Rheological Properties of Coatings During Drying Processes

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Synopsis

Coatings such as paints and printing inks transferred on substrates change from viscous liquids to viscoelastic solids during drying processes and finally become a hardened film. In order to investigate more precisely the viscoelastic properties of coatings during liquid-to-solid conversion, we developed the same type of ultrasonic rheometer as employed by Mason et al., in which the reflection coefficient technique is utilized. The complex modulus can be determined by the reflection coefficient and the phase shift. Using this rheometer, we can obtain the viscoelastic properties of coatings at various stages of drying at infinitesimal shear strain at the frequency of 3 MHz.

The viscoelastic properties of a commercial offset litho ink which was dried by oxidative polymerization were measured at various temperatures. From the results of viscoelastic measurements, the drying of ink seems to be accelerated remarkably with increasing temperature. As the drying processes progress, a three-dimensional network structure may be formed in the ink film with the aid of oxidative polymerization. The drying-time dependence of G' is different from that of G''. From the drying-time dependences of G' and G'', we can quantitatively deduce the internal structure of printing ink films during drying processes and provide a physical explanation for various drying stages. The dispersed pigments in a coating seem to play an important role in film formation and affect the mechanical properties of the drying film.

INTRODUCTION

Coatings such as paints and printing inks transferred on substrate change from viscous liquids to viscoelastic solids during drying processes and finally become hardened films. Previously, we reported this phenomenon as viscoelastic transition processes, and succeeded in interpreting the change of mechanical properties of ink films at various stages of drying processes with physical quantities such as sound velocity and coefficient of ultrasonic attenuation.[1-3] In order to investigate more precisely the drying mechanisms of coating, it is necessary to measure continuously the viscoelastic properties of coatings changing from the liquid to the solid state, with a rheometer. Mason, Baker, McSkimin,[4] and Barlow and collegues[5-6] presented an acoustic technique, using a fused-quartz delay line, in order to investigate these viscoelastic properties. The storage modulus G' and loss modulus G'' can be determined by measuring the reflection coefficient and phase shift. Myers and co-workers measured the change of the reflection coefficient during the drying process for various coatings, using an apparatus of the same design.[7-8] They pointed out that the ultrasonic attenuation becomes progressively larger with drying of the coatings.

However, in order to investigate precisely the structural change of coatings during drying, quantitative evaluation of viscoelastic properties is necessary. Not only the storage modulus but also the loss modulus for the coatings must be examined.

We have developed the same type of ultrasonic rheometer by the aid of recent electrocircuit and microcomputer techniques, so that accurate measurements of the reflection coefficient and phase shift during film drying can be performed automatically.

Our apparatus has the following characteristics: Because the measurements are performed in the ultrasonic frequency region, an instantaneous alteration of mechanical properties can be detected. The formation of a three-dimensional network structure in coatings may not be affected by the periodic strain, as the applied shear strain is infinitesimal. Furthermore, viscoelastic properties of coatings can be determined independently of the mechanical properties of substrate. As a result, we can evaluate more precisely the viscoelastic properties of coatings at various stages of drying and then clarify the drying mechanism of coatings.

In this study, the viscoelastic properties of a commercial offset litho ink are investigated. Many offset litho inks are dried with the aid of oxidative polymerization. As the drying processes progress, a three-dimensional network structure may be formed in the ink film. From the viscoelastic measurements, we intend to determine quantitatively the relation between the viscoelastic properties and the internal structure of printing ink films during drying processes, and to provide a physical explanation for various drying stages.

