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Performance

Glass Fiber Having Isocyanate Group on the Surface.

Preparation and Reaction with Amino Acid

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Summary

Reaction of silanol groups on the surface of glass fiber with diisocyanates were investigated. It was found that the effect of organometallic catalysts upon the reaction varied with their metal ions or their ester substituents. Then the addition reaction of isocyanate group on glass fiber surface with amino acid was carried out successfully to prepare a glass fiber-amino acid adduct.

1. Introduction

Organometallic compounds are well-known as most effective catalysts for reactions of isocyanates with alcohols [1-5].

Mechanisms were proposed for the reactions in which a ternary complexe consisting of alcohol, isocyanate and metal compound play a role, or in which rapid equilibrium formation of a binary complex between the catalyst and the alcohol or the isocyanate first occurs and the followed by a slow bimolecular reaction of the complex with the other reagents.

We previously reported that the reactivity of silanol groups on the surface of glass fibers toward diisocyanates was quite similar to that of ordinary hydroxyl group toward diisocyanates [6]. In the present paper, the effects of metal ions, carboxylate moiety and others on the reaction of silanol groups with isocyanates were examined. Then, the addition reactions of amino acids with the isocyanate groups which are present on the surface of glass fiber was investigated. Thus, the possibility to prepare complexes of glass fibers with various amino acids was investigated.

2. Experimental

2.1 Materials

The same materials of glass fiber, diisocyanates (P-MDI and H-MDI) and solvents (DMF, DMSO etc.) as those described in the previous paper [6] were used. As organometallic compounds, laurates of Ca, Cd, Ba, Zn, Pb and Mn, dibutyltin dilaurate, dibutyltin diacetate, dibutyltin maleate, dibutyltin 2 - ethylhexoate etc. of special grade chemicals (Tokyo Kasei Co., Ltd.) were used without further treatments. Methionine methyl ester hydrochloride and glycine methyl ester hydrochloride (special grade chemicals, Tokyo Kasei Co., Ltd.), were used without further purification.

2.2 Reactions of glass fiber with diisocyanate compounds

They were carried out similarly as described in the previous paper [6].

2.3 Analysis

All kinds of analyses except the following were carried cut according to the previous paper [6].

Measurement of incorporated amino acid ester

To 1g of the glass fiber-amino acid adduct was added 50ml of 0.05N NaOH in 50% ethanol solution, and the mixture was stirred at room temperature (about 24°C) for 24 hrs. After the termination of the reaction, the reaction mixture was filtrated, 10ml of the filtrate was taken out and titrated with 0.2N-H_2SO_4, by use of phenolphthalein as an indicator and the amount of amino acid reacted with 1g of isocyanate-glass fiber was determined.

2.4 Addition reaction of amino acids with isocyanate groups on glass fiber

One gram of glass fiber having isocyanate group, 50 ml of solvent, 1 to 5 g of various amino acids and a prescribed catalyst were added, and the mixture was reacted at 30°C for a prescribed period in a nitrogen atmosphere. The reaction mixture was washed sufficiently with dioxane to remove unreacted materials, and vacuum dried at 40°C. The reaction product was analyzed by weight change and infrared spectrum.

3. Results and Discussion

3.1 Catalytic effects of organometallic compounds

By use of various metal laurates, reactions of P-MDI and H-MDI with glass fiber were carried out at 30°C in DMSO and the amounts of combined isocyanates were determined. The results in the case of P-MDI are shown in Figure 1. As can be seen from Figure 1, the catalytic effects fairly differ from one another by the nature of metal ions, and according to the present results of P-MDI, the catalytic effects decreased in the order of $Mn^{2+} > Pb^{2+} > Ca^{2+} > Cd^{2+} > Ba^{2+} > Zn^{2+}$. Also, for the reaction of H-MDI with glass fiber, almost the same tendency was observed. Further, the relation of the catalytic effect with the amount of free isocyanate groups present on the glass surface in the case of P-MDI is shown in Figure 2. It can be seen that, in the reaction system with more catalytically effective metal ion, the amount of free isocyanate groups tends to decrease in the later period of the reaction. This fact suggests that, in the presence of catalytically active metal ions, the bridging reaction between the two silanol groups on the surface of glass fiber and diisocyanates may proceed easily.

