

Crosslinking of Amidated Polybutadiene with Resole. I

HAJIME HARA, YOSHIHIKO ARAKI, and SHINGO ORII, *Central Technical Research Laboratory, Nippon Oil Company, Ltd. 8, Chidori-cho, Naka-ku, Yokohama, Kanagawa 231 Japan*

Synopsis

Various liquid polybutadiene derivatives were examined as modifiers to improve the brittleness of phenolic resins. Amidated polybutadienes obtained from a maleinated polybutadiene and ammonia had the highest curing tendency when they were reacted with resole under mild conditions. The cured resins were homogeneous and the brittleness of the phenolic resins was remarkably improved. Crosslinking efficiency was closely related to the succinamic acid group of the amidated polybutadiene. Thermal behavior of the succinamic acid group was also related to the effects of curing temperature and curing time on crosslinking. From these observations, cross-condensation between the succinamic acid group of an amidated polybutadiene and resole seemed to have occurred to a great extent than the self-condensation of resole itself and oxidative crosslinking of the amidated polybutadiene.

INTRODUCTION

Studies have been made on modifiers to improve the brittleness of phenolic resins. Tung oil is an excellent modifier.¹ Low molecular weight polybutadienes have also been examined as modifiers. Two acceptable methods have been proposed for the reaction between a polybutadiene derivative and 2-methylolphenol or resole. One of the methods involves a thermal reaction between the carbon—carbon double bond of polybutadiene and the 2-methylolphenol group of resole via a chromane or a quinone—methide intermediate.² The other method involves a phenol-modified polybutadiene.³ Using a Friedel—Crafts catalyst, phenols are alkylated with the carbon—carbon double bond of polybutadiene, and the resulting polybutadiene derivative is then involved in the condensation reaction with resole. Patents⁴ have been published on the methods, which, however, are not free from drawbacks. In the first method, higher reaction temperatures (ca. 200°C) than those for condensation of resole itself are required; thus, efficient crosslinking cannot be expected under mild reaction conditions (100–150°C). In the second method, the Friedel—Crafts catalyst may effect undesirable polymerization or cyclization of polybutadiene double bonds during alkylation.² These undesirable reactions decrease the amount of phenols added to the double bonds of polybutadiene and the flexibility of the phenol-modified polybutadiene.

It was found that amidated liquid polybutadienes derived from maleinated polybutadiene and ammonia were compatible with resole, and the crosslinked product formed between amidated polybutadiene and resole improved the brittleness of the phenolic resin remarkably.

EXPERIMENTAL

Materials

The liquid polybutadienes (PB) whose number-average molecular weights were roughly from 1000 to 3000 (rounded as 1000, 2000, and 3000) and their vinyl contents ranged from 60 to 70% were used.

Phenol, aqueous formaldehyde (35%), aqueous ammonia (25%), and amines were of commercial reagents and used without further purification.

Preparation of Resole

Resole was prepared conventionally using aqueous ammonia as the catalyst.

Ammonia (0.2 mol) (25% aqueous solution) was added to 2 mol of phenol and 2.4 mol of formaldehyde (35% aqueous solution) in a flask equipped with a reflux condenser and an agitator, and mixed. The mixture was maintained at 90°C for 30 min; the unreacted materials and water were then removed at about 50°C *in vacuo*.

Preparation of Polybutadiene Derivatives

Maleinated polybutadiene was prepared conventionally by reacting the polybutadiene with maleic anhydride at 190°C without solvent. A dicarboxylic acid derivative and a half ester derivative were prepared by reacting the maleinated polybutadiene with an excess of water or *n*-butanol (2–5 mol equivalent of succinic anhydride group), respectively, in the presence of a small amount of triethylamine as the catalyst at 90°C. After confirming that the succinic anhydride group was consumed completely by infrared analysis, the excess water or *n*-butanol was removed under reduced pressure at 120°C. Half amide derivatives were prepared by reacting the maleinated polybutadiene with amine (equal mol amount of succinic anhydride group) at 90°C until confirming that the succinic anhydride group was consumed completely by infrared analysis.

Preparation of Amidated Polybutadiene from Ammonia

Aqueous ammonia was added dropwise to the maleinated polybutadiene dissolved in an inert solvent such as toluene or tetrahydrofuran at 40°C, and after maintaining the mixture at 40°C for 1 h, the solvent and water were removed under reduced pressure. Evaporation was carried out at bath temperatures below 100°C to prevent the formation of an imide derivative and to obtain a solid or semisolid amidated polybutadiene. Ammonia conversion was calculated from the nitrogen content of the amidated polybutadiene. The succinamic acid group content of the amidated polybutadiene was calculated from the acid value, which was determined by titrating the solution of amidated polybutadienes in xylene with a potassium ethoxide solution using phenolphthalein as indicator.

