

Effect of Method of Synthesis of Unsaturated Fatty Acid-Modified Alkyd Resin on the Crosslinking Behavior of Prepolymer: Correlation of Molecular Weight Distribution of Prepolymer and Degree of Crosslinking of the Derived Film

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Synopsis

The viscoelastic properties of films of unsaturated fatty acid-modified alkyd resins prepared by different synthetic procedures are examined. The films prepared by the fatty acid method have a higher glass transition temperature and greater degree of crosslinking than those prepared by the monoglyceride method. It is suggested the molecular weight distribution of prepolymer prepared by the monoglyceride method would be broader than that prepared by the fatty acid method, and this was verified by the results of $[\eta]/\bar{M}_n$ and fractionation of prepolymers. The differences in viscoelastic properties of films is explainable on the basis of the molecular weight distribution and the distribution of crosslinking functional groups of prepolymers.

INTRODUCTION

An alkyd resin can be prepared in several ways by modifying the order of introduction of the alkyd ingredients. Three methods were used in the present study. In method A (fatty acid method), the reactants such as glycerol, phthalic anhydride, and fatty acid are reacted together; in method B (fatty acid monoglyceride method), the glycerol and fatty acid are reacted first, then phthalic anhydride is added; in method C (oil monoglyceride method) glycerol and oil are reacted first, then phthalic anhydride is added.

Some differences are observed between the products (resin, varnish or paint) when either method B or method C was used in place of method A: (1) the resin was softer and tackier; (2) the resin tolerated more aliphatic hydrocarbon thinner, and its solution had a lower viscosity; (3) the drying of the varnish was not so rapid and the film was somewhat softer and tackier. Also, when method B or C replaced method A, the rate of esterification decreased and gelation occurred at somewhat higher acid values.

These differences may be interpreted as due to (1) the difference in structure of the prepolymer owing to the reaction of the phthalic half ester or fatty acid with the primary or secondary hydroxyl of glycerol in the alkyd

synthesis;¹ (2) the presence of natural antioxidants, such as tocopherol present in the oil;² (3) the difference of chemical composition between drying oils and fatty acids;³ or (4) the degree of dimerization of unsaturated aliphatic chain in the cooking stage.

Generally, the mechanical properties of crosslinked polymers are affected by the fine structure of the prepolymer.

In the present study, a series of unsaturated fatty acid-modified alkyd resins were synthesized by method A, B, or C and the viscoelastic properties or the degree of crosslinking of the derived films compared by means of dynamic-mechanical measurement. The molecular weight distribution was considered as a factor in the difference in the products.

EXPERIMENTAL

Raw Materials

Linseed oil fatty acid was a commercially available product, iodine value 187 or 168 (Wijs method).

Linseed oil was a commercial product, iodine value 183.

Glycerol, phthalic anhydride, and stearic acid were chemically pure.

Synthesis of Prepolymers

Oil length 60 or 56 (expts. A-3 and B-3) linseed oil fatty acid-modified alkyd resin was synthesized by various procedures.

The apparatus consisted of a four-necked 500-ml. flask equipped with a sealed glass stirrer, a thermometer, a nitrogen gas inlet tube, and a Stark-Dean trap. The flask containing the reactants was heated in an oil bath. The conditions of reaction were shown as follows:

Fatty Acid Method (A)

Expt. A-1. An equimolar mixture of linseed oil fatty acid (I.V. 187), glycerol, and phthalic anhydride was put in the flask, and heated at a rate of 1°C./min. from 130°C. and kept at 230°C. for 9 hr.

Expts. A-2-1, A-2-2. Conditions were the same as in expt. A-1, except that a part of linseed oil fatty acid was replaced with stearic acid (10% by weight of fatty acid ingredient in Expt. A-2-1, and 25% in expt. A-2-2).

Expt. A-3. A mixture of linseed oil fatty acid (I.V. 168, 1.78 mole), phthalic anhydride (2.1 mole), and glycerol (2.1 mole) was put in the flask and heated at 200°C. for 1 hr. and then kept at 230°C. for 10 hr. A small amount of xylene was added for refluxing; no nitrogen gas was bubbled through in this case.

