UDC 667.612. 6'13 : 536.08

Measurement of Viscoelastic Properties of Coating Films During the Curing Process by a Free Damped Oscillation Method using a Rigid-Body Pendulum

Seiji Ushiama*

Abstract

A rigid-body flexural pendulum apparatus was designed and fabricated for following the viscoelastic behavior of coating films during the curing process by the measurement of damped free oscillations. The knife-edge from which the pendulum is suspended, is immersed in a reaction mixture, and the change of the viscoelastic behavior of the specimen brings on those of the period (T) and logarithmic decrement (Δ) of the damped free oscillations of the pendulum.

The values of T and Δ obtained are related to the dynamic modulus (E') and modulus loss (E'') by the following equation:

$$E' = (I \tan \theta_1 / bh^2)[(4\pi^2 - \Delta^2)/T^2 - Mgl/I]$$

$$E'' = (4\pi I \tan \theta_1 / bh^2)\, \Delta / T^2$$

where, h and b are the thickness and width of the specimen, respectively, and M, l, I and θ_1 are the mass, length, moment of inertia, and knife-edge angle of the pendulum, respectively.

Examples, including the viscoelastic behavior of acrylic-melamine coatings during the curing process, are shown to illustrate the usefulness of the technique.

Overview

An apparatus was designed and fabricated to measure the viscoelasticity of coating films during the curing process by the measurement of damped free oscillations of a rigid-body flexural pendulum. When a coating film is formed at the rotational axis of the pendulum and the pendulum is freely oscillated, the oscillation period T and logarithmic decrement Δ of the pendulum change in response to the changes in viscoelasticity of the coating film. By treating the dynamic response of the coating film at the rotation axis of the pendulum as the oscillation movement of the pendulum, the obtained values of T and Δ were related to equations for the dynamic storage modulus (E') and the loss modulus (E'') of the coating film. By using this measurement method and these equations, the changes in viscoelasticity during the curing process of an acrylic thermosetting coating were tracked. The measured E' and E" were clearly characterized by changes in curing temperature and cross-linker system of the coating.

Furthermore, from the measured results of E'

Accepted on February 13, 1978

*Institute of Vocational Training 1960, Aihara, Sagamihara, Kanagawa

and E'' it was possible to evaluate differences in hardness of coating films that differed in curing temperature or formulation.

1. Introduction

The measurement of dynamic viscoelasticity provides important clues when tracking the mechanism of the curing process. However, the change in viscoelasticity during the curing process is extremely wide, so it is difficult to grasp all aspects by using just a single measurement method. Lewis et al.[1,2], Saxon et al.[3], Imai et al.[4,5] and Hirada et al.[6] have all reported the use of dynamic viscoelasticity to track the curing process.

In a previous report[7], the author investigated the measurement of viscoelasticity during the curing process by using the flexural pendulum method. In this method, the lower the thickness of the test piece, the more the bending of the test piece concentrates in the microscopic areas near the fixed end and it was pointed out that this oscillation resembles that of a pendulum. In addition, it was reported that it was possible to measure the viscoelasticity from the oscillation period and the logarithmic decrement, even if there were microscopic local deformations in such samples.

Therefore the author analyzed the dynamic response of coatings at the rotation axis of a rigid pendulum and then tried to measure the changes in viscoelasticity during the curing process by using the damped free oscillation of the pendulum. As a result, it became clear that the evaluation of changes in viscoelasticity during the curing process was definitely possible from the measurement of the oscillation period and logarithmic decrement of the pendulum. This method has some special characteristics. Firstly, the use of oscillation analysis, to take account of the oscillation behavior about the substrate, is not required. Secondly, the changes in viscoelasticity can be sufficiently measured on films of around only 50μm thickness. Here the author reports the measurement principles, apparatus and results.

2. Measurement principles and device

2-1. Measurement principles

Figure 1 shows the knife edge of a rigid pendulum placed on a flat substrate surface.

