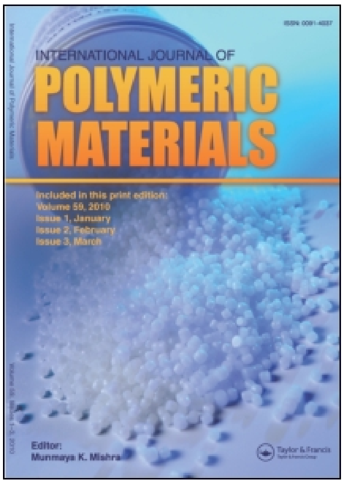

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EFFECTS OF GLASS MICROFILLERS ON THE WATER-TRANSPORT BEHAVIOR OF POLYURETHANE COMPOSITES

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Glass microspheres with unique composition and diameter, and modified by different surface treatments, were blended with polyurethane (PU) in various proportions to improve the liquid transport properties of the PU composites. Transport properties such as diffusion, permeability, and sorption coefficient were measured on various filler-filled PU composites at three different temperatures. These temperature-dependent parameters were used to provide a quantitative way to examine the effects of filler loading and the surface properties on the improvement of the water transport properties of PU composites. Results show that due to trapping at interfacial boundaries between filler and polymer, a high water affinity and large space for water activity is expected inside all the filler-filled composites. As a result, lower water diffusion (or high water resistivity) was found among all the filler-filled composites compared to that of filler-free composites. Besides, the more filler present in the composite, the longer the paths of the water molecules within the composites as the water penetration proceeds. Thus, lower diffusion coefficient values were observed for composites with large amounts of filler addition.

Keywords: glass microfiller, diffusion coefficient, sorption solubility, polyurethane (PU) composite

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INTRODUCTION

There has been a remarkable growth in the use of polymer materials in aerospace, transportation, and structural construction industry applications. Especially when polymers need to be immersed in liquid for a long period of time, they encounter the diffusion of small-molecular penetrants inside the polymers that cause the polymer networks to swell. In addition, the polymers used as components for underwater vehicles are expected to be light-weighted to provide the necessary buoyancy, yet possess satisfactory mechanical strength and dimensional stability. Therefore, transport and mechanical properties of polymers are key factors in determining their applications. To ensure the proper usage of polymers in applications such as these, a knowledge of thermal stability and environmental adaptability of polymers is essential.

For a single polymer to satisfy the demands of such various applications is difficult. As a result, polymer composites with the addition of suitable fillers or fibers [1–2] were designed to integrate the components' characteristics and provide unique combinations of properties. Polymer composites with the addition of appropriate amounts of inorganic fillers are considered to effectively enhance their water resistivity. These inorganic fillers are responsible for the retardation of liquid penetration due to the interactions of fillers with aggressive media. Water resistance of the polymer composite is thus enhanced by this barrier mechanism. To quantitatively evaluate the extent of solvent-diffusion in these composites, an appropriate characterization method is required to provide the quantitative solvent-resistivity information. This information will be useful in the design of a composite with an optimum combination of types of fillers and amounts of fillers loaded. Among the methods of the transport property measurement, the gravimetric method is an efficient way to elucidate the rate of solvent transport in the polymer. Based on this method, Aminabhavi et al. investigated the transport properties of various polymers with different types of solvents [3]. They found that the blending of the fibril fillers improved the resistivity to solvent by reducing the liquid-transportation and thus delaying the penetration rate inside the polymers. Furthermore, Kalenda and Kalendova applied a thin layer of inorganic film [4] on the surface of polymers. They found the sizes and shapes of inorganic fillers as well as their reactivity with solvents influenced the transport behavior.

