

Viscoelastic Properties of UV-Curing Ink Systems

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Synopsis

Mechanical properties such as tensile strength, relaxation modulus, creep compliance, and storage and loss moduli of UV-curing ink systems were examined at various drying stages. Acrylic-based binder consisting of epoxy acrylate prepolymer and trifunctional monomer were used as UV-curing systems. For the UV-cured specimen containing a large quantity of trifunctional monomer a highly crosslinked network structure was formed at comparatively short irradiation time, however, the sample lacks toughness and nonlinear rheological behavior was observed. On the other hand, for the specimen containing a large amount of epoxy prepolymer, a uniform network structure was formed and the ultimate strength increased with the growing network structure. In the temperature sweep experiments for storage and loss moduli, two transitions were observed. The transition observed above 10°C shifts to higher temperature and becomes broader with increasing irradiation time. The transition which is associated with a relaxation in the crosslinks was observed at -70°C and the height of the G'' peak increased with increasing irradiation time.

INTRODUCTION

Printing inks can be dried in a number of ways, i.e., evaporation, absorption, oxidative polymerization, polycondensation, and crosslinking. Most inks dry by a combination of mechanisms. During the drying processes, printing ink changes from a viscous suspension to a viscoelastic solid and finally to a hardened film. Previously, we have ascribed this phenomenon to viscoelastic transition of printing ink and succeeded in evaluating the viscoelastic properties of ink films at various stages of drying.¹⁻² From creep experiments of the ink films cured by oxidative polymerization, it is concluded that their mechanical properties depend on the network structure and drying processes.³

Recently, printing inks cured by irradiation of ultraviolet (UV) light are used frequently in screen printing and printing on metal plates. Mechanical properties of UV-cured printing inks and coatings depend on binder systems, which consist of reactive prepolymer, oligomer, and monomer. Acrylic based compounds are most often used and are capable of radical polymerization. The final properties of UV-cured films depend mainly on the properties of the prepolymers which form the main constituent of the binder systems. The admixing of monomer and oligomer also affect the curing process and the final network structure.

In order to investigate the roles of prepolymer and monomer in the properties of UV-cured ink films, stress-strain relationship, relaxation modulus, creep and creep recovery, and dynamic viscoelastic properties were measured at various

drying stages for the cured films obtained from different binder systems. The relations between the mechanical properties and the crosslinked structure were discussed.

EXPERIMENTAL

Sample

Acrylic-based binder systems consisting of epoxy acrylate prepolymer (Epiclon 1050 from Dai-Nippon Ink and Chemicals Inc., molecular weight 500) and monomer (trimethylolpropane triacrylate) at various composition rates as shown in Table I were used.

In the UV-curing systems, the reactive radicals are initially formed by irradiation of high intensity UV light with the aid of photoinitiators and the polymerization proceeds by the radical mechanism. In this study, 10% of 2,2-dimethoxy-2-phenyl-acetophenone was used as the photoinitiator for convenience. The excess photoinitiator did not affect the mechanical properties in this study.

Sample binder systems were coated by an applicator on tin plates up to 30 μm in thickness. Since the polymerization is inhibited by oxygen, UV light irradiation was under a nitrogen atmosphere using a high pressure mercury lamp. In this UV-curing binder system, the 365 nm absorption is of primary importance, therefore a UV D-35 filter was used. The sample films were exposed for various times ranging from 1 min to 10 min. Thereafter, the cured films were peeled off from the tin plates and cut into strips (35 mm \times 5 mm).

Measurements

Tensile properties and relaxation modulus were measured by the TENSILON tensile tester (Toyo Measuring Instrument Co., Model UTM-4). In the tensile test, extension was performed at a constant speed of 5 mm/min at the temperature of 30°C.

Creep and creep recovery measurements were performed at a constant stress of 3.3×10^6 Pa using an apparatus which is a modification of a chemical balance. The details of the apparatus and method of measurement have been described elsewhere.³

TABLE I
Composition of Binder Systems

Sample	Prepolymer ^a (wt %)	Monomer ^b (wt %)
B-55	50	50
M-64	60	40
B-73	70	30

^a Modified Bisphenol A Epoxy Acrylate (Epiclon 1050, $\bar{M}_n = 500$).

^b Trimethylolpropane triacrylate.

Dynamic viscoelastic properties were measured at a constant frequency of 10 Hz using a Rheometrics Solid Analyzer (RSA-II). The dynamic measurements was performed in the temperature sweep mode at a strain amplitude of 0.1%. The specimen were quenched to -100°C and heated up to 200°C at a heating rate of $2^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Gel Fraction

Before going on to investigate the mechanical properties of cured films, degree of gelation for the specimens at various curing stages was estimated as follows. Specimens were dipped into methyl ethyl ketone for 48 h in order to extract a sol fraction. The weight of specimens before and after dipping was measured and gel fraction was calculated from the reduction of weight. Figure 1 shows the dependence of the gel fraction on the irradiation time for the various binder systems.

Generally, structure and mechanical properties of UV-cured films depend on the concentration of reactive radicals in the system. Since the monomer contains three reactive functional groups, the network density in the specimen may increase with increasing monomer content. After 1 min irradiation of UV light, the gel fraction exceeds 70% for all specimens. The photo-crosslinking reaction is particularly noteworthy in the B-55 specimen in the initial irradiation time region. However, the gel fractions for B-55 and M-64 seem to level off at 90% after 10 min irradiation. It is thought that the mobility of the chain radical is restricted with increasing network density. However, for the B-73 specimen the gel fraction seems to increase slightly even after 20 min of irradiation.

