Viscoelastic Investigation on the Cure of Unsaturated Polyester Coatings

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Synopsis

The change of the viscoelastic behavior of an unsaturated polyester resin during curing was followed by a vibrometric technique, while the portion converted to gel in applied films was also determined by means of extraction with a solvent. Some relationship between the viscoelastic properties and the amount gelling has been found to exist. The dependency of the curing rate of polyesters on the concentration of initiator as well as accelerator seemed not to be unity. A marked delay in cure has been observed in the region of low concentrations of initiator and accelerator.

INTRODUCTION

During the curing stages of network polymers, an increase in viscosity and elasticity is believed to take place with introduction of crosslinks into the systems. The changes in such properties in the gelled state, however, have not been shown quantitatively because of experimental difficulties and in the paint industry, the degree of hardening of coated films is evaluated by means of a touch test. Previously we[1] reported that it is possible to determine the viscoelastic properties of applied paint films by using a vibrometric technique. The technique was also accepted as being applicable for semicured systems.[2] In this study, the rate of polymerization of an unsaturated polyester resin has been investigated from the point of view of viscoelasticity.

EXPERIMENTAL

Vibrometric Technique

Vibrometric techniques, such as the vibrating-reed method, have often been employed in the rheological investigation of polymers.[3] Becker[4] has given the equations for calculating the complex modulus of paint films coated on both sides of a steel substrate. If coatings were applied on one side of substrate, the neutral axis of the specimen consisting of a steel substrate and a paint layer would be displaced compared to that of the substrate alone. The distance of this displacement, which depends on the differences in elasticity and thickness between paint film and steel substrate, appeared so small as to make it possible to ignore its influence.[2] Therefore

in this study, specimens coated on one side were used without correction for the displacement of the neutral axis.   The dynamic and loss modulus of the coated films on a steel substrate were calculated by using eqs. (1) and (2):[2,4,5]

$$E = \frac{[(w/w_s)(\nu/\nu_s)^2 - 1]E_s}{1/2\{[1 + (2h/h_s)]^3 - 1\}} \tag{1}$$

$$E' = \frac{[(w/w_s)(\nu/\nu_s)^2(\Delta\nu/\nu) - \tan\delta_s]E_s}{1/2\{[1 + (2h/h_s)]^3 - 1\}} \tag{2}$$

where E is the dynamic (Young's) modulus of film, E' is the loss (Young's) modulus of film, E_s is the dynamic (Young's) modulus of the substrate (steel), δ_s is the mechanical loss angle of the substrate, w is the weight of specimen (film + substrate), w_s is the weight of substrate, h is the thickness of film, h_s is the thickness of substrate, ν is the natural resonance frequency of the specimen, ν_s is the natural resonance frequency of the substrate, and $\Delta\nu$ is the bandwidth of the specimen. $\Delta\nu$ represents the range of frequencies for which the resonance amplitude falls within limit not less than $1/\sqrt{2}$ of its maximum value.

Apparatus

The apparatus employed is shown diagrammatically in Figure 1.   The specimen to be tested was suspended on threads attached at the nodes. Two electromagnets positioned under the ends of the specimen were utilized as a vibrator and a receiver.   A vibrating current from a variable audio-oscillator was fed to drive an electromagnet.   The vibration of the specimen was received electrically by another electromagnet.   The natural
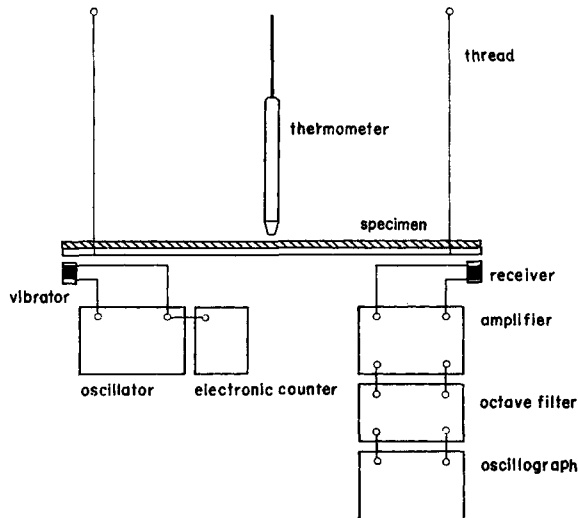