Crosslinking of Amidated Polybutadiene

Resole and amidated polybutadiene were dissolved in toluene-methanol (1:1 weight ratio) to make a 50% resin solution. A few grams of the solution was placed on an aluminum plate which was then heated. The cured resin (about 500 μm in thickness) was crushed into small pieces which were immersed in acetone at ambient temperature. The acetone insoluble fraction was dried under reduced pressure at 80°C.

Evaluation of Cured Resin Performance

A resin solution containing resole and amidated polybutadiene was coated on a steel panel using a doctor blade to form a film which was heated at 150°C for 1 h. The physical properties of the cured film were determined by the methods described in JIS K-5400. The DuPont impact test was carried out using a 500 g plummet of 0.5 in. diameter.

RESULTS AND DISCUSSION

Crosslinking of Amidated Polybutadiene

A variety of polybutadiene derivatives was examined to study the crosslinking phenomenon with resole. The results of a number of maleinated polybutadiene derivatives are shown in Figure 1. Mixtures of the polybutadiene derivatives and resole formed before heating a completely compatible phase which was retained even after curing. Among the polybutadiene derivatives investigated, a half amide derivative (NH_3) gave the largest acetone insoluble fraction at the higher concentrations.

Among the various amide and/or ammonium salt derivatives having roughly the same amount of functional group, the cured resin obtained from an ammonium salt derivative gave the largest acetone insoluble frac-

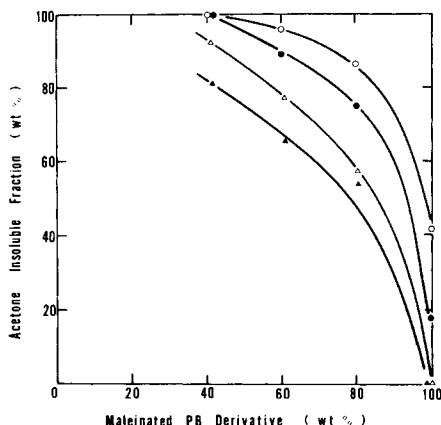


Fig. 1. Reactivity of various maleinated PB derivatives with resole at curing temperature of 150°C for 1 h, \bar{M}_n of PB = 2000, 3.3 mol of functional group on polymer chain: (O) a half amide derivative (NH_3); (●) a dicarboxylic acid derivative; (Δ) an acid anhydride derivative; (▲) a half ester derivative (*n*-BuOH).

tion followed by a polybutadiene derivative containing a succinamic acid (a half amide made from ammonia). The acetone insoluble fraction obtained from a cured mixture of resole with an amide or with an ammonium salt polybutadiene derivative was always much larger than that expected from such a cured mixture in absence of cross-condensation. Amide derivatives obtained from aliphatic amines showed a poor curing tendency (Fig. 2) while aniline derivatives showed a good curing tendency.

The effect of polybutadiene molecular weight on crosslinking was investigated. Polybutadiene derivatives having 2.2 and 3.3 mol of succinamic acid group, respectively, were mixed with resole, and the mixtures were heated at 150°C for 1 h. The results are shown in Figure 3. Amidated polybutadienes having the same number of functional group in their polymer chains gave almost the same result for the acetone insoluble fraction. Such observation suggests that crosslinking be closely related with the amide functional group.

The effects of ammonia added to the succinic anhydride group of mal-inated polybutadiene on crosslinking are plotted in Figure 4. The plots show that more than 0.5 eq of ammonia to 1 eq of succinic anhydride group will have about the same crosslinking efficiency.

The effects of curing temperature on the amidated polybutadiene are shown in Figure 5. The crosslinking reaction occurred slightly at 100°C but almost completely after heating at about 130°C for 1 h. While the cured resins became hard and brittle at higher temperatures, the acetone-insoluble fraction increased but slightly with increasing temperature.

At 150°C the crosslinking was almost complete after 15 min as shown in Figure 6. In the absence of a drier such as a cobalt or manganese salt, the carbon—carbon double bonds of vinyl rich polybutadienes could hardly be involved in oxidative crosslinking at temperatures below 160°C. In Figure 1, the observation that polybutadiene derivatives, except those containing a half amide group, exhibited hardly any crosslinking tendency in the absence of resole, supported the view that oxidative crosslinking could be neglected in this system. Moreover, thick crosslinked films (about 500 μm) were formed. These observations suggest that some crosslinking involving the amide functional group be more dominant than the oxidative crosslinking in this system.