Further, the catalytic effect of the metal ion is analyzed according to the previous paper. Assuming that the time required to form a certain intermediate in reaction is inversely proportional to the rate of reaction, then the following equations hold:

$$k/k_o = t_o/t \qquad (1)$$

where k and k_o are the rate constants for the catalyzed and uncatalyzed reactions, respectively, and t and t_o correspond to the times required for formation of the intermediate species in the catalyzed and uncatalyzed reactions. From the catalysis law,

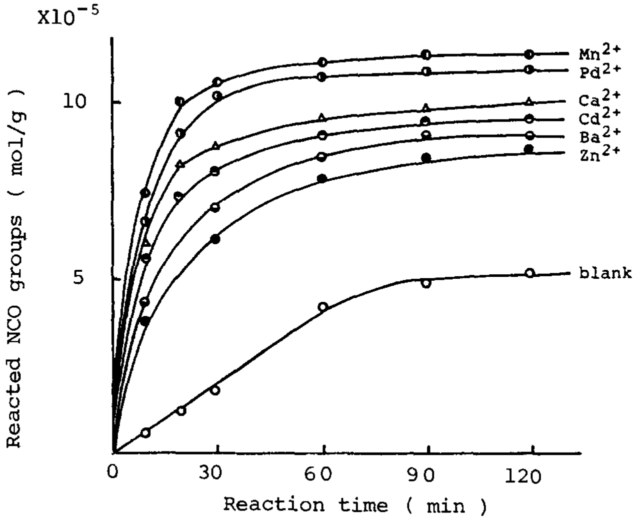


Fig. 1 Effects of metal-laurates on the diisocyanate-glass fiber reaction

(1% Cat./P-MDI; in DMSO at 30°C)

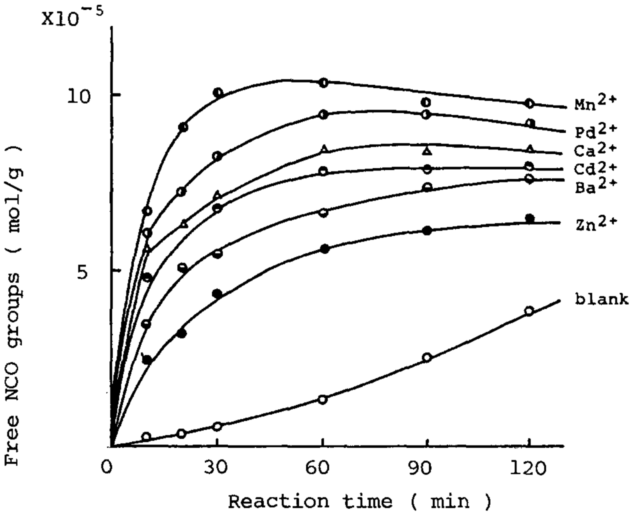


Fig. 2 Effects of metal-laurates on the free NCO groups of the glass fiber

(1% Cat./P-MDI; in DMSO at 30°C)

$$k = k_o + k_c[C]^x \qquad (2)$$

where k_c is the catalytic coefficient, [C] is the concentration of catalyst, and x is the order of catalysis. Dividing eq.(2) by k_o

