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Oxidative Polymerization of Polybutadiene and Its Derivatives

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The oxidative polymerization or peroxide curing for such prepolymers as polybutadiene consisting mainly of 1, 2-structure, or esters containing the butadiene units was studied by means of infrared spectral analysis and dynamic mechanical measurements. Films of the cross-linked polybutadiene formed by the oxidative polymerization reaction show a high glass transition temperature and a high degree of crosslinking. This is considered to be the result of the larger amount of double bonds that are involved in the prepolymers and which suffer cross-linking, and the result of the presence of such polar groups as those of carboxyl, carbonyl and hydroxyl groups in the dried film, which are formed in the course of oxidative polymerization. When *t*-butylperbenzoate was used as a catalyst for cross-linking polybutadiene, some cyclization of vinyl groups was observed, leading to a less effective cross-linking. A greater reactivity was observed for *trans*-ethylenic double bonds than for vinyl groups in these reactions. Polybutadiene, being of larger molecular weight, gave a film of a higher $(T_g)_d$ value.

The drying oils, the usual naturally occurring oxidative-polymerizable materials, have been widely employed in the coating industry for a long time. This may have been because of the ready availability of the material and their merits as paints. Recently, a few synthetic resins, which can be oxidatively polymerized, have been developed as coating materials in the course of utilizing the products resulting from the petroleum industry.

As to the drying oils, the physical properties of films of drying oil or drying oil-modified resins were studied by the present authors with respect to the correlation of the physical properties and the chemical structure.[1-5] A similar approach will be used for the study of synthetic oxidative-polymerizable resins developed or to be developed.

In the present study, polybutadiene or its derivatives are employed, as they contain polymerizable double bonds introduced with the polymerization of butadiene. The study of these films will be an aid to the understanding of the oxidative polymerization. Polybutadienes of different molecular weights, the polyester derived from a diol of polybutadiene, and an ester derived from the diacid of polybutadiene are employed in this study.

In order to study the correlation between the physical properties of film and the chemical structure of the prepolymer, dynamic mechanical measurements and an infrared spectral analysis were carried out.

Experimental

Prepolymers. *Polybutadienes.* They were prepared by an anionic polymerization, using sodium as a catalyst, according to the method described by Kurtz.[6] The micro structure of the polybutadienes was determined by means of the infrared spectral analysis reported by Morero *et al.*[7]

Sample A. $\overline{M}_n$ 1650*, vinyl, 92.2%; *trans*-ethylenic, 7.8%; *cis*-ethylenic, trace.

Sample B. $\overline{M}_n$ 900, vinyl, 90.0%; *trans*-ethylenic, 9.2%; *cis*-ethylenic, 0.8%.

Sample C. $\overline{M}_n$ 7200, vinyl, 89.0%; *trans*-ethylenic, 11.0%; *cis*-ethylenic, trace.

Polyesters Derived from a Diol of Polybutadiene. An equimolar mixture of a diol of polybutadiene ($\overline{M}_n$ 685; hydroxyl value, 164) and phthalic anhydride and a small amount of xylene, which is used for removing water formed during esterification from the reacting system, were placed in a four-necked flask equipped with a glass-sealed stirrer, a thermometer, a nitrogen-gas inlet tube, and a Stark & Dean trap, then the mixture was heated at 230°C for 3.5 hr in an oil bath. The resulting product was light yellow and had an acid value of 10.4. In this heating procedure, about 10% of the vinyl groups, as measured by the infrared spectral method, reacted.

Esters Derived from a Diol of Polybutadiene. The diacid of polybutadiene, consisting mainly of 1, 2-structure (I) was supplied by the Nihon Soda Co. ($\overline{M}_n$ 2100, vinyl-, 91.9%; *trans*-ethylenic, 8.1%; *cis*-ethylenic,