EXPERIMENTAL

Measurement

Briefly, the principles of the measuring technique are as follows: If a shear wave is reflected at a solid/liquid interface at oblique incidence with the direction of vibration parallel to the interface, the characteristic mechanical shear impedance of sample Z_L can be given by eq. (1) as a function of the magnitude of the reflection coefficient (R) and phase change (θ) caused by application of the liquid.[9]

$$Z_L = R_L + iX_L = Z_Q \cos\phi \, (1 - R^2 + 2iR\sin\theta)/(1 + R^2 + 2R \cos\theta) \quad (1)$$

where Z_Q is the shear mechanical impedance of solid (fused quartz), and ϕ is the angle of incidence. Assuming a plane shear wave, the complex shear modulus G^* of liquid can be represented by

$$G^* = G' + iG'' = Z_L^2/\rho \quad (2)$$

where ρ is the density of the medium. Therefore, the real and imaginary parts of the shear modulus are given as follows:

$$G' = Z_Q^2 \cos^2\phi[(1-R^2)^2 - 4R^2\sin^2\theta]/\rho(1+R^2 + 2R \cos \theta)^2 \quad (3)$$

$$G'' = Z_Q^2 \cos^2\phi[4R(1-R^2) \sin \theta]/\rho(1+R^2 + 2R \cos \theta)^2 \qquad (4)$$

A schematic diagram of the measuring system is given in Figure 1. This system permits measurements of the changes of the reflection coefficient and the phase when an ink is applied to the reflecting surface of a fused-quartz bar. Rectangular Y-cut quartz crystal plates are bonded to each end of the fused-quartz bar with silver solder. The quartz transducers resonate in the thickness-shear mode of vibration at 3 MHz. Displacement in the wave is perpendicular to the plane of the paper. The basic frequency of 3 MHz is generated by a highly stable synthesizer. The continuous wave is gated to form a modulated high-frequency pulse of some 13.5 μs in duration by a transmitter gating circuit, and the output of this unit is amplified and applied to a quartz crystal transducer. After propagation through the fused-quartz bar, the shear wave is received by a second transducer at the opposite end. The pulse envelope of the receiving signal is obtained through a filter, and its amplitude is determined by a voltmeter using a peak-detecting circuit. The magnitude and phase of the received signal changes with the viscoelastic properties of the ink film on the fused-quartz bar. For the measurement of phase shift, a reference signal is derived from an identical fused-quartz bar used as a fixed delay line. The pulse from the reference bar opens the gating circuit of the counter, and the pulse from the test bar closes this gating circuit. Therefore, we can determine the phase change from the time interval between two signals. Using a high-resolution universal counter (Takeda Riken Co. Ltd., TR-5830), we can measure the time interval with the precision of 100 ps, so that the phase shift can be detected to a precision of about 1°. The digital data from the voltmeter and the universal counter are transferred into a personal computer through a general-purpose interface bus (GP-IB). The values of R_L and X_L for the mechanical shear impedance of the ink film are predominantly determined by the changes in amplitude and phase, respectively. From these values, the complex shear modulus of the sample ink can be calculated.

Material

A commercial offset litho printing ink for printing on plastic film (POP Yellow, Dainippon Ink Kagaku Kogyo Co. Ltd.) was used as the sample. This printing ink is dried by oxidative polymerization and does not contain
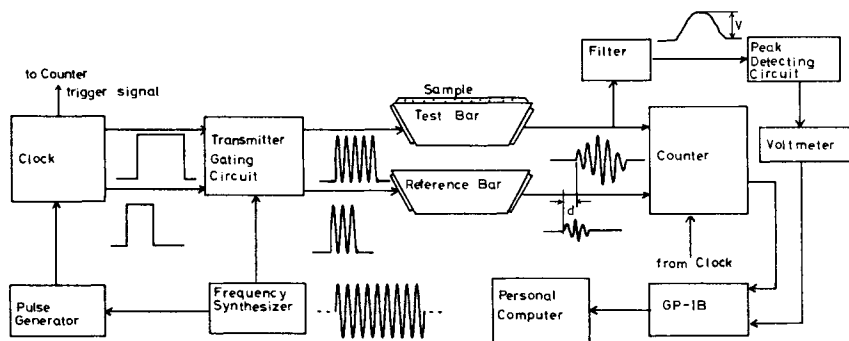

