

New Catalysts for Urea Formation Reactions.

II. Catalytic Activity of Carboxylic Acids

YOJI WATABE, *New Products Development Division, Bridgestone Tire Company Ltd., 2800-1 Ogawahigashi, Kodaira, Tokyo 187, Japan*, and MICHIO ISHII and YUTAKA ISEDA, *Tire Designing Department, Bridgestone Tire Company, Ltd., 2800-1 Ogawahigashi, Kodaira, Tokyo, Japan*

Synopsis

Carboxylic acids with weak acidities showed large catalytic activity. For instance, for chlorine-substituted acetic acid the activity increased with decreasing chlorine content. For benzoic acid derivatives, electron acceptor substituents, such as NO₂, Cl, and OH, lowered the catalytic activity, while electron donor substituents such as alkyl and alkoxy groups increased it. Detailed study on the cure rate of polyureaurethane, with 2-methyl benzoic acid as a catalyst, showed that pot life (PL) and the minimum demolding time (DT) had a correlation with the catalyst amount [X] represented by the following equation:

$$PL^{-1} \text{ (or } DT^{-1}) = A + B[X]$$

where *A* and *B* are constants. Further, use of appropriate amounts of the catalyst enhanced tensile strength at break for polyureaurethane.

INTRODUCTION

Tertiary amines and salts of alkali metal, tin, cobalt and lead, are known catalysts for isocyanate-hydroxyl reactions. Only a few studies^{1,2} have been published for the isocyanate-amine reaction, probably because the urea-forming reaction is much faster than the urethane-forming one. There is a need, however, for new catalysts for the urea-forming reaction, since catalysts shorten demolding time and cure time of polyureaurethane. Catalysts are indispensable for urea-forming reactions since there are competing reactions in some systems such as the *in situ* polymerization of vinyl monomer.^{2,3}

Since benzoic acid shows some catalytic activity,¹ we examined the catalytic activity of other carboxylic acids and phenol compounds with different acidities. In this article, catalytic activity was evaluated by pot life (PL) and the minimum demolding time (DT). Further, mechanical properties of polyureaurethanes with and without catalyst were compared. Significant differences in molecular structures, as reported previously,⁴ were observed.

EXPERIMENTAL

Materials

Coronate 4090 from Nihon Polyurethane Co. Ltd. was used as an isocyanate-terminated prepolymer derived from 1 mole poly(oxytetramethylene)glycol and 2 mole 2,4-tolylenediisocyanate. The content of isocyanate group (NCO content) was 4.12, 4.33, or 4.39% by weight depending on the lot of the prepolymer. 3,3'-Dichloro-4,4'-diaminodiphenylmethane (MOCA) was used as a chain extending agent. The molar ratio of amino groups of MOCA to isocyanate groups of the prepolymer (NH_2/NCO) was 1.00. All the carboxylic acids and phenol compounds (Tables I–III) were reagent-grade materials. Cure was carried out in the same way as previously reported.⁴

Measurements

Pot life (PL) equaled the time for viscosity of the prepolymer–MOCA mixture to reach 1000 P. It was determined at 80°C by a BL type viscometer made by Tokyo Keiki Co. Ltd. The minimum demolding time (DT) was the time for the torque of the prepolymer–MOCA mixture to reach 90% of its value at 180 min. The cure curve (torque–time curve) was measured by a Curastometer⁵ manufactured by Japan Synthetic Rubber Co. Ltd. Tensile strength at break [T_B (kg/cm^2)] and elongation at break [E_B (%)] were measured at 25°C with a 50 mm/min extension speed, using test pieces cut from a 2-mm thick slab sheet with

TABLE I
Catalytic Activities of Chlorine-Substituted Acetic Acids^a

Acids	pKa	PL at 80°C (min)	DT at 100°C (min)
Without acid		23.1	76.1
Acetic acid	4.76	12.1	64.0
Monochloroacetic acid	2.87	14.3	55.4
Dichloroacetic acid	1.26	14.9	65.4
Trichloroacetic acid	0.64	24.2	87.4

^a Amount of acid, 1.37 mmole per 100 g of prepolymer; NCO content, 4.12%.

TABLE II
Catalytic Activities of Alkyl- or Alkoxy-Substituted Benzoic Acid Derivatives^a

Acids	pKa	PL at 80°C (min)	DT at 100°C (min)
Without acid		17.0	68.6
Benzoic acid	4.20	5.0	25.0
2-Methyl benzoic acid	3.91	5.0	18.0
3-Methyl benzoic acid	4.27	4.4	14.8
3,5-Dimethylbenzoic acid	4.30	4.3	19.4
4-Methoxy benzoic acid		3.7	15.3
3,5-Dimethoxybenzoic acid		3.9	14.5
2-Ethoxybenzoic acid		7.2	21.9
4-Ethoxybenzoic acid		4.4	10.7

^a Amount of acid, 4.12 mmole per 100 g of prepolymer; NCO content, 4.39%.