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[1] J. Kumanotani, L. W. Chen and T. Kuwata, This Bulletin, **35**, 8, 1341 (1962).
[2] L. W. Chen and J. Kumanotani, *ibid.*, **39**, 10, 2085 (1966).
[3] L. W. Chen and J. Kumanotani, *J. Appl. Polymer Sci.*, **9**, 2785 (1965).
[4] L. W. Chen and J. Kumanotani, *ibid.*, **9**, 3519 (1965).
[5] L. W. Chen and J. Kumanotani, *ibid.*, **9**, 3645 (1965).
[6] D. Morero, A. Santambrogio, L. Porri and F. Clampell, *Chim. e. Ind.*, **41**, 758 (1959).
[7] Irving Kuntz, *J. Polymer Sci.*, **54**, 569 (1961).
* Measured by a vapor-pressure osmometer, Mechrolab, Inc.

trace; neutralization value, 49.7). (I) was mixed with an excess amount of butanol (1 : 15 in molar ratio), plus a small amount of toluenesulfonic acid as a catalyst. The mixture was then refluxed for 10 hr and submitted to vacuum distillation to remove *n*-butanol; the resulting product was dissolved in benzene, neutralized with an aqueous sodium bicarbonate solution, and washed with water several times, and then the benzene solution was distilled in a vacuum in a water bath to remove benzene.

The diacid of polybutadiene with a 1, 4-structure (II) employed was H-434 ($\overline{M}_n$ 3770, vinyl-, 24.6%; *trans*-ethylenic, 53.4%; *cis*-ethylenic, 22.0%; COOH eq./100 g 0.05—0.06), which was produced by the Thiokol Chem. Corp. A prepolymer of the butylester type was prepared from this acid by the same procedure as was used for I.

Film-forming Character. The varnishes made by dissolving each of the prepolymers in an equal weight of xylene, with or without drying agents (naphthenates of cobalt, 0.08%; manganese, 0.08%), were coated on rock salt, and then the xylene was removed from the coated sample at room temperature at a pressure of 10 mmHg. The change in the functional groups in the course of film formation was measured by the technique of infrared spectroscopy, and was reflected in the changes in optical density (*D*).

The characteristic absorption bands employed were; vinyl group, 911 cm^{-1}, 990 cm^{-1}; *trans*-ethylenic double bond, 967 cm^{-1}, hydroxyl, hydroperoxo, carboxyl, 3400 cm^{-1}; carbonyl group, 1720 cm^{-1}; hydroxyl group 1050 cm^{-1}; carboxylate, 1580 cm^{-1}, 1400 cm^{-1}; and *cis*-ethylenic double bond, 745 cm^{-1}.

Preparation of Films. Each varnish was coated on tin plates. Baked films (105°C for 6 hr; coating 6 times) and air-dried film were prepared. The films were split off by an amalgam method.

Cross-linking Character of Prepolymers. Since the double bonds involved in the prepolymer are considered to be the functional groups for oxidative polymerization, the diminishing of the double bonds was analyzed by infrared spectral analysis. In the case of the prepolymer consisting mainly of 1, 2-structure, the analysis of the change in *cis*-ethylenic double bonds was omitted since only traces were present. The cross-linking character was studied by dynamic mechanical measurements[2,8] and by measurements of the stress-strain curve of the swollen film.[9,10]

An implicit comparison will be made of the results of the present study and the results on the films of drying oils and oil modified resins.

Results and Discussion

Polybutadiene. *Infrared Spectral Analysis.* The infrared spectra and the functional group analysis in the course of air drying are shown in Figs. 1 and 2 respectively. It was found that: D911, D990 and D967 decreased as the time elapsed, while D3200—3600 and D1050 increased.

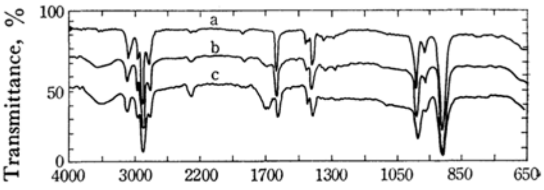

Fig. 1. Infrared spectra of air dried films of polybutadiene ($\overline{M}_n$ 1650) with addition of naphthenates of Co 0.08% and M_n 0.08%. a, after coating; b, 1 day; c, 5 days