Fig. 1. Diagrammatic sketch showing method of determining viscoelastic properties of applied paint films.

resonance frequency was determined as the frequency for which the resonance amplitude attained a maximum value. To determine the loss modulus, the bandwidth has been measured; however, it can also be determined in different ways, such as measuring the logarithmic decrement under free oscillation. The difference in the values measured in each of the above two methods, however, has been found to be insignificant.[1]

Polyester Resin

The polyester resin studied was synthesized from maleic anhydride, phthalic anhydride, diethylene glycol, and propylene glycol in a molar ratio of 2:5:5:2. The above resin (70 parts) was dissolved in 30 parts of styrene monomer. Hydroquinone (100 ppm on resin) and *p-tert-*buthylcatechol (0.01 part on resin solution) were added as inhibitors. Methyl ethyl ketone peroxide and cobalt naphthenate were used as a radical initiator and an accelerator, respectively. The MEK peroxide solutions were prepared as 60, 37.5, and 23.1 wt.-% solutions in dimethyl phthalate, and each of the solutions was added in the proportions of 5, 3.2, and 2.6 parts per 100 parts resin solution, respectively, in order to derive the films containing the same amount of dimethyl phthalate, while one part of Co naphthenate solutions, prepared to contain variable amounts of metal cobalt, as 6, 2.4, 1.2, and 0.6 wt.-% in xylene, was added per 100 parts of resin solution. Polyester films were applied with a special applicator to steel panels, 200 mm. in length, 20 mm. in width and 0.4 mm. in thickness so as to obtain cured film about 0.4 mm. thick.

Determination of Solvent-Insoluble Portion

It is interesting to examine the relation between the viscoelastic behavior and the portion converted to gel in the applied film. For this purpose a number of steel panels, 30 mm. in length, 20 mm. in width, and 0.4 mm. thick, were coated at the same time that the specimen for the vibrometric measurement was prepared. At given times the panels were immersed one after another into a solvent as cure proceeded. Acetone was used as a solvent. After extracting the soluble material and drying the remainders, the portion converted to gel was determined.

RESULTS

Immediately after coating, the specimens were mounted on the measuring apparatus, and the variations of natural resonance frequency and bandwidth were followed during the stages of cure. To fix the measuring frequency is impossible owing to the nature of vibrometric technique. The quantities of natural resonance frequency measured, however, have been observed to lie within a range of 440–520 cps. for all experiments. The measurments were carried out on the third overtone of oscillation. The temperature was kept at 20 ± 1°C. during the experiments in a conditioned room. Details of a calculating sheet are shown in Table I.

TABLE I
Typical Results (Sample I-1)[a]

