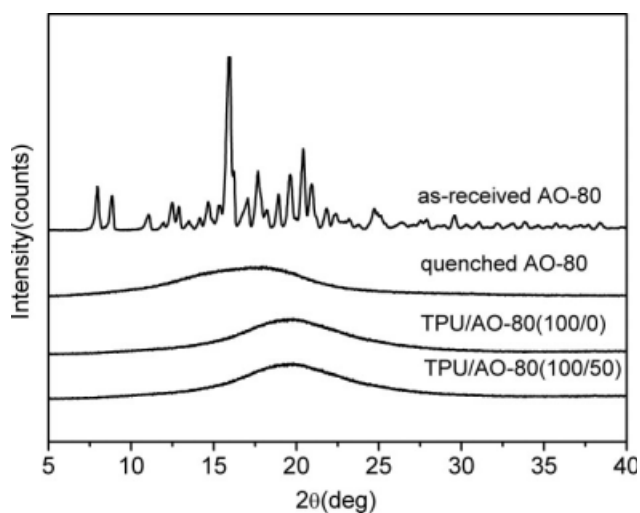


Figure 4 X-ray diffraction (XRD) curves of AO-80 and TPU/AO-80 hybrids.

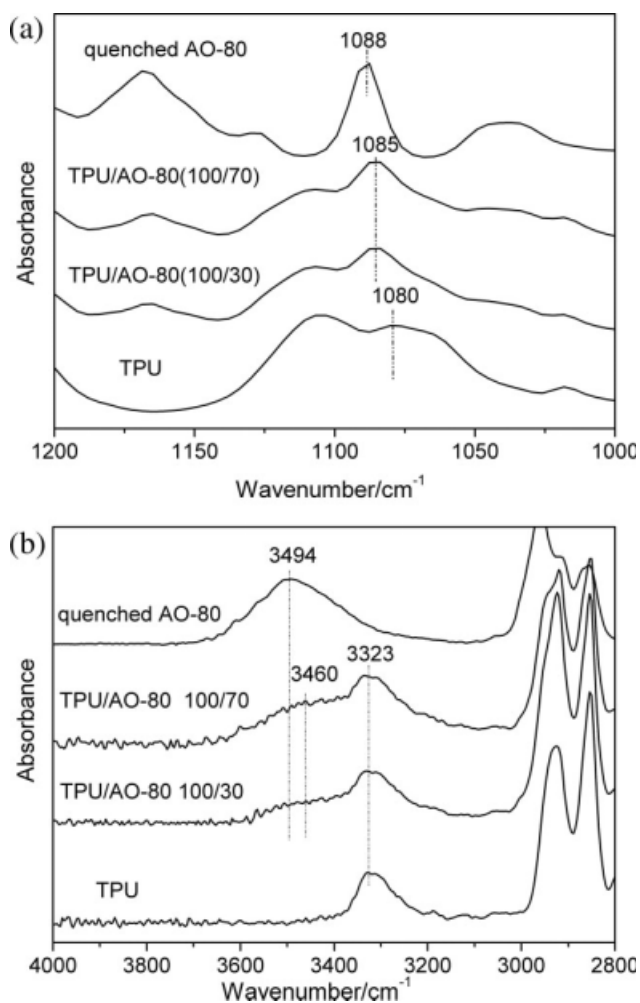


Figure 5 Infrared spectrum in the ether (a) and amido (b) groups stretching region for quenched AO-80, TPU and TPU/AO-80 hybrids.

Dynamic mechanical properties of TPU/AO-80 hybrids

Figure 6 shows the temperature dependence of the $\tan\delta$ values of the hybrids with various mass ratios of TPU/AO-80. All the TPU/AO-80 hybrids displayed only one $\tan\delta$ peak, which was corresponding to the glass transition of soft segments of TPU. With an increasing amount of AO-80 in the hybrids, the $\tan\delta$ peak gradually shifted to higher temperatures and the temperature range of $\tan\delta > 0.3$ became broader. Particularly, when the AO-80 amount in the TPU/AO-80 hybrids increased from 0phr to 100phr, the $\tan\delta$ value increased from 0.4 to 1.6. In addition, the temperature range of the $\tan\delta$ value larger than 0.3 was broadened from 26°C to 38°C when the ratio of TPU/AO-80 was from 100/0 to 100/100. Such an unexpected change of $\tan\delta$ peak was very interesting. It is well known that the damping performance of a polymeric material is mainly determined by its viscoelastic behavior in a