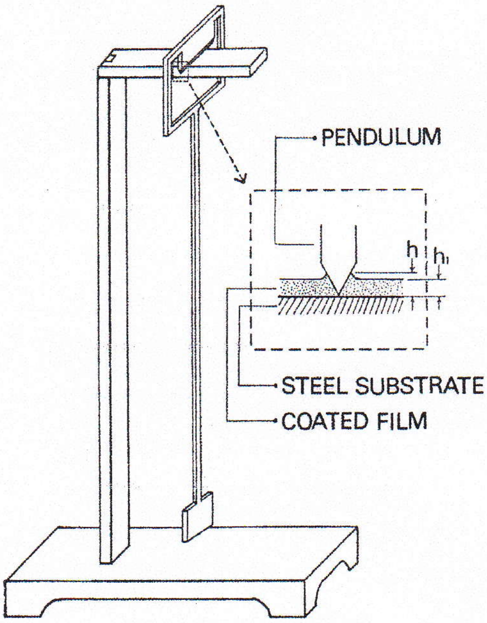

Fig. 1. Rigid-body pendulum.

At the point of contact between them the pendulum freely oscillates. When a coating material is present between the substrate surface and the knife edge, as shown in Figure 1, the oscillation of the pendulum changes in response to changes in the dynamic properties of the coating film.

If the pendulum in this system is displaced from the static point by the swinging angle θ, the coating film generates a stress perpendicular to the contact side of the knife edge in proportion to the displacement speed and displacement amount. If an oscillation model, such as that shown in Figure 2, is considered and the substrate and the pendulum are joined just like a spring , a movement equation (1) can be developed from the point of view of the rotational movement of the pendulum at the point A axis.

$$Id^2\theta/dt^2 + 2F_1 h/2\sin\theta_1 + Mgl\theta = F\sin\omega t \tag{1}$$

I: moment of inertia at the rotation axis of the pendulum
F_1: stress of the coating film over knife edges AB and AC
h: thickness of the coating film
θ_1: angle formed by the knife edge of the static pendulum and the substrate
M: mass of the pendulum
l: distance from rotation axis to the center of gravity position of the pendulum
F: external force applied to the pendulum swing
ω: angular frequency
t: time

If the fluctuation angle θ is extremely low, F_1 can be expressed by equation (2)

$$F_1 = E^* S\cos\theta_1 \cdot \theta \tag{2}$$

Here, E* is the complex modulus and is represented by $E^* = E' + iE''$, where E' is the dynamic storage modulus and E'' is the loss modulus. S is the cross-section area when the coating is considered a spring. If the width of the film coating is assumed to be b, the expression becomes $S = bh/\sin\theta_1$.
When equation (2) is inserted into equation (1), equation (1') is obtained.

$$Id^2\theta/dt^2 + (E^* S\cos\theta_1 h/\sin\theta_1)\theta + Mgl\theta = F\sin\omega t \tag{1'}$$

Since equation (1') is considered as the equation for free oscillation, equation (3) is formed when the substitutions $S\cos\theta_1 h/\sin\theta_1 = K$ and $E^* = E' + iE''$ are made.

$$Id^2\theta/dt^2 + K(E'+iE'')\theta + Mgl\theta = 0 \tag{3}$$

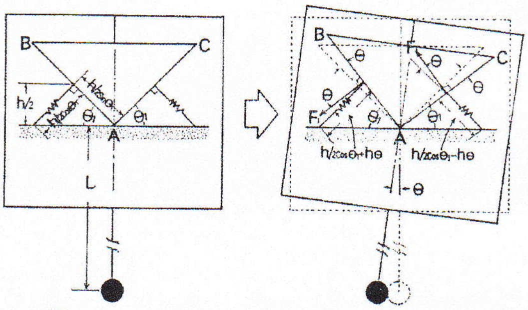

Fig. 2. Mechanical model of a rigid-body pendulum.

