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The Effect of Glyceride Composition on the Mechanical Properties of Alkyd Resin Films

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Summary

The dynamic mechanical properties of dried films prepared from alkyd resins made by the reaction of phthalic anhydride with synthetic mixtures of the mono-, di-, and trilinoleates of glycerol of the same overall composition are reported. The properties of the films dried at room temperature correlate with the microgel content of the resins, which is a function of the monoglyceride content of the original reaction mixture. Films dried at 120°C show smaller differences in mechanical properties.

Contrary to popular belief alkyd resins prepared by different methods from the same raw material composition do not always have the same solution properties; these differences have been attributed to variation in the molecular weight distribution of the alkyds (*1*). The different distributions arise because the interchange reactions are comparatively slow under the conditions used for the commercial polymerization of alkyd resins. The relatively fast interchange found by Flory (2) for linear polyesters occurred under conditions not normally used in alkyd manufacture (strong acid catalysis, cooking for more than 14 hr). In addition, recent studies have shown that many alkyd resins are not homogeneous but contain a dispersed phase microgel. This is not soluble in the continuous phase of low molecular weight polymer; hence microgel is not readily susceptible to interchange reactions. Because of the difficulties encountered in interconverting alkyd resins of different molecular weight distributions, the polymer-forming reactions must be carefully controlled to obtain consistent molecular weight distributions, and hence polymer properties, from batch to batch.

In nature fatty acids occur widely as the glyceride esters, e.g., vegetable oils, and commercially it is often desirable to use oils in alkyd manufacture rather than to first isolate the fatty acid. Direct use of vegetable oils is achieved by first reacting them with a polyol to give a partial ester. When glycerol is the polyol a "monoglyceride mixture" is formed.

Recently it has been shown by Solomon and Swift (3) that the composition of the monoglyceride mixture varies with the reaction conditions and the catalyst used, and that contrary to previous opinion an equilibrium composition is not reached under practical conditions. The consequences of this, taken in conjunction with the comparatively slow interchange reactions, is that the molecular weight distribution (including microgel content) of an alkyd would vary with the composition of the monoglyceride mixture. This prediction has been substantiated by recent studies (*4*) in which alkyd resins of the same overall composition have been processed from a number of glyceride mixtures. The present study was aimed at relating the glyceride composition used to prepare these resins to the microgel content and to the structure and mechanical properties of the films formed from these resins by autoxidation. In the previous investigation (*4*), subjective tests had indicated differences in the film properties and prompted us to measure the mechanical properties of the free films.

EXPERIMENTAL

The alkyd resins had a mole ratio of linoleic acid/glycerol/phthalic anhydride of 1.0:1.36:1.11. They were prepared by conventional solution process polyesterification from the glyceride mixtures shown in Table 1. The solution properties of the resins and the type of microgel present are shown in Table 2.

TABLE 1

Mole Compositions Used to Prepare Resins

Resin	α-Monoglyceride	α-α' Diglyceride	Triglyceride	Glycerol	Phthalic anhydride
1	6.0	0	0	2.16	6.66
2	4.5	0	0.5	3.16	6.66
3	3.0	1.5	0	3.66	6.66
4	4.5	0.75	0	2.91	6.66
5	3.0	0.75	0.5	3.91	6.66

The free films were prepared by coating tin-plated iron panels with the resin solution, which contained oxidation catalysts [0.2% cobalt and 1.5% lead (metal content) added as the naphthenates]. The film specimens were stripped from the panels by the amalgamation method after drying at room temperature or 120°C.

The complex Young's modulus was measured at 138 cps over a temperature range −80°C–100°C by a direct-reading tan δ meter (5).

RESULTS

The results are shown in Figs. 1 to 7, where storage and loss

TABLE 2

Solution Properties of Resins

Resin	Viscosity (Stokes)[a]	Acid value	Hydroxyl value	Cloud point[b] acetone/water	Cloud point[b] n-pentane	Appearance under electron microscope at 7500×
1	1.4	10.6	35.0	4.18	32.5	Large number of particles 1.0 μ
2	1.65	9.9	51.0	5.43	23.5	Small number of particles 1.0 μ
3	4.70	10.3	47.7	5.51	15.8	Small number of particles 1.0 μ
4	2.25	10.5	37.0	5.14	24.2	Small number of particles 1.0 μ
5	5.0	10.2	54.0	7.14	14.6	Large number of small particles

[a] Measured at 25°C at 55% solids content in mineral spirit.

[b] Measured as described in Ref. 4.