transitional region between the glassy and the rubbery states. In this region, the macromolecular chain segments, not entire macromolecules, tend to vibrate in phase with an external vibration. However, the movement of molecular segments usually cannot keep up with the imposed vibration, resulting in the increase of the internal friction and energy dissipation.¹ The stronger the internal friction is, the higher the $\tan\delta$ value and the better the damping performance of the material would be. For the TPU/AO-80 hybrids, the strong intermolecular interactions between AO-80 and TPU reduced the mobility of TPU chain segments and caused the high energy dissipation (destruction and re-construction of hydrogen bonding) under dynamic deformations. These results are in an increase of the $\tan\delta$ value. Additionally, the broadening of the $\tan\delta$ peaks with the increase of AO-80 amounts could be attributed to the numerous types of interactions existed in the TPU/AO-80 hybrids. Taken together, high $\tan\delta$ value and broad transition temperature ranges suggested that the TPU/AO-80 hybrids could possess excellent damping properties. Moreover, the $\tan\delta$ peak corresponding to the T_{gh} of TPU did not show up. This phenomenon presented by DMA again supported the fact that AO-80 mainly dispersed in and interacted with the soft regions of TPU. The reason why the glass transition of hard segments of TPU didn't appear was already suggested in DSC part.

Table I summarized the DMA results of the neat TPU and the different hybrids. The peak area (TA) from the $\tan\delta \sim$ temperature curves could be considered as a damping index. It was a measure of the energy dissipation of a transition process.¹⁷ As shown in Table I, compared with the neat TPU, TPU/AO-80 hybrids exhibited unusually high TA

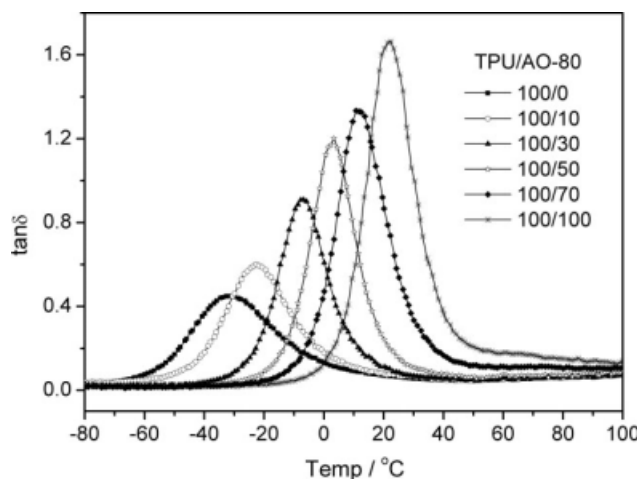


Figure 6 Temperature dependence of the loss tangent ($\tan\delta$) values for TPU and TPU/AO-80 hybrids with varied mass ratios of TPU/AO-80.

TABLE I
Damping Properties of Neat TPU and TPU/AO-80 Hybrids

TPU/AO-80 phr/phr	Tan δ max		Temperature range of tan δ > 0.3			Area
	value	T/°C	T1/°C	T2/°C	$\geq T/°C$	TA
100/0	0.45	-32.0	-43.6	-17.4	26.2	23.8
100/10	0.60	-22.7	-35.0	-7.1	27.9	26.0
100/30	0.91	-6.8	-20.0	7.1	27.1	27.8
100/50	1.20	3.3	-10.4	19.3	29.7	32.4
100/70	1.33	10.8	-3.2	31.9	35.1	40.3
100/100	1.66	22.4	5.9	43.0	37.1	47.8
	Tan δ max ^a		Frequency ranges of tan δ value >0.3 ^a			
	value	Freq/Hz	Freq1/Hz		Freq2/Hz	
100/0	0.52	1.0×10^5	7.6×10^2		3.1×10^7	
100/50	1.05	1.1×10^3	1.0×10^1		1.6×10^6	

^a The reference temperature was 10°C.

value. The TA value of the hybrids increased from 23.8 to 47.8 when the AO-80 amount in TPU/AO-80 hybrids increased from 0phr to 100phr. On the other hand, the TPU/AO-80 hybrids had efficient damping (tan δ > 0.3) over a relatively wider temperature range.

Figure 7 shows the frequency dependence of tan δ and the storage modulus (E') for neat TPU and TPU/AO-80 (100/50) hybrid at reference temperature 10°C calculated from the WLF equation. The character frequency was 1.0×10^5 and 1.1×10^3 Hz, and the frequency ranges of tan δ value >0.3 are $7.6 \times 10^2 \sim 3.1 \times 10^7$ Hz and $1.0 \times 10^1 \sim 1.6 \times 10^6$ Hz, respectively. Compared with the neat, the frequency range of tan δ value larger than 0.3 of TPU/AO-80(100/50) hybrid was wider and also located at a

lower frequency position. Besides, the tan δ peak value of TPU/AO-80(100/50) hybrid was 1.05, which was almost 2 times higher than that of neat TPU matrix. This implied that TPU/AO-80 (100/50) hybrid could present a good damping performance with wider range at low frequency. Commonly, for normal organic small molecules filled polymer hybrids,¹⁸ such as plasticized polymer system, the glass transition temperature of the matrix was moved to lower location, as well as a lower tan δ value and storage modulus. However, TPU/AO-80 hybrids showed novel dynamic mechanical properties, which was attributed to the strong intermolecular interactions between AO-80 and matrices.