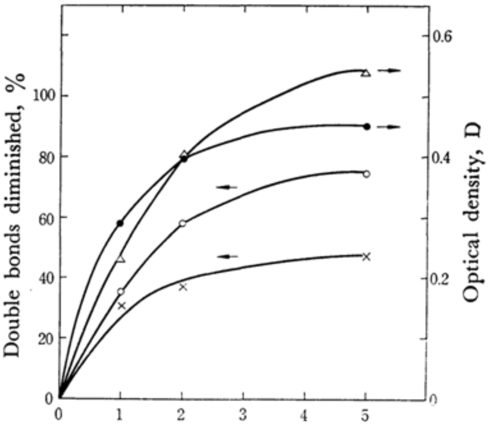

Fig. 2. The functional group analysis of air dried films of polybutadiene ($\overline{M}_n$ 1650) with addition of naphtenates of Co 0.08% and M_n 0.08%. × vinyl, ○ *trans*-ethylenic, ● D_{OH}, △ $D_{\mathrm{C=O}}$

The infrared spectra and the functional group analysis in the course of baking the polybutadiene are shown in Figs. 3 and 4 respectively. In the case of air drying, similar results were obtained except that the intensive absorption was observed at 1150—1200 cm^{-1}.

In order to obtain further information on these absorption characteristics, the air-dried film was ground and dipped in alkaline alcohol for 2 days, then the resulting samples were filtered and washed

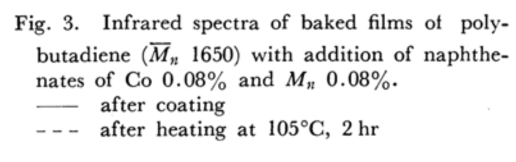

Fig. 3. Infrared spectra of baked films of polybutadiene ($\overline{M}_n$ 1650) with addition of naphthenates of Co 0.08% and M_n 0.08%.
—— after coating
- - - after heating at 105°C, 2 hr

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[8] Y. Inoue, *Kobunshi Kagaku (J. Soc. Polymer Sci., Japan)*, **10**, 140 (1953).

[9] L. Mullins, *J. Polymer Sci.*, **19**, 225 (1965).

[10] A. Ciferri, and P. J. Flory, *J. Appl. Physics*, **30**, 1498 (1959).

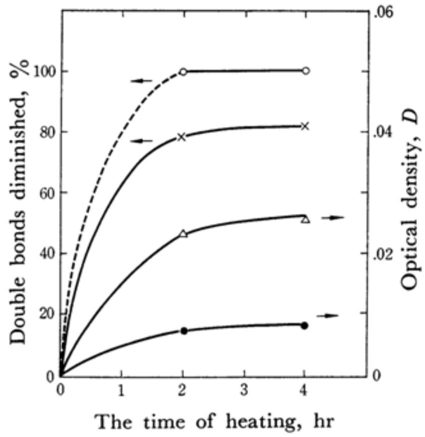

Fig. 4. The functional group analysis of baked films of polybutadiene ($\overline{M}_n$ 1650) with addition of naphthenates of Co 0.08% and *Mn* 0.08%.
× vinyl, ○ *trans*-ethylenic, ● D_{OH},
△ $D_{C=O}$

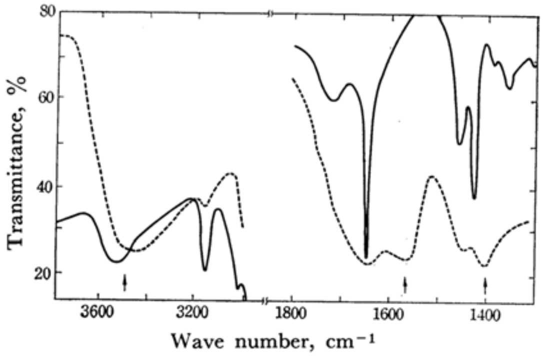

Fig. 5. Infrared spectra of alkaline alcohol treated film of polybutadiene.
—— untreated, - - - treated

with acetone until the filtrate became colorless on the phenolphtalein indicator. The sample thus obtained was dried in a vacuum and the infrared spectrum was measured.