Ultimate Strain and Strength

The dependence of ultimate strain and strength for the cured specimens on the exposure time is shown in Figures 2 and 3, respectively. With increasing

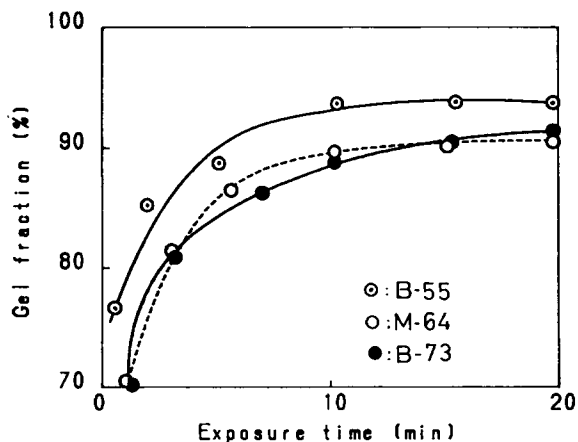


Fig. 1. The relation between the gel fraction and the exposure time for the various binder systems as indicated.

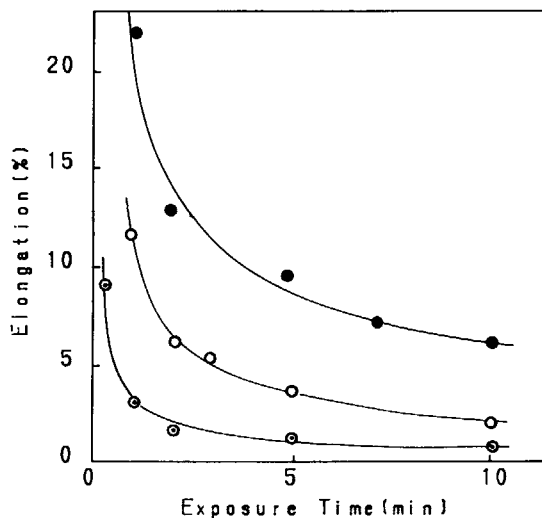


Fig. 2. Plots of the ultimate strain against the exposure time for the various binder systems. Binder systems; (●) B-73, (○) M-64, (⊙) B-55.

exposure time, the ultimate strain decreases drastically at first and gradually reaches the equilibrium value. The ultimate strain decreases with the weight ratio of monomer. At the initial stage of irradiation, the value of ultimate strength for B-55 is largest but, however, it rapidly levels out to a low level. On the other hand, the ultimate strength of B-73 increases in proportion to the irradiation time, and reaches the largest value of all after 10 min of irradiation. This phenomenon may be attributable to the differences in the curing process and the crosslinked structure. The network structure of cured specimens is markedly affected by the rate of reaction. Faster curing reaction causes a local increase in network density. The locally denser structure disturbs motion of chain radicals and crosslinking reaction is restricted to a narrow region. Con-

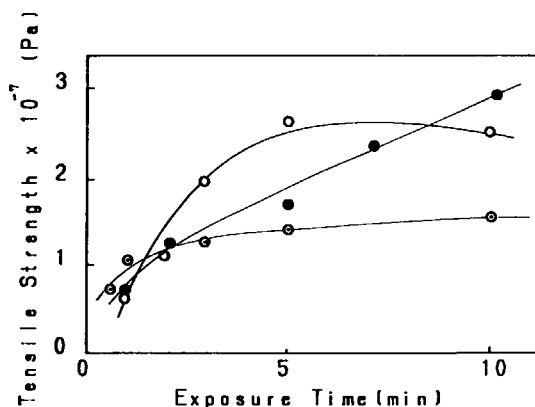


Fig. 3. Plots of the ultimate strength against the exposure time for the various binder systems. Binder systems; (●) B-73, (○) M-64, (⊙) B-55.

sequently, irregular network structures may be formed. Therefore, in B-55 which contains the largest quantity of trifunctional monomer, the irregular network structure is deduced. On the other hand, for B-73 containing a large amount of epoxy prepolymer, both the curing rate and the structural density are not so high as those for B-55, but the comparatively uniform chain length between crosslinking points behaves as an elastically effective strand. Therefore, the ultimate strain is higher than the other and the ultimate strength becomes larger with growing network structure.

Relaxation Modulus

The network density can be also evaluated from an equilibrium modulus in a stress relaxation measurement. Figure 4 shows the stress relaxation curves for B-73 at various exposure times. The equilibrium modulus in the long time region is observed irrespective of exposure times. Therefore, three dimensional network structure may be constructed within 1 min of irradiation. With increasing exposure time, the equilibrium relaxation modulus increases and the viscoelastic transition region shifts toward the longer time region. The same phenomena were observed for B-55 and M-64.

For a rubber elastic material, the crosslinking density can be estimated from the equilibrium modulus G_e by Eq. (1).⁴

$$\nu = G_e / \Phi RT \quad (1)$$

where ν is the moles of network strands in the unit volume, Φ is a numerical factor not far from unity, R is the gas constant, and T is the absolute temperature. For highly crosslinked polymer in which the network strands are too short for the statistical theory based on Gaussian distributions be applied, Eq. (1) is theoretically invalid. However, an approximate proportionality of G_e and T is reported for several densely crosslinked polymers.⁵⁻⁷ Then, we can empir-