In this research, three types of inorganic glass bubbles—hollow microspheres with higher strength-to-weight ratio—were embedded in the PU polymer network. These microspheres were all made of soda-silica with an average diameter of 40 μm. These microfillers have true densities ranging from 0.32 to 0.5, which were expected to reduce the density of the composite. Two of the microfillers were chemically treated on their surface, epoxy silane and methacrylate chromic chloride (MCC) respectively, whereas the one without chemical treatment was taken as the control group. The microfillers with appropriate hydrophilic surface treatment are considered to improve the degree of wettability with polar solvents, which determines the extent of molecular attractive forces between the liquid-penetrant and filler surface. These trapping forces are responsible for retarding water transportation due to the presence of filler and thus prolong the time for water penetration through the composites. These factors were believed to be the reasons for the enhancement of water resistivity of PU/filler composites. To quantitatively characterize the effects of filler concentration and chemical property of filler surface, different transport parameters such as diffusion, sorption and permeation coefficients were measured at various environmental temperatures.

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 two minutes. The mixtures were then molded to disks of 2 mm thickness by a compression molding machine for two days. Three types of microfillers used in this study were obtained from 3M Co. with trade names of D32, H50, and K37. They are all made of soda-lime-borosilicate glasses. However, the filler K37 was modified by epoxy silane on its surface and the surface of D32 was modified by methacrylate chromic chloride (MCC) treatment. Their microstructures were studied using a scanning electron microscope (JEOL JSM-T330A) with an accelerating voltage of 15 to 20 kV as shown in Figure 1. The densities of composites can be reduced to 80% of their original density by the addition of filler concentrations to 12 phr due to the hollow structure of microfillers.

Diffusion Experiments

The diffusion of water molecules into polymer composites can be quantitatively evaluated by a one-dimensional Fick's second law. The

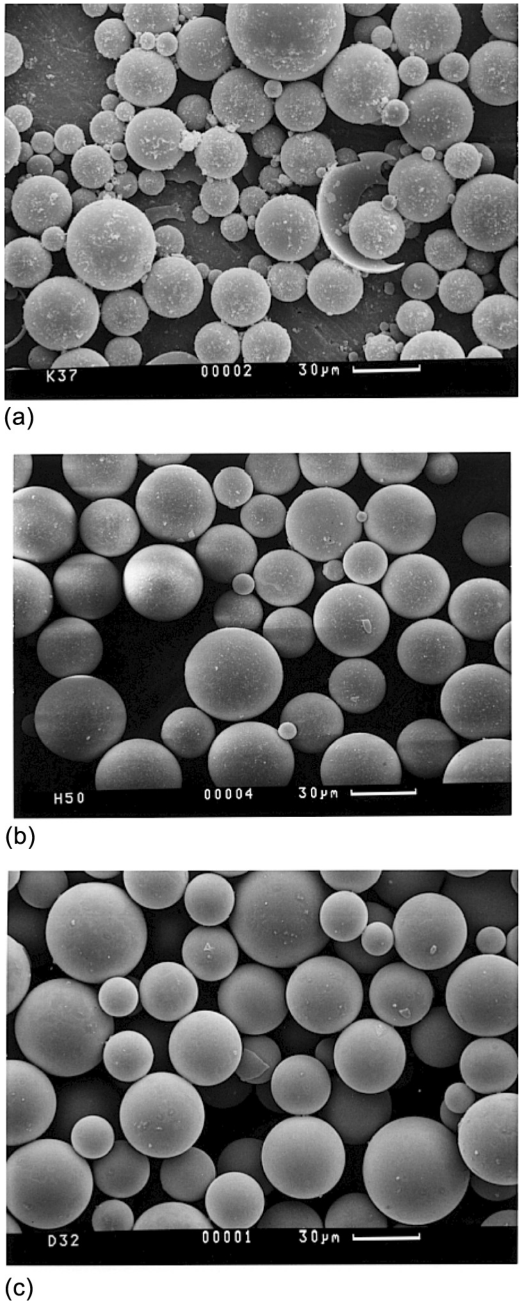

FIGURE 1 The SEM images of glass ceramics of (a) K37, (b) H50, and (c) D32.

