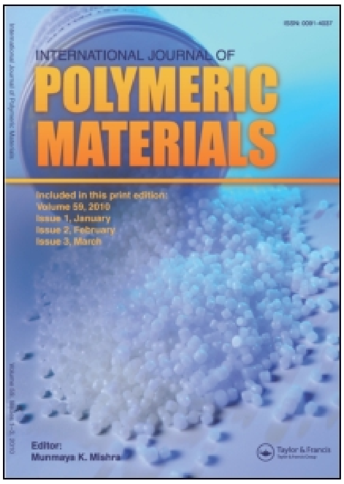

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DYNAMIC MECHANICAL STUDIES OF POLYURETHANE COMPOSITES FILLED WITH GLASS MICROFILLERS

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Ceramic microspheres with unique composition and diameter, modified by different surface treatments, were blended with polyurethane (PU) in various proportions to improve the visco-elastic and mechanical properties of PU composites. Results of dynamic mechanical spectra indicate that the introduction of microbeads H50, D32 and K37 into the PU network leads to the shift of glass transition temperature. Besides, the intensity of loss $\tan\delta$ *of PU composites decreased as a function of the filler's concentration, due to reduced concentration of polymer backbones. Both the shift of Tg as well as the changes of loss* $\tan\delta$ *show that the introduction of microspheres not only creates physical bonding with PU but also causes steric effects due to the adsorption of N–H and C=O functional groups of PU on the filler surface. However, the introduction of various microfillers shows the composites to have different Young's modulus. This evidence shows that the rigidity and elasticity of polymer composite can be finely tuned by the introduction of various surface-treated microfillers as well as the amount of filler added.*

Keywords: glass microfiller, PU composite, dynamic mechanical analysis, glass transition temperature, Young's modulus

INTRODUCTION

Polymer materials have been widely applied in the industries of aerospace, transportation, and structural construction. To meet the

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increasing demands of various working environments, polymers with added suitable fillers or fibers are designed to enhance the overall performance of composites. For instance, polymer composites embedded with carbon fiber generate strong mechanical strength and dimensional stability. As a result, they are considered as candidates of structural enforcement materials [1]. Besides, polymer substrates with added reactive inorganic fillers can considerably improve their water resistivity due to a relatively strong bonding between fillers and diffusive liquids [2–4]. In addition, with the addition of hollow fillers, the apparent density of polymer composites is reduced and the associated buoyancy property makes them eligible for underwater applications. Furthermore, the changes of the viscoelasticity and flow property of polymer composites by fillers also play an important role in material processing. Finally, the environmental temperature affects the vibration of the polymer molecules and the polymeric microstructures, which would affect their transport [5] and mechanical behavior [6]. As a result, the characteristics of fillers such as diversity in shapes, apparent density, as well as the distribution of particle size directly determine the range of their end applications [7]. To examine and assure the proper usage of polymers in these applications, a knowledge of their mechanical modulus, thermal stability, and environmental adaptability is very essential.

In this paper, inorganic glass hollow microspheres with high strength to weight ratio, were embedded in a PU polymer network. The extent of the interaction force between functional groups of polymer backbones and surface-coated fillers are determined by the compatibility of micro-heterogeneous networks. Therefore, dynamic mechanical spectra were carried out and the effects of filler addition on the dynamic glass transition temperature, storage and loss modulus and, Young's modulus were evaluated.

EXPERIMENTAL PROCEDURES

Sample Preparation

The polyurethane (PU) polymer used in the study was procured from Fuller Co. with a trade name of URALITE FH-3593, which is a two-component, liquid type, and curable elastomer. It was blended with different types of microfillers at various proportions at room temperature for 2 minutes. The mixtures were then molded to disks of 2 mm thickness by a compression molding machine for 2 days. Three types of microfillers used in this study were obtained from 3M Co. with trade names of D32, H50 and K37, respectively. They are all made up of soda-lime-borosilicate glasses. However, the filler H50 was modified by epoxy silane on its surface and the surface of D32 was modified by methacrylato chromic chloride (MCC) treatment. They all contain the main elemental compositions of Na, Al, Si and Ca by the EDS analysis. Some extra trace elements depending on the types of surface treatment were found in the D32 and H50 fillers. For instance, C and N elements were found in the D32 microfiller (MCC treatment) while C, O and relatively high concentrations of Si elements were found in the H50 system (epoxy silane treatment). The median size of fillers is 40 μm and the true density of fillers and their related properties are summarized in Table 1. Besides, their microstructures were studied using a scanning electron microscope (JOEL JSM-T330A) with an accelerating voltage of 15 to 20 KV as shown in Figure 1. The figure indicates that the shape of microfillers is sphere and the particle distribution is homogeneous. Additionally, the hollow structure of microfillers leads to the densities of composites being reduced by 20% of their original density with the addition of filler concentration to 12 phr.