$$k/k_o - 1 = k_c/k_o[C]^x \qquad (3)$$

or

$$\log(k/k_o - 1) = \log(k_c/k_o) + x\log[C] \qquad (4)$$

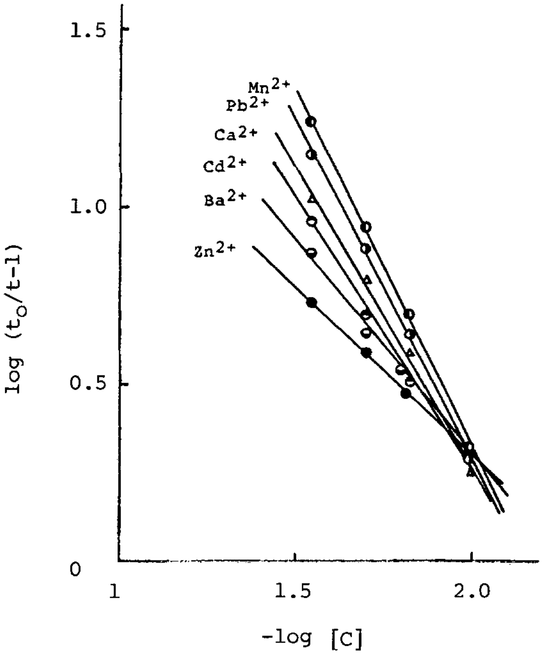


Fig. 3 Plots of log(t_o/t-1) vs.-log(C) of various metal-laurates in the reaction between glass fiber and P-MDI. (in DMSO at 30°C)

From these equations, the order of catalysis, x, and relative catalytic coefficient are derived by plotting log(k/k_o - 1) or log(t_o/t - 1) against the logarithm of catalyst concentration [C].

As shown in Figure 3, the relation between log(t_o/t - 1) and -log[C] is almost linear for each metal ion. Similarly, the effect of the metal ion concentration on the reaction of H-MDI with glass fiber was studied. The results were summarized in Table 1. It can be seen from Table 1 that both the reaction order x and the ratio k_c/k_o vary appreciably with the nature of the metal ion, though the cause of these phenomena is not known yet.

Table 1. Catalystic parameters for various metal ions

Catalyst	P-MDI		H-MDI	
	(k_c/k_o) x10^{-3}	x	(k_c/k_o) x10^{-3}	x
Mn-Laurate	4.95	2.0	5.02	2.0
Pb "	4.14	2.0	4.22	2.0
Ca "	3.02	1.6	3.16	2.0
Cd "	1.42	1.5	1.99	2.0
Ba "	0.32	1.1	0.32	1.5
Zn "	0.11	1.0	0.25	1.0

The catalytic effects of metal ions on the reaction of isocyanates with hydroxyl groups depend, in general, on the structure of the hydroxyl compounds. In butanol - isocyanate reaction systems, $(n\text{-}C_4H_9)_2\cdot Sn^{2+}$ and Mn^{2+} are most effective, while Zn^{2+}, Cu^{2+} etc. are almost ineffective. Further, it has been known that, in ethylene glycol-isocyanate systems, $(n\text{-}C_4H_9)_2\cdot Sn^{2+}$ and Pb^{2+} are most effective and, next to them, Zn^{2+}, Cu^{2+} etc. are also effective.

Based on the results described in the previous paper, and also on the fact that silanol groups on the surface of glass fiber are similar to hydroxyl groups in their reaction behavior, it can be considered that ternary complexes consisting of isocyanate, silanol group and metal ion may be formed and also that the complexion ability may depend on the nature of the metal ion.

3.2 Effect of the structure of organometallic compound

Overmars et al. [7,8], based on the fact that phenyllead triacetate was more active than tributyllead acetate as the catalyst for the reactions of alcohols with isocyanates, suggested that the carboxylic moiety of the catalyst may affect seriously the reactions of alcohols with isocyanates. In the present experiments, by use of organometallic compounds of $(n\text{-}C_4H_9)$ SnX_2 type, where X=carboxylate, the effect of X on the reactions of isocyanates with glass fiber was investigated.