specific diffusion process is described by:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \tag{1}$$

where C is the liquid concentration in the polymer matrix at time t, X indicates the distance of the diffusion, and D represents the diffusivity. The initial and boundary conditions are given as follows:

$$C = 0 \qquad 0 < X < h \qquad t < 0$$

$$C = C_m \qquad X = 0, X = h \qquad t > 0$$

where h symbolizes the thickness of specimen, and C_m shows the concentration of the liquid in the polymer at equilibrium time. Based on the above-mentioned constraints [5], Eq. (1) is solved to give C_t, the concentration of the liquid in the polymer at time t, as

$$\frac{C_t}{C_m} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\exp\left[-\frac{D(2n+1)^2\pi^2}{h^2}t\right]\sin\left[\frac{(2n+1)\pi}{h}x\right] \tag{2}$$

or in terms of gravimetric weight of the liquid in the specimen:

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{D(2n+1)^2\pi^2}{h^2}t\right]. \tag{3}$$

However, a short-time equation can be applied to approximate the diffusivity before the completion of 55% sorption at equilibrium:

$$\frac{M_t}{M_m} = \frac{4}{h}\sqrt{\frac{Dt}{\pi}} \tag{4}$$

where M_t is the total amount of liquid in the specimen expressed in weight percentage (wt%) at time t and M_m is the corresponding amount of the liquid at equilibrium. Thus, the diffusion constant, D, can be calculated from a rearrangement of Eq. (4) as

$$D = \pi\left[\frac{h\theta}{4M_m}\right]^2 \tag{5}$$

where θ is the slope of the plot of M_t versus $t^{1/2}$.

Sorption and Permeation Coefficients

In order to understand the extent of interactions between the polymer and solvents due to the addition of glass spheres, the sorption coefficient was calculated by using the relation of

$$S = \frac{W_m - W_0}{W_0} \tag{6}$$

where W_0 is the net-weight of the specimen and W_m is the total weight of the specimen embedded in the solvent at the equilibrium. Furthermore, permeability coefficients [6] of solvent molecules, P, can be determined by the values of diffusivity (D) and sorption coefficient (S) using the relationship

$$P = D \cdot S. \tag{7}$$

RESULTS AND DISCUSSION

Figure 2 represents the kinetics of water uptake by a filler-free PU polymer with respect to immersion time under different environmental temperatures. The feature figure is a typical Phase I diffusion process [7], where liquid medium homogeneously diffuses through the polymer matrix until saturation. The final equilibrium weight indicates the maximum capacity of water occupied in the polymer matrix, which implies the extent of water activity within hydrophilic sites of the polymer. As a result, the polymer network that contains micropores or micro-cracks leads to an increase in the effective water diffusion due to free trapping and additional free space for water transport activity. In the perspective of thermal effects, the filler-free PU polymer at lower environmental temperature (30°C) had a higher water absorption capacity (20 wt%) than at higher temperatures, as shown in Figure 2. This tendency suggests that PU polymer chains are thermally more active at higher temperatures due to increased molecular vibration, which consequently leaves less space for water molecules to occupy. As a result, the water uptake for PU was less at the temperature of 60°C than it was at 30°C. The extent of water sorption at various temperatures was summarized in Table 1, where the mean sorption coefficient is $0.198\,\text{cm}^2/s$ at 30°C and $0.072\,\text{cm}^2/s$ at 60°C. According to the slope of the weight-gaining curve in Figure 2, the rate of water uptake indicates the extent of water activity at given temperatures with respect to the immersion time. Results show that a PU polymer network at lower temperature has a greater water uptake rate that is almost two times the slope of PU at a high temperature.

