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Reactions

Carbon Fiber Having Isocyanate Group on the Surface.
Preparation and Application for Composites

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Summary

Reaction between diisocyanate and the hydroxyl groups on the surface of carbon fiber oxidized by nitric acid was investigated. It was found that polar solvents were favorable for the reaction. Stronger amines and Ba-laurate catalysts gave good results.

Further, rigid polyurethane foam reinforced by the carbon fiber thus prepared was found to show improved bending properties.

1. Introduction

Carbon fiber is now effectively used as reinforcement in the preparation on lightweights composite materials because of its high strength, high elastic modulus and low density. As well known, the mechanical properties of the composite materials depend greatly on the interaction between the components of the composite, i.e. carbon fiber and resin matrix, at the interface. For this reason, carbon fiber is usually treated with coupling agents or with sizing agents such as epoxy resin and Nylon resin to increase the affinity between the two components of composite material (1).

In previous papers (2-4), the preparations of the reactive carbon fibers having various functional groups on the surface, and their applications were reported. In the present paper, the reaction of oxidized carbon fiber with diisocyanate was examined. Namely, the effect of solvent utilized for this reaction as well as the catalytic activities of amines and metal carboxylates were investigated. One of two isocyanate groups of the reagent was reacted with the OH group of carbon fiber, and the other isocyanate group remained unreacted. The carbon fiber thus treated was utilized to reinforce polyurethane resin.

2. Experimental

2.1 Materials

Carbon fiber (TORAYKA,F-3000, Toray Co. Ltd., Japan) was oxidized with 20% nitric acid for 2hr at 100°C, which was thoroughly washed with water and dried.

Diphenylmethane 4,4'-diisocyanate (P-MDI) and hydrogenated diphenylmethane 4,4'-diisocyanate (H-MDI) of Sumitomo Bayer Urethane Co. Ltd., were used without further purification. The same materials of solvents (DMAc, DMSO etc.), amines(quinoline, pyridine etc.) and metal carboxylates as those described in the previous papers (5,6) were used.

2.2 Reactions of the oxidized carbon fiber with diisocyanate

They were carried out similarly as described in the previous paper (5).

2.3 Analysis

All kinds of analysis were carried out accoring to the previous papers (2,5).

2.4 Fabrication of composite and methods for mechanical properties measurements

Preperation of carbon fiber reinforced rigid polyurethane foam and the measurement of its bending properties were carried out similarly as described in the previous paper (7).

3. Results and Discussion

3.1 Reaction between the hydroxyl group on the surface of the oxidized carbon fiber and diisocyanate

It is well known that hydroxyl group and carboxyl group are formed by the oxidation of carbon fiber (2,8). Reaction of the oxidized carbon fibers with diisocyanate was pursued as a function of temperature and time. The result are shown in Table 1. With inceasing temperature and time, the formation of urethane linkage increased as the result of the reaction of diisocyanate with the hydroxyl groups on the surface of the oxidized carbon fiber.

Table 1. Change of the concentration of hydroxyl groups, carboxylic groups and uretane linkage during the reaction of the oxidized carbon fiber with P-MDI.

Condition		Concentrations in 10^{-5} mol/g			
temp. in °C	time in min.	hydroxyl groups	carboxylic groups	urethane linkages	free NCO fixated on the surface
30	0	0.67	9.1	-	-
	10	0.45	8.9	0.24	0.15
	20	0.37	8.9	0.28	0.28
	30	0.31	8.7	0.33	0.21
	60	0.26	8.2	0.39	0.24
60	10	0.27	8.8	0.42	0.33
	20	0.14	8.5	0.54	0.38
	30	0.06	8.5	0.61	0.40
	60	0.02	8.2	0.67	0.46

* Reaction Condition; Oxidized carbon fiber 12.5g/l,
P-MDI 10g/l in DMSO.