Fig. 1.   A schematic diagram of a measuring system for determination of the viscoelastic properties at a frequency of 3 MHz.

any nonvolatile component such as mineral oil. (Such a component can migrate preferentially to the interface between the fused quartz and the ink film during ink drying and cause undesirable effects in the measurements.) From the theory of the plane wave reflection method, the medium must be isotropic and have a large attenuation per wavelength. The 10-μm thickness of sample layer is assumed to be sufficient to attenuate the shear wave. Experiments were carried out with film thicknesses ranging from 20 to 40 μm and with drying at various temperatures (30–50℃). In order to confirm the accuracy of this method, two kinds of liquid are examined. One is a typical Newtonian liquid, which is usually used to calibrate an apparatus (Syowa Sekiyu Co. Ltd., JS 50 - JS 2000). The other is an epoxy resin adhesive (Cemedaine Co. Ltd., High Super).

RESULTS AND DISCUSSION

Evaluation of the Dynamic Shear Viscosity of a Newtonian Liquid

Several precautions are required to ensure reliable measurements. To get accurate data, adequate temperature stabilization of the acoustic system and also stabilization of the electronic apparatus are most important. The fused-quartz delay line is placed in a water jacket, where water at a constant temperature is circulated. The temperature of the sample is controlled with a precision of 0.1℃ and is monitored by the output voltage from a thermocouple attached to the fused-quartz delay line.

Figure 2 shows the relation between dynamic viscosity, η', measured by the reflection coefficient technique and steady-state viscosity η for viscosity-standard liquids. The values of η' and η seem to agree well with each other. For viscosity-standard liquids with higher viscosity, the value of η' is somewhat smaller than that of η. This phenomenon may be attributed to viscoelastic relaxation of the standard liquids. From these results, the accuracy of the present technique is assumed to be satisfactory.