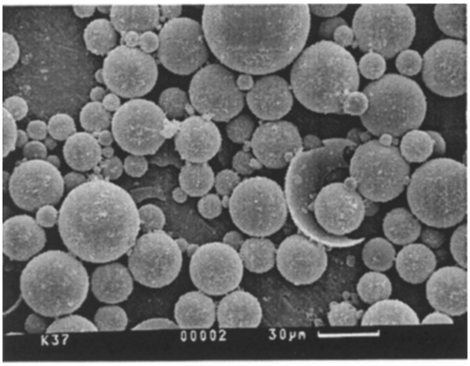
Dynamic Mechanical Analysis

The dynamic mechanical data were studied with the aid of Perkin-Elmer DMA 7 and a stainless-steel parallel plate. The spectra of samples were run with a temperature range from $-100°C$ to $0°C$ at a frequency of 1 Hz. The heating rate for all the runs was $1°C/min$. The samples have the dimension of 20 mm by 5 mm with a thickness of 3 mm to provide the measurement consistency. The storage modulus (E'), loss modulus (E'') and loss $\tan\delta$ were recorded versus temperature. The temperature corresponding to peak of loss $\tan\delta$ is considered

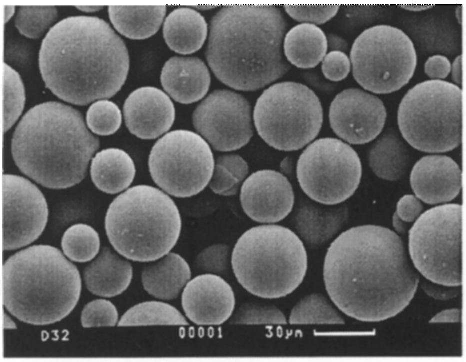
TABLE 1 Basic Information for Microfillers

Sample ID	True density	Composition	Median particle size	Effective top particle size
K37	0.37	Soda-lime-borosilicate glass	40 μm	85 μm
D32	0.32	Same as K37 with MCC* surface treatment	40 μm	85 μm
H50	0.50	Same as K37 with epoxy silane surface treatment	40 μm	60 μm

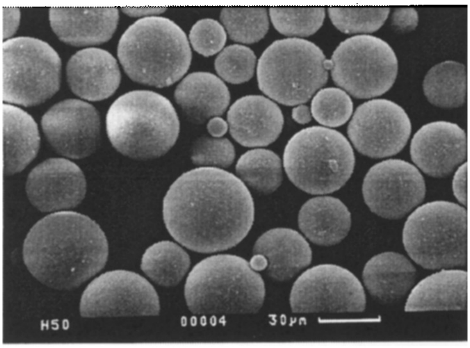
The volume fraction of void for all three microfillers is around 0.8.
*MCC represented methacrylato chromic chloride.



(a) K37



(b) D32



(c) H50

FIGURE 1 Microstructures of microfillers K37, D32, and H50.

as the dynamic glass transition temperature (T_g). Additionally, Young's modulus, an elastic modulus indicating the deformation (strain) of specimen produced by a force, was also measured for all specimen at room temperature.