Fatty Acid Monoglyceride Method (B)

Expt. B-1. A mixture of linseed oil fatty acid (1 mole) and glycerol (1 mole) was heated at a rate of 1°C./min. from 160°C. to 230°C. and maintained at that temperature for 30 min., cooled to room temperature,

and phthalic anhydride (1 mole) was added. The mixture was again heated (1°C./min.) to 230°C. and maintained at that temperature for 9 hr.

Expt. B-2. The procedure of expt. B-1 was followed, except that 0.5% by weight of sodium hydroxide was added as catalyst in synthesizing the monoglyceride.

Expt. B-3. A mixture of linseed oil fatty acid (I.V. 168, 1.78 mole), and glycerol (2.1 mole) was heated at 250°C. for 30 min., and cooled to 170°C., and phthalic anhydride (2.1 mole) added. Then the mixture was heated at 230°C. for 9 hr. A small amount of xylene was added for refluxing, and no nitrogen gas was bubbled through in this case.

Oil Monoglyceride Method (C)

Expt. C-1. A mixture of linseed oil (878 parts) and glycerol (184 parts, 2 mole) with 0.5% by weight of litharge (to oil) was heated at a rate of 1°C./min. from 160°C. to 230°C., maintained at that temperature for 60 min., and cooled to 130°C., at which point phthalic anhydride (3 mole) was added.

The reaction was then allowed to proceed as in expt. A-1, the mixture being maintained at 230°C. for 9 hr. The reaction product was filtered to remove the litharge.

Expt. C-2. This experiment was the same as expt. C-1, except that 0.5% of lithium naphthenate replaced the litharge, and the reaction time for alcoholysis was 30 min.

The end point of alcoholysis was determined by examination of solubility in methanol.⁴ Alternatively, the end point was checked by an infrared method in which one part of the sample was dissolved in 9 parts of chloroform and the infrared spectrum of the colored chloroform solution measured until the absorptions at 1050 cm.⁻¹ (primary hydroxyl) and at 1100 cm.⁻¹

TABLE I
Properties of Prepolymers and the Derived Films of Unsaturated Fatty Acid-Modified Alkyd Resins (Oil Length 60)

Sample	Acid value, mg. KOH/g. resin	Number-average molecular weight \bar{M}_n^a	$(T_g)_d$, °C.	G_h , dyne/cm. ² × 10 ⁻⁷	Degree of swelling, %	Chloroform soluble portion of film, %
A-1-9	17.0	1300	2	6.0	400	5.4
A-2-1-9	10.3	1300	-8	4.8	460	9.7
A-2-2-9	18.8	1300	-10	3.2	510	18.7
B-1-7	17.1	1200	-7	4.0	470	10.0
B-1-9	14.0	1700	-20	3.8	430	8.5
B-2-7	8.4	1300	-12	2.0	690	21.0
B-2-9	6.2	1200	-20	4.3	510	17.3
C-1-9	6.2	1600	-1	4.7	430	8.5
C-2-9	5.9	1500	-10	5.2	450	10.5

^a Measured by cryoscopic method (benzene).

(secondary hydroxyl) give maximum absorbance. No difference was observed between the products obtained after 30 min. and 60 min. reaction time.

Sample varnishes were prepared by dissolving each prepolymer in an equal weight of xylene. The acid value, number-average molecular weight, and iodine value of the prepolymers are shown in Table I and II. (In the first column, the last number noted for each sample is the reaction time in hours at 230°C.)

TABLE II
Properties of Prepolymers and the Derived Films of Unsaturated Fatty Acid-Modified Alkyd Resins (Oil Length 56)

Sample	Acid value, mg. KOH/g. resin	Number-average molecular weight \bar{M}_n^a	Iodine value (Wijs')	Intrinsic viscosity $[\eta]$	$[\eta]/\bar{M}_n \times 10^6$	Gelation time, min.	$(T_g)_d$, °C.	G_h , dyne/cm. ² $\times 10^{-7}$	Degree of swelling, % ^b
A-3-8	9.3	2080	85.5	0.054	2.60		23	5.6	190
A-3-10	7.2	2530	86.4	0.062	2.45	>600	25	8.0	180
B-3-8	11.9	2380	84.5	0.098	4.04		22	4.2	230
B-3-9	11.8	2720	83.9	0.132	4.86	550	22	4.1	200

^a Measured by vapor pressure osmometer, Mechrolab, Inc.