Figure 8 shows the temperature dependence of the storage modulus (E') of the TPU/AO-80(100 : 0-100)

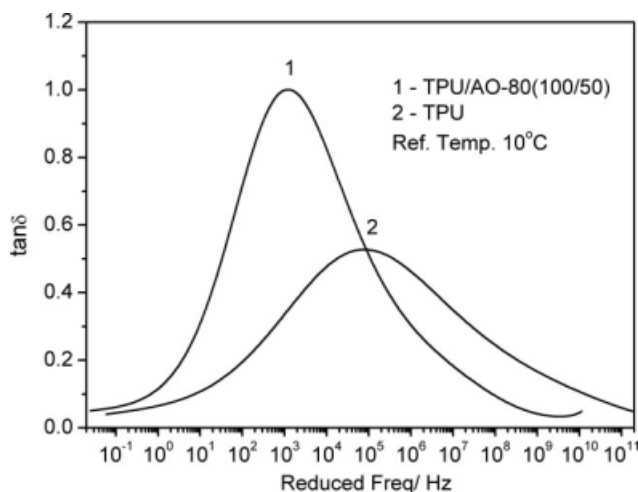


Figure 7 Frequency dependence of loss factor of neat TPU and TPU/AO-80(100/50) hybrid.

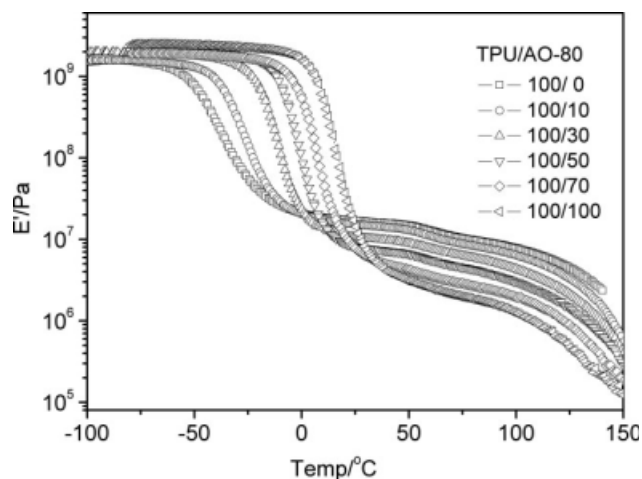


Figure 8 Temperature dependence of the storage modulus (E') for TPU and TPU/AO-80 hybrids with varied mass ratios of TPU/AO-80.

TABLE II
Mechanical Properties of TPU/AO-80 Hybrids

Properties	TPU/AO-80 hybrids					
	100/0	100/10	100/30	100/50	100/70	100/100
Hardness (Shore A)	82	80	79	70	74	69
Tensile strength (MPa)	35.5	30.0	27.7	25.6	23.6	18.3
Stress at 100% strain (MPa)	5.2	5.0	3.7	3.8	2.7	1.9
Elongation at break (%)	637	751	774	747	787	747
Permanent set (%)	32	48	48	36	28	32
Tear Resistance(KN/m)	89.3	86.1	72	54	50	40

hybrids. All of the storage modulus curves displayed two transitions. The first transition located at lower temperature was related to glass transition of soft segments of TPU, and the second transition at higher temperature corresponded to the destruction of ordered structure of the hard phase of TPU. In the glass transition region, the curves gradually moved toward higher temperatures with the increase of AO-80 amount and the hybrids exhibited higher modulus than that of the neat matrix. However, the E' values in rubbery regions of the hybrids significantly decreased as the amount of AO-80 increased. This was because the physical interactions between AO-80 molecules and soft segments of TPU were destroyed and the AO-80 acted as a plasticizer when the temperature was higher than the glass transition temperature of AO-80 (40.9°C). As a result, E' values were decreased when the amount of AO-80 increased.