When E' and E'' are assumed to be independent of frequency, the solution of equation (3) is given by equation (4).

$$\theta = \theta_0 e^{-\alpha t} e^{i\omega t} = \theta_0 e^{(i\omega - \alpha)t} \tag{4}$$

By substituting this equation into equation (3), equation (5) is obtained.

$$I(\alpha^2 - \omega^2 - 2i\omega\alpha) + KE' + iKE'' + Mgl = 0 \tag{5}$$

If this equation is separated into real and imaginary numbers, equations (6) and (7) are obtained.

$$E' = (I/K)(\omega^2 - \alpha^2 - Mgl/I) \tag{6}$$

$$E'' = 2\alpha I\omega/K \tag{7}$$

Here, oscillation period T and logarithmic decrement Δ are represented by equations (8) and (9).

$$\Delta = \alpha T \tag{8}$$

$$T = 2\pi/\omega \tag{9}$$

When equations (8) and (9) are substituted into equations (6) and (7), equations (6') and (7') are obtained.

$$E' = (I/K)[(4\pi^2 - \Delta^2)/T^2 - Mgl/I] \tag{6'}$$

$$E'' = 4\pi I\Delta/KT^2 \tag{7'}$$

Next, considering the situation when the oscillation system has no coating material between the substrate and pendulum, the oscillation period T_0 of the pendulum is given by equation (10).

$$T_0 = 2\pi\sqrt{I/Mgl} \tag{10}$$

When equation (10) is transformed, $4\pi^2/T_0^2 = Mgl/I$ is obtained and therefore equation (6') becomes equation (11).

$$E' = (I/K)[(4\pi^2 - \Delta^2)/T^2 - 4\pi^2/T_0^2] \tag{11}$$

Furthermore, since $\Delta^2 << 4\pi^2$, equation (11) can be approximated to equation (12).

$$E' = (4\pi^2 I/K)[1/T^2 - 1/T_0^2] \tag{12}$$

In order to measure and evaluate the relative change in the viscoelasticity, the relative values of E' and E'', namely Er' and Er'' can be obtained from equations (13) and (14) by setting a reference point.

$$Er' = (1/T^2 - 1/T_0^2)/(1/T_1^2 - 1/T_0^2) \tag{13}$$

$$Er'' = T_1^2\Delta/T^2\Delta_1 \tag{14}$$

T_1: oscillation period of the pendulum at the reference point
Δ_1: logarithmic decrement of oscillation at the reference point

As shown above, it is possible to measure the viscoelasticity during the curing process by treating the dynamic response of the coating as an oscillation movement of the pendulum.

2.2 Overview of the measurement device

Figure 3 shows the structure of the measuring system. This measuring system was designed and fabricated for the purpose of measuring the viscoelasticity of thermosetting coatings during the curing process.

The measurement procedure is as follows.

On the hotplate ③, place a test piece ② (cold rolled steel plate, 20 x 5 x 0.8 mm) on which the test sample ① is coated.

Next, place the knife edge of the rigid pendulum ④ perpendicular to the coating surface as shown in Figure 1.

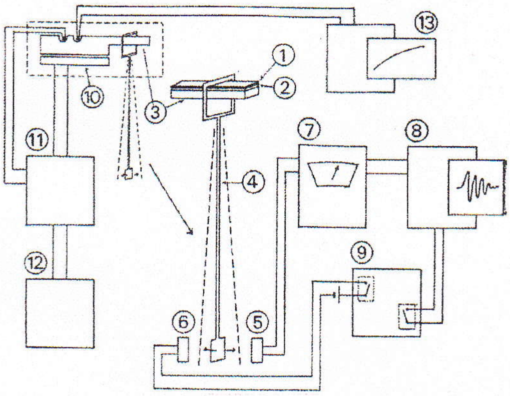

Fig. 3. Block diagram of the measuring system.
1. coated film.
2. steel substrate.
3. hot plate.
4. pendulum.
5. probe.
6. magnetic coil.
7. detector.
8. oscillograph.
9. timer.
10. heater.
11. thermostat.
12. transformer.
13. recorder.

After setting the pendulum, leave the test sample at room temperature for a fixed period in order to volatilize the solvent in the test sample.

Then, begin to heat the hotplate and periodically measure the changes in T and Δ of the pendulum during the curing of the sample.

The measurement of oscillation is similar to that previously reported.[7] Displacement of the lower end of the pendulum is detected by a probe ⑤ and displacement gauge ⑦ and recorded by the oscillograph with an electromagnetic pen ⑧. Excitation of the pendulum is performed by providing electricity to the electromagnet ⑥. The timer ⑨ automatically controls the excitation of the pendulum and the recording of oscillation.

