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Amidations of Rosin with Isocyanates*

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Amidations of abietic acid and rosin with isocyanates, a novel approach to modify rosin, were investigated using three isocyanates, namely cyclohexyl isocyanate, phenyl isocyanate, and tolyl isocyanate. The experimental results demonstrate that abietic acid and rosin reacted with the three isocyanates at 100 to 150 °C for 1 to 5 h to produce rosin amides in yields of 90 to 100%. The reaction temperatures were **much** lower than 200 to 300 °C at which conventional modifications of rosin are carried out. The amidation of abietic acid with phenyl isocyanate in toluene proceeded much faster than that in acetone or dioxane. The addition of triethylamine or N-methylpiperidine as a catalyst greatly accelerated the amidation rates of abietic acid and rosin with phenyl isocyanate. Molten rosin could react, with phenyl isocyanate without using a solvent, which can shorten synthetic route of rosin amides, and reduce reaction times. The rosin amides prepared under these conditions were in light color, and suffered from little oxidation and decarboxylation.

INTRODUCTION

Rosin is a biochemical material derived from some coniferous trees, and has found wide applications in paper, ink, adhesive, coating and paint industries. In the paper industry, rosin with alum has been used as a dominant sizing agent to provide paper and paperboard with resistance to liquid wetting, penetration, and absorption since 1807. However, this familiar rosin sizing is effective only under acidic conditions, and is meeting the problem as pH values in papermaking systems, in recent years, are rapidly shifting from acidic to neutral-alkaline regions. Although many neutral rosin sizes were developed for the neutral-alkaline papermaking systems (Nakajima, 1993; Zhu et al., 1994; Tahara et al., 1996), few of them were successful in the industrial application for economic and technologic reasons.

One of the reasons for the difficulties to prepare practical neutral rosin sizes is that rosin esters, which are the major components for the neutral rosin sizes, have to be produced at very high reaction temperatures (Hind et al., 1954; Huang, 1994). The major component of rosin is a family of tricyclic acid called rosin acid. Abietic acid as shown in Fig. 1 is a typical structure of the rosin acids. Owing to steric hindrance of the large hydrophobic bulk in the rosin acids, the reactions of the carboxyl groups with other compounds are usually carried out at high temperatures (ZOO-300°C) for 3-15 h. Furthermore, abietic acid has a conjugated double bond, and is a tertiary carboxyl acid. The high reaction temperatures for long reaction times consume a large amount of

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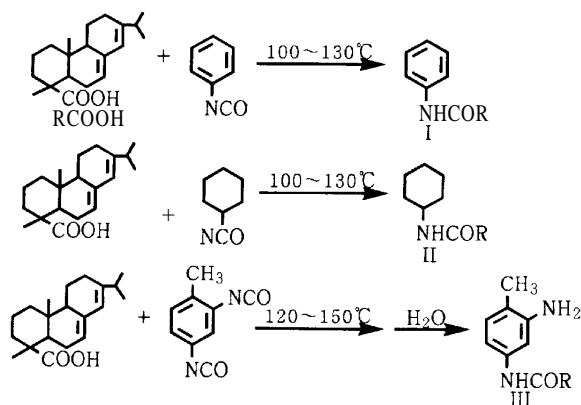


Fig. 1. The amidations of abietic acid with isocyanates applied in this study.

energy, and may cause oxidation and decarboxylation of rosin acids. The modification of rosin at lower reaction temperatures, therefore, is a key technique to produce neutral rosin sizes, and has been the subject of many studies (Zhou *et al.*, 1984; Wu and Tanaka, 1995).

Considering the large steric hindrance of rosin acids, rosin was allowed to react with isocyanates with high reactivity at moderate reaction temperatures. Figure 1 shows the scheme of amidations of abietic acid with three isocyanates, phenyl isocyanate, cyclohexyl isocyanate, and tolyl diisocyanate, to give Amides I, II, and III. The amidation yields of abietic acid with the three isocyanates were 90 to 95% at 100 to 150°C in the reaction times of 1 to 3 h. These results illustrate that the amidation of rosin with isocyanates, that is, a novel modification of rosin could proceed well at lower reaction temperatures as expected. The rosin amides had been applied to neutral rosin sizes, and exhibited good sizing effectivenesses in the region of pH 4 to 8 (Wu and Tanaka, 1996). In this paper, we will describe the amidation of abietic acid and rosin with phenyl isocyanate under various reaction conditions in details.