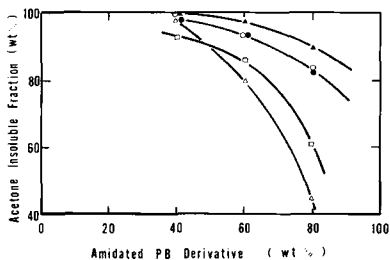


Fig. 2. Reactivity of various amidated PB derivatives with resole at curing temperature of 150°C for 1 h, \bar{M}_n of PB = 2000, 3.3 mol of functional group on polymer chain: (○) a half amide of ammonia; (▲) an ammonium salt; (●) a half amide of aniline; (△) a half amide of *n*-butylamine; (□) a half amide of diethylamine.

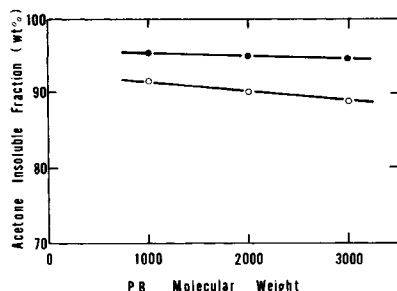


Fig. 3. Effects of PB number-average molecular weight on crosslinking at amidated PB/resole wt ratio = 60/40: (●) 3.3 mol of succinamic acid group on polymer chain; (○) 2.2 mol of succinamic acid group on polymer chain.

Structure of Amide Group and Its Thermal Behavior

Ammonia, primary amines, and secondary amines react with the succinic anhydride group under mild conditions to give a half amide derivative (succinamic acid made from ammonia). Under the experimental conditions, a small amount of succinic acid and its ammonium salt group must be present, because aqueous ammonia was used as an amidation agent.

The acid values of amidated polybutadienes derived from ammonia were always larger than the calculated acid values of half amide derivatives, indicating that an appreciable amount of succinic acid group was also included in the amidated polybutadiene. From these acid values, the composition of the half amide group and that of the dicarboxylic acid group were calculated (Table I).

When amidated polybutadiene derived from ammonia was heated on a hot plate at 150°C, infrared absorption bands of the ammonium salt and amide disappeared in the first 30 min. On the other hand, the absorption band of the imide group increased remarkably after heating for 30 min. Table II shows changes in nitrogen content by heat treatment. In the first 30 min, the nitrogen content decreased markedly, but it remained almost constant thereafter. From these observations, it was concluded that free ammonia or the ammonium salt was either removed or converted to succinamic acid in the first 30 min, and the succinamic acid group was then converted to an imide group on further heating. Since crosslinking was

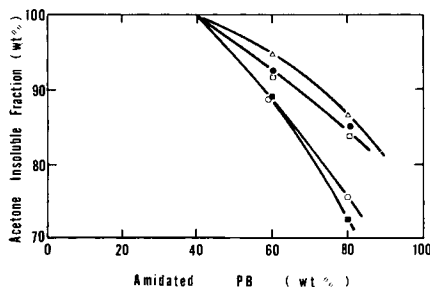


Fig. 4. Effects of ammonia added to succinic anhydride group on crosslinking efficiency, \bar{M}_n of PB = 2000, 3.3 mol of succinic anhydride group on polymer chain: (□) 1.5 mol equivalent to succinic anhydride group; (△) 1.0 eq; (●) 0.5 eq; (◻) 0.25 eq; (■) none.

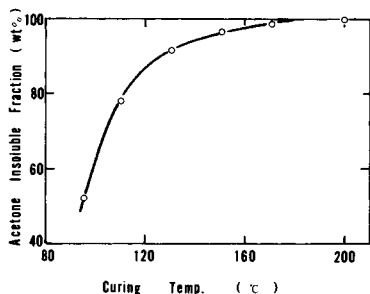
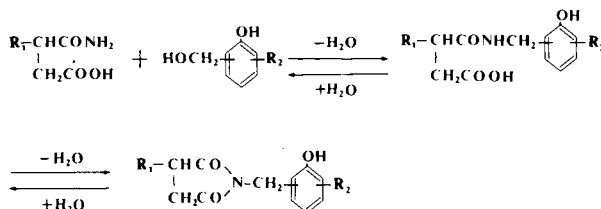


Fig. 5. Effects of temperature on crosslinking for curing time of 1 h, \bar{M}_n of PB = 2000, 3.3 mol of succinamic acid group on polymer chain, amidated PB/resole wt ratio = 60/40.

completed by heating in the first 30 min as shown in Figure 6, the crosslinking seemed to be more closely related to the succinamic acid group than to the imide group. Actually, it was confirmed that imide compounds were not directly involved in the condensation with resole at 150°C.

When a mixture of resole and amidated polybutadiene derived from ammonia was heated, the same change occurred in the infrared spectrum as in the amidated polybutadiene when it was heated. Thus, the following cross-condensation reactions were assumed:



where R_1 is the polybutadiene moiety and R_2 is the resole moiety. Since all reactions were carried out in an open system, the final products were presumed to be imide compounds.

