

Infrared Study of the Cure of Unsaturated Polyester

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Synopsis

The infrared spectra of unsaturated polyesters in process of cure have been taken of samples free from unreacted portion. Styrene and polyester fractions in the curing polyester films were assessed from comparison of the band intensities at 695 and 740 cm.^{-1} . The styrene fraction in curing films was found to increase as cure proceeded, and the delayed curing was seen to be accompanied by a build-up of films of lower styrene content. The differences between samples observed in the mechanical behavior were considered attributable for the most part to the difference in styrene content.

INTRODUCTION

In a previous paper,¹ the change in mechanical behavior of an unsaturated polyester during cure was reported; it was found that a film dried more quickly tended to require a higher gel content to attain the same complex modulus as a more slowly dried film. In another paper,² we reported that the rapidly dried film also was found to possess a higher transition temperature in loss modulus and a somewhat lower dynamic elasticity in the region of elevated temperatures than the latter. The results of measuring the dependency of complex modulus on temperature for two samples (II-1 and II-4), which had been employed in the previous study, are shown in Figure 1; here a similar relationship is seen to exist.

The curing of polyesters is considered to be affected by the inhibitive action of oxygen in air and the evaporation of styrene monomer accompanied by the variation of chemical composition of systems. The differences in the mechanical behavior described above may be assumed to be related to the manner of curing to which the films are subjected. In this investigation, it was attempted to analyze the process of cure by use of infrared spectroscopy to elucidate the correlation between chemical composition and mechanical properties of unsaturated polyester resin.

EXPERIMENTAL

The gelled portions of the curing films which had been studied in the previous paper¹ were used for the infrared spectroscopy. The stage of cure, namely, the times for which each sample was immersed in the solvent, are given in Table I. II-1 denotes the series of samples containing 0.06 parts Co metal in 100 parts resin solution as an accelerator and II-4 de-

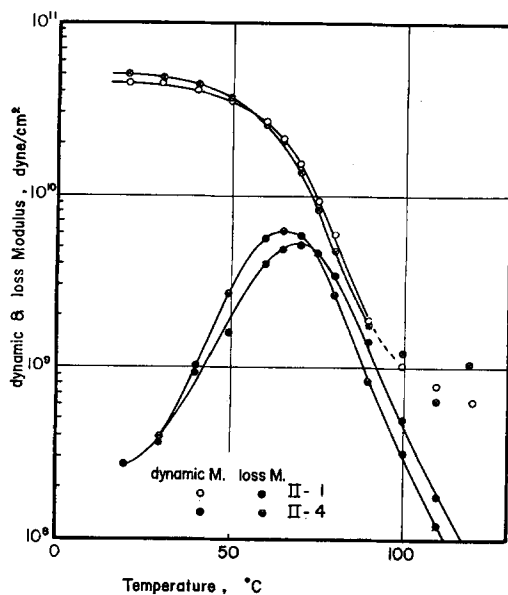


Fig. 1. Dependence of dynamic and loss moduli on temperature for films of II-1 and II-4. Measurements were carried out after heat treatment at 120°C. for 4 hr.

notes a series containing 0.006 phr Co. In Table I, various properties of each sample are also listed. A density gradient tube was used for the measurement of density of samples. A number-average molecular weight

TABLE I
Properties of Polyester Films During Cure

Series	No.	Time, min.	Dynamic modulus, $\times 10^{-9}$, dyne/cm. ²	Loss modulus $\times 10^{-9}$, dyne/cm. ²	Density, g./cm. ³
II-1	1	40	0.8	0.32	1.265
	2	50	1.4	0.95	1.262
	3	60	2.9	1.85	1.253
	4	70	4.9	2.96	1.257
	5	90	12.0	4.76	1.244
	6	110	18.7	4.93	1.242
	7	420	36.6	2.38	1.234
	8	14,400	47.3	0.53	1.226
II-4	1	90	—	0.09	1.278
	2	120	1.1	0.39	1.264
	3	150	1.7	1.20	1.257
	4	180	3.9	2.19	1.256
	5	240	12.4	5.25	1.250
	6	300	20.7	5.53	1.247
	7	1,440	40.9	2.75	1.243
	8	43,200	52.4	0.67	1.236

of about 1400 was obtained for the original polyester resin, and a polyester molecule contains two maleic units on the average.