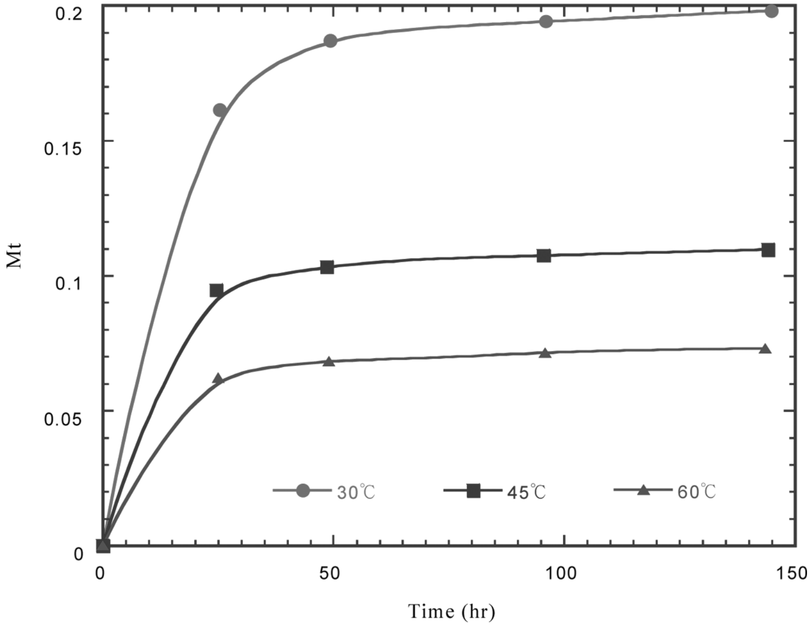

FIGURE 2 The effect of environmental temperatures on water diffusion in filler-free PU.

However, the effective diffusion coefficient has an inverse temperature dependence. As seen in Table 2, the mean diffusion coefficient for neat PU is $5.47 \times 10^{-8}\,\mathrm{cm}^2/s$ at 30°C and $6.56 \times 10^{-8}\,\mathrm{cm}^2/s$ at 60°C. This is due to the fact that the diffusion coefficient is not only a function of water penetration rate but also inversely proportional to the final equilibrium weight, as shown in Eq. (5). At the high temperature,

TABLE 1 Sorption Coefficient in Polymer Composites

Type	Temperature°C	0 phr	3 phr	6 phr	9 phr	12 phr
	30	0.198	0.231	0.230	0.241	0.273
PU/K37	45	0.112	0.167	0.185	0.215	0.234
	60	0.072	0.139	0.159	0.193	0.232
	30	0.198	0.235	0.279	0.320	0.381
PU/D32	45	0.112	0.162	0.179	0.225	0.235
	60	0.072	0.134	0.193	0.245	0.309
	30	0.198	0.216	0.211	0.239	0.244
PU/H50	45	0.112	0.149	0.155	0.162	0.168
	60	0.072	0.106	0.118	0.127	0.129

TABLE 2 Diffusion Coefficient, D $\times 10^8$ (cm^2s^{-1}), in Polymer Composites

Type	Temperature°C	0 phr	3 phr	6 phr	9 phr	12 phr
PU/K37	30	5.47	4.22	3.81	2.77	2.50
	45	6.18	3.28	2.86	2.61	2.67
	60	6.56	3.47	2.94	2.76	2.41
PU/D32	30	5.47	4.36	3.42	3.03	3.08
	45	6.18	3.47	2.34	3.03	2.92
	60	6.56	3.31	2.39	2.02	1.81
PU/H50	30	5.47	4.89	4.33	3.67	3.56
	45	6.18	3.50	3.22	3.17	3.08
	60	6.56	3.67	3.56	3.28	3.03

thermal energy induced the molecular vibration of water to a status that favored the water transport activity through the bulk polymer matrix. Therefore, a filler-free PU at a temperature of 60°C produces a higher value of diffusion coefficient that that of PU at lower temperatures.