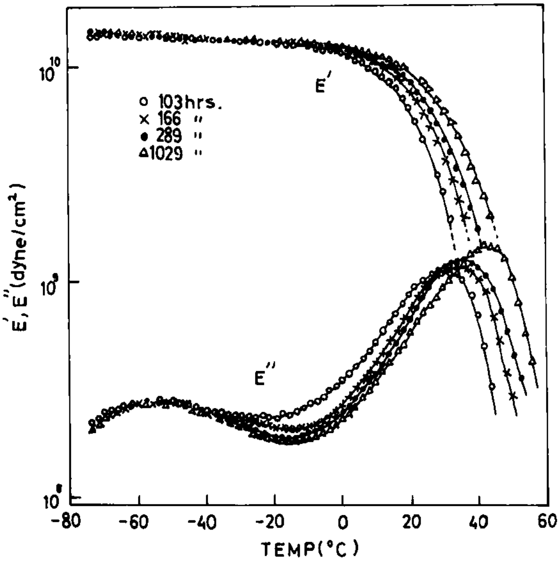

FIG. 1. Complex modulus vs. temperature curves for specimens derived from resin 1 and dried at room temperature.

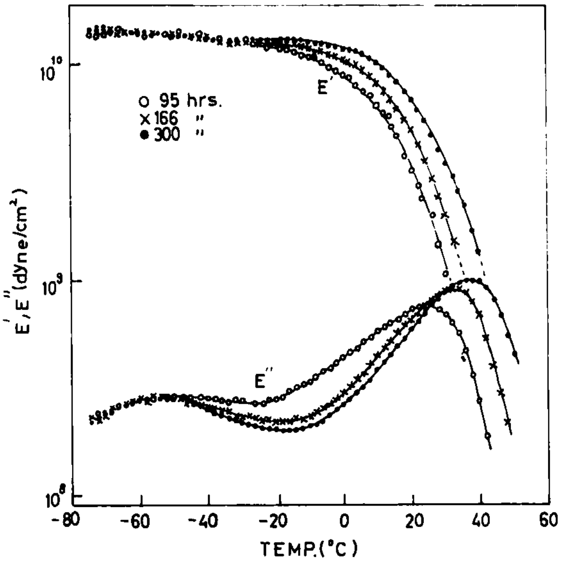

FIG. 2. Complex modulus vs. temperature curves for specimens derived from resin 2 and dried at room temperature.

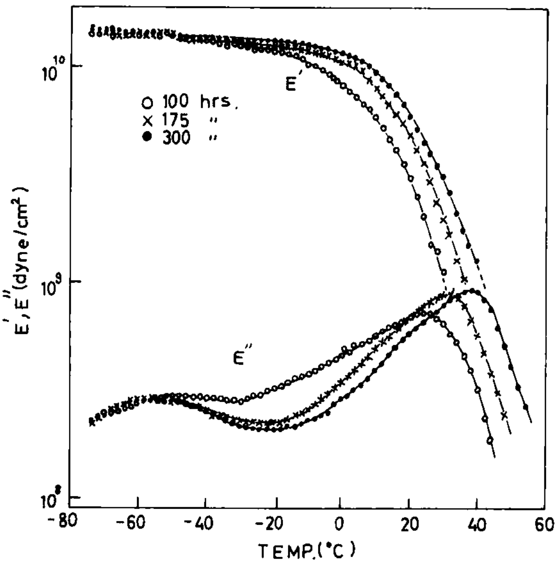

FIG. 3. Complex modulus vs. temperature curves for specimens derived from resin 3 and dried at room temperature.

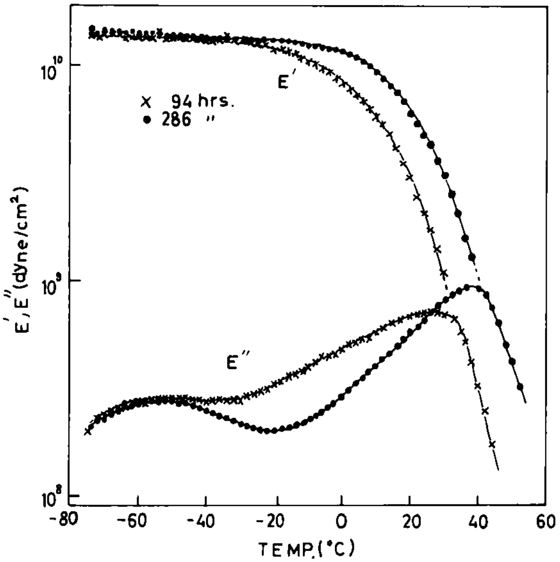

FIG. 4. Complex modulus vs. temperature curves for specimens derived from resin 4 and dried at room temperature.