The hotplate ③ is heated by a nichrome heater (300W) ⑩. The heating temperature is controlled by a thermistor ⑪ (TP-673 from Iuchi Seieido Co., Ltd.). A transformer ⑫ is used to control the rate of temperature increase. The plate temperature is recorded by an equilibrium recorder ⑬.

3. Determination of the measurement conditions

Changes in oscillation period T and logarithmic decrement Δ of the pendulum which occur in response to the change in viscoelasticity of the coating film are affected by the size of the pendulum (M, l, θ_1) and shape of the test sample (b, h). For this measurement method, the changes in T and Δ should be as large as possible in order to best evaluate the change in viscoelasticity of the test sample

By substituting the functions $K = S\cos\theta_1 h/\sin\theta_1 = bh^2/\tan\theta_1$ and $I = T_0{}^2Mgl/4\pi^2$ into equation (12), equation (15) is obtained.

$$T_0/T = \sqrt{(E'bh^2/Mgl\tan\theta_1) + 1} \tag{15}$$

Equation (15) shows that the oscillation period of the pendulum changes in response to the factor $E'bh^2/Mgl\tan\theta_1$, that is determined by b, h and E' of the sample and M, l, and θ_1 of the pendulum.

Under measurement conditions where $E'bh^2/Mgl\ \tan\theta_1 \ll 1$ it is impossible to determine the dynamic storage modulus of the test sample from the oscillation cycle because T is approximately equal to T_0. Figure 4 shows the relationship between E' and T of the sample using equation (15). When E' of the sample decreases, T gradually nears T_0 until they are finally about the same value. Furthermore, the range in which the values of T and T_0 become almost the same depends largely on the measurement conditions. Figure 4 shows that the larger the Mgl value of the pendulum used for measurement, the larger the range of E' where T is approximately T_0. This is also true if the bh^2 value of the measurement sample is decreased.

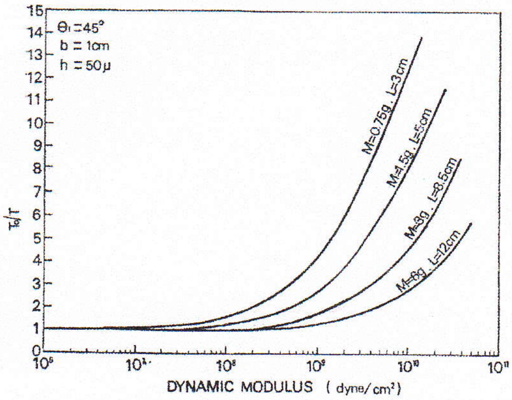

Fig. 4. Relation between the period (T) and dynamic modulus of damped free oscillation calculated according to Eq (15).

Next, exchanging the dynamic viscosity of the sample for η', and substituting the relationship $E'' = 2\pi\eta'/T$ into equation (7) produces equation (16).

$$\Delta = \eta' T b h^2 / 2 I \tan\theta_1 \qquad (16)$$

Logarithmic decrement Δ is determined by b, h and η' of the sample and T, I and θ_1 of the pendulum. When the measurement conditions are such that the pendulum is large and bh^2 of the sample is small, Δ becomes extremely small and the measurement sensitivity decreases. Conversely, when the measurement conditions are such that the pendulum is small and bh^2 of the sample is large, free oscillation conditions are no longer satisfied and the measurement is essentially impossible if the η' of the sample is large.

With this measurement method, it is necessary to determine the pendulum size (M, l, θ_1) and sample shape (b, h) that matches the range in which the viscoelasticity of the measured sample changes. Equation (15) is used to check the measurement conditions. If measurement conditions are such that T is close to T_0, E' cannot be calculated. Therefore, measurement of E' requires measurement conditions where T_0/T is greater than 1. In practice, as there are some measurement errors in T, the setup requires measurement conditions such that T_0/T is equal to or greater than 1.005. This necessitates that $E'bh^2/Mgl\tan\theta_1$ in equation (15) is equal to or greater than 0.01. Accordingly, the measurement range of E' by this measurement method is approximated by equation (17).