In order to prepare standard samples containing a specified amount of styrene in the cured films, the same polyester as used in the previous experiment was dissolved in styrene monomer in the different proportions (90:10, 80:20, and 70:30). These samples were then dried, care being taken to prevent the evaporation of styrene monomer by using cellophane paper as covers. Infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer; samples were in the form of potassium bromide disks, except for liquid samples.

RESULTS

Figure 2 shows the spectra for styrene monomer, the original unsaturated polyester resin, and its 70 wt.-% solution in styrene monomer; and the spectra for standard samples are given in Figure 3.

From a comparison of these spectra, we can obtain some information to analyze the curing of polyesters. The most remarkable change in band

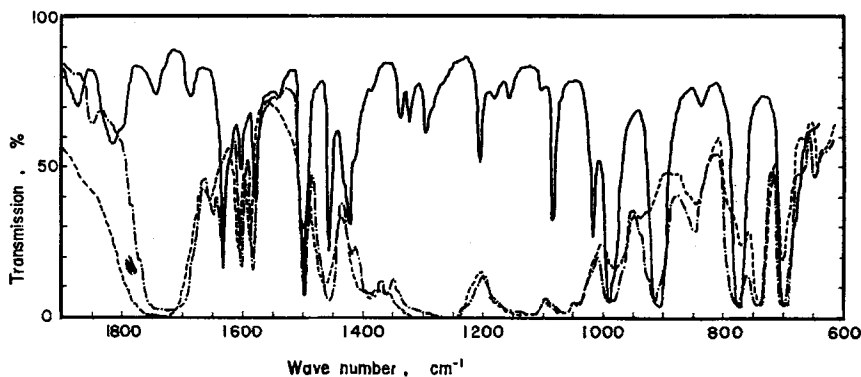


Fig. 2. Infrared spectra for styrene monomer, original polyester resin, and its solution.

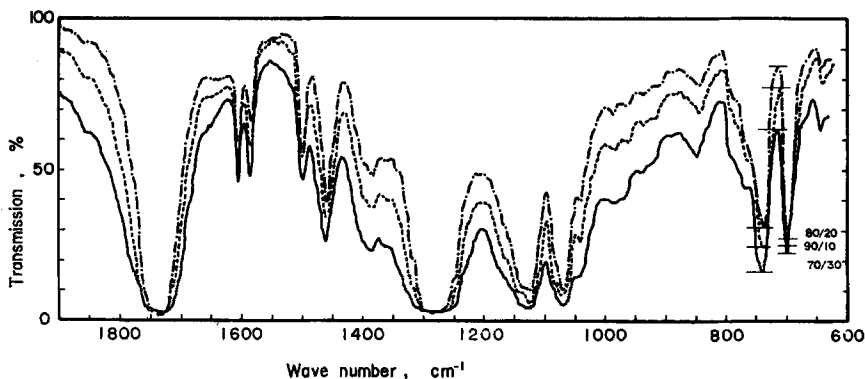


Fig. 3. Infrared spectra for standard samples.

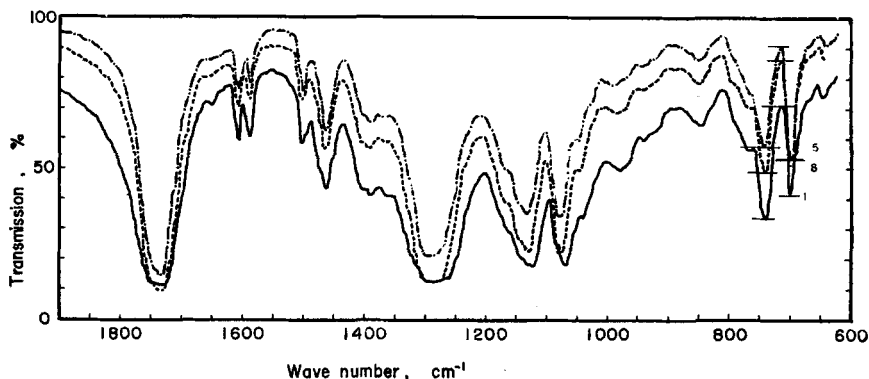


Fig. 4. Infrared spectra for series II-1.