For the cases of PU composites with the filler addition, their water penetration phenomena are obviously different from that of filler-free PUs. Figure 3 gives the kinetic plot of the weight gain versus square root of the immersion-time. These curves are a typical Phase II diffusion process [7], where the second linear tangent line of the water uptake curve occurs before the achievement of equilibrium plateau. The formation of the second curve is due to the water retardation by the filler and its slope, indicating the extent of water hindrance, is proportional to the filler concentrations. Due to the trapping at interfacial boundaries between filler and the polymer network, a high water-interaction inside the filler-filled composites is expected. As a result, it would lead to a decrease in the effective water diffusion. Furthermore, the more filler is added to the composite, the longer the paths of the water molecules within the composites. Thus, the time for water molecules to penetrate through specimen is prolonged and as a result, lower diffusion coefficient values were obtained. This effect is especially noticeable for the composites with large volume fraction of filler, as summarized in Table 2. The diffusion coefficient of PU/K37 composites at 12 phr filler content (2.50×10^{-8} cm^2/s) is one half the value of the filler-free PU (5.47×10^{-8} cm^2/s). Similar tendency was found among the PU/D32 and PU/H50 composites. However, PU/D32 and PU/K37 composites have lower water-diffusion (better water resistivity) than that of PU/H50 because of the unique surface property on the microfillers (D32 and K37). The microfillers with appropriate hydrophilic surface treatment are selieved to improve the

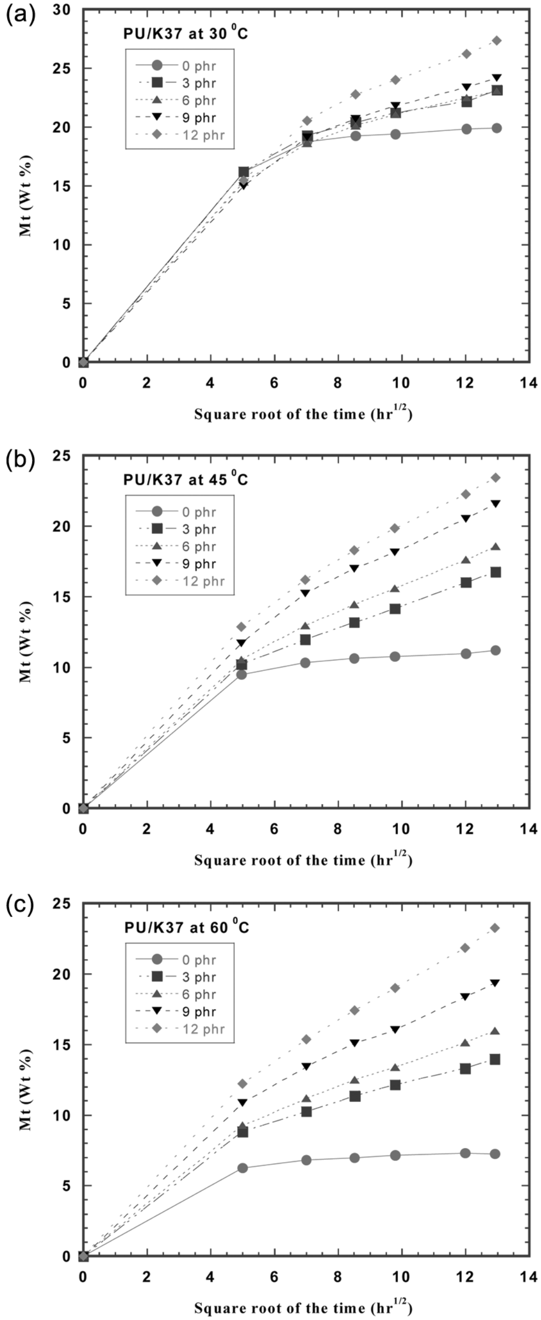

FIGURE 3 The effect of the microfiller addition on water diffusion in PU composites at (a) 30°C, (b) 45°C and (c) 60°C.