The results obtained are shown in Figure 4 and Table 2. These results show that the reaction aspects of P-MDI and H-MDI are similar to each other, their catalytic activities decrease in the order of dibutyltin dilaurate > dibutyltin di-2-ethylhexoate > dibutyltin maleate > dibutyltin diacetate, and the reaction behavior also varies with the nature of the carboxylic moiety.

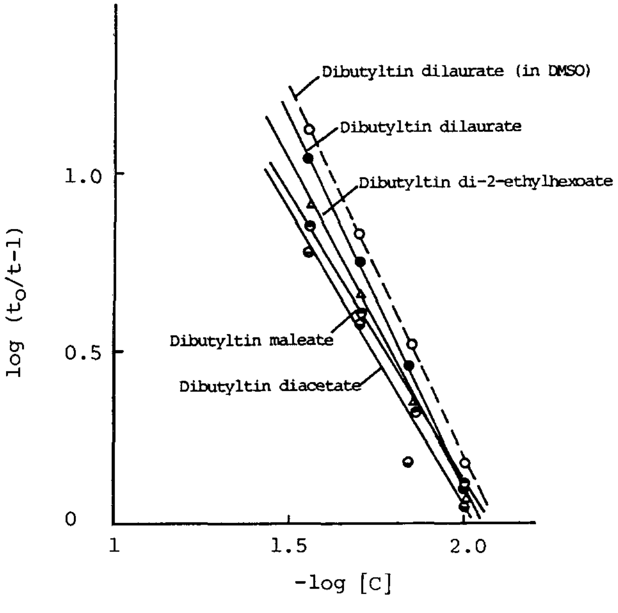


Fig. 4 Plots of $\log(t_o/t-1)$ vs. $-\log(C)$ of various dibutyltin dicarboxylates in the reaction between glass fiber and P-MDI (in DMF at 30°C)

Table 2. Catalystic parameters for dibutyltin dicarboxylate

Catalyst (in DMF)	P-MDI		H-MDI	
	$(k_c/k_o)\text{x}10^{-3}$	x	$(k_c/k_o)\text{x}10^{-3}$	x
Dibutyltin diacetate	2.83	1.5	0.526	1.5
Dibutyltin maleate	2.15	1.5	1.35	1.5
Dibutyltin di-2-ethylhexoate	2.88	1.6	1.42	1.6
Dibutyltin dilaurate	3.05	2.0	2.38	2.0
" (in DMSO)	3.80	2.0	2.75	2.0

Further, in similar reactions carried out in DMSO by use of dibutyltin dilaurate (shown in Figure 4 with dotted line), it appeared that the reaction order was not changed, while the value k_c/k_o changed. Based on this fact, it is suggested that solvents may affect only the reaction rate and not the order of the reaction of isocyanates with glass fiber, while the carboxylic moiety affect the reaction order itself.

Nesterov et al. [9], investigating the catalytic action of R_2SnX_2 type catalysts in the reactions of alcohols with isocyanates, reported that the substituent X affected the reaction little. On the other hand, Borhent et al. [10], investigating the catalytic action of dibutyltin dilaurate, reported that a tin-containing cation, formed by the dissociation of the catalyst according to the following equation, contributed to the formation of urethane.

$$(n\text{-}C_4H_9)_2\ Sn\{OCO(CH_2)_{10}\cdot CH_3\}_2 \rightarrow \{(n\text{-}C_4H_9)_2\ Sn\ OCO(CH_2)_{10}\cdot CH_3\}^+ + CH_3(CH_2)_{10}\cdot COO^-$$

Also, in the present experiments, it is considered that the dissociation degree of the substituent may affect the reactions of isocyanates with silanol groups.

3.3 Effects of binary catalysts of organometallic compound and amine

It is well-known that reactions of isocyanates and alcohols are, in general, promoted remarkably by the simultaneous use of organometallic compounds and amines [11,12]. In the present study, dibutyltin dilaureate was used together with various amines. The results are shown in Table 3. These data show that, the reactivity is far larger than that with each of organometallic compound or amine. Also, it is evident that catalysts of the organometallic compound - amine binary mixture system promote the reaction of isocyanates with silanol group. Although the mechanism of such a promoting action of binary catalysts is not clear yet, the catalytic activity may be raised by some mutual actions of all four components, namely, isocyanate, amine, metallic salt and silanol group [2].