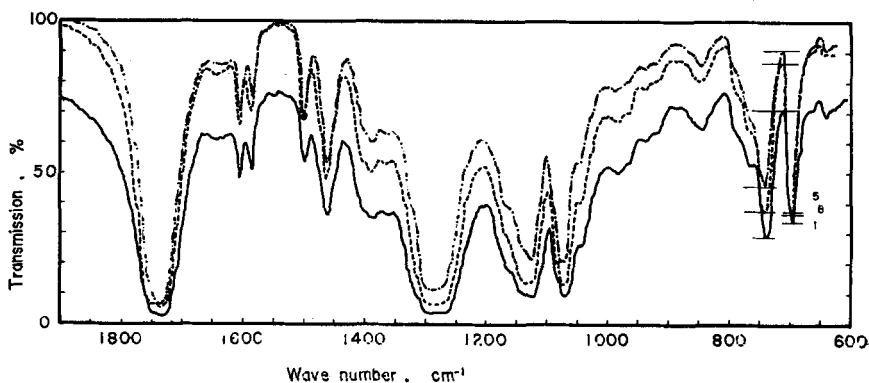


Fig. 5. Infrared spectra for series II-4.

intensity can be observed in the regions of 690 and 770 cm^{-1} . The band at 770 cm^{-1} , which is characteristic of the C—H out-of-plane bending mode for monosubstituted benzene, can be seen in the styrene spectrum, and the band at 740 cm^{-1} , which is due to that of *o*-disubstituted benzene, can be seen in the spectrum of polyester, as expected. Here, disubstituted benzene refers to the phthalic residue existing in the polyester molecules. The band at 695 cm^{-1} , which is characteristic of styrene and ought not to appear in the *o*-phthalic spectrum, appears in both spectra of styrene and polyester; the reason for this, however, is not clear. Other bands noted in Figure 2 are those at 1630 and 1650 cm^{-1} . The former is attributed to the —C=C— stretching mode in styrene monomer and the latter is considered due to that of maleic unsaturation in polyester chains. Absorptions other than the above-described can also be assigned, but as they are not of concern in the following discussion, further description is omitted.

Typical spectra of curing polyesters selected are shown in Figures 4 and 5. Here, the band intensity at 770 cm^{-1} is seen to decrease significantly with cure, while as observed in the case of standard samples, an

inversion in the relative intensity of the bands at 740 and 695 cm^{-1} is found to take place. Figures 4 and 5 indicate that the concentration of maleic unsaturation decreases as cure proceeds; no styrene monomer remains in the curing films after treatment with acetone.

DISCUSSION

Chemical Composition of Curing Films

The variations observed in the band intensity at the given wave numbers suggest that they enable estimation of the change in chemical composition with cure. As mentioned above, although the band at 695 cm^{-1} is observed as it is subjected to the superposed contribution of styrene as well as polyester components in films, it is considered to be more suitable for estimation of the styrene concentration rather than the band at

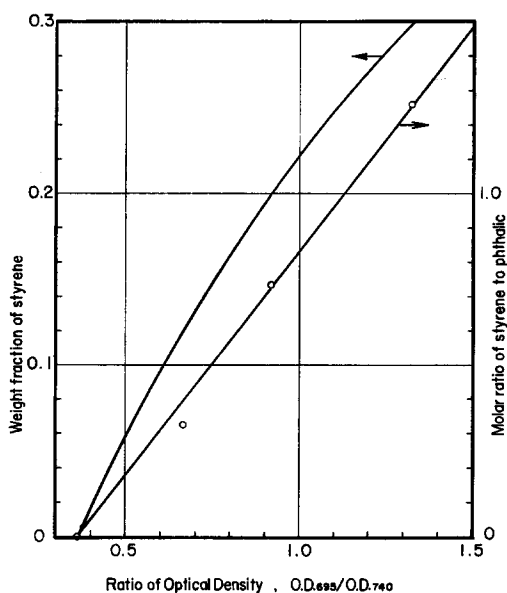


Fig. 6. Calibration curves for estimation of styrene content.