Date	Time	ν, cps	$E \times 10^{-9}$, dyne/cm.^{2}	$d \log E/dt$	$\Delta\nu$, cps	$E' \times 10^{-9}$, dyne/cm.^{2}	$d \log E'/dt$
1	10:00 AM			Mixing			
"	10:03 "			Application			
"	10:15 "	455.88	0.03	—	0.54	0.01	0.074
"	10:20 "	455.90	0.04	—	0.63	0.05	0.074
"	10:25 "	455.91	0.04	—	0.92	0.17	0.074
"	10:30 "	456.32	0.7	—	1.21	0.28	0.074
"	10:35 "	457.13	1.3	—	2.33	0.73	0.059
"	10:40 "	457.83	1.9	—	3.65	1.24	0.044
"	10:45 "	459.41	3.2	0.053	5.65	2.04	0.038
"	10:50 "	462.11	5.3	0.039	7.83	2.93	0.028
"	10:55 "	465.77	8.2	0.031	10.01	3.82	0.017
"	11:00 "	469.78	10.7	0.024	11.09	4.38	0.011
"	11:10 "	477.84	18.2	0.009	12.72	5.03	0.001
"	11:20 "	481.71	21.4	0.005	12.40	4.95	−0.002
"	11:30 "	485.73	24.7	0.003	11.62	4.66	−0.002
"	11:40 "	488.16	26.8	0.002	10.95	4.40	−0.002
"	11:50 "	489.91	28.3	0.001	10.40	4.19	−0.002
"	0.00 PM	491.98	30.0	0.001	9.82	3.98	−0.002
"	0:30 "	495.10	32.7	"	8.37	3.38	−0.002
"	1:00 "	497.53	34.8	"	7.30	2.94	−0.001
"	1:30 "	498.08	35.2	"	7.04	2.83	−0.001
"	2:00 "	499.49	36.5	"	6.84	2.75	−0.001
"	3:00 "	500.90	37.7	"	6.12	2.45	<0.001
"	4:00 "	502.32	38.9	"	5.58	2.21	"
"	5:00 "	502.61	39.2	"	5.84	2.34	"
2	10:05 AM	507.02	43.0	"	3.99	1.55	"
3	9:40 "	509.32	45.0	"	3.23	1.22	"
4	9:45 "	509.79	45.4	"	3.12	1.18	"
6	9:25 "	510.86	46.3	"	2.52	0.92	"
8	9:50 "	511.34	46.8	"	2.40	0.86	"
11	9:40 "	511.25	46.6	"	2.47	0.89	"

[a] $E_s = 2.1 \times 10^{12}$ dyne/cm.^{2}, tan $\delta_s = 0.0011$, $\nu_s = 489.23$ cps, $w = 14.690$ g., $w_s = 12.493$ g., $h = 0.385$ mm., $h_s = 0.403$ mm.