RESULTS AND DISCUSSION

Effects of Filler Addition on Tg

Figure 2 is a typical loss tan δ spectrum for all PU composites as a function of working temperature. The corresponding temperature of the peak is considered as a dynamic transition temperature of the specimen. Furthermore, the intensity of the peak height represents the specimen's mechanical damping properties. For composite systems such as PU/K37, PU/D32, and PU/H50, the glass transition temperature tends to increase with the filler concentration, while that of tan δ goes in an opposite direction. The spectra of PU composites were

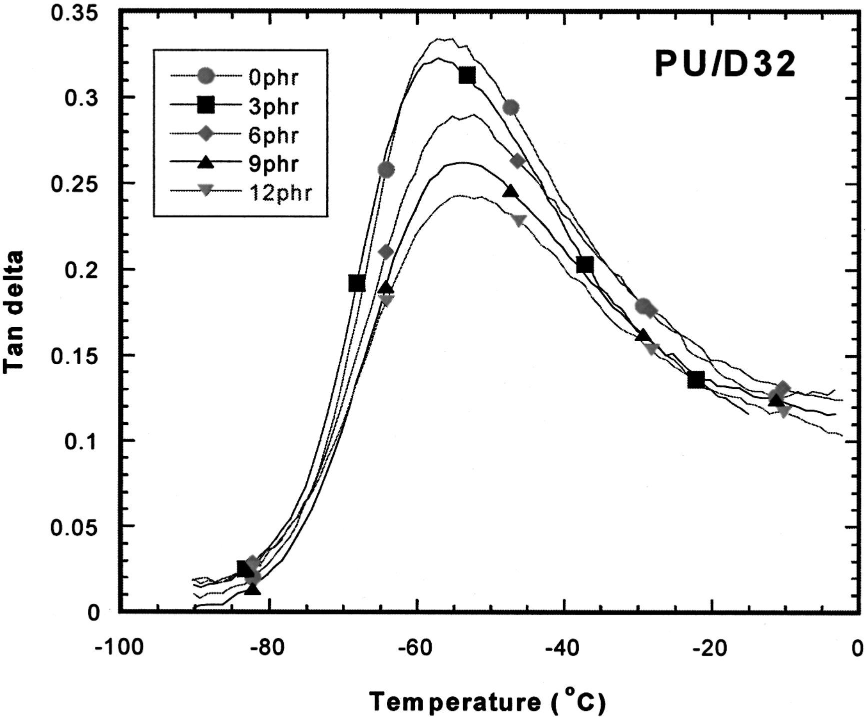


FIGURE 2 Loss tan δ *vs*. temperature.

TABLE 2 Dynamic Mechanical Properties of PU Composites with Various Filler Loadings

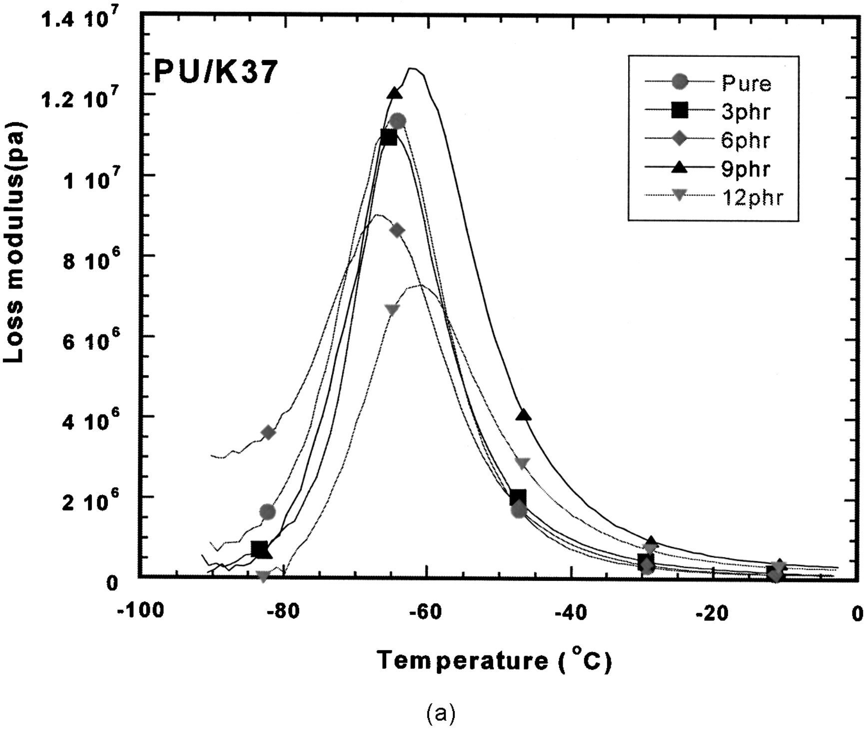
		Filler content (phr)				
Type	Parameter	0	3	6	9	12
PU/K37	Tg (°C)	−56	−55.28	−55.026	−51.721	−51.149
	Tan delta	0.332	0.321	0.35	0.268	0.255
	Young's modulus ($*10^{-7}$ Pa)	2.1782	2.7292	2.8302	2.7685	2.8177
PU/D32	Tg (°C)	−56	−56.811	−53.602	−52.913	−52.870
	Tan delta	0.332	0.320	0.290	0.262	0.242
	Young's modulus ($*10^{-7}$ Pa)	2.1782	1.8791	1.3261	1.0366	1.0034
PU/H50	Tg (°C)	−56	−53.188	−51.777	−52.036	−51.502
	Tan delta	0.332	0.338	0.253	0.226	0.184
	Young's modulus ($*10^{-7}$ Pa)	2.1782	2.2572	2.0200	2.2408	2.0376