^b The films were dipped in benzene.

Preparation of Films

Each of the varnishes without the addition of drying agents was coated on a tin plate and heated at 105°C. for 8 hr. in air and the procedure repeated six times. The films were stripped off by the amalgam method.

Viscoelastic Properties of Films

The temperature (T) dependence of shear modulus G , and logarithmic decrement λ of the films were measured by the torsional pendulum method.⁵ From G - T and λ - T curves, the shear modulus in the plateau region G_h which is a measure of degree of crosslinking of films⁶⁻⁸ and glass transition temperature measured by dynamic-mechanical methods $(T_g)_d$ were obtained.⁹

Degree of Swelling and Film Solubility

The degree of swelling and the film solubility were measured as follows.

The film of weight W_0 was dipped in chloroform at room temperature for more than a week, then the swollen film was weighed in another covered weighing bottle filled with chloroform until its weight was constant (W_s). The degree of swelling is expressed by $(W_s/W_0) \times 100$.

The swollen film was then dried in vacuum to the dry weight W_d . The soluble portion of the film is expressed as $(W_0 - W_d)/W_0 \times 100$. The result is shown in Table I.

Intrinsic Viscosity

The prepolymers were dissolved in xylene and the concentration c varied from 8 to 25 g./100 cc. The intrinsic viscosity was obtained from the log

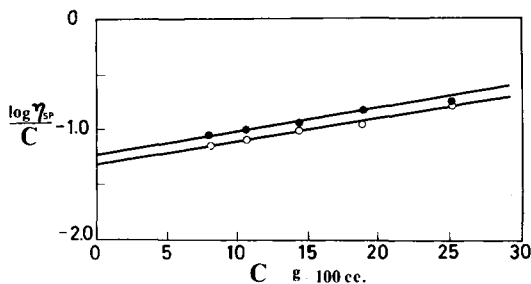


Fig. 1. Plot of $\log \eta_{sp}/c$ vs. concentration of prepolymer prepared by fatty acid method: (●) A-3-10; (○) A-3-8.

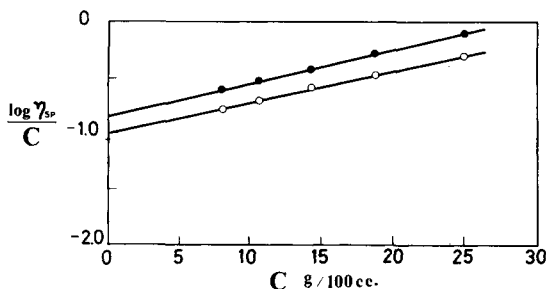


Fig. 2. Plot of $\log \eta_{sp}/c$ vs. concentration of prepolymer prepared by fatty acid monoglyceride method: (●) B-3-9; (○) B-3-8.

η_{sp}/C versus c relation (Figs. 1 and 2). The ratio $[\eta]/M_n$ was used as a measure of molecular weight distribution.^{10a}

Fractionation of Prepolymers

The prepolymers were fractionated by the system of acetone solution (1.25 or 1.50%) and water. Each fraction was weighed after being dried in vacuum at room temperature. The infrared spectra of several fractions were obtained.

RESULTS AND DISCUSSION

Viscoelastic Properties of Films

Figures 3 and 4 and Table I show that higher values of $(T_g)_d$ and larger values of G_h were observed in the film of expt. A-1-9 compared with those obtained from the films of the B or C series. The results obtained from measurement of the degree of swelling of film as well as the soluble portion of the film were in agreement with the results obtained from the G_h values.