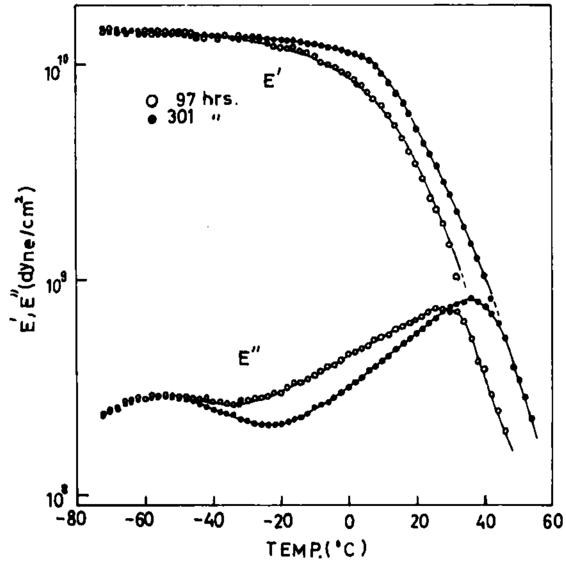

FIG. 5. Complex modulus vs. temperature curves for specimens derived from resin 5 and dried at room temperature.

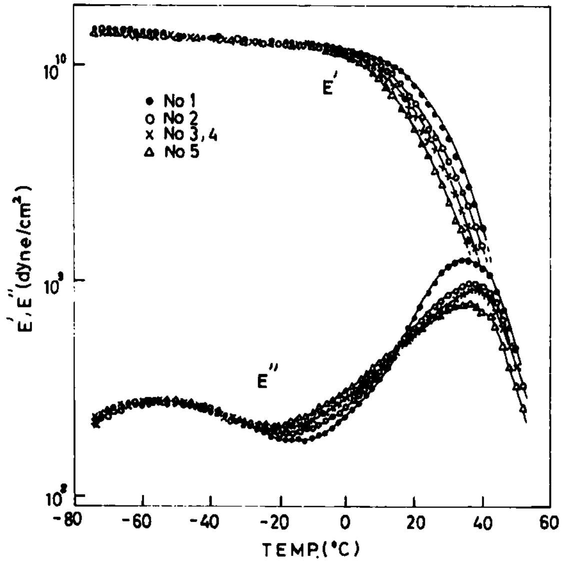

FIG. 6. Complex modulus vs. temperature curves for specimens derived from different resins and dried at room temperature for about 300 hr.

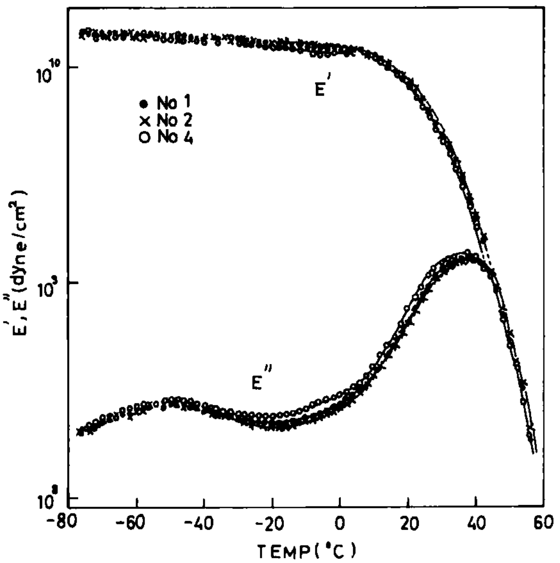

FIG. 7. Complex modulus vs. temperature curves for specimens derived from different resins and baked at 120°C for 0.5 hr.

moduli, E' and E'', are plotted vs. temperature. Two absorption peaks are observed in E'' vs. temperature curves for all the specimens. The position and intensity of the absorption which appears at about −50°C, denoted β absorption, does not depend on the resin or the drying conditions. The other absorption, which appears at about 40°C and will be denoted α absorption, increases its intensity and shifts toward higher temperatures with increasing drying time at room temperature, as can be seen in Figs. 1 to 5. In a region intermediate between α and β absorption, E'' decreases and the slope of E'' vs. temperature curve increases with drying. Figure 6 shows the differences among the resins at the same drying level (300 hr at room temperature), where a steady dry state seems to be first achieved. It is found that the resin also affects the α absorption and the intermediate region between the two absorptions. The peak height of the α absorption is a maximum for resin 1, which contains the maximum amount of monoglyceride. This trend in the magnitude of E'' is reversed in the intermediate region. The differences among specimens prepared from different resins are diminished in the case of heat drying, as shown in Fig. 7.