3.2 Solvent effect on the reaction of the oxidized carbon fiber with diisocyanate

Reaction was carried out in various solvents to prepare carbon fiber having isocyanate groups. Results with P-MDI are shown in Table 2. The weight of the reaction product in dioxane scarcely changed, and the IR absorptions assigned to urethane (1710cm^{-1}) and isocyanate (2250cm^{-1}) (9)

were not recognized. On the contrary, the weight of the reaction product in monochlorobenzene, N,N-dimethylacetamide and dimethylsulfoxide showed considerable increase, and the characteristic IR absorptions assigned to urethane and isocyanate groups were clearly recognized. Thus, carbon fiber having isocyanate groups has been prepared. It is suggested from Table 2 that the urethane and free isocyanate group were increased when a more polar solvent is used. It is known that polar solvent solvates the isocyanate group to increase the activity (10).

Table 2. Solvent effect on the reaction of the carbon fiber with P-MDI

Solvents	Dielectric constants (ε)	Dipole moments (μ)	Reaction temp. (30°C)		Reaction temp. (60°C)	
			urethane linkage	free NCO fixated	urethane linkage	free NCO fixated
			on the surface (mol/g) x 10^{-6}		on the surface	
Dioxane	2.21	0.45	0	0	0	0
Chlorobenzene	5.62	1.56	2.50	1.20	4.22	2.27
DMAc^{b}	37.8	3.79	3.18	2.05	6.15	3.54
DMSO^{c}	48.6	40.3	3.90	2.42	6.72	4.65

a: Reaction Condition; Carbon fiber 12.5g/l, solvent 50ml, reaction time 60min..

b: N,N-Dimethylacetamide

c: Dimethylsulfoxide

3.3 Catalystic effect of amine and metal carboxylates

It is well known that amine and metal carboxylates are effective catalysts for the reaction of isocyanate compounds with hydroxy compounds. Thus, the catalytic activities of various amines and metal carboxylates were examined.

As an example, triethylamine in various amounts was added to reaction systems of P-MDI and oxidized carbon fiber at 30°C in dimethylsulfoxide, and the urethane linkage and free isocyanate group were measured, and results are shown in Figure 1 and Figure 2. As shown in Figure1, the rate of urethane formation increase with increase in the concentration of triethylamine. As shown in Figure2, the free isocyanate group also increase with increase in the concentration of triethylamine, but that it tended to decrease in the latter stage of reaction when amine was used at higher concentrations. From this result it is obvious that amine exhibits the catalytic effect remarkably also on the reaction system of the oxidized carbon fiber-diisocyanate.

To cleare the catalytic reaction mechanism, the order of catalysis (x), and relative catalytic coefficient (k_c/k_o) were calculated according to the previous report (5). 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;

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

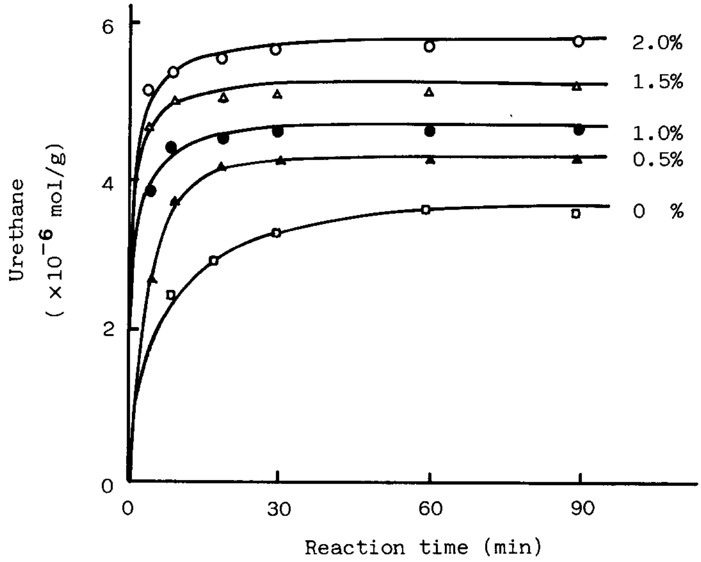

Fig. 1. Effect of triethylamine on the reaction of carbon fiber with P-MDI.