$$E' \geqq 0.01 Mgl \tan\theta_1 / bh^2 \qquad (17)$$

The measurement conditions are checked using the relationship shown in equation (17). The measurement of the change in viscoelasticity shall be performed on a coating film having an E' value greater than 1×10^6 dyne/cm^2 and a shape that is similar to an actual coating film. If the conditions of the pendulum used in the measurement are set using $E' = 1 \times 10^6$ dyne/cm^2, $h = 50\mu$m and $b =$

1cm, $Mgl \tan\theta_1$ is less than or equal to 2.5 x 10^3dyne・cm. Here, if $\theta_1 = 45°$, Ml is less than or equal to 2.6g・cm and the size range of the pendulum can roughly be determined.

Pendulum design and prototyping were done based on these results. The conditions of the prototype were as follows: $\theta_1 = 60°$, $M = 0.9$g, l = 7.2cm. This pendulum had a T_0 of 0.655s and a moment of inertia around the rotation axis of about 68dyne・cm. The oscillation of the prototype pendulum on steel substrate alone due to air viscosity and friction had a logarithmic decrement Δ_0 of about 0.015 but this value was ignored when obtaining equation (7).

4. Measurement results and observations

4.1. Oscillation period T and logarithmic decrement Δ

An acrylic thermosetting coating was chosen for the measurement sample and the changes in viscoelasticity during the curing process were measured as changes in T and Δ of the pendulum. Before measurement, a test piece was coated and then left at room temperature for 30 minutes. Next, a hot plate was heated and the changes in T and Δ were measured. An example of the results is shown in Figure 5. In this measurement the curing temperature was set at 140 °C and was kept for around 60 minutes. The measurement sample was an acrylic thermosetting coating which was cross-linked with epoxy modified melamine resin. The coated thickness h_1 of the measurement sample was 75µm and the sample width was 0.5cm.

As shown in Figure 5, the temperature of the sample starts to rise in the 3 minutes after the start of heating. After these 3 minutes the curing process begins. No change in T was seen during the heating-up stage and T was about equal to T_0. About 3 minutes after the temperature of the hot plate reached the curing temperature, T gradually decreased. Δ gradually decreased during the heating-up stage and then conversely increased when the curing temperature was reached. The dotted portion of the Δ line in Figure 5 is the measurement range where $\Delta = \Delta_0$.

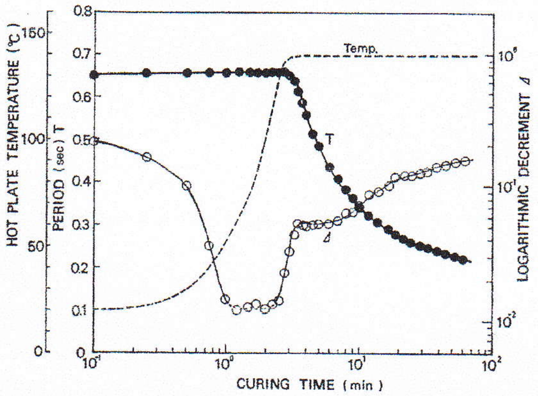

Fig. 5. Changes of the period (T) and the logarithmic decrement (Δ) of epoxy modifid acrylic melamine coating during the curing process.

The degree of curing occurring during the heating-up stage is considered to be quite small. Accordingly, the changes in T and Δ in these 3 minutes can be considered the responses to the changes in viscoelasticity of the sample that accompany the increase of the temperature. Furthermore, the changes in T and Δ beyond 3 minutes can be considered the responses to the changes in viscoelasticity that accompany the curing of the sample.

4.2 Dynamic storage modulus E' and dynamic loss modulus E''

Figure 6 shows the changes in E' and E'' of the sample determined from the values of T and Δ shown in Figure 5. In this study it was difficult to accurately measure the film thickness *h* at the knife-edge portion of the pendulum. Therefore, the change in viscoelasticity was denoted as a relative value using equations (13) and (14). The result where the standard point was set at 30 minutes after the start of heating is shown in Figure 6.