The absorptions at 1500 cm^{-1} and 1400 cm^{-1}, which are the characteristic bands of carboxylate groups, were present in the infrared spectrum of the alkaline-treated film (Fig. 5). In view of these results, and in view of the fact that the absorption at 3200—3600 cm^{-1} was still present, it may be suggested that the hydroxyl and carboxyl groups were found in the oxidative polymerization of polybutadiene. These results are similar to those presented in the description of a patent, that the formation of hydroxyl, and carboxyl groups was found in the oxidation of polybutadiene in a liquid state (with oxygen and with the naphthenates of cobalt and manganese).[11]

As for the reactivity of vinyl and trans ethylenic double bonds, the percentage of the double bonds diminishing *versus* the time was plotted (Figs. 2 and 4). As the *trans*-ethylenic double bonds diminished faster, it may be suggested that the *trans*-ethylenic double bonds are apt to be oxidized.

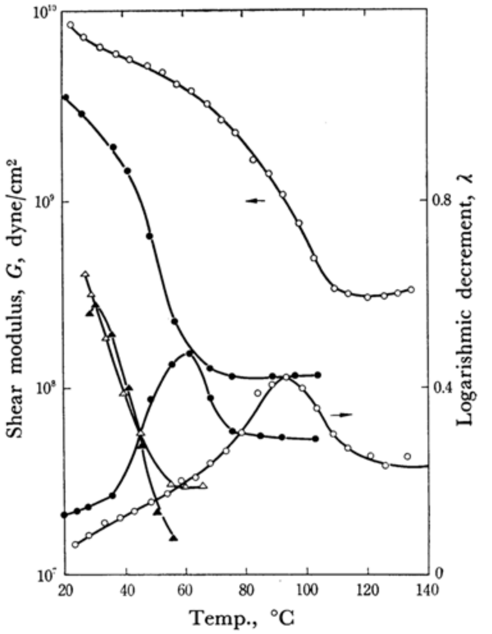

Fig. 6. The *G-t* and *λ-t* curves of air dried films of polybutdiene ($\overline{M}_n$ 1650) with addition of naphthenates of Co 0.08% and *Mn* 0.08%
● Exposed in air for one month
○ Exposed in air for six months
△▲ Baked film of polyester derived from diol of polybutadiene without addition of drying agent (105°C, 6 hr, coating 6 times)

The diminishing of *cis* double bonds (745 cm^{-1}) was also observed in the course of oxidative polymerization (Fig. 1).

The Viscoelaslic Properties of the Film. The *G-t* and *λ-t* curves of the air-dried films are shown in Fig. 6. The films exposed in air for one month and for six months showed $(T_g)_d$ values of 60°C and 93°C and *Gh* (the rubbery plateau modulous in the curves of modulous *versus* the temperature) values of 1.25×10^8 and 3.0×10^8 dyne/cm^2 respectively. The $\overline{M}_c$ (the number-average molecular weight between cross-links) of the film exposed in air for six months is about 1000. These results revealed that the film of polybutadiene is highly cross-linked.

These results suggest that the polar groups formed in the oxidative polymerization of the prepolymers also contribute to raising the $(T_g)_d$ values of the dried films.

Peroxide-catalyzed Cross-linking of Polybutadiene. The polybutadiene (C) with *t*-butyl-perbenzoate (7% to polybutadiene) was dissolved in an equal weight of benzene, coated on tin plates, and heated at 105°C for 1.5 hr in

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[11] Esso, Brit. Pat. 824287 (1959).

air. This coating procedure was repeated 4 times.

The $(T_g)_d$, $\overline{M}_c$, and the amounts of diminished vinyl groups were -30°C, 3740, and 80% respectively. The film has a lower degree of cross-linking density and a lower $(T_g)_d$ value, yet most of the vinyl groups diminished. These results suggested that the cyclization of vinyl groups occurs in this peroxide-catalyzed cross-linking of polybutadiene consisting mainly of 1,2-structure.

The Effect of the Molecular Weight of the Prepolymer on the Viscoelastic Properties of Films. Generally speaking, the polymeric material prepared by anionic polymerization using sodium as a catalyst show a narrow distribution of molecular weight. Therefore, in employing such samples, the effect of a broad distribution of molecular weight can be avoided. Figure 7 shows the *G-t* and *λ-t* curves of films of polybutadiene (A) and (B), in which the films were derived from prepolymers of different molecular weights. The films were prepared under the same drying conditions. The prepolymer of a high molecular weight gave a film with a high $(T_g)_d$ value. nevertheless, no distinguishable difference was observed.