On the other hand, the poor curing tendency of the amidated polybutadienes derived from aliphatic amines seems to be attributed to the poor

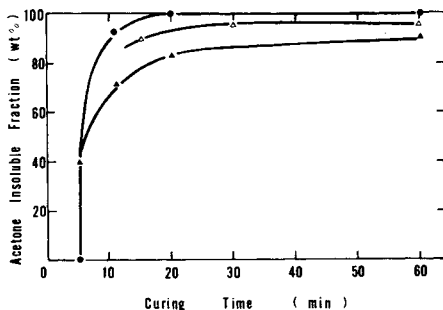


Fig. 6. Effects of time on crosslinking efficiency at 150°C, 3.3 mol of succinamic acid group on polymer chain, amidated PB/resole wt ratio = 60/40: (●) resole; (Δ) amidated PB ($\bar{M}_n=2000$); (▲) amidated PB ($\bar{M}_n=1000$).

TABLE I
Analysis of Amidated PB^a

NH ₃ /SAG ^b (mol ³ ratio)	Ammonia conversion (%)	Succinamic acid group (%)	Succinic acid group (%)
1.0	89	84	16
1.5	83	94	6

^a Amidation agent: aqueous ammonia; \bar{M}_n of PB: 2000; SAG^b: 3.3 mol on polymer chain.

^b SAG = succinic anhydride group on PB.

reactivity of the secondary amide group toward the above first condensation reaction. Moreover, the final imide compound could not be expected for them.

The amidated polybutadiene derived from aniline can react with the methylol group of resole through the nuclear substitution of aniline moiety as well as through the condensation reaction mentioned above. That seems to be the reason why the aniline derivative showed the excellent curing tendency.

Detailed cross-condensation studies involving resole and amidated polybutadiene derived from ammonia will be described in the subsequent paper.

Mechanical Properties of Cured Resins

The mechanical properties of coating films were measured. All the cured resin films in Table III were clear and homogeneous. Amidated polybutadienes with the same number of succinamic acid group on the polymer chains were used in these experiments. Amidated polybutadienes, especially, of higher molecular weights, remarkably improved the brittleness of phenol resin films. This phenomenon also suggested the crosslinking with the succinamic acid group, because the larger the molecular weight of the amidated polybutadiene was, the larger its molecular weight between the crosslinking points.

CONCLUSION

Amidated polybutadienes, which were derived from maleinated derivatives and ammonia, reacting with resole under mild curing conditions formed a number of homogeneous crosslinked products. The brittleness of

TABLE II
Heat Treatment of Amidated PB^a

Heating time (h)	Nitrogen contents of amidated PB (wt %)		
	NH ₃ /SAG=1.0	NH ₃ /SAG=1.5	NH ₃ /SAG=2.0 ^b
0.0	1.7	2.4	2.8
0.5	1.4	1.4	1.2
1.0	1.7	1.4	1.4
2.0	1.3	1.6	1.0
4.0	1.3	1.6	1.2

^a Amidation agent: aqueous ammonia; \bar{M}_n of PB: 2000; SAG: 3.3 mol on polymer chain; at 150°C.

^b 2 mols of ammonia added to one succinamic acid group.

TABLE III
Mechanical Properties of Cured Resin Films^a

PB \overline{M}_n	Resole/amidated PB (wt ratio)	Pencil hardness	Elicksen indentation (mm)	DuPont impact (cm)
1000	100/0	4H	0.5	10
	60/40	2H	0.6	20
	40/60	H	3.5	30
2000	20/80	2B	8.8	Above 50
	60/40	B	1.8	30
	40/60	Below 6B	6.8	Above 50
3000	20/80	Below 6B	9.0	Above 50
	60/40	Below 6B	3.0	40
	40/60	Below 6B	7.4	Above 50
	20/80	Below 6B	8.8	Above 50

^a Obtained from amidated PB and resole; amidated PB having 3.3 mol of succinamic acid group; film thickness: about 50 μm ; curing condition: 1 h at 150°C.

the cured phenolic resins was improved remarkably by addition of an amidated polybutadiene. Based on the following, namely, curing conditions, the effect of the succinamic acid functional group on curing efficiency, and the behavior of the succinamic acid group on heating, it was concluded that cross-condensation between the succinamic acid group and the methylol group of resole was the predominant reaction, and a cross-condensation scheme was proposed for this system.

References

1. Y. Yoshimura, *J. Appl. Polym. Sci.*, **29**, 1063 (1984).
2. C. G. Schwarzer, *J. Paint Technol.*, **29**, 523 (1967).
3. P. Sander-Plassman and G. Peitscher, *Angew. Macromol. Chem.*, **24**, 205 (1972).
4. Jpn. Pat. 741419 (1970).

Received September 19, 1985

Accepted January 11, 1986