analyzed and summarized in Table 2. Results show that the glass transition temperature (T_g) of filler-free PU was ~ −56°C. With more filler added in the polymer network, the glass transition temperatures of composites increased to −51.5°C for PU/H50 (12 phr), −51.2°C for PU/K37 (12 phr), and −52.9°C for PU/D32 (12 phr). The shift of T_g toward higher temperatures is normally observed in the case of polymers when reinforced by dispersed inorganic fillers [8, 9]. This indicates the chain mobility was suppressed by the physical bonding due to the adsorption of N−H and C=O groups of PU onto the filler surface. Based on the shift of T_g toward higher temperatures, the introduction of microfillers into PU network not only affects the physical bonds but also changes the microstructure. However, the variation of T_g between each composite system looks so little, implying that only slight interfacial bonding occurred between polymer backbones and various surface treated microspheres.

Effects of Filler Addition on the Mechanical Properties

Dynamic mechanical spectra of filled and unfilled PU were studied as functions of filler content and temperature. Storage modulus, an index of elastic behavior, was found to decrease with increasing temperature. Whereas the loss modulus (E″), property of viscous characteristic, of neat PU and filled PU has a maximum in between −65 to

−60 °C. The relative heights of the loss tan δ, ratios of loss modulus to storage modulus, are an index of mechanical damping or capability of energy dissipation within microstructures. In the case of additive loading at 3 phr level for all types of microfillers, loss modulus of PU composites become weaker than that of neat PU. As more additives loading into PU networks (6 phr, 9 phr), the composites have an astonishing increase in loss modulus for the case of D32/PU and H50/PU systems as shown in Figures 3 (a), (b) and (c). Yet, the changes of loss modulus for additives loading at 12 phr become gentle for all PU composites at room temperature. Addition of fillers into PU network results in an increased loss modulus in composites, assuring a high mechanical damping characteristic. While the corresponding loss tan δ still maintains values ranging from 0.1 to 0.3, which represents that the composites are moderately rigid without provoking internal friction as the deformation occurs.



(a)

FIGURE 3 Loss modulus *vs.* temperature as function of filler loading.