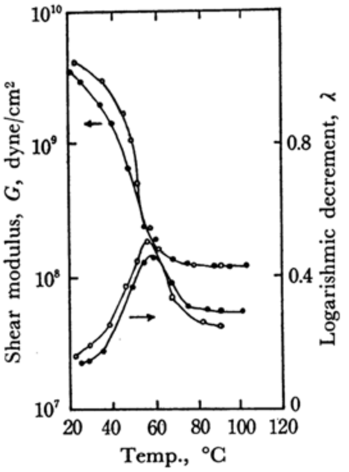

Fig. 7. The *G-t* and *λ-t* curves of air dried films (exposed in air for one month) of polybutadiene polybutadiene with addition of naphthenates of Co 0.08% and M_n 0.08%.
○ $\overline{M}_n$ 900, ● $\overline{M}_n$ 1650

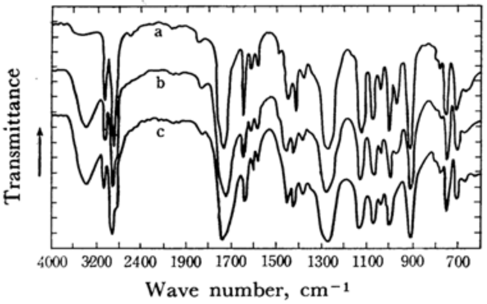

Fig. 8. Infrared spectra of air dried film of polyester derived from diol of polybutadiene with addition of naphthenates of Co 0.08% and M_n 0.08%.
a, after coating; b, 1 day; c, 6 days

A Polyester Derived from a Diol of Polybutadiene. *Infrared Spectral Analysis.* As is shown in Figs. 8, 9 and 10, the change in the infrared spectra in the course of air drying was similar to that of polybutadiene. Exposure in air for 6 days decreased the amounts of vinyl- and *trans*-ethylenic double bonds by 40% and 68% respectively.

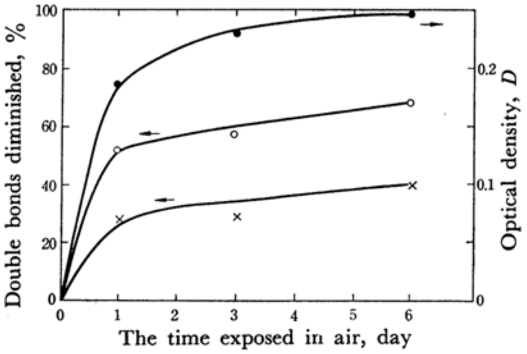

Fig. 9. The functional group analysis of air dried films of polyester derived from a diol of polybutadiene with addition of naphthenates of Co 0.08% and M_n 0.08%.
× vinyl, ○ *trans*-ethylenic, ● D_{OH}

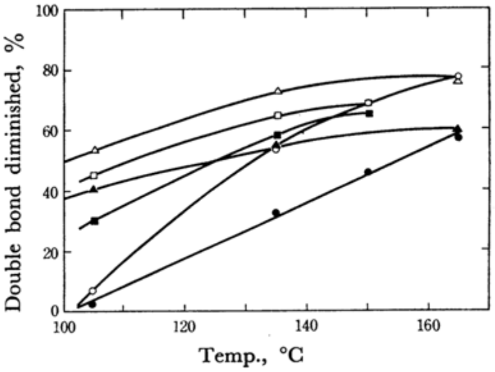

Fig. 10. The functional group analysis of baked films (baked at specified temperature for 2 hr) of a polyester derived from a diol of polybutadiene.