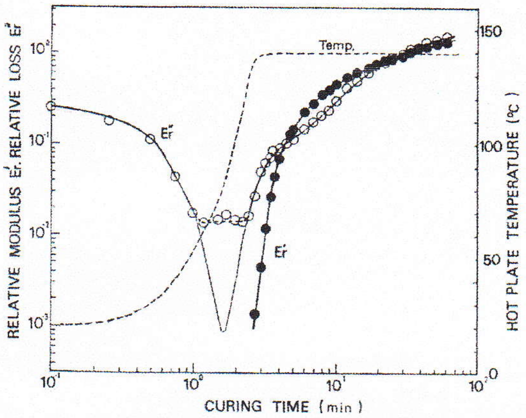

Fig. 6. Viscoelastic properties during cure of epoxy modified acrylic melamine coating at 140°C.

In Figure 6, the first 3 minutes represent the heating-up stage and the sample viscosity and elasticity decrease. In this measurement, the change in the viscoelasticity during the heating-up stage could not be measured except for a portion of the changes in the viscosity because *T* was around T_0 or Δ was around Δ_0 as shown in Figure 5. After 3 minutes the curing process started and the sample viscosity and elasticity increased greatly. As seen in Figure 6, the change in viscoelasticity accompanying this curing was observed as clearly characterized changes in Er' and Er".

As mentioned earlier, the degree of curing occurring during the heating-up stage is considered to be quite small. Accordingly, the changes in *Er'* and *Er"* measured from 3 minutes onwards as shown in Figure 6 are considered to represent the entire curing process of the sample. However, the change in viscoelasticity during the heating-up stage could not be measured except for a portion of the change in viscosity. This was a problem caused by the measurement conditions. When aiming to measure the small changes in viscoelasticity in such a heating-up process, it will in future be necessary to select a bigger value of $bh^2/Mgl\tan\theta_1$ (equation 15) than that used in this study in order to increase the sensitivity of measurement. By increasing the sensitivity of measurement it may be possible to measure the changes in *Er"* shown as the dotted curve estimated in Figure 6.

Next, the change in viscoelasticity indicated by the changes in relative values as shown in Figure 6 was investigated in terms of *E'* and *E"*. The measurement sample was cured for 60 minutes at 140 °C and the film was isolated. *E'* and *E"* of the film at 140 °C were measured using a Rheovibron DDV-II-C (Toyo Baldwin KK), a direct reading dynamic viscoelastometer. At a measurement frequency of 3.5Hz, *E'* was 4 x 10^8dyne/cm^2 and *E "* was 9 x 10^6dyne/cm^2 at 140 °C. Furthermore, sample T_g was 68 °C. Here, *E'* and *E "* measured by a direct reading dynamic viscoelastometer were equated to *Er'* and *Er"* at 60 minutes in Figure 6 and the change in viscoelasticity shown in Figure 6 replaced the change of *E'* and *E"*. The dynamic storage modulus shown in Figure 6 changed in the range of around 5 x 10^5dyne/cm^2 to 4 x 10^8dyne/cm^2. The dynamic loss modulus is considered to change at around 9 x 10^4dyne/cm^2 to 9 x 10^6dyne/cm^2. This shows that the changes in viscoelasticity during the curing process determined by this method are comparatively small.

Next, measurement reproducibility will be discussed. Measurement reproducibility was investigated by curing an identical sample under identical conditions. Results of the repeated measurements are shown in Figure 7. Although an identical sample was cured under identical conditions, viscoelastic changes were slightly different. This is likely to be the result of slight differences in the curing conditions which subtly influenced the changes in viscoelasticity during the curing process.

4.3 Changes in viscoelasticity of an acrylic thermosetting coating during the curing process

The changes in viscoelasticity during the curing process were measured while changing the curing temperature and the coating formulation of the acrylic thermosetting coating.