The gelation time, which was supposed to correspond to the time at which the bandwidth began to increase, could not be defined accurately because of the uncertainty of experimental data. The rates of increase of dynamic and loss modulus seem to be constant in the early stages of cure, then they fall gradually according as cure proceeds. The result to be emphasized is that loss modulus decreases after reaching a maximum value. This fact can be interpreted by assuming that the system enters the freezing region of molecular movement at that point. After a long period of cure, both dynamic and loss moduli appear to approach given limits. The experimental results are given in Figures 2–4 in which E and E' are plotted versus time on a log–log scale.
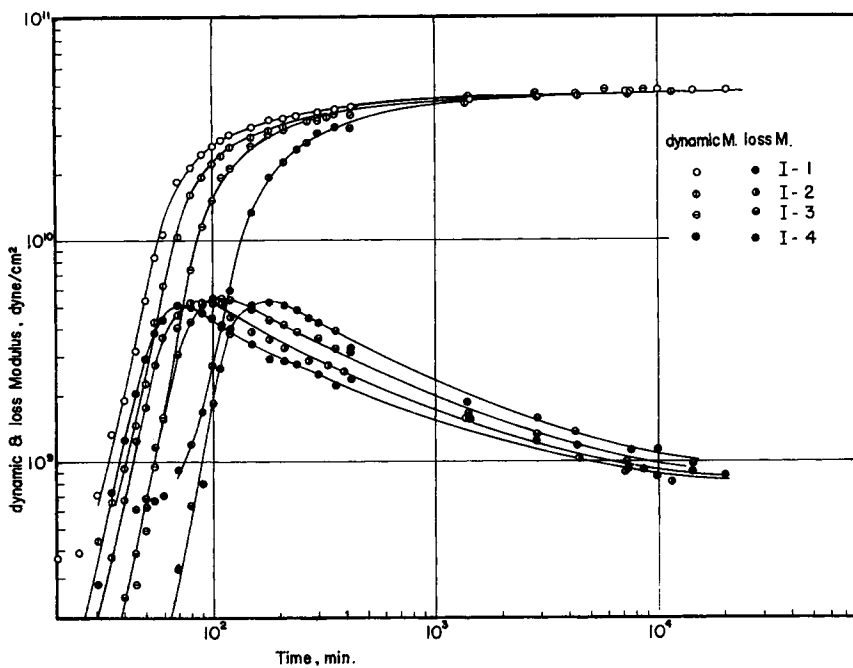
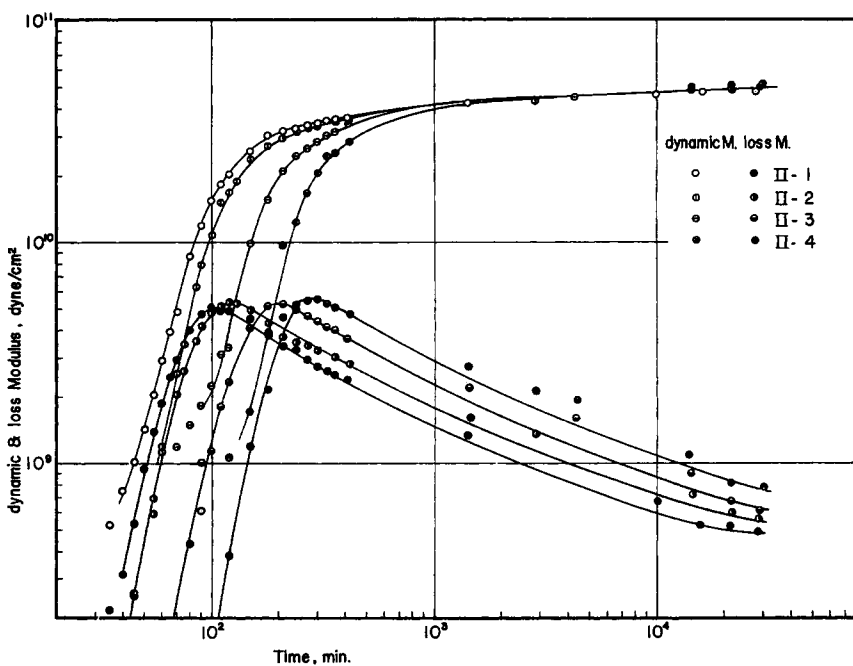Fig. 2. Dynamic and loss moduli vs. time for series I.

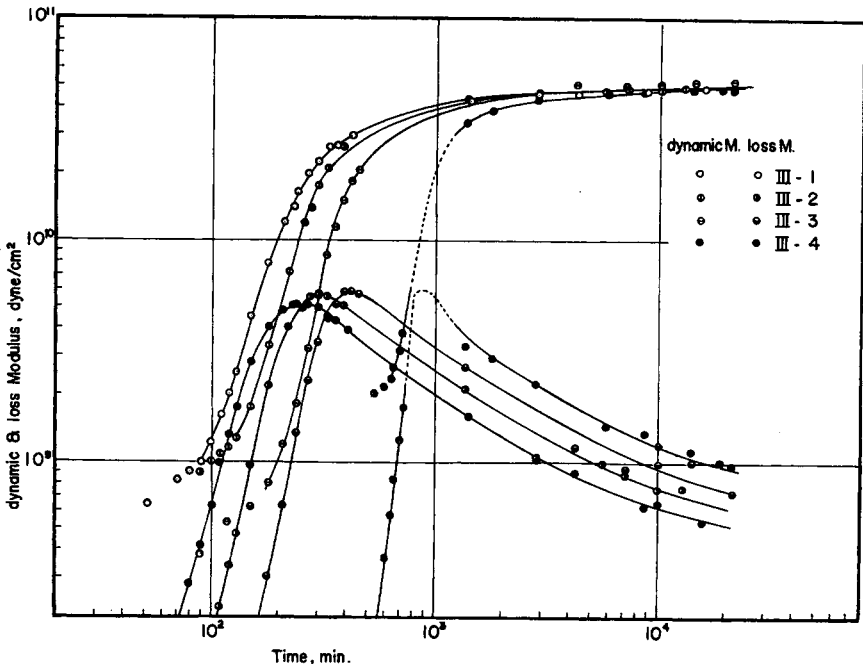Fig. 3. Dynamic and loss moduli vs. time for series II.