The Effect of Temperature on the Drying of Printing Ink

The sample ink was coated on the surface of fused quartz with a thickness of 30 μm and dried at temperatures ranging from 30° to 50℃. Figures 3 and 4 show the plots of values for the reflection coefficient and phase shift, respectively, versus the drying time (t_d) at various drying temperatures. The values of R measured immediately after coating seem to be constant. However, with increasing drying time, the R values decrease rapidly and then increase again after showing a minimum. With decreasing temperature, the minimum shifts to longer drying time, and the change in R becomes slower. On the other hand, the values of θ decrease slightly at the initial stage of drying. After a certain period, the values of θ increase abruptly, but finally an equilibrium is reached. The region preceding the drastic changes of R and θ may correspond to the induction period for oxidative polymerization. Because this method is based upon the measurement of the complex reflection coefficient of an incident shear wave at a solid (fused quartz) – liquid (sample) interface, the values of R and θ are
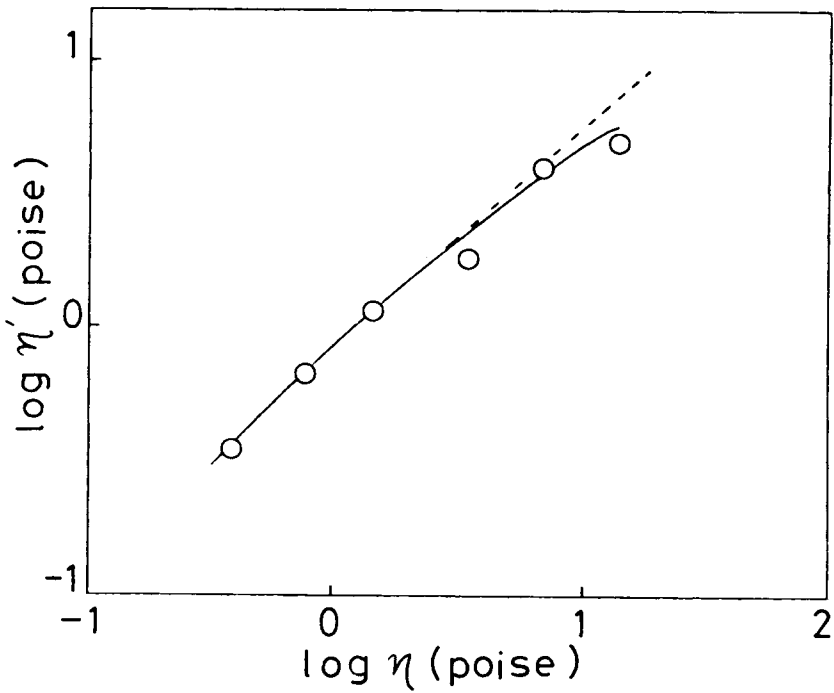
Fig. 2.   The relation between dynamic viscosity measured at 3 MHz by the reflection coefficient technique, and steady-state viscosity for a viscosity-standard liquid.
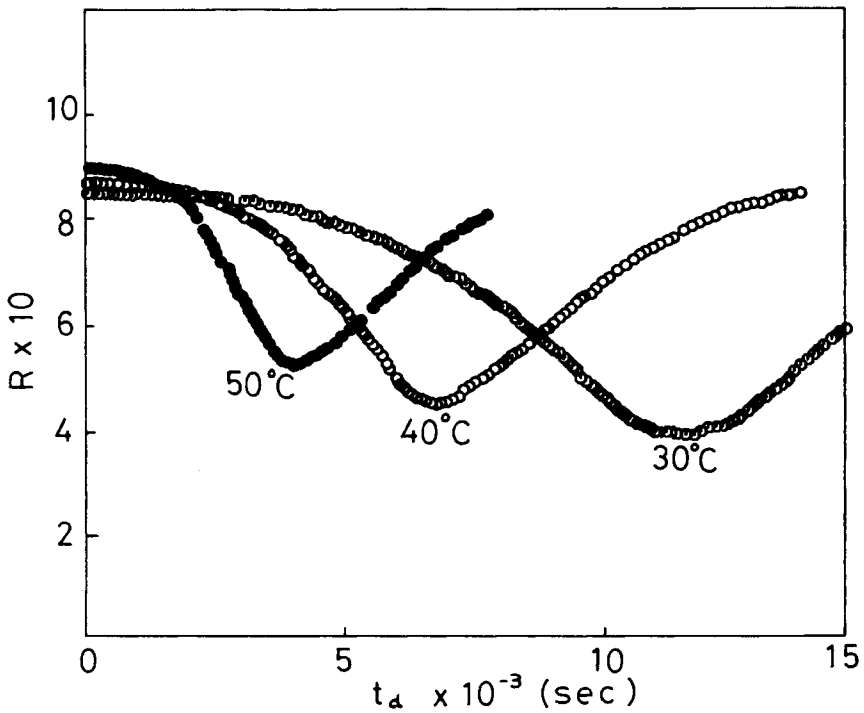