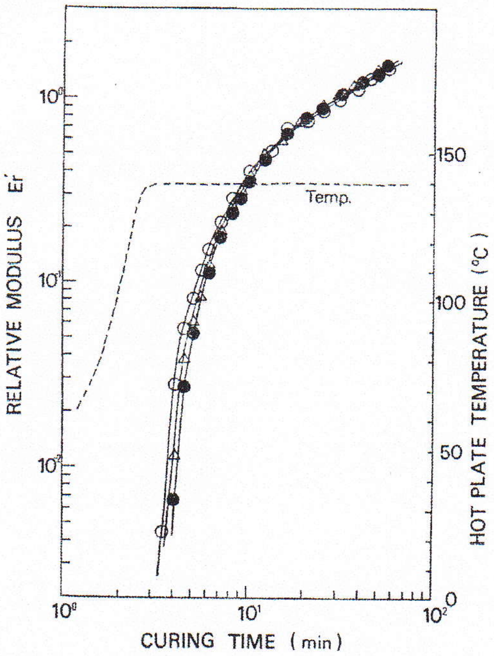

Fig. 7. Reproducibility of the measurements of dynamic modulus on the same batch of epoxy modified acrylic melamine coatings under the same curing conditions.

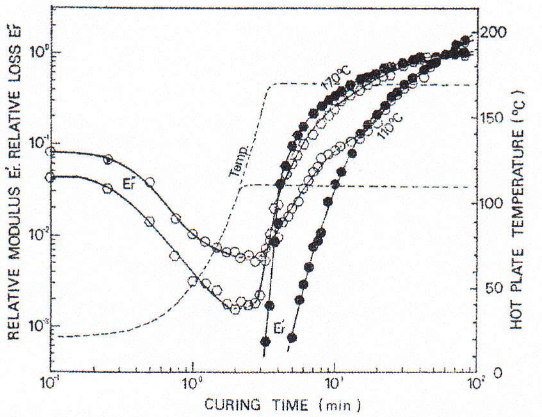

Fig. 8. Viscoelastic properties during cure of epoxy modified acrylic melamine coatings at various temperatures.
○● : 110°C ○● : 170°C

Samples were acrylic thermosetting coatings based on an acrylic copolymer of hydroxyethyl methacrylate, butyl methacrylate and acrylic acid, with differing compositions of epoxy modified melamine resin, hexamethylolmelamine, isobutylated melamine, etc.

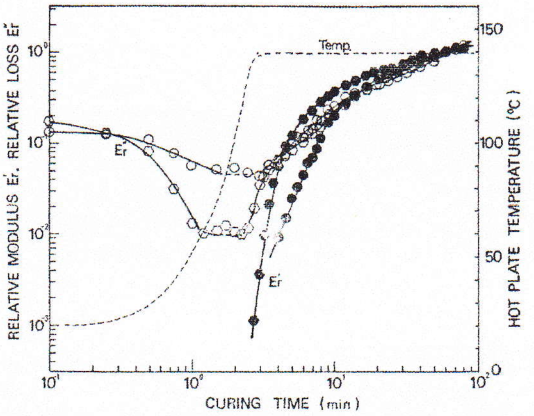

Fig. 9. Viscoelatic properties during cure of epoxy modified acrylic melamine coatings at 140°C.
○● : Acrylic/Epoxy modified melamine (70/30 wt%)
○● : Acrylic/Epoxy modified melamine (80/20 wt%)

Figure 8 shows the differences in the change in viscoelasticity caused by varying the curing temperature. The measurement sample was an acrylic/epoxy modified melamine coating (70/30% by weight). The diagram shows the curing reaction for 60 minutes. Curing was almost completed at 170 °C but was still continuing at 60 minutes in the case of 110 °C. Figure 9 shows the measurement results of samples with different melamine resin content. The measurement samples were similar to those for Figure 8. At a lower melamine resin content, the curing was somewhat delayed and the change in the relative dynamic storage modulus grew smaller. Figure 10 and 11 show the results for Er' and Er" for coatings formulated with various types of melamine resin. The differences of Er' and Er" between hexamethoxy methyl melamine and isobutylated melamine are shown in Figure 10 and the differences between two types of hexamethoxy methyl melamine with mineral spirit tolerances (MST) of 0 and 0.5 are shown in Figure 11. The results show that the curing of the coatings formulated with hexamethoxy methyl melamine was slower than those with isobutylated melamine or epoxy-modified melamine. Furthermore, when the same type of melamine resin was used, the differences in chemical structure, expressed as differences in MST, were associated with differences in the curability.