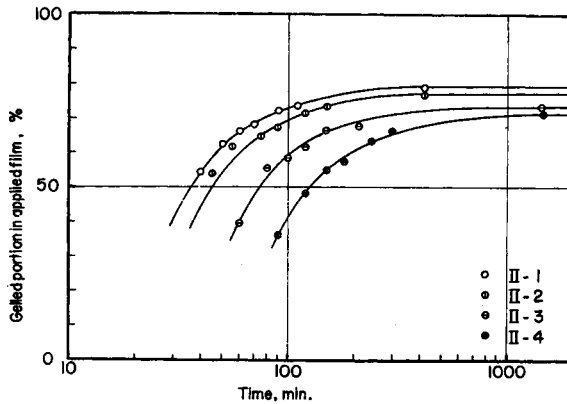Fig. 4. Dynamic and loss moduli vs. time for series III.

Fig. 5. Gel portion vs. time for series II.

The data indicating the increase of the insoluble portion in curing films with time are shown in Figure 5.   The results of plotting the corresponding values of E and E' against the amount of gelled portion are illustrated in Figures 6 and 7, respectively.   A nearly linear relationship was obtained between the amount of gelled portion and log E as well as log $E;$ except at stages of advanced cure.   The values of E and E', however, appeared to depend on the amount of gelled portion in different ways when the concentration of accelerator varied.
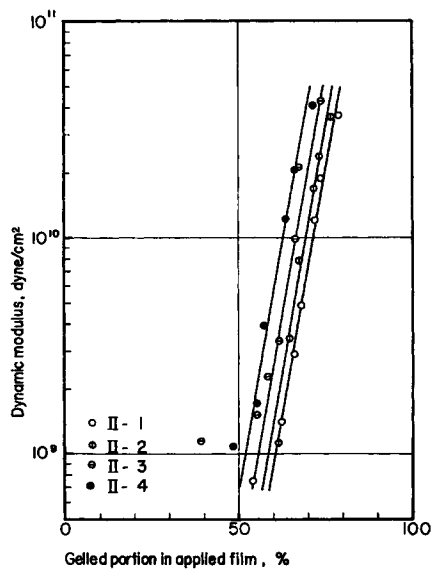
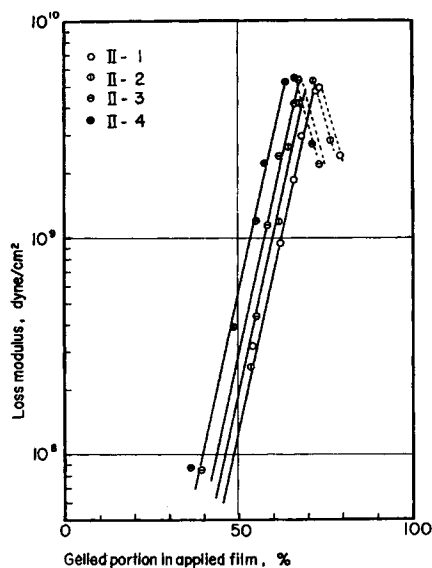Fig. 6. Dynamic modulus vs. gel portion for series II.

Fig. 7. Loss modulus vs. gel portion for series II.