Fig. 3.   Drying-time dependences of the reflection coefficient for a printing ink at the various temperatures shown.
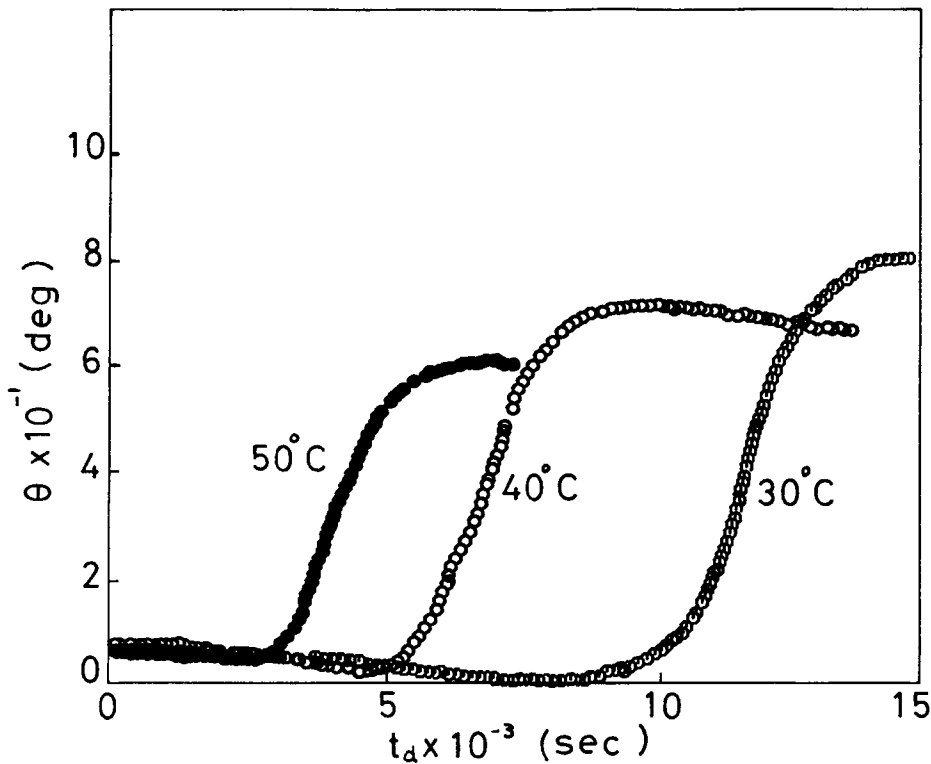
Fig. 4. Drying-time dependences of phase shift for a printing ink at the various temperatures shown.

remarkably affected by the drying stage of the boundary ink layer. Therefore, the drastic change in R and θ can be explained as follows: Oxidative polymerization, which starts at the surface of the ink film, reaches the interface between film and fused quartz, and the three-dimensional network structure becomes denser in the ink film. On the other hand, the increase of R and the existence of an equilibrium value of θ in the longer-drying-time region can also be explained as follows: From the theory of the plane wave reflection method, the measuring medium should be isotropic and should have a large attenuation per wave length. The well-dried part at the surface of the ink film seems to be more rigid and to have less attenuation. Therefore, diverging or secondary reflection of a plane wave may occur. Furthermore, the film-forming process is accompanied by shrinkage of the film itself and fails to establish intimate contact with the fused-quartz surface, as pointed out by Myers and Schultz.[7] These effects appear as undesirable components which are superimposed on an output signal, and the accuracy of phase measurements may be extremely restricted. Therefore, we excluded this region in the following studies of the viscoelastic properties of ink films in the course of drying; i.e., data in the increasing R region was disregarded.

Figures 5 and 6 show the drying-time dependences of G' and G'' at various temperatures. In Figure 5, the values of G' increase with drying time. At the initial drying stage, the value of G' is larger for lower temperatures.

In this drying stage, the density of the structural networks may be similar in each film. Therefore, the value of G' depends mainly on temperature. However, with increasing drying time, the G' value for higher temperatures increases more rapidly. The same tendency is observed in Figure 6. In this figure, at the initial drying stage, the values of G'' are not only independent of drying time, but also show a minimum before they increase abruptly. The time at which G'' increases abruptly, shifts to a shorter drying time with increasing temperature. From these results, the drying of ink seems to be accelerated remarkably with increasing temperature. With the progress in the drying processes, a three-dimensional network structure may be formed in the ink film with the aid of oxidative polymerization, and thus the soft ink layer turns to a hard, solid film. The drying-time dependence of G' is different from that of G'', especially at the initial drying stage; thus, the region where the value increases remarkably is observed at an earlier drying time for G', and the value of G'' is comparatively constant irrespective of temperature but decreases temporally before the abrupt increase occurs. It is thought that these phenomena are attributed to the peculiarity of an internal structure or temporary nonuniformity of the ink film, in which an uncured part remains in the inner part of the ink film as a sol fraction.