MATERIALS AND METHODS

Materials

A Chinese gum rosin (Grade W) was kindly provided by Arakawa Chem. Ind. Co. Ltd. Abietic acid (>70%) was obtained from Tokyo Kasei Ind. Co. Ltd., and purified on a silica column using a mixture of n-hexane, ethyl acetate and methanol (6:4:1 in volume) as a eluting solvent. Cyclohexyl isocyanate, phenyl isocyanate, and tolyl diisocyanate (>98%, Tokyo Kasei Ind. Co. Ltd.) were used for the amidations without purification.

Analytical procedures

Mass spectra (MS) were recorded on a Shimadzu QP-1000 gas chromatography mass

spectrometer operating under DI conditions (70 eV). Infrared spectra were obtained using a Perkin-Elmer system 2000 Fourier-transform spectrometer. High performance liquid chromatography (HPLC) was carried out on a JASCO TRIROTAR-II with a column of DEVELOSIL-60-3 (ϕ 20 x 250 mm) using a mixture of n-hexane, ethyl acetate and methanol (6:4:1 in volume) as a eluting solvent. Quantitative analyses were made on the HPLC. Abietic acid and phenyl abietic amide were used as standard materials. Color of rosin amides was measured according to JIS K5902.

General procedure for preparation of rosin amides

The solvents were distilled and stored in the containers containing molecular sieve 5A. All of glasswares were dried in a oven at 105 °C overnight.

To a 200 ml three-necked flask, desired amounts of abietic acid, a catalyst and a solvent were charged, and a condenser with CaCl_2 dryer and a thermometer were equipped. The flask was heated in a oil bath to desired temperatures, and then phenyl isocyanate was added dropwise over 15 min with stirring. The reaction was carried out under an atmosphere of nitrogen. The samples were taken at desired times and analyzed by the HPLC. After the reaction was completed, the flask was cooled to room temperature, and the reaction mixture was washed with 0.1 N NaOH solution, dried over Na_2SO_4 , and filtered. The solvent in the filtrate was evaporated under vacuum to give the product.

In the case that phenyl isocyanate was reacted with rosin, a 200 ml four-necked flask equipped with the condensator, the thermometer, and a glass stirrer was used. Rosin and a catalyst were charged to the flask, and heated to melten state. Then phenyl isocyanate was added dropwise over 15 min with stirring, and the flak was heated to required temperatures. After the reactions were carried out under an atmosphere of nitrogen for desired times, the reaction mixture was cooled to room temperature, and stored for applications.

Identification of rosin amide I

The chemical structure of rosin amide is shown in Fig. 1. Because rosin, even the abietic acid used, is a mixture of tricyclic acids as mentioned above, it is difficult to identify the rosin amide with a NMR spectroscopy. The structure of Amide I was determined by MS and IR spectroscopy. MS m/z (%): 377 (M^+ , 21), 285 (9), 258 (14), 257 (6), 241 (7), 174 (13), 120 (4), 119 (100), 92 (48), 77 (26), 65 (18), 45 (17), and 43 (12). IR ν_{max} cm^{-1} : 3302 (NH), 1670 (amide), 1510 (phenyl), and 1158 (CON).

RESULTS AND DISCUSSION

Effects of temperature and solvent on the amidation of abietic acid with phenyl isocyanate

Table 1 gives amidation yields of abietic acid with phenyl isocyanate in four different solvents, namely acetone, dioxane, ethyl acetate, and toluene, at different temperatures. The reactions in acetone and dioxane at 25 °C proceeded very slowly. The amidation yields of abietic acid in the two solvents for 24 h were only 6.5% and 4.3%, respectively.