DISCUSSION

The changes in dynamic or loss modulus with curing are considered useful for the purpose of analyzing the mechanism of cure of polyesters. But when a combined specimen consisting of polyester and steel is used, it can be said that the values less than 10^9 dyne/cm.^{2} for dynamic modulus and

less than 10^8 dyne/cm.^{2} for loss modulus were of uncertain character by reason of the experimental technique in itself.   Hence for determinations at early stages of cure, the values of loss modulus may be considered to be preferable.   The loss modulus of the system has been also related to the real part of the complex viscosity as

$$E' = 2\pi\nu\eta \tag{3}$$

where η is dynamic tensile viscosity.   Then the quantity $d \log E'/dt$ was used as an index representing the rate of reaction.   As shown in Table I, an interval of time over which $d \log E'/dt$ is constant was found to exist. The values of $d \log E'/dt$ in this region are listed in Table II.   In Table II the time $t_{E'}$ for which loss modulus reaches a maximum value is also shown.

TABLE II
Compositions and Curing Rates of Samples

Sample No.	MEK peroxide, g./100 g. resin soln.	Metal Co, g./100 g. resin soln.	$d \log E'/dt$, min.$^{-1}$	$t_{E'}$, min.
I-1	3.0	0.06	0.074	70
I-2	3.0	0.024	0.065	90
I-3	3.0	0.012	0.053	110
I-4	3.0	0.006	0.037	180
II-1	1.2	0.06	0.051	100
II-2	1.2	0.024	0.042	125
II-3	1.2	0.012	0.033	200
II-4	1.2	0.006	0.021	285
III-1	0.6	0.06	0.021	260
III-2	0.6	0.024	0.016	300
III-3	0.6	0.012	0.013	420
III-4	0.6	0.006	0.006	—

In Figure 8, the values of $d \log E'/dt$ mentioned above are plotted against the concentration of initiator used, employing that of accelerator as parameters.   The slopes of the dotted lines drawn in Figure 8 indicate the dependency of $d \log E'/dt$ on initiator concentration, i.e., if a curve can be drawn parallel to the dotted line C, a dependency on the square root of initiator concentration is shown to be present.

In vinyl-type polymerization, it has been said that if chain radicals disappear through bimolecular reaction the rate of polymerization should depend upon the square root of initiator concentration.[6]   In the case of this investigation, the rate of generation of radicals may be written

$$R_i = k_k[I][A]^n \tag{4}$$

where k_d is the rate constant for initiation, $[I]$ and $[A]$ represent the concentration of initiator and accelerator, respectively, and n is the order of reaction with respect to accelerator.   As shown in Figure 8, the rate of polymerization indicated by $d \log E'/dt$ seems to depend on the square root
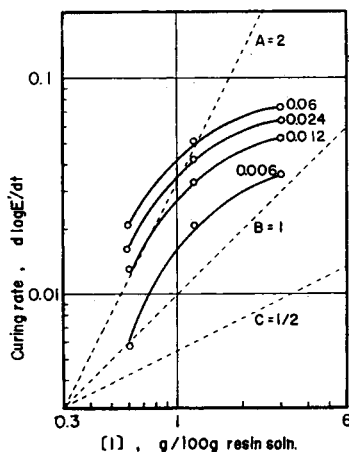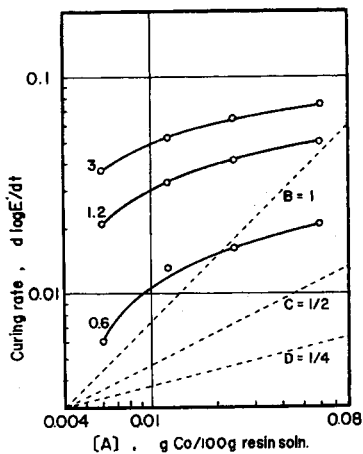
Fig. 8. Curing rate vs. initiator concentration.