Curing Process of Epoxy Resin Adhesive

Figure 7 shows logarithmic plots of G' and G'' versus elapsed time after a curing agent for the epoxy resin adhesive is added. Measurement was carried out at a temperature of 30°C. Initially, the value of G' increases
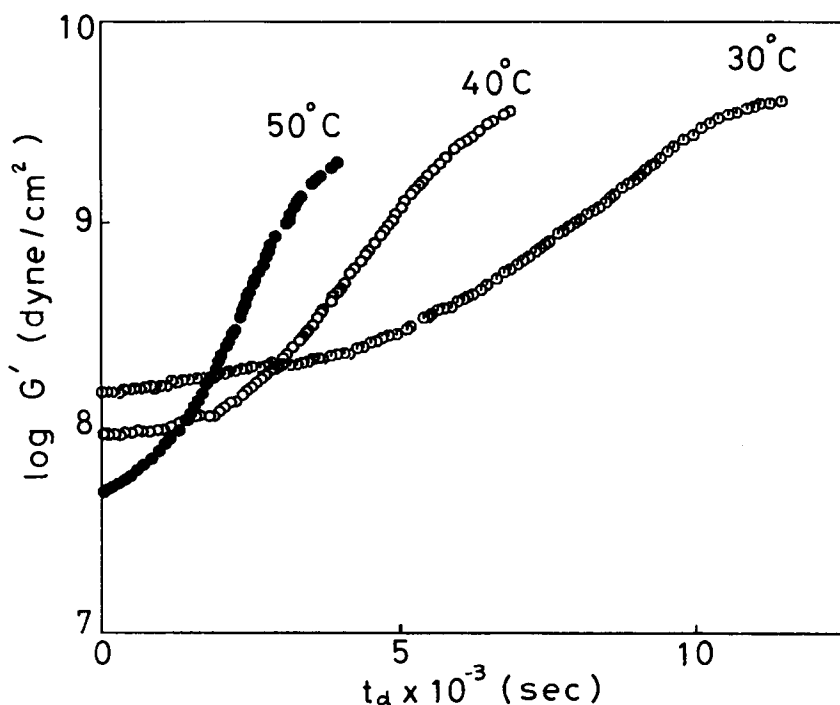

Fig. 5.   Drying-time dependences of G' at 3 MHz for the various temperatures indicated.
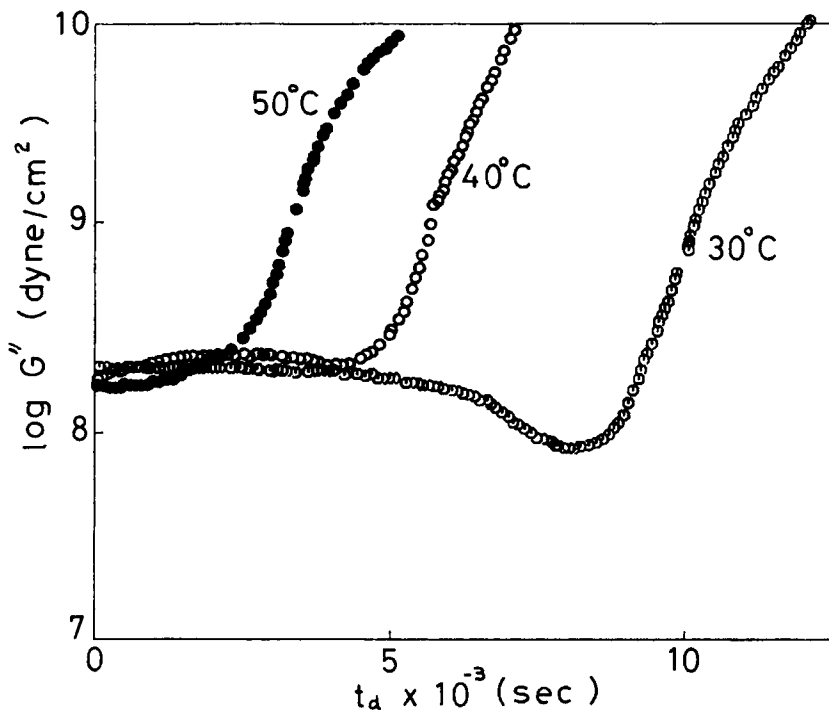
Fig. 6. Drying-time dependences of G'' at 3 MHz for the various temperatures indicated.