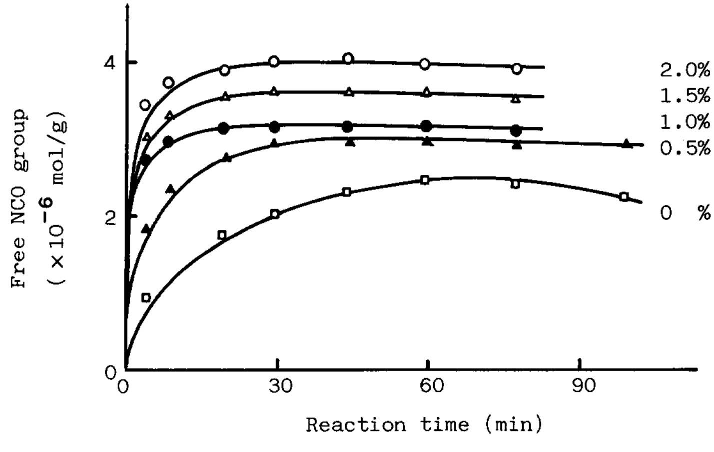

Fig. 2. Effect of triethylamine on the reaction of carbon fiber with P-MDI.

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 to for formation of the intermediate species in the catalyzed and uncatalyzed reactions. From the catalysis law,

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

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

$$\log(t_o/t-1) = \log(k_c/k_o) + x\log[c] \qquad (4)$$

As shown in Figure 3, the relation between log(t_o/t-1) and catalyst concentration (c) is almost linear for each amine.

According to the same method, the catalytic activity for the reaction between the oxidized carbon fiber and H-MDI was examined, the result is shown in Table 3. These results indicate that the catalytic activity of amine increases with its basicity. This result is similar to the case of catalytic activity in the reaction between isocyanates and alcohols. Comparatively small values in the tables for the relative catalytic effect of N,N-dimethylaniline would be caused from the steric hindrance of a complex formed of isocyanate and N,N-dimethylaniline (11).

The catalytic effects of various metal laurates and dibutyltin dilaurate were also investigated in the reaction between the oxidized carbon fiber and P-MDI or H-MDI at 30°C in dimethylsulfoxide.

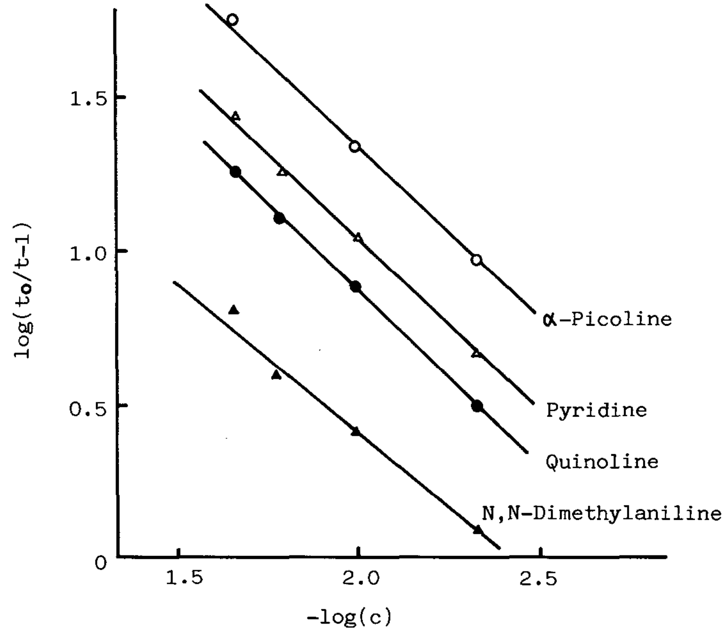

Fig. 3. Plots of catalysis law for various amine to the oxidized carbon fiber with P-MDI.

Table 3. Catalytic parameters for various amines.

Catalyst	P-MDI		H-MDI	
	k_c/k_o	x	k_c/k_o	x
Quinoline	935	1.0	1090	1.0
Pyridine	1778	1.0	1736	1.0
α-Picoline	3632	1.0	2085	1.1
N,N-Dimethylaniline	210	0.9	182	0.9