TABLE III
Catalytic Activities of Phenol Compounds^a

Phenol derivatives	pKa	PL at 80°C (min)	DT at 100°C (min)
Without acid		21.1	79.3
2-Methylbenzoic acid	3.91	6.1	23.6
Phenol	9.99	15.7	72.1
2-Chlorophenol	8.48	13.4	57.7
2,4-Dichlorophenol	7.85	13.0	66.9
2-Nitrophenol	7.23	17.6	81.8

^a Amount of phenol 4.12 mmole per 100 g of prepolymer; NCO content, 4.33%.

a ring dumbbell. Tear energy [Γ (kg/cm)] was measured according to the method proposed by Agei and Ninomiya⁶ and Nishi and Naito,⁷ using test pieces (80 × 10 × 2 mm) having a 2-mm length cut at its margin perpendicular to tensile direction.

RESULTS AND DISCUSSION

Catalysts for Urea-Forming Reactions

In order to study the relationship between acidity of carboxylic acids and catalytic activity, pot life and minimum demolding time were determined on chlorine substituted derivatives of acetic acid represented by $\text{CH}_n\text{Cl}_{3-n}\text{COOH}$. The amount of each acid employed was 1.37 mmole per 100 g of the prepolymer. As shown in Table I, the catalytic activity is the largest for acetic acid, but decreases with increasing acidity; finally, even the retardation of cure rate is observed with trichloroacetic acid, the acid with the strongest acidity.

The same measurements were carried out on ortho- or para-substituted benzoic acid (Table II). The minimum demolding time for polyureaurethane is decreased linearly with increasing pKa of the acid [Fig. 1(b)], though large differences in slopes can be seen between ortho- and para-substituted derivatives. The methyl group, an electron donor, heightens the catalytic activity of benzoic acid.

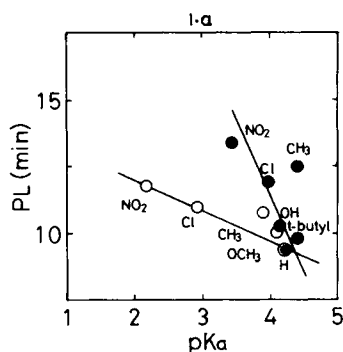


Fig. 1. Effect of acidity of ortho- or para-substituted benzoic acid derivatives on pot life (PL) and minimum demolding time (DT). (○) ortho; (●) para; catalyst amount: 1.37 mmole per 100 g of prepolymer; NCO content: 4.12%; PL and DT without catalyst are 23.1 and 76.1 min, respectively.

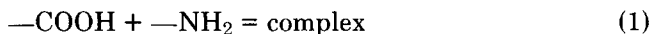
In contrast, electron-acceptor substituents such as nitro, chloro, and hydroxyl groups lower the activity. The same results are obtained when pot life is plotted against pK_a [Fig. 1(a)].

Since carboxylic acids of weaker acidity shows larger catalytic activity, we examined benzoic acid derivatives substituted with other electron-donor groups such as alkyl and alkoxy groups. As expected, any benzoic acid derivatives (Table II) shorten pot life and minimum demolding time much more than unsubstituted benzoic acid. Further, several acidic phenol compounds were subjected to the same tests (Table II), since their acidities are still weaker than the carboxylic acids (Table II). Contrary to our expectation, however, they do not surpass the carboxylic acids in catalytic activity (Table III), though 2-chlorophenol and 2,4-dichlorophenol shorten pot life and minimum demolding time to some extent. The lower catalytic activity of phenol compounds will be discussed in considering the reaction mechanism.

Reaction Mechanism

Reaction mechanism is inferred (Fig. 2) though no experiments have been conducted. The urea-forming reaction occurs by a nucleophilic attack of the nitrogen atom of the amino group on the carbon atom of the isocyanate group. Therefore, the reaction will be accelerated by increasing the basicity of the nitrogen atom. Figure 2 represents a complex from an amine and a carboxylic acid which attacks the carbonyl group of the isocyanate. Hydrogen bonding A between carbonyl group of carboxylic acid and hydrogen of amino group is based on the fact that the phenol compound, which does not have a carbonyl group, shows only slight catalytic activity in spite of its weaker acidity. The basicity of the nitrogen atom is strengthened by the hydrogen bonding A, but is weakened by the hydrogen bonding B. The electron-donor substituent R then tends to strengthen the hydrogen bonding A and subsequently weakens the hydrogen bonding B, resulting in enhancement of catalytic activity. Although the hydrogen bonding B is not favored because of the neutralization of the basicity of the amino group, it may play a role in facilitating the approach of isocyanate to the complex by preventing the amino group from inversion.