degree of wettability with polar solvents, which determines the extent of molecular attractive forces between the liquid-penetrant and filler surface. These trapping forces would delay the rate of water transportation due to the presence of filler, and thus prolong the time of water penetration through the composites. These effects are believed to be responsible for the enhancement of water resistivity of PU/filler composites. Thus, water-retardation condition was more prominent for the PU/K37 composites than PU/D32, because the epoxy-silane surface treatment is believed to be a stronger hydrophilic reagent than MCC. As a result, the water diffusivity in PU/K37 is lower than that in PU/D32, and PU/H50 (plain microsphere) under the same loading condition. As more fillers are added inside the composites, the retardation of water-transportation is more obvious. The diffusivity of PU/K37 at 3 phr is $4.22 \times 10^{-8}\,\mathrm{cm^2/s}$, with more filler addition, the diffusivity of PU/K37 at 12 phr dropped to $2.50 \times 10^{-8}\,\mathrm{cm^2/s}$ as shown in Table 2. Similar tendency may be found in the cases of PU/D32 and PU/H52 composites.

With respect to the effect of thermal energy in the filler-filled composites, the PU composites at high temperature (60°C) show a lower diffusion coefficient than that of PU composites at a low temperature (30°C), which is contrary to the water-diffusion resulting of the filler-free PU. This opposite tendency indicates that the increased water transportation activity due to a high thermal environment is still not sufficient to overcome the extended pathlines result from the micro-porous fillers. As a result, the PU composites with various filler additions all manifest the same effect on the respective diffusion and the sorption coefficients as the temperature increases. However, the microfiller H50, which is different from that of D32 (modified by the MCC) and K37 (epoxy silane treated), was the plain hollow bubbles without surface treatment. As a result, its PU composites exhibit less water interactive activity and thus a greater extent of water diffusivity is expected. On the other hand, the PU composites with the filler D32 and K37 addition have a stronger water activity, which favors water trapping at filler-matrix interfaces. As a result, lower diffusion coefficients are expected for PU/D32 and PU/K37 composites.

Furthermore, the water permeability of PU and PU composites is a combined effect of the diffusivity and the sorption coefficient. Results in Table 3 show that the water 12 permeation capability of PU and PU composites all characterize such a behavior. The values decrease as the concentration of fillers increase and also decrease as the environmental temperatures increase.

TABLE 3 Permeability Coefficient, $P \times 10^9 (cm^2 s^{-1})$, in Polymer Composites

Type	Temperature°C	0 phr	3 phr	6 phr	9 phr	12 phr
PU/K37	30	10.87	9.78	8.78	6.69	6.83
	45	6.90	5.50	5.28	5.61	6.25
	60	4.70	4.86	4.69	5.33	5.61
PU/D32	30	10.87	10.2	9.53	9.64	11.8
	45	6.90	5.64	4.19	6.83	6.83
	60	4.70	4.44	4.61	4.94	5.58
PU/H50	30	10.87	10.6	9.14	8.72	8.67
	45	6.90	5.19	5.00	5.14	4.72
	60	4.70	3.92	4.22	4.17	3.92

CONCLUSION

The addition of glass microfillers to polymer improves the liquid transport properties of the PU composites. Transport properties such as diffusion, permeability, and sorption coefficient were measured at various filler-filled PU composites on three different temperatures. These temperature-dependent parameters were used to provide a quantitative way to examine the effects of microspheres and their surface properties on the improvement of the water transport properties of PU composites. Results show that due to the trapping at interfacial boundaries between filler and polymer, a high water affinity and space for water activity inside all the filler-filled composites is expected. This effect could decrease the effective water diffusion in filler-filled composites more than those of compounds without microfiller addition. Besides, the PU composites with the addition of epoxy-surface-treated filler (K37) and the filler (D32) containing the methacrylate chromic chloride (MCC) show a better water resistivity than that of PU composites with the plain microsphere (H50). Generally speaking, filler-filled PU composites have a higher water resistivity (lower water diffusion coefficient) than that of filler-free PU. With respect to the effect of loading amounts of fillers in polymer compounds, apparently the more filler present in the composite, the longer the paths of the water molecules within the composites as the water penetration proceeds. Thus, lower diffusion coefficient values were observed for composites with larger amounts of filler addition.

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