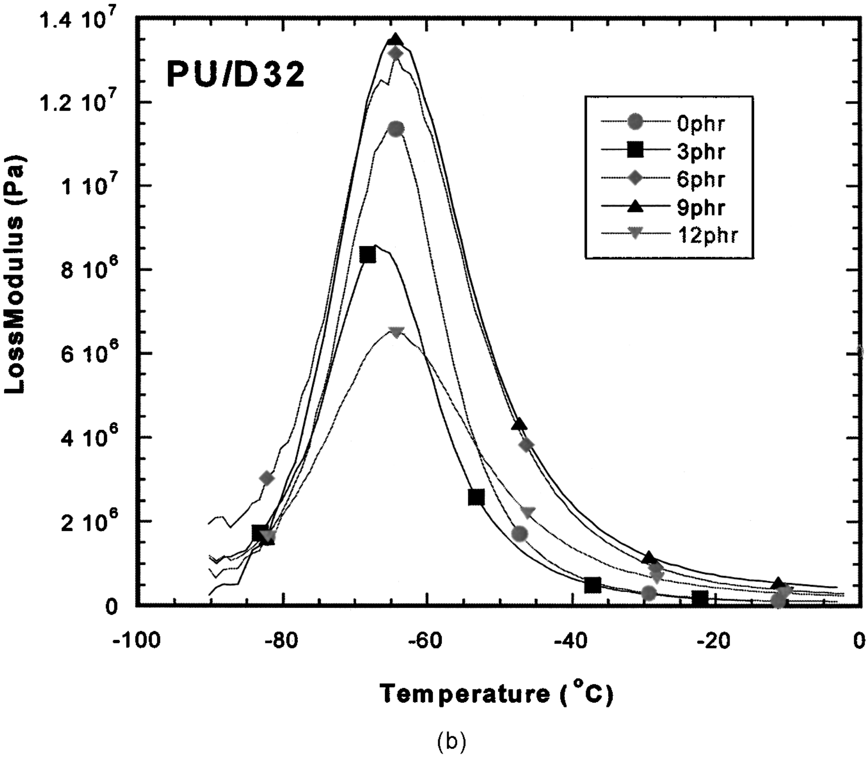
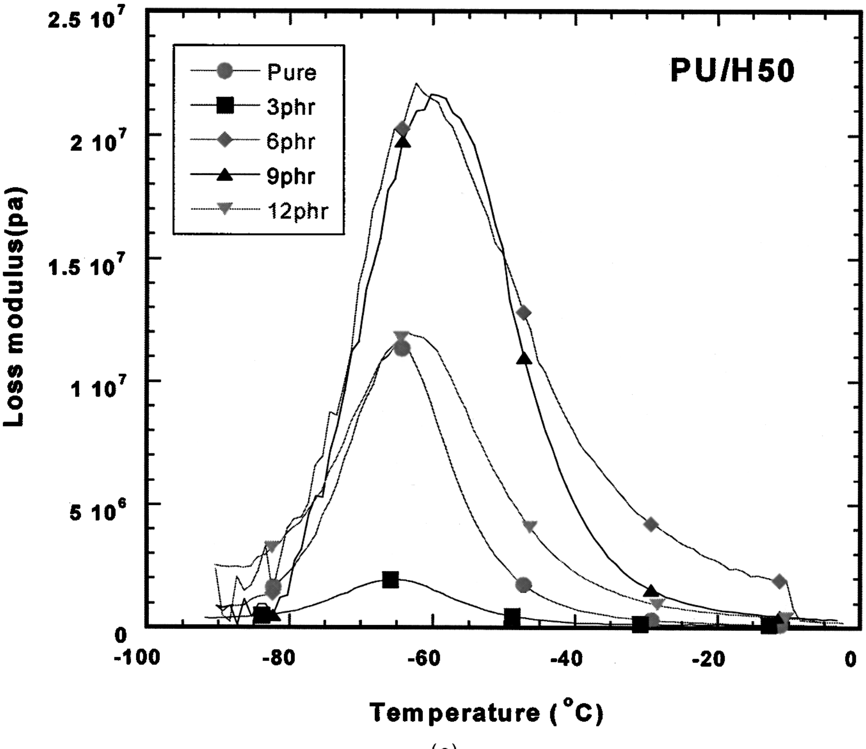


FIGURE 3 (*Continued*).

However, the Young's modulus of composites with various filler addition showed a very different tendency according to the filler's concentrations as shown in Table 2. The Young's modulus of PU/D32 composites decreased from 2.18×10^7 Pa (0 phr) to 1.0×10^7 Pa as the amount of D32 was added to 12 phr, whereas that of PU/K37 increased slightly to 2.8×10^7 Pa at the concentration of 12 phr. Only the addition of H50 micro bubbles gives no effect to PU composites in Young's modulus. This observation shows that the characteristics of microfillers are responsible for the rigidity and viscoelasticity of polymer composite, which can be finely tuned through different surface-treated microfillers as well as the loading amount.

CONCLUSIONS

The addition of microfillers in polymers affects the mechanical properties and density of composites. Fillers with various surface-treatments



(c)

FIGURE 3 (*Continued*).

affect the microstructure, elasticity and phase shift of composites when adding into polymer backbones. With regard to the effect on mechanical properties, the D32 microfiller can increase the Young's modulus of composites, but that of K37 addition goes in the opposite direction. Furthermore, the addition of microfiller would reduce the apparent density of the composite by $10 \sim 20\%$ and increase its glass transition temperature. Results of loss modulus as well as $\tan\delta$ also show that PU polymer containing various fillers not only changes the mechanical damping properties of the composite but also enhances its energy absorbing characteristics.

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