DISCUSSION

The molecular mechanism of α absorption can be attributed to the diffusional motion of main chain segments corresponding to the glass to rubber transition, since the value of E' decreases rapidly in this temperature region.

The behavior observed for β absorption leads to the conclusion that the absorption arises from local chain motions which do not depend on structural features brought about by drying conditions or resin composition. A local relaxation mode due to the torsional oscillation of the main chain as proposed recently (6,7) seems to explain the present case.

The variables in this study show appreciable effects on the behavior at temperatures around the α absorption peak. It is more natural to regard the intermediate region as part of the α absorption than to regard it as a separate mechanism. Therefore, the intermediate region (−20–10°C) and the peak region (20–50°C) will be referred to as the α_L and α_H regions, respectively.

The drying of alkyd resin films is caused by the autoxidation of fatty acid chains producing cross-links. The α absorption as a whole is shifted to higher temperatures by the formation of cross-links and polar groups as a direct result of autoxidation. Another, and more essential, feature observed in the mechanical behavior as a consequence of the drying process is the decrease in the α_L absorption and the increase in the α_H absorption intensity. It can be presumed that the motion of free fatty acid chains contributes to absorption in the α_L region. As the drying process proceeds, the motion of the fatty acid chains will become more restricted and contribute to absorption in the α_H region. At present it is not certain whether the restriction on the motion of the fatty acid is caused by cross-links or intermolecular forces due to the polar groups.

Comparison of the resins (Fig. 6) shows a regular correlation between the glyceride composition used to prepare the alkyd and the α absorption behavior. The inverse relationship between the intensity of the α_L and α_H regions is similar to those observed in Figs. 1 to 5. In Fig. 6, however, the position of the absorption peak is the same for all specimens. Since the temperature of the α absorption peak is determined by the cohesive energy density and the cross-linking density, these structural parameters are roughly constant for all the specimens included in Fig. 6. Therefore, it can be concluded that as the monoglyceride content of the initial reaction mixture is increased, structures are formed during drying of the resin film in which the motion of the fatty acid chains is more restricted.

The ratio of the absorption intensity in the α_H region to that in the α_L region for the specimens compared in Fig. 6 shows a more precise correlation with the amount of microgel previously found (*4*) to exist in the resin solutions. This correlation leads us to assume that the restriction on the motion of the fatty acid chains is caused by a certain structure which is similar in its nature to, and would be formed by or from, the microgel. The exact nature of microgel is not clear at present. Sufficient data are not yet available to decide whether the microgel particle is insolubilized by infinite network formation through covalent bonds or by aggregation of molecules through intermolecular forces.

The effects of microgel on the film-forming process are considered to be largely diminished at higher temperatures, since the differences among the specimens baked at 120°C are very small, as is seen from Fig. 7. This is consistent with either fusion of the microgel particles at elevated temperature and/or less enhancement of the oxidation rate by microgel with increasing temperature.

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Zusammenfassung

Es wird über die dynamisch-mechanischen Eigenschaften von getrockneten Filmen berichtet, die durch Reaktion von Phtalsäureanhydrid und synthetischen Mischungen von Mono-, Di-, und Trilinolenaten des Glyzerins hergestellt worden waren. Die Eigenschaften der bei Zimmertemperatur getrockneten Filme stimmen mit dem Mikrogelgehalt des Harzes überein, wobei letzterer eine Funktion des Monoglyzeridgehalts der Ausgangsreaktionsmischung ist. Bei 120°C getrocknete Filme zeigen kleinere Unterschiede in den mechanischen Eigenschaften.

Résumé

On fait un rapport sur les propriétés dynamiqes et mécaniques des films en résines alkydes sechés, preparés par la réaction d'anhydride phthalique avec des mélanges synthétiques de mono-, di, et tri-linoléates de glycérol, à composition globale identique. Les proprietés de ces films, sechés à température ambiante, sont en corrélation avec le montant en microgel de ces résins, lui-meme une fonction du taux en monoglycérides du mélange réactionnel originel. Les films sechés a 120°C possèdent des différences plus faibles de leurs proprietés mécaniques.

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