Fig. 9. Curing rate vs. accelerator concentration.

of [I] in the higher concentration region, whereas at lower concentrations a dependency on one or much higher power of [I] was observed to exist. With regard to accelerator, a similar relationship can be seen in Figure 9; the quantity n, however, is assumed to be less than unity on comparing Figure 9 with Figure 8. In this study, experiments were carried out in open air because it was desired to elucidate the drying performance of polyesters as coating materials. Therefore variation of experimental conditions resulting from oxygen uptake and styrene evaporation during the cure could not be avoided. The marked delay of curing reaction observed in the low concentration regions of [I] and [A] is considered to be attributable to the unavoidable variation of experimental conditions.

In the period after the time $t_{E'}$, a notable decline of loss modulus has been shown, in spite of the insignificant change in dynamic modulus.

This suggests the continuation of reaction in the gelled state, and the difference of the reaction rate arising from the variation of [A] seems to become more distinct when less initiator was used.

As described above, it is unfortunate that a direct relationship between the gel portion of the coatings and the viscoelastic properties could not be defined.   Polyester films cured at high polymerization rate seem to require a large portion converted to gel in order to attain the same values of viscoelastic properties as films cured at low polymerization rate.   The reason for this can be interpreted partially by the fact that the polyester films dried at different rates of cure would possess different chemical compositions.[2]

CONCLUSIONS

It may be concluded that the vibrometric technique is useful for studying the reaction mechanism at the post-gelation stages of polymers.   In this region, the change in loss modulus is more marked than that in dynamic modulus.   In the pre-gelation region, however, to determine the viscoelastic behavior is difficult by reason of the technique in itself; therefore the induction period and accurate gelation time could not be obtained. The conclusions drawn from this investigation may be summarized as follows.

(1) At the early stages of cure, the logarithms of dynamic- and loss modulus increase proportionally with the increase of the portion converted to gel in an applied film.

(2) The dependency of curing rate of polyester on initiator and accelerator is found to vary with the initial concentration of each.

(3) The marked delay of curing rate observed with low initial concentrations of initiator and accelerator is considered to be attributable to oxygen uptake and styrene evaporation occurring in the course of cure.

References

1. T. Imai and T. Okawa, *J. Japan Soc. Colour Material*, **38**, 424 (1965).
2. T. Imai and T. Okawa, *J. Japan Soc. Colour Material*, **39**, 383 (1966).
3. M. Horio and S. Onogi, *J. Appl. Phys.*, **22**, 977 (1951).
4. G. W. Becker and K. Frankenfeld, *Farbe u. Lack*, **66**, 443 (1960).
5. T. Imai, *J. Japan Soc. Colour Material*, **38**, 80 (1965).
6. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 115.

Résumé

On a étudié le changement du comportement viscoélastique d'une résine de polyester insaturé à diverses phases du traitement thermique en utilisant une technique vibrométrique.   On a également déterminé la portion convertie en gel dans des film appliqués en utilisant l'extraction par solvant.   On a trouvé une réaction entre les propriétés viscoélastiques et la quantité de gel formé.   Il semble que la dépendance de la

vitesse du traitement thermique du polyester vis à vis de la concentration en initiateur et en accélérateur, n'est pas unitaire. On a également observé un certain retard de la réaction de traitement thermique lorsque la concentration en initiateur et en accélérateur est basse.

Zusammenfassung

Die Änderung des visko-elastischen Verhaltens ungesättigter Polyesterharze in den verschiedenen Härtungsstadien wurde mit einer vibrometrischen Methode verfolgt. In den verwendeten Filmen wurde auch der in ein Gel umgewandelte Anteil durch Extraktion mit einem Lösungsmittel bestimmt und es wurde eine gewisse Beziehung zwischen den visko-elastischen Eigenschaften und der Menge des Gelanteiles gefunden. Es scheint keine strenge Proportionalität zwischen der Härtungsgeschwindigkeit der Polyester und der Initiator- und Beschleunigerkonzentration zu bestehen. Im Bereich niedringer Initiator- und Beschleunigerkonzentration wurde eine ausgeprägte Verzögerung der Härtung beobachtet.