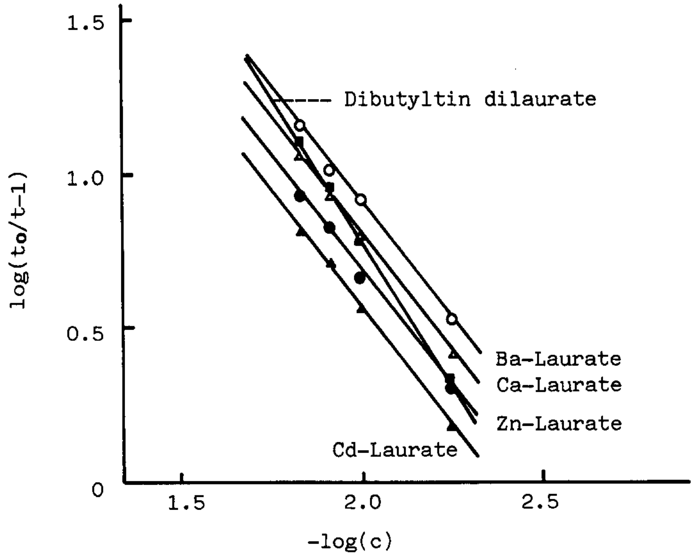

Fig. 4. Plots of catalysis law for metal carboxylates to the reaction of oxidized carbon fiber with H-MDI.

Table 4. Catalytic parameters for metal carboxylates.

Catalyst	P-MDI		H-MDI	
	k_c/k_o	x	k_c/k_o	x
Ba-Laurate	1020	1.0	1820	1.2
Ca-Laurate	650	1.1	1010	1.1
Zn-Laurate	340	1.1	720	1.1
Cd-Laurate	240	1.0	430	1.0

As shown in Figure 4, the relationship between $\log(t_o/t-1)$ and log(c) was found nearly linear for each metal carboxylates as in the cases of amines. Table 4 shows the order of catalysis and the relative catalytic coefficient calculated from the relationship in Figure 4 for each metal carboxylates. The catalytic effect was found in the decreasing order of Ba-laurate > Ca-laurate > Zn-laurate > Cd-laurate, varying considerably with the change of metallic ions. It is known that the catalytic effect of metal carboxylates is usually dependent on the chemical structure of hydroxy compound to react with isocyanate (12). As described in our previous paper (6), the formation of complex consisting of isocyanate, hydroxyl group of the oxidized carbon fiber and metallic ion, would be dependent here also on the nature of the metallic ion, resulting in the difference in the catalytic effect between metal carboxylates examined.

3.4 Mechanical properties of the oxidized carbon fiber reinforced rigid polyurethane foam

The interfacial shearing strength of the composite which has been reinforced by the oxidized carbon fiber is already known to increase with increasing the hydroxyl group on the surface of the carbon fiber (13). Thus it was tried to prepare rigid polyurethane foam composite uniformly reinforced by the oxidized carbon fiber according to the method described in our previous paper (7). Table 5 shows the bending properties of the composite. The oxidized carbon fiber reinforced rigid polyurethane foam was found nearly the same as the composite reinforced by epoxy resin treated carbon fiber in flexural strength as well as in flexural modulas, and the former showed considerable higher interfacial shearing strength than the latter. The aging treatment in the boiling water showed a big difference in the bending properties between those two composites. In case of the composite reinforced by epoxy resin treated carbon fiber, partial interfacial separation of the adhesive strength between carbon fiber and resin matrix would have occurred by the penetration of water, resulting in the deterioration of the bending properties. In case of the oxidized carbon fiber reinforced composite, on the contrary, the existence of sufficiently strong urethane linkage between carbon fiber and resin matrix would have prevented the aggressive penetration of water.

Table 5. Bending properties of the carbon fiber reinforced rigid polyurethane foam.

Carbon fiber treatment	Carbon fiber content (vol%)	Flexural strength (Kg/mm^2)	Flexural modulus (Kg/mm^2)	Interfacial shear strength (Kg/mm^2)
Epoxy resin treatment	5.8	11.4 (10.2)	387 (375)	0.85 (0.45)
	3.3	9.6 (9.2)	355 (346)	0.84 (0.44)
	1.6	8.4 (7.0)	307 (285)	0.74 (0.38)
Oxidation followed by diisocyanate treatment	5.8	12.5 (12.0)	390 (384)	0.89 (0.88)
	3.3	10.4 (9.8)	362 (352)	0.88 (0.86)
	1.6	8.8 (8.5)	315 (308)	0.80 (0.75)

* The values in parenthesis are for the samples after the boiling water treatment for 30 hr.

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