

Controlled-Release Polyurethane Created by Absorbing Transition-Metal Acetate and Benzyl Carbinol

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ABSTRACT: Three kinds of the transition-metal acetates were absorbed into polyurethane to investigate its effect on the desorption velocity of benzyl carbinol and ethyl alcohol from polyurethane. The results show that a small amount of transition-metal acetate can enhance the absorption amount of benzyl carbinol and ethyl alcohol in polyurethane. With the existence of transition-metal acetate, benzyl carbinol and ethyl alcohol desorb from polyurethane more slowly. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1170–1173, 2002

Key words: absorption; transition-metal acetate; polyurethane; controlled-release systems

INTRODUCTION

Absorption of some organic solutes such as fragrances, pest-control agents, and pharmaceutical drugs into polymers has received considerable attention, as these solutes release from polymers in a controlled manner. The controlled-release systems have many practical applications, for example, agricultural uses, including the release of pesticides, herbicides, and fertilizers from a polymer base to the surrounding soil.¹ The desorption velocity of solutes from polymers depends on the interaction between solutes and polymers, so enhancing the interaction forces will decrease the desorption velocity. Some solutes have good response to organometallic compounds; it will indirectly enhance the interaction between solutes and polymers if solutes and organometallic compounds are absorbed into polymers together. Then solutes should be expected to desorb from

polymer more slowly with the existence of organometallic compounds.

Furthermore, the impregnation of organometallic compounds into a polymer matrix offers considerable possibilities for the modification or tailoring of specific polymer properties. The earlier reported works showed that it is not only of great importance in the development of polymer catalysts,² but also offers a new method to prepare functional materials, such as metal/polymer nanocomposites³ and metal polymer films.⁴ However, the impregnation of organometallic compounds into polymers to prepare controlled-release system was not addressed.

EXPERIMENTAL

Materials

Polyurethane (PU; Bagflex 50T) used was the product of Bayer Chemical Corp., Germany. Carbon dioxide gas (99.9% purity; The Nitrogenous Fertilizer Corp. of Guangzhou, Guangdong Province, China) used in all experiments was purified by molecular sieve. Benzyl carbinol (chemically

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pure) and nickel acetate (chemically pure) were products of Chemical Reagent Corp. of Shanghai, Shanghai, China. Copper acetates (chemically pure) and ethyl alcohol (analytically pure) were products of Chemical Reagent Corp. of Guangzhou, Guangdong Province, China. Cobaltous acetate (chemically pure) was a product of Guanghua Chemical Corp. of Shantou, Guangdong Province, China.

Methods

Polyurethane was pressed into sheets by compression molding with a planet vulcanizing machine at 170°C. The sheets were cut into 1 × 2 cm pieces to have a uniform surface area for all the samples. The polyurethane used in all the experiments was purified with ethyl alcohol before the absorbing experiment and had the same thickness of 1.0 mm and weight of about 0.24–0.25 g. All the transition-metal acetate was dissolved in benzyl carbinol/ethyl alcohol solution. Then, polyurethane was put in a 1.0 mL benzyl carbinol/ethyl alcohol solution of $M(\text{Ac})_2$ ($M = \text{Cu}, \text{Ni}, \text{Co}$). After absorbing the solution for several hours, the polyurethane was removed from the solution and its surface washed with ethyl alcohol. Then, the weight of polyurethane was monitored gravimetrically (by taking the weights up to 0.1 mg) at once, and then again at different time intervals. The experiments were repeated twice at the same conditions, and the reported data was an average of two values, with a standard deviation of 4.0%. The polyurethane after absorption was stored in a clean, dust-free room where the temperature varied from 23 to 26°C and relative humidity varied from 65 to 70%.

Table I Weight Changes of Polyurethane After Absorbing $M(\text{Ac})_2$ Solution^a

$M(x, y, z)$	Weight Change of PU with $M(\text{Ac})_2$ (%)		
	$\text{Cu}(\text{Ac})_2$	$\text{Ni}(\text{Ac})_2$	$\text{Co}(\text{Ac})_2$
$M(0, 0.2, 0.8)$	45.0	45.0	45.0
$M(0.02, 0.4, 0.6)$	71.6	69.5	69.5
$M(0.02, 0.2, 0.8)$	60.8	53.4	62.4
$M(0.04, 0.2, 0.8)$	46.3	45.2	44.4
$M(0.06, 0.2, 0.8)$	—	48.0	—
$M(0.10, 0.2, 0.8)$	—	49.6	—

^a Absorbing for 12 h at 40°C. x , the mass of $M(\text{Ac})_2$ (g); y , the volume of benzyl carbinol (mL); z , the volume of ethyl alcohol (mL).