3.4 Addition reaction of amino acid with isocyanate group on glass fiber surface

Generally, isocyanate groups can react with active hydrogen-containing compounds, but the reactivity decreases in the order of amine, alcohol, water, thiol and carboxylic acid. Thus, reactivities of amino acids containing these functional groups to glass fibers containing isocyanate

Table 3. Effects of dibutyltin dilaurate (DBTDL) - amine catalysis on the isocyanate - silanol reactions

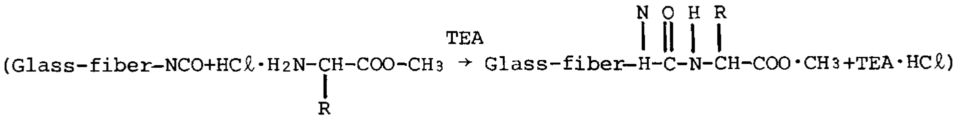
DBTDL	Amine Catalyst		Reacted NCO (x 10^{-5} mol/g)	Free NCO (x 10^{-5} mol/g)
1%	Without Amine		11.5	10.9
"	Quinoline	1%	12.6	11.8
	"	2%	14.9	14.0
"	Pyridine	1%	12.5	12.2
	"	2%	16.6	15.2
"	Triethylamine	1%	12.8	11.5
	"	2%	13.5	13.6

Solvent : DMSO, temperature: 30°C, reaction time: 30 min.

Table 4. Reactions of glass-fiber having isocyanate groups with amino acid esters*.

Amino acid ester	Solvent	Saponification method	
		Bound amino acid (m mol/g)	Yield of reaction (%)
Methionine methyl ester hydrochloride	DMF	0.625	42
	DMSO	0.711	48
Glycine methyl ester hydrochloride	DMF	0.871	74
	DMSO	0.880	76

* Reaction conditions: Glass-fiber having isocyanate group 1.0g (free NCO 9.2×10^{-5} mol/g); amino acid ester 3.0m mol; Triethyl amine 3.0 m mol; Solvent 30 ml, temperature 30°C, reaction time 12 hrs.



$$(\text{Glass-fiber-NCO}+\text{HC}\ell\cdot\text{H}_2\text{N-}\underset{\underset{\displaystyle R}{|}}{\text{CH}}\text{-COO-CH}_3 \xrightarrow{\text{TEA}} \text{Glass-fiber-}\overset{\overset{\displaystyle N}{|}}{\text{H}}\text{-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-}\overset{\overset{\displaystyle H}{|}}{\text{N}}\text{-}\overset{\overset{\displaystyle R}{|}}{\text{CH}}\text{-COO}\cdot\text{CH}_3+\text{TEA}\cdot\text{HC}\ell)$$

groups were investigated. From a consideration of low solubilities of amino acids in organic solvents, and for the purpose to make only amino acids to react selectively, carboxyl groups were previously protected by esterification.

Results of investigations on the reactivity of amino acids esters to glass fibers containing isocyanate groups are summarized in Table 4. Solvents used were DMSO and DMF. The rate of reaction of methionine methyl ester with glass fiber containing isocyanate groups amounted to 40 ∿ 50% in these solvent. Thus, it was proved that free isocyanate groups on the isocyanate - containing glass fiber react easily with amino groups of amino acids. Also, the reaction rate of isocyanate groups with glycine methyl ester was about 75% in these solvents.

Based on the above results, it was shown that, by the addition reaction of isocyanate -containing glass fiber with amino acid esters, glass fiber - amino acid adducts can be synthesized easily in good yield at relatively low temperature.

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