In other words, a larger degree of crosslinking and higher glass transition temperature were observed for the film derived from varnish prepared by the fatty acid method compared with those of films derived from the varnishes prepared by the monoglyceride methods. The $(T_g)_d$ and G_h of the

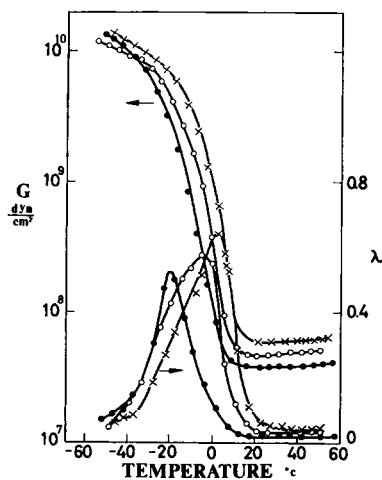


Fig. 3. G - T and λ - T relations of films of unsaturated fatty acid-modified alkyd resins prepared by various methods: (X) fatty acid method, A-1-9; (●) fatty acid monoglyceride method, B-1-9; (O) oil monoglyceride method, C-1-9.

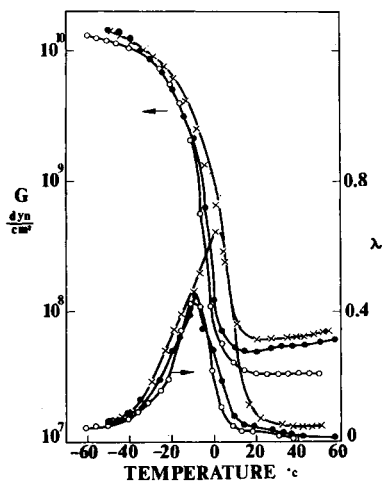


Fig. 4. G - T and λ - T relations of films of unsaturated fatty acid-modified alkyd resins in which a part of linseed oil fatty acid is replaced by stearic acid: (X) 0% stearic acid, A-1-9; (●) 10% stearic acid, A-2-1-9; (O) 25% stearic acid, A-2-2-9.

films of expts. A-2-1-9 and A-2-2-9 were tabulated for comparison (Table I and Fig. 4).

As there is no definite relation between $(T_g)_d$ and G_h , it is suggested that factors other than the degree of crosslinking of film affect the $(T_g)_d$.

The above results indicate that structural differences in the prepolymer introduced by varying the method of synthesis affects the viscoelastic properties and the degree of crosslinking of film.

Effect of Molecular Weight Distribution on the Degree of Crosslinking of Film

As the rate of esterification of phthalic half ester to β -hydroxyl of glycerol is slower than that of fatty acid, Goldsmith¹ suggested that the β -hydroxyl of glycerol is esterified with fatty acid by method A and α -hydroxyl by method B or C. He also suggested that the phenomenal difference between the synthetic methods mentioned previously could be explained by the fact that the prepolymer obtained in the fatty acid method is more regular while that formed in the monoglyceride method is branched and distorted. If a regular arrangement of prepolymer would accompany the regular arrangement of aliphatic chains, the difference in crosslinking behavior for the various synthetic methods could be explained by the difference in the distribution of the crosslinking group, i.e., the double bond.

An unsaturated fatty acid-modified alkyd resin may be considered a polyester derived from phthalic anhydride and glycerol with an unsaturated aliphatic group as side chain. Since the unsaturated aliphatic side chain linked to the glyceride portion by the ester linkage rotates freely, and the double bond, the source of crosslinking, is far from the glyceride portion, it is rather difficult to tell the difference in degree of crosslinking of the film from the structural differences in the prepolymer as pointed out by Goldsmith.

Comparisons of Stuart models of alkyds to test Goldsmith's speculation showed that no steric hindrance to rotation of the aliphatic chain exists.

Published kinetic data related to alkyd synthesis suggest, rather, that the molecular weight distribution of the prepolymer may explain the differences in crosslinking behavior.

Relation of Alkyd Synthesis to Molecular Weight Distribution

In preparation of monoglyceride with oil and glycerol, it is said a random distribution among monoglyceride, diglyceride, triglyceride, and glycerol exists. The same concept is applied to the esterification of fatty acid and glycerol. For example, the resulting composition from an equimolar mixture of fatty acid and glycerol is as follows:

glycerol:monoglyceride:diglyceride:triglyceride = 29.7:44.3:22.2:3.8 (mole-%) or 7.7:44.4:38.6:9.3 (wt.-%) where stearic acid is the fatty acid ingredient.