770 cm^{-1} , which seemed to be insufficiently sharp. In this study, therefore, the ratio of optical density at 695 cm^{-1} to that at 740 cm^{-1} is employed as an index expressing the chemical composition of polyesters. By making use of the spectra for standard samples, a reliable calibration line as shown in Figure 6 can be obtained. The optical densities of the bands at 695 and 740 cm^{-1} were determined by using a base line drawn in parallel with the abscissa at the point of peak of 715 cm^{-1} . The amounts of styrene and polyester converted to gel were calculated on the basis of the original weight of the applied polyester. The optical densities obtained and the estimated styrene and polyester fractions are summarized

TABLE II
Optical Density and Composition of Curing Polyesters

Series	No.	O.D. ₆₉₅	O.D. ₇₄₀	Styrene reacted, %	Polyester reacted, %	Ratio styrene polyester	Extractables, %	Weight loss, %
II-1	1	0.328	0.394	9.5	44.6	0.21	43.6	2.3
	2	0.190	0.209	12.1	50.3	0.24	35.2	2.4
	3	0.213	0.237	12.9	53.6	0.24	31.2	2.4
	4	0.162	0.181	13.0	55.4	0.24	29.2	2.4
	5	0.366	0.364	15.9	56.2	0.29	25.4	2.5
	6	0.524	0.473	18.2	55.7	0.34	23.6	2.5
	7	0.383	0.306	22.2	57.0	0.39	18.2	2.6
	8	0.398	0.299	25.1	57.6	0.44	14.0	3.2
II-4	1	0.239	0.324	5.3	30.8	0.17	56.7	7.2
	2	0.201	0.276	6.9	41.7	0.16	43.9	7.5
	3	0.314	0.409	8.5	46.6	0.18	37.3	7.6
	4	0.226	0.286	9.2	48.2	0.19	34.9	7.7
	5	0.207	0.249	11.1	52.6	0.21	28.5	7.8
	6	0.294	0.317	13.1	53.2	0.25	25.7	7.9
	7	0.223	0.204	17.4	54.4	0.32	20.3	7.9
	8	0.234	0.199	19.3	54.0	0.37	18.2	8.5

in Table II. Each series of samples showed considerable loss of weight during the cure, as shown in Table II.

The data in Table II show clearly that the major part of weight loss occurred in the very early stages of cure, perhaps in the induction period, and the styrene fraction in the gel portion increased as cure proceeded. These aspects can be observed more conveniently by drawing the scheme as Figure 7.

The curves representing the manner of reaction of polyester molecule appear to reach a limiting value at given points of time, and the point

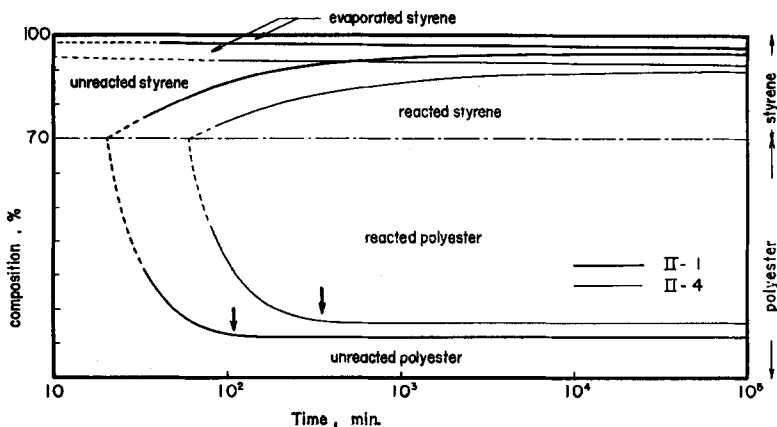


Fig. 7. Scheme expressing the variation of film compositions during cure.

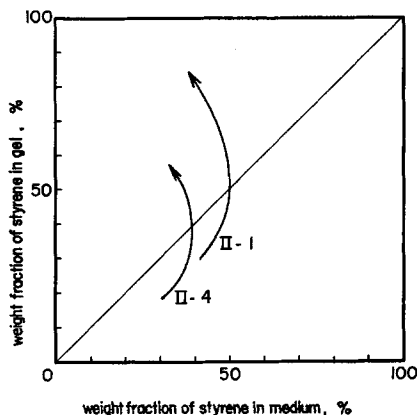


Fig. 8. Plots of styrene fraction in producing gel vs. styrene fraction in medium.

is seen to concur with the time t_E , which has been defined in a previous paper as the time at which the loss modulus reaches its maximum value and is indicated by arrows in Figure 7. Whereas styrene monomer seems to be able to react even at a fairly late stage of cure, this is considered to express the difference of molecular mobilities at the diffusion controlled stage.