- ● without addition of drying agent, vinyl
- ○ without addition of drying agent, *trans*-ethylenic
- ▲ 6.6 wt%, *t*-butyl perbenzoate added, vinyl
- △ 6.6 wt%, *t*-butyl perbenzoate added, *trans*-ethylenic
- ■ naphthenates of Co 0.1, M_n 0.1 and Pb 1.7 wt% added, vinyl
- □ naphthenates of Co 0.1, M_n 0.1 and Pb 1.7 wt% added, *trans*-ethylenic

TABLE 1. THE FUNCTIONAL GROUP ANALYSIS OF THE POLYESTER DERIVED FROM A DIOL OF POLYBUTADIENE IN BAKING

Baking condition	Catalyst	The double bonds diminished, %	
		vinyl	*trans*-ethylenic
105°C—2 hr	none	2	7
	BPO 6.6 wt%	41	54
	Co 0.1, Mn 0.1, Pb 1.7 wt%	30	45
135°C—2 hr	none	33	54
	BPO 6.6 wt%	54	73
	Co 0.1, Mn 0.1, Pb 1.7 wt%	58	64
150°C—2 hr	none	46	69
	Co 0.1, Mn 0.1, Pb 1.7 wt%	65	68
150°C—4 hr	none	53	75
	Co 0.1, Mn 0.1, Pb 1.7 wt%	77	73
165°C—2 hr	none	57	78
	BPO 6.6 wt%	60	75

TABLE 2. ELEMENTARY ANALYSIS OF BAKED FILMS (105°C, 6 hr, Co 0.08%, Mn 0.08%) OF THE ESTER DERIVED FROM A DIACID OF POLYBUTADIENE

Sample	Prepolymer, %			Film, %			Number of oxygen atom combined per butadiene
	C	H	O	C	H	O	
1,2 structure (I)	86.1	11.0	2.9	72.81	8.89	18.30	0.67
1,4 structure (II)	87.4	11.0	1.6	74.76	9.24	16.0	0.60

When the prepolymer was heated with or without drying agents (*t*-butyl-perbenzoate or naphtenates of cobalt, manganese and lead) at various temperatures and for various times, the easy oxidation of *trans*-ethylenic double bonds was also observed (Figs 9 and 10).

Viscoelastic Properties of the Film. The *G-t* and *λ-t* curves of the baked films are shown in Fig. 6. The $(T_g)_d$ and *Gh* values are 30°C and 3×10^7 dyne/cm^2 respectively. Compared with the oil-modified alkyd resin with the same phthalic anhydride content ($(T_g)_d$, -30°C: *Gh*, 6×10^7 dyne/cm^2), the film has a higher $(T_g)_d$ value and a lower cross-linking-density value. The higher value in $(T_g)_d$ is considered to be due to the effect of polar groups obtained in the oxidative polymerization.

Esters Derived from the Diacid of Polybutadienes. The functional group analysis is shown in Fig. 11.

In the oxidative polymerization of esters of the diacid of polybutadiene, essentially of 1, 2-structure, the *trans*-ethylenic double bonds diminished faster than the vinyl groups. This result is the same as the result obtained in the oxidative polymerization of polybutadiene of 1, 2-structure.

In the oxidative polymerization of esters of the diacid of polybutadiene with less 1, 2-structure, the amount of vinyl groups and that of *trans*-ethylenic double bonds diminished to almost the same extent. Since the *cis-trans* isomerization of double bonds may be involved in this case, the analysis of the reactivity is difficult.

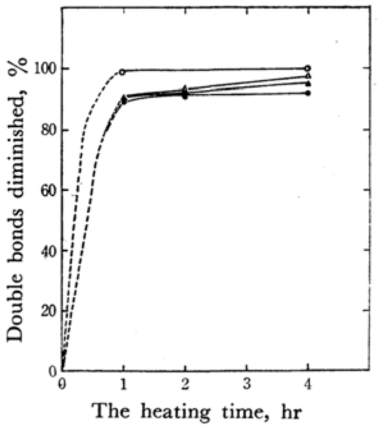

Fig. 11. The functional group analysis of baked films (135°C) of an ester derived from a diacid of polybutadiene with addition of naphthenates of Co 0.08% and M_n 0.08%.

● mainly, 1, 2 structure, vinyl
○ mainly, 1.2 structure, *trans*-ethylenic
▲ more 1, 4 structure, vinyl
△ more 1, 4 structure, *trans*-ethylenic

Elementary Aanalysis of Films. The elementary analysis of the baked films is shown in Table 1. The oxygen atom combined per butadiene unit is 0.6—0,7. This result indicates that the prepolymers are highly oxidized.

Again, the suggestion that the film of polybutadiene with high $(T_g)_d$ value is due to the polar groups formed in the oxidative polymerization was supported.