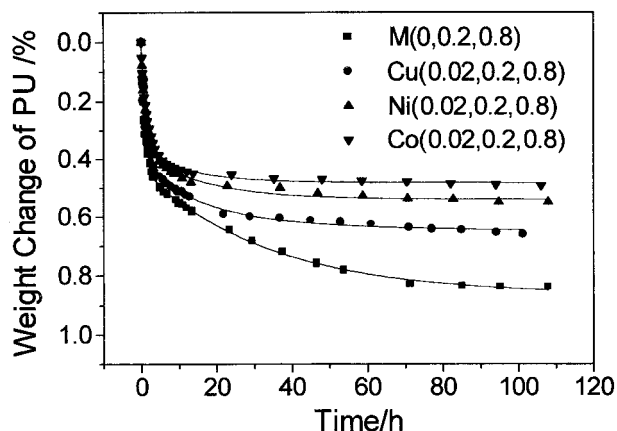


Figure 1 Weight change (wt %) of PU after absorbing transition-metal acetate for 12 h at 40°C [x , the mass of $M(\text{Ac})_2$ (g); y , the volume of benzyl carbinol (mL); z , the volume of ethyl alcohol (mL)].

RESULTS AND DISCUSSION

Weight Changes of Polyurethane

The weight change of polyurethane can be ascertained from the data noted in Table I. The fundamental mechanisms that contribute to the weight changes are as follows: (1) small molecules are absorbed by the polyurethane, which leads to an increase in the weights of the samples; and (2) either the polymers or some agents, such as monomers, oligomers, additive, or plasticizers, in the polymers are dissolved into the benzyl carbinol/ethyl alcohol solution of $M(\text{Ac})_2$ ($M = \text{Cu}, \text{Ni}, \text{Co}$), which leads to a decrease in the weight of the

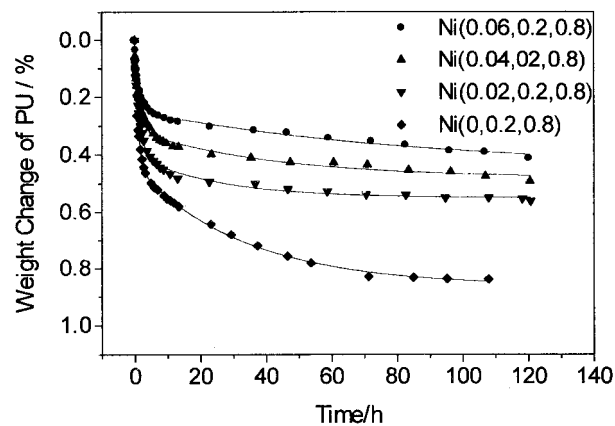


Figure 2 Weight changes of PU after absorbing $\text{Ni}(\text{Ac})_2$ solution for 12 h at 40°C [x , the mass of $\text{Ni}(\text{Ac})_2$ (g); y , the volume of benzyl carbinol (mL); z , the volume of ethyl alcohol (mL)].

Table II The Weight Change of PU After Absorbing Copper Acetate Solution^a

Condition	Weight Change of PU/%			
	Cu(0, 0.2, 0.8)	Cu(0.02, 0.2, 0.8)	Cu(0.04, 0.2, 0.8)	Cu(0.02, 0.4, 0.6)
SC-CO ₂	60.1	66.0	63.6	84.3
Air	30.5	41.9	38.6	47.5

^a Absorption time, 5.33 h; temperature, 40°C; pressure of SC-CO₂, 8.0 MPa.

samples. In general, the second mechanism had little contribution to the weight changes. Table I indicated that the weight change showed a similar trend for different acetates; that is, the weight changes had the order: $M(0.02, 0.4, 0.6) > M(0.02, 0.2, 0.8) > M(0.10, 0.2, 0.8) > M(0.06, 0.2, 0.8) > M(0.04, 0.2, 0.8)$. The result shows that a small mass of transition-metal acetate can enhance the absorption amount of benzyl carbinol and alcohol in polyurethane, but cannot increase the absorption amount of transition-metal acetate.