In order to see the effect of the catalyst amount on reaction rate, pot life and the minimum demolding time were measured using 2-methyl benzoic acid. The plot of the reciprocal of pot life against the catalyst amount [Fig. 3(a)] is linear. It can be explained as follows: It is inferred that the carboxylic group of the catalyst and amino group of MOCA reversibly form the complex (Fig. 2) [eq. (1)]:



$$K = [\text{complex}]/[\text{COOH}][\text{NH}_2] \quad (2)$$

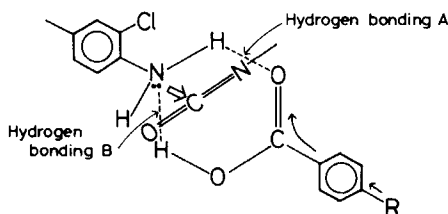


Fig. 2. Inferred complex of amino group and carboxylic acid attacking isocyanate.

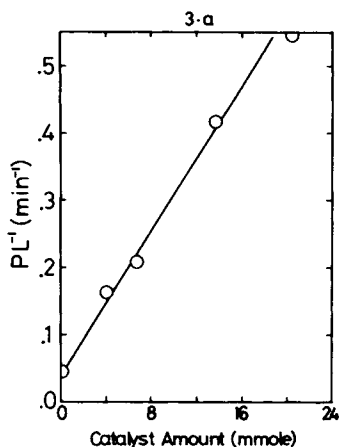
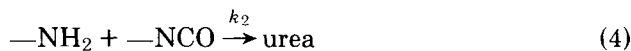
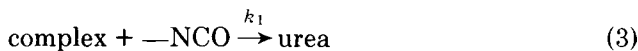


Fig. 3. Relationship between reciprocal of PL or DT and amount of 2-methylbenzoic acid. The catalyst amount shows a value per 100 g of prepolymer. NCO content: 4.33%; DT was determined at 100 °C (O) and 120 °C (●).

where K is the equilibrium constant. The urea bond is formed by reaction of the complex with the isocyanate group [eq. (3)] as well as reaction of the amino group with the isocyanate group [eq. (4)],



where k_1 and k_2 are rate constants. The reaction equation can be written [eq. (5)] as second order:

$$-\frac{d[\text{NCO}]}{dt} = k_1[\text{complex}][\text{NCO}] + k_2[\text{NH}_2][\text{NCO}] \quad (5)$$

Equation (5) can be written as eq. (6) using eq. (2) and considering that $[\text{NCO}]$ is equal to $[\text{NH}_2]$:

$$-\frac{d[\text{NCO}]}{dt} = (k_2 + k_1K[\text{COOH}])[\text{NCO}]^2 \quad (6)$$

Assuming that the equilibrium in eq. (1) lies to the left, $[\text{COOH}]$ will be regarded as its initial value $[\text{COOH}]_0$. Support for the assumption is obtained by IR analysis of an equimolar mixture of 2-chloroaniline and acetic acid as model compounds (Fig. 4). Absorption spectra of the amino group at 3400 and 3490 cm^{-1} are neither broadened nor shifted to a lower frequency region by acetic acid. This indicates that the content of the complex is very small. Thus, integration of eq. (6) with respect to time from 0 to PL yields eq. (7), since $[\text{NCO}]/[\text{NCO}]_0$ at PL is found to be almost constant, that is, 0.35 ± 0.04 regardless of the catalyst amount employed:

$$\text{PL}^{-1} \propto k_2 + k_1K[\text{COOH}]_0 \quad (7)$$

Equation (7) explains the linear relationship between the reciprocal of pot life and the catalyst [Fig. 3(a)]. Cure curves at 100°C with and without the catalyst

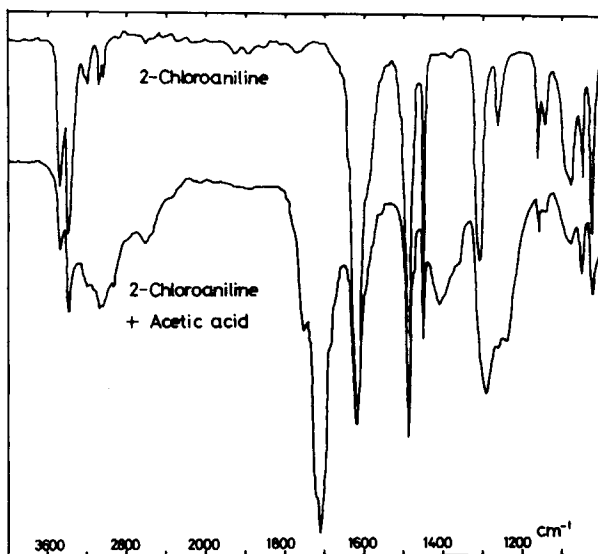


Fig. 4. Infrared spectra for 2-chloroaniline and equimolar mixture of 2-chloroaniline and acetic acid.