As shown in Figure 8, the results of plotting the weight fractions of styrene in the increment of gel formed at a given stage versus that of the unreacted styrene in the medium give a peculiar pattern differing from the one ordinarily indicated.³ This suggests a curing mechanism in which styrene monomer takes part in network structure progressively at the early stages of cure and comes to play a leading role at the late stages of cure.

Mechanical Behavior

Takahashi⁴ reported that the polyesters of higher styrene contents give films of lower rubberlike elasticity compared with those of lower styrene contents, and for this reason he stated that the molecular weight between crosslinks increases with increasing styrene content. In this investigation, II-4 had lost apparently a considerable amount of styrene through evaporation in the early stages of cure, and infrared spectra show that the films of series II-4 contained relatively less of the styrene component than those of series II-1. In order to estimate the molecular weight between crosslinks, measurement of the degree of swelling was attempted, but this could not be done because of the occurrence of a heavy solvent cracking. A strange result has been obtained from the measurement of densities as indicated in Table I, that is, an unexpected decrease in density was observed during the cure. The density of polyesters seems to be related to the concentration of styrene in the films. This is considered as it is a problem which has to be solved.

Figure 1 indicates that II-1 possesses a somewhat higher transition temperature than II-4, and this temperature may be considered to be related to the glass transition temperature T_g . T_g is believed to increase with introduction of crosslinks and/or ring structures into systems. If the difference in the transition temperature observed above was supposed to be due to the effect of crosslinks, II-1 should have a higher dynamic modulus than II-4 at elevated temperatures. Figure 1, however, shows only an insignificant difference between the two. Further, the above supposition is not compatible with the observations regarding the process of cure. Hence, the increase observed in transition temperature is concluded to be due to the steric effect of the styrene molecules.⁴ In the copolymerization reaction of unsaturated polyesters, it seems that the increasing styrene content in feed does not increase the crosslinking density but lengthens the styrene chains which connect the polyester chains. From the results of this study, it would be safe to presume that the mechanical properties of films would be governed by the styrene-to-polyester ratio, the quantity of which is considered to depend on the length of induction period; thus a higher styrene fraction gives a film of lower rubberlike elasticity and higher transition temperature.

CONCLUSIONS

The work described in this paper has been carried out as a follow-up study to the previous paper¹ for the purpose of relating the film behavior with the chemical composition or structure. Some aspects of the manner of copolymerization occurring in the cure of polyesters could also be obtained. The film behavior of a polyester are affected by curing conditions such as temperature and concentration of initiator and accelerator. However, when curing was carried out in air, the differences observed between behaviors of films are assumed depend on the variation of chemical composition resulting from the evaporation of styrene.

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References

1. T. Imai, *J. Appl. Polymer Sci.*, in press.
2. T. Imai and T. Okawa, *J. Japan Soc. Colour Material*, **39**, 383 (1966).
3. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 180.
4. S. Takahashi, *J. Japan. Soc. Colour Material*, **37**, 155 (1964).

Résumé

Les spectres infrarouges de polyesters insaturés pris au cours de leur recuit ont été pris sur des échantillons ne contenant pas de parties qui n'auraient pas réagi. Les fractions en styrène et polyesters au sein de films de polyesters ont été établis par comparaison des intensités de bande à 695 et 740 cm^{-1} . Expérimentalement, on montre que

a fraction styrénique des films recuits croît à mesure que la recuité progresse; un recuit retardé s'accompagne d'une teneur en styrène plus faible des films obtenus. Les différences observées entre les divers échantillons en ce qui concerne leurs comportements mécaniques étaient attribués principalement à la différence en teneur en styrène.

Zusammenfassung

Infrarotspektren ungesättigter Polyester wurden während des Härtungsprozesses an vom nicht-reagierten Anteil befreiten Proben aufgenommen. Der Styrol- und der Polyesterbruchteil in den härtenden Polyesterfilmen wurden aus dem Vergleich der Bandenintensität bei 695 und 740 cm^{-1} ermittelt. Die Versuche zeigten, dass der Styrolbruchteil in den härtenden Filmen mit fortschreitender Härtung zunahm und dass eine Verzögerung der Härtung von einem Aufbau von Filmen mit niedrigerem Styrolgehalt begleitet war. Es wird angenommen, dass die beobachteten Unterschiede im mechanischen Verhalten der Proben grösstenteils auf Unterschiede im Styrolgehalt zurückzuführen sind.

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