It is predicted from the equation for gelation of condensation derived statistically by Flory^{10b} that the gelation occurs at the same extent of esterification for the same initial composition with respect to functional groups, regardless of the reaction procedure. Experimentally, however, gelation occurred at a lower extent of esterification when method B or method C was used than when method A was used, as shown in the results of Goldsmith¹ and the present study (Table II).

An attempt to explain this phenomena is based on the reaction occurring at high temperature (250°C.):



as described by Schönfeld.¹¹ As a result, the amount of glycerol, a trifunctional species, increases. This would cause gelation to occur at a lower extent of esterification.

There are two reasons why reaction (1) is mentioned.

(1) The amount of diglyceride is relatively large as the result of random distribution. If method A is followed, the esterifications of phthalic half ester and fatty acid proceed at the same time, resulting in a smaller amount of free diglyceride.

(2) From the results obtained by Goldsmith, the diglyceride-rich mixture is no more than half esterified by phthalic anhydride, as measured by acid value. This suggests that the phthalic half ester reacts only with difficulty with the β -hydroxyl of α, α' -diglyceride.

From the consideration of the chemical behavior of glycerol and triglyceride formed by reaction (1), it is obvious that the molecular weight distribution of the prepolymer prepared by method B or C is broader.

Effect of Method of Synthesis on the Distribution of Molecular Weight of Prepolymer

Experiments A-3 and B-3 were carried out to compare the distribution of molecular weight in relation to the method of preparation. The comparison of method A with method B only was carried out to avoid such other factors as unsaturation, natural antioxidant, and conjugation arising from the employment of oil. The properties of prepolymers and films are shown in Figures 5 and 6 and Table II. As acid value, number-average molecular weight, and iodine value of the prepolymers were nearly the same, no appreciable effect of polymerization of fatty acid was found.

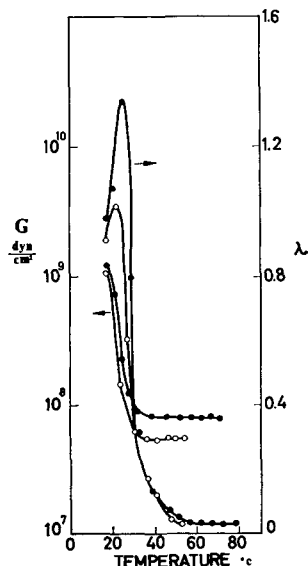


Fig. 5. G - T and λ - T relations of films of unsaturated fatty acid-modified alkyd resin prepared by the fatty acid method (oil length 56), film baked at 105°C. for 8 hr.: (O) A-3-8; (●) A-3-10.

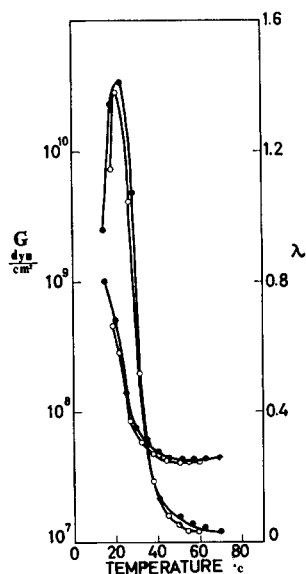


Fig. 6. G - T and λ - T relations of films of unsaturated fatty acid-modified alkyd resin prepared by fatty acid monoglyceride method (oil length 56), film baked at 105°C . for 8 hr.: (O) B-3-8; (●) B-3-9.

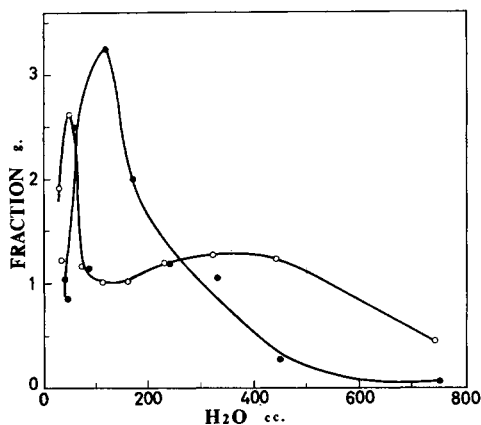


Fig. 7. Fractions vs. H_2O added (differential); 15 g. sample/1000 cc. acetone: (●) A-3-8; (O) B-3-8.