Static mechanical properties of TPU/AO-80 hybrids

Table II shows the static mechanical properties data of the TPU/AO-80 hybrids with various TPU/AO-80 mass ratios. The tensile strength and elongation at break of neat TPU were 35.5MPa, 637%, respectively. These values were high but reasonable because of the special hard segment and soft segment microphase separation structure. Hard phase of TPU as physical crosslinking points and reinforcing phase provides high tensile stress, while soft phase as rubbery phase provides large elasticity and elongation at break. As shown in Table II, the introduction of AO-80 had a significant impact on the tensile strength. The tensile strength of the hybrids decreased along with the ratios of AO-80 increasing. This was because the content of hard segment in the hybrids decreased with increasing the AO-80 amount, and led to the decrease of the tensile strength of the hybrids. However, the tensile strength of TPU/AO-80 (100/100) hybrid still kept 18.3 MPa. Generally, these stress values were higher than that of normal rubber composites^{19,20} and enough high for many engineering application.

Besides, it also led to the decrease of hardness, stress at 100% strain and tear resistance along with the content of AO-80 increasing. The results also indicated that the hybrids had high elongation ratio and relative large permanent deformations.

CONCLUSIONS

In this study, TPU/AO-80 organic hybrids were successfully prepared through melt blending, which was followed by hot and cold pressing procedure. AO-80 was completely dissolved in the matrix. When the amount of AO-80 increased, the glass transition of the soft segments of TPU shifted to higher temperature, while the glass transition of the hard segments exhibited no evident change. This was attributed to the selectively dispersing of AO-80 in the soft phase of TPU and the forming of the intermolecular interactions (hydrogen bonding) between the hydroxyl groups of AO-80 and the polar groups of the TPU's soft segment. With the increase of AO-80 amount in the hybrids, the $\tan\delta$ peak gradually shifted to higher temperatures and the maximal $\tan\delta$ value increased from 0.4 to 1.6. Meanwhile, the glass transition temperature ranges were broadened and the TA value increased greatly with the content of AO-80 increasing. The hybrids displayed excellent comprehensive performance and were expected to have potential applications as high performance damping materials.

References

1. Lv, Y.-H.; Wang, T.-F. Handbook of Control Device and Material of Noise and Vibration; 2nd ed.; Mechanic and Industry Press: Beijing, China, 1999; pp 286–93.
2. Sperling, L.-H.; Fay, J.-J. Polym Adv Technol 1991, 2, 49.
3. Alex, C.-F.; Williams, H.-L. J Appl Polym Sci 1976, 20, 3387.
4. Chen, Q.-M.; Ge, H.-H.; Chen, D.-Z.; He, X.-D.; Yu, X.-H. J Appl Polym Sci 1994, 54, 1191.
5. Chern, Y.-C.; Tseng, S.-M.; Hsieh, K.-H. J Appl Polym Sci 1999, 74, 328.
6. Song, M.; Hourston, D.-J.; Schafer, F.-U. J Appl Polym Sci 2001, 81, 2439.
7. Tung, C.-J.; Hsu, T.-J. J Appl Polym Sci 1992, 46, 1759.
8. Xie, H.; Wang, G.; Guo, J. Angew Makromol Chem 1994, 91, 221.

9. Hourston, J.-D.; Schafer, F.-U.; Bates, J.-S. *J Appl Polym Sci* 1996, 60, 2409.
10. Klempner, D.; Berkowski, L.; Frisch, K. C. *Rubber World* 1985, 16, 192.
11. Wu, C.-F.; Otani, Y.; Namiki, N.; Emi, H.; Nitta, K.; Kubota, S. *J Appl Polym Sci* 2001, 82, 1788.
12. Wu, C.-F.; Mori, K.; Otani, Y.; Namiki, N.; Emi, H. *Polymer* 2001, 42, 8289.
13. Wu, C.-F.; Yamagishi, T.; Nakamoto, Y.; Ishida, S.; Nitta, K.; Kubota, S. *J Polym Sci Part B: Polym Phys* 2000, 38, 2285.
14. Wu, C.-F. *J Polym Sci Part B: Polym Phys* 2001, 23, 39.
15. Zhao, X.-Y.; Xiang, P.; Tian, M.; Fong, H.; Jin, R.-G.; Zhang, L.-Q. *Polymer* 2007, 48, 6056.
16. Xiang, P.; Zhao, X.-Y.; Xiao, D.-L.; Zhang, L.-Q. *J Appl Polym Sci* 2008, 109, 106.
17. Kaneko, H.; Inoue, K.; Tominaga, Y.; Asai, S.; Sumita, M. *Mater Lett* 2002, 52, 96.
18. Monteiro, E. E. C.; Fonseca, J. L. C. *J Appl Polym Sci* 1997, 65, 2227.
19. Koberstein, J. T.; Galambos, A. F.; Leung, L. M. *Macromolecules* 1992, 25, 6195.
20. Yu, Z.-C. *World Rubber Ind* 2006, 3, 43.