are shown (Fig. 5). The abrupt increase in torque arises mainly from ordering of hard segments involving urea and urethane groups. The reciprocal of the minimum demolding times from cure curves at 120 and 100°C (Fig. 5) is plotted against the catalyst [Fig. 3(b)]. The linear relationship is obtained at 120°C, but only in the small catalyst range at 100°C. The deviation from the line in the larger catalyst range at 100°C arises from a failure of the rapid ordering of hard segments after the accelerated urea-forming reaction.

Mechanical Properties for Polyureaurethane with Catalyst

In order to cure conditions after demolding, we studied the effect of postcure time on mechanical properties for polyureaurethane with 2-methyl benzoic acid. Before measuring mechanical properties, all test pieces were aged at 30°C, under 50% humidity atmosphere for one week. Ten percent modulus (M_{10}) is almost constant from 23.6 to 180 min (Fig. 6). Tensile strength at break (T_B) and

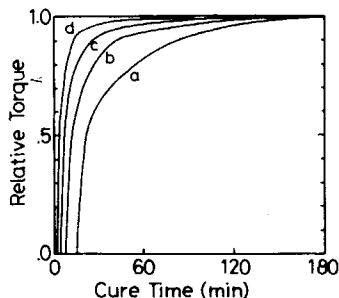


Fig. 5. Cure curves of polyureaurethane with and without 2-methylbenzoic acid. Catalyst amount per 100 g of prepolymer (mmole): (a) 0.0, (b) 1.37, (c) 4.12, (d) 13.6; NCO content: 4.33%.

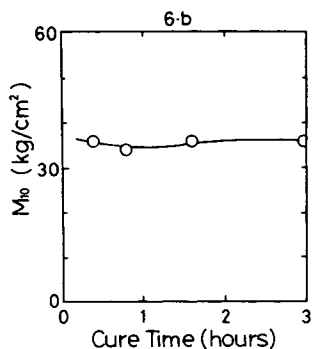


Fig. 6. Effect of post cure time on mechanical properties for polyureaurethane. Amount of 2-methyl benzoic acid: 4.12 mmole per 100 g of prepolymer; NCO content: 4.33%; DT at 100°C: 23.6 min.

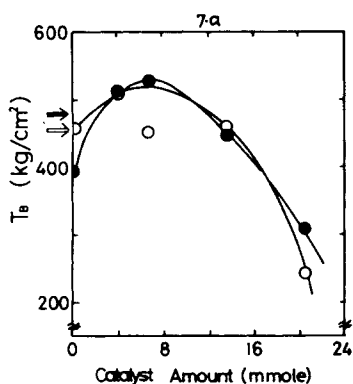


Fig. 7. Effect of the amount of 2-methyl benzoic acid on mechanical properties for polyureaurethane cured for a period corresponding to each minimum demolding time. The catalyst amount shows a value per 100 g of prepolymer. NCO content: 4.33%; arrows in coordinate show mechanical properties of polyureaurethane cured for 180 min without the catalyst. Cure temperature: 100°C (O, ⇒); 120°C (●, ⇒).

elongation at break (E_B) decrease with increasing postcure time. All properties, however, were as excellent as those for polyureaurethane without the catalyst. Thus, the postcure appears to be unnecessary.

Effect of the catalyst amount on mechanical properties are studied using the same samples (Fig. 3). Cure is carried out for a period corresponding to each minimum demolding time at 100 and 120°C, respectively. In the catalyst range from 4.12 to 13.6 mmole T_B for polyureaurethane with the catalyst is somewhat larger than that for polyureaurethane without the catalyst [Fig. 7(a)]. However, it is decreased considerably in the catalyst amount of 20.5 mmole. The former result is confirmed since 2-methyl benzoic acid greatly increases molecular weight of polyureaurethane. Values of T_B for nylon⁸ and polyethylene⁹ are enhanced by increasing the molecular weight. The latter is attributed to deficiency of cure time requisite for sufficient ordering of hard segments. E_B and tear energy (Γ) are less affected by the catalyst amount [Figs. 7(b) and 7(c)].

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