The values of $[\eta]/M_n$ obtained with method B were larger than those obtained with method A; i.e., the distribution of molecular weight of prepolymer obtained by method B is broader than that by method A. The result of fractionation also agrees in the result obtained from $[\eta]/M_n$ values (Figs. 7-10). The distribution curves of expt. B-3 shown in Figures 7 and 8 show two peaks of distribution of molecular weight may be caused by reaction (1); glycerol, being the chain extender, contributes the formation of large molecules, and triglyceride remains as a low molecular weight part.

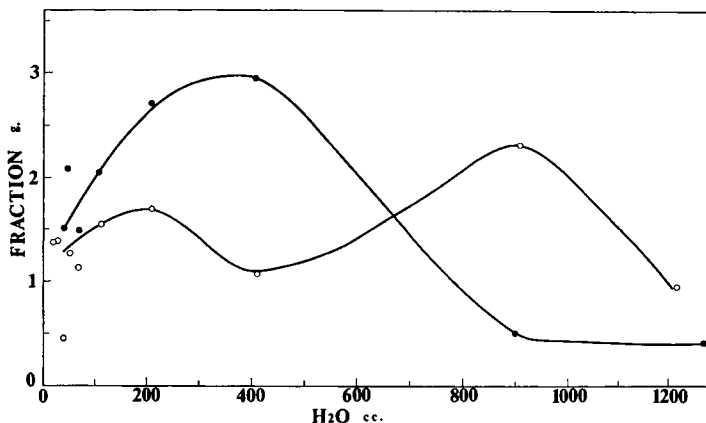


Fig. 8. Fractions vs. H₂O added (differential); 15 g. sample/1200 cc. acetone: (●) A-3-10; (○) B-3-9.

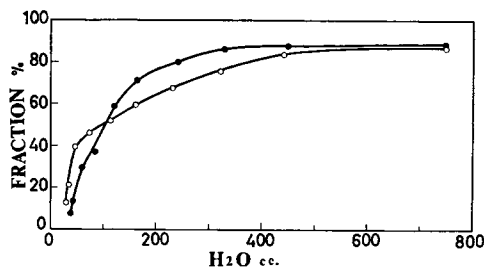


Fig. 9. Fractions vs. H₂O added (cumulative); 15 g. sample/1000 cc. acetone: (●) A-3-8; (○) B-3-8.

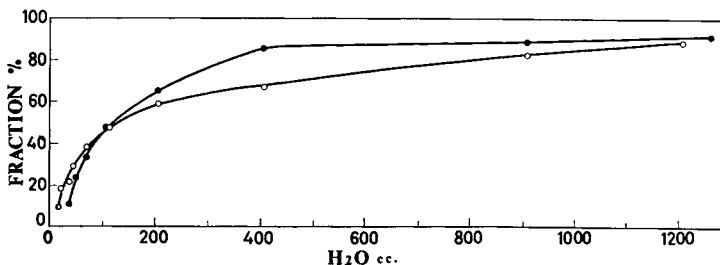


Fig. 10. Fractions vs. H₂O added (cumulative); 15 g. sample/1200 cc. acetone: (●) A-3-10; (○) B-3-9.

The recovery of fractions is 90% of the sample; the remainder (10%) is considered to be present as prepolymer remaining in the solution and that adhering to the apparatus.

Degree of Crosslinking of Film and Molecular Weight Distribution of Prepolymer

(T_g)_a and G_b of films B-3 were smaller than those of films A-3 (Figs. 5 and 6 and Table II). An analogous result is observed as in the previous experi-

ments in the relation of G_h and $(T_g)_d$ of the films with the method of preparation of prepolymer.

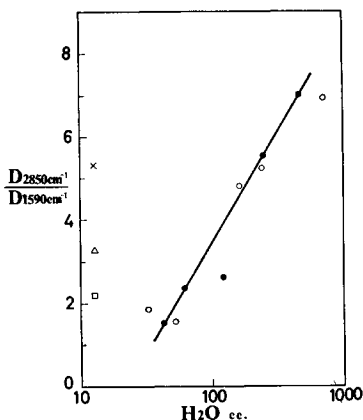


Fig. 11. D_{2850}/D_{1590} of fractions vs. H_2O added: (●) A-3-8; (○) B-3-8; (□) oil length 40, not fractionated; (Δ) oil length 50, not fractionated; (×) oil length 60, not fractionated.