The results shown in Figures 8 to 11 sufficiently demonstrate the changes in viscoelasticity during the curing process of acrylic thermosetting coatings. As mentioned earlier, these results show that it is possible to investigate the curing behavior of coatings caused by differences in the coating formulations as well as the curing conditions. It is believed that the use of this method to track the changes in the viscoelasticity provides useful data for the elucidation of the curing mechanisms of coatings.

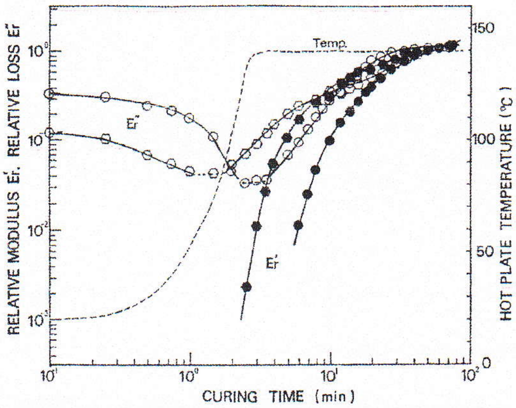

Fig. 10. Viscoelastic properties during cure of acrylic-melamine coatings at 140°C.
○● : Acrylic/Hexamethoxy methyl melamine (75/25 wt%)
○● : Acrylic/Isobutylated melamine (75/25 wt%)

5. Conclusion

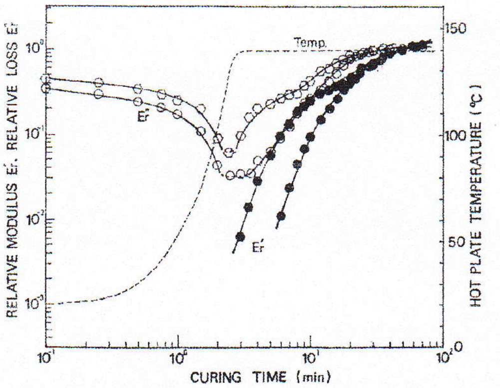

Fig. 11. Viscoelastic properties during cure of acrylic-hexamethoxy methylol melamine coatings at 140°C.
●○ : Mineral spirit tolerance 0
○● : Mineral spirit tolerance 0.5

The theory, apparatus and interpretation of results related to the measurement of viscoelasticity during the curing process as a dynamic response of a coating at a pendulum knife edge still requires further discussion. However, this simple method is able to detect the change in the viscoelasticity of the coating film during the curing process with a high degree of sensitivity. It can also measure changes in viscoelasticity using sample shapes similar to actual coatings but does not need oscillation analysis to take account of the oscillation behavior about the substrate as is required by traditional methods. Furthermore, it is possible to evaluate the cross-linking state from the changes of the dynamic modulus during the curing process because the measured dynamic modulus can be considered to lie roughly in the rubber elastic region. This means that tracking the cross-linking of coatings is comparatively easy.

It is believed that with further investigation of measurement conditions and mechanisms, this method can be a useful method with which to measure the viscoelasticity during the curing process over a wide measurement range. Furthermore, it is clear that this measurement method can be applied not only to coatings, but also for comparatively large samples such as putty, adhesive and cement materials.

Acknowledgements

The author wishes to thank Takeyuki Tanaka of Nippon Oil and Fats Co., Ltd. for help and to thank
Nippon Oil and Fats Co., Ltd. for providing measurement samples.

References

1. A. F. Lewis, J. K. Gillham : *J. Appl. Polymer Sci.*, 6, 422 (1962)
2. J. K. Gillham, A. F. Lewis : *J. Appl. Polymer Sci.*, 7, 685 (1963)
3. R. Saxon, F. C. Lestienne : *J. Appl. Polymer Sci.*, 8, 475 (1964)
4. Takeo Imai : Colour material, 38 [2], 80 (1965)
5. Takeo Imai, Toshio Okawa : Colour material, 38 [10], 424 (1965)
6. Sadao Hirata, Akira Kishimoto : Colour material, 42 [10], 463 (1969)
7. Seiji Ushiama : Colour material, 51 [1], 10 (1978)