Desorption of Benzyl Carbinol and Ethyl Alcohol

The absorption/dissolution of benzyl carbinol and ethyl alcohol in polyurethane was indirectly indicated by the weight change of polyurethane after absorption. In accordance with Fickian diffusion kinetics, this change versus the square root of desorption time ($t^{1/2}$) was initially linear.^{5,6} However, in our experiments, this change in mass with time showed a dependence on the logarithm of time (see Figs. 1–2), which is consistent with the results of Shieh.⁷ The desorption velocity of benzyl carbinol and ethyl alcohol decreased with the existence of transition-metal acetate. For example, after 120 h, the desorption amount of benzyl carbinol and ethyl alcohol in polyurethane without absorbing transition-metal acetate was 85%, whereas it was 40% after absorbing solution Ni(0.06, 0.2, 0.8). Figure 1 showed that Co(Ac)₂

can decrease the desorption velocity more than Ni(Ac)₂, whereas Ni(Ac)₂ decreased more than Cu(Ac)₂. Generally, the transition-metal acetate has a strong interaction with benzyl carbinol, so the transition-metal acetate trapped in polyurethane indirectly enhances the interaction between benzyl carbinol and polyurethane. However, the transition-metal acetate not absorbed in polyurethane will decrease the absorption amount of benzyl carbinol and ethyl alcohol in polyurethane, which is why a small mass of transition-metal acetate can enhance the absorption amount of benzyl carbinol and ethyl alcohol in polyurethane. The role of transition-metal acetate in the absorption process provides another approach to enhance the interaction between small molecules and polymer. It can also offer a new route to prepare the controlled-release system.

Absorption in Supercritical Carbon Dioxide

Applications of supercritical carbon dioxide (SC-CO₂) have received considerable attention during the past 20 years, not only because of the inherent potential of itself, but also because of an environmentally benign alternative to organic solvents.^{8,9} It was found that CO₂ accelerates the absorption of many molecules into a number of polymers.⁵ In here, absorption of Cu(Ac)₂ solution into polyurethane in SC-CO₂ was compared with that in the air. Tables II and III indicated that SC-CO₂ could accelerate the absorption of benzyl

Table III The Uptake of Cu in PU after Absorbing Copper Acetate Solution^a

Condition	Uptake of Cu in PU/%		
	Cu(0.02, 0.2, 0.8)	Cu(0.04, 0.2, 0.8)	Cu(0.02, 0.4, 0.6)
SC-CO ₂ (8.0 MPa)	0.20	0.29	0.13
Air	0.29	0.27	0.28

^a Absorption time, 5.33 h; temperature, 40°C.

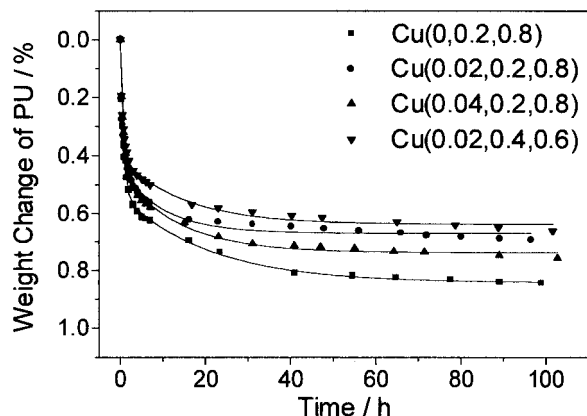


Figure 3 Weight changes of PU after absorbing $\text{Cu}(\text{Ac})_2$ solution for 5.33 h in supercritical carbon dioxide [x , the mass of $\text{Cu}(\text{Ac})_2$ (g); y , the volume of benzyl carbinol (mL); z , the volume of ethyl alcohol (mL)].

carbinol and ethyl alcohol, but could not increase the absorption amount of $\text{Cu}(\text{Ac})_2$. The weight change of polyurethane after absorption in SC-CO_2 in mass with time showed a dependence on the logarithm of time also. Copper acetate could also play a role in controlled-release of benzyl carbinol and ethyl alcohol (see Fig. 3).

CONCLUSIONS

1. A small mass of transition-metal acetate can enhance the absorption amount of benzyl carbinol and ethyl alcohol in polyurethane.
2. With the existence of transition-metal ace-

tate, benzyl carbinol and ethyl alcohol desorb from polyurethane more slowly.

3. Absorption of transition-metal acetate into polyurethane provides another approach to enhance the interaction between small molecules and polymer. It can also offer a new route to prepare a controlled-release system.

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