markedly. However, after 500 s, it increases more slowly. On the other hand, the time dependence of G'' is rather complicated. Initially the value of G'' increases gradually with increasing time. However, after 300 s it decreases, but then increases again after 1000 s. The same tendency can be observed in the drying-time dependence of G'' for the printing ink film at the initial drying stage. For ink films the peculiar time dependence of G'' was attributed to the structural nonuniformity of the sample film, because ink drying proceeds at the surface of the ink film. However, from the results with epoxy resin adhesive in which the curing reaction proceeds uniformly, the peculiar drying-time dependence of G'' must be attributed to the mechanical properties due to the network structure in the sample film. Thus, a three-dimensional network structure is produced throughout the sample film, and the mechanical loss is reduced temporarily. Inasmuch as the network strands behave like the chain predicted by the rubber elastic theory, with increasing cross-linking couplings the value of G' may increase, but that of G'' may be constant or may decrease. However, as the structural networks become more dense, both G' and G'' increase with increasing drying time. When we compare the curing process of the epoxy resin adhesive with that of printing ink, the increasing of G'' in the adhesive is less than that in printing ink. This phenomenon may be attributed to the role of pigments as filler particles. It is suggested that filler particles may be bridged to others by many polymer chains, and therefore act as multiple cross-links as well as a rigid occupier of space.[10] Therefore, drying ink films
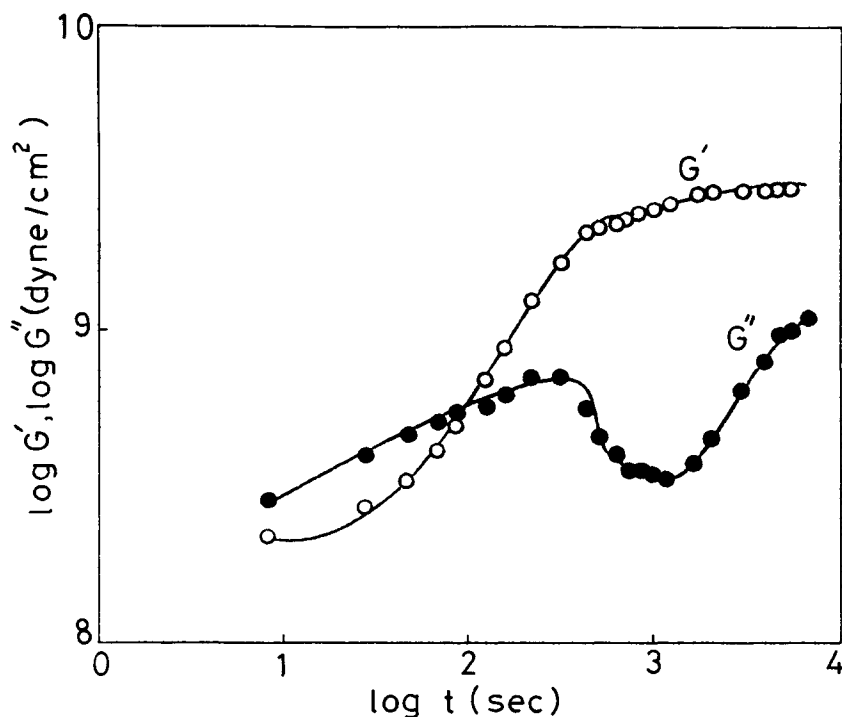
Fig. 7. Logarithmic plots of G' and G'' versus elapsed time after a curing agent for the epoxy resin adhesive is added.

with pigments become more rigid and brittle. This conclusion agrees well with that of creep measurements for hardened films.[11,12]

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