The reaction in toluene went best of the four solvents used. The yield of Amide in toluene was 26.1% after reaction at 25 °C for 3 h, and increased to 45.2% for 24 h. These results indicate that solvents greatly influence the amidation rates. The efficiency of the solvents used were higher in the order of toluene>ethyl acetate>acetone>dioxane. This is agreement with the results in the reactions of a phenyl isocyanate with alcohols in these solvents (Arnold *et al.*, 1957; Ephraim *et al.*, 1958).

Table 1. The amidation yields of abietic acid with phenyl isocyanate in the different solvents.*

Solvent	Reaction temperature(C)	Amidation yield (%)		
		Reaction time (h)		
		3	8	24
Acetone	25	2.5	3.7	6.5
	50	7.9	9.2	14.3
Dioxane	25	2.0	2.5	4.3
	105	21.4	43.2	73.0
Ethyl acetate	25	7.8	10.2	14.3
	75	24.1	38.5	69.4
Toluene	25	26.1	31.3	45.2
	75	42.3	65.7	80.5
	105	64.3	90.3	100

* Abietic acid and phenyl isocyanate were in equimolar amounts.

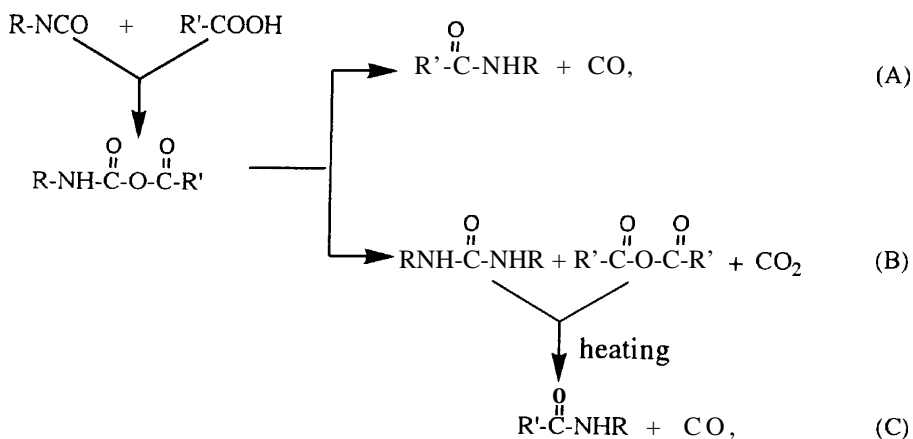


Fig. 2. Proposed mechanisms of reactions of an isocyanate with a carboxylic acid in equimolar amounts.

The results described above show that though phenyl isocyanate is considerably reactive, it can not react with abietic acid easily at room temperature. By raising reaction temperatures, the amidation rates of abietic acid with phenyl isocyanate in the four solvents were enhanced remarkably. As shown in Table 1, the amidation yield of abietic acid with the isocyanate in toluene for 3 h increased from 26.1% at 25°C to 42.3% at 75 °C, and 64.3% at 105°C. Figure 2 shows proposed mechanisms of the reaction of an isocyanate with a carboxylic acid in equimolar amounts (Agre et al., 1955; Sorenson, 1959). The first product of the reaction is a carbamic-carboxylic anhydride which is unstable in most cases. The decomposition of the anhydride proceeds through two paths to give a amide in (A), and a symmetrical urea and the anhydride of the acid in (B). Carbon dioxide is evolved in both cases. The products of path (B) can react with each other on heating to give the amide 'in path (C). Thus, under severe conditions, the ultimate product of the reaction is the amide. However, considering oxidation and decarboxylation of rosin at high reaction temperatures, the suitable temperatures for the amidations of rosin with isocyanates were 100 to 150°C as stated in following sections.

Catalyzed amidation of abietic acid with phenyl isocyanate

From the data in Table 1, it can be seen that the amidation of abietic acid with phenyl isocyanate in toluene even at 105°C had to be carried out for more than 8 h to obtain the products in amidation yields of above 90%. To reduce reaction times, catalyzed amidation of abietic acid with phenyl isocyanate was tried. It is well known that reactions of alcohols with an isocyanate were catalyzed by tertiary amines (Burkus, 1961; Milena et al., 1994). Therefore, two typical tertiary amines, triethylamine and N-methylpiperidine which showed large catalysis activity in the reactions of the alcohols with the isocyanate, were chosen for the amidation of abietic acid with phenyl isocyanate.