In view of experimental data relating the G_h value of film and the molecular weight distribution of prepolymer, it is found the prepolymer of narrow molecular weight distribution gave film of higher crosslinked network. Since G_h is related to the number-average molecular weight between crosslinks \overline{M}_c by the relation $G_h = \rho RT/\overline{M}_c$, where ρ is density of the film, R is the gas constant, and T is absolute temperature, G_h is a measure of effective crosslinks and rather of physical nature. If the network structure is not uniformly or regularly crosslinked, some chemical crosslinks are of no contribution to the effective crosslinks.^{10c} Moreover, the crosslinking functional group (double bond) is shown by Figure 11 not to be uniformly distributed; this figure is a plot of D_{2850}/D_{1590} versus the amount of water added in fractionation, and is a measuring scale for molecular weight of fractions. D_{2850} is the optical density at 2850 cm.^{-1} in the infrared spectrum and is due to the methylene or methyl of aliphatic chain, D_{1590} is due to the phthalate group, and the ratio is a measure of the aliphatic to phthalate ratio of the prepolymer. It is found that large molecules are rich in phthalate groups and small molecules in aliphatic chains. If the double bonds are uniformly distributed over aliphatic chains, the crosslinking functional groups are not uniformly distributed over the molecules involved in the prepolymer. Therefore, it is suggested that the derived film would not be uniformly crosslinked.

Thus, the differences in crosslinking behavior of prepolymers could be explained by the molecular weight distribution or the distribution of crosslinking functional group.

The lower value of $(T_g)_d$ of films prepared by method B may thus result partly from the lower degree of crosslinking of the films.

The above discussion indicates that the method of preparing alkyd resin (fatty acid and fatty acid monoglyceride method) affects the molecular weight distribution of prepolymer, and as the result, affects the glass transition temperature and the degree of crosslinking of the film.

Therefore, some of the marked differences between resins prepared by different methods, such as gelation in cooking and hardness of prepolymer or film, could be explained on the basis of molecular weight distribution in the prepolymer instead of Goldsmith's model.

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Résumé

On a examiné les propriétés viscoélastiques de films de résines alkydes modifiés par des acides carboxyliques non-saturés, préparés par différents procédés. On a trouvé que les films provenant de la synthèse en présence d'acide carboxylique ont une température de transition vitreuse plus élevée et un degré de pontage plus grand que ceux provenant de la synthèse en présence de monoglycéride. Après examen de la réaction des glycérides, on a suggéré que la distribution des poids moléculaires du prépolymère préparé en présence de monoglycéride pourrait être plus large que celle du prépolymère préparé en présence d'acide carboxylique, ce qui a été vérifié par les résultats de $[\eta]/\bar{M}_n$ et par le fractionnement des prépolymères. La différence dans les propriétés viscoélastiques des films est expliquée par la distribution du poids moléculaire et par la distribution des groupes fonctionnels responsables du pontage dans les prépolymères.

Zusammenfassung

Die viskoelastischen Eigenschaften von nach verschiedenen synthetischen Verfahren hergestellten, mit ungesättigten Fettsäuren modifizierten Alkydharzen werden untersucht. Es wird festgestellt, dass die nach der Fettsäuremethode erhaltenen Filme eine höhere Glasumwandlungstemperatur und einen grösseren Verzweigungsgrad besitzen als die nach der Monoglyzeridmethode hergestellten. Ein Überblick über die Reaktionen der Glyceride zeigt, dass die Molekulargewichtsverteilung des nach der Monoglyzeridmethode hergestellten Präpolymeren breiter sein sollte als diejenige des nach der Fettsäuremethode hergestellten; diese Erwartung wurde durch $[\eta]/\bar{M}_n$ und Fraktionierungsergebnisse an Präpolymeren bestätigt. Die Unterschiede der viskoelastischen Eigenschaften von Filmen werden als Folge der Molekulargewichtsverteilung und der Verteilung funktioneller Vernetzungsgruppen der Präpolymeren erklärt.

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