The catalyzed amidations were carried out in toluene at 105°C and the results were given in Table 2. The addition of triethylamine or N-methylpiperidine (10 mg/g abietic acid) reduced the reaction times from 10 h without the catalysts to 3 h to reach amidation yields of about 95%. The catalysis activity of N-methylpiperidine was a little larger than

Table 2. Catalyzed amidations of abietic acid with phenyl isocyanate in toluene at 105 °C.*

Catalyst	addition amount (mg/g abietic acid)	Reaction time (h)	Amidation yield (%)
—	—	10	94
Triethylamine	5	3	85
	10	3	93
	20	3	95
N-methyl piperidine	5	3	89
	10	3	95
	20	3	98

* Abietic acid and phenyl isocyanate were in equimolar amounts.

that of triethylamine. No significant difference in catalysis efficiency could be observed for the addition amounts of the catalysts between 10 and 20 mg/g abietic acid. The results demonstrate that the tertiary amines can greatly accelerate the reaction rate of abietic acid with phenyl isocyanate.

Amidation of rosin with phenyl isocyanate

Table 3 shows the results of amidation of rosin with phenyl isocyanate in toluene. Based on the comparison of the data in Table 3 with those in Tables 1 and 2, it is found that the amidation of rosin with phenyl isocyanate could also proceed well, but a little slower rate than that of abietic acid with the isocyanate. For example, rosin and abietic acid reacted with phenyl isocyanate in toluene for 11 h and 10 h to reach the amidation yields of 95% and 94%, respectively. This may be because rosin is a mixture of tricyclic acids including abietic acid which have different amidation rates.

On the other hand, rosin melts at about 90°C. If molten rosin may react directly with an isocyanate without using a solvent, the synthetic route for rosin amide can be shortened, and the cost for industrial production of the amide can be cut down. The experimental data in Table 3 shows that rosin reacted with the isocyanate at 105 °C for 7 h to give amidation yield of 91% compared with 95% for 11 h for the reaction in toluene. By raising reaction temperature to 200°C, the reaction time to give product with the same amidation yield was reduced to 1 h. The addition of N-methyl piperidine greatly accelerated the amidation rate of rosin with phenyl isocyanate. These results proved that rosin can react with phenyl isocyanate well without using a solvent as expected.

Table 3. The amidation yields of rosin with phenyl isocyanate*.

Solvent	Reaction conditions			Amidation yield (%)	Color number
	Catalyst	Temperature (°C)	Time (h)		
Toluene	—	105	11	95	35
Toluene	Triethylamine	105	4	94	25
Toluene	N-Methyl-piperidine	105	3	94	25
—	—	105	7	91	35
—	—	150	4	92	50
—	—	200	1	92	>70
—	N-Methyl-piperidine	150	1	93	35

* COOH/NCO=1

Oxidation and decarboxylation of rosin during the amidation

Color is an important indication of modified rosin products, which somewhat reflects oxidation of rosin (Hind *et al.* 1954; Nakamura, 1970). In this study, we used color number according to JIS K5902 to monitor color changes of the reaction products of rosin with phenyl isocyanate as shown in Table 3. The unmodified rosin melted at about 90°C, and had the color number of 10. The data in Table 3 shows that the color numbers of the rosin amide prepared at 105°C were smaller than 35, indicating that oxidation occurred during the amidation was small. But the color number of the modified product was dramatically increased to >70 when the amidation temperature was 200°C. It was observed that the color of reaction mixtures rapidly became darkened at about 180°C. Thus, it is important to control the reaction temperature below 150°C in order to obtain light colored products.

The results of HPLC separation of the reaction mixtures produced at 105°C revealed that the amounts of decarboxylated products were below 1%, but increased to 3% for the products made at 200°C, which meant that the decarboxylation in the amidation of rosin with phenyl isocyanate was small. This is consistent with the results that significant decarboxylation of rosin usually occur at above 220 °C (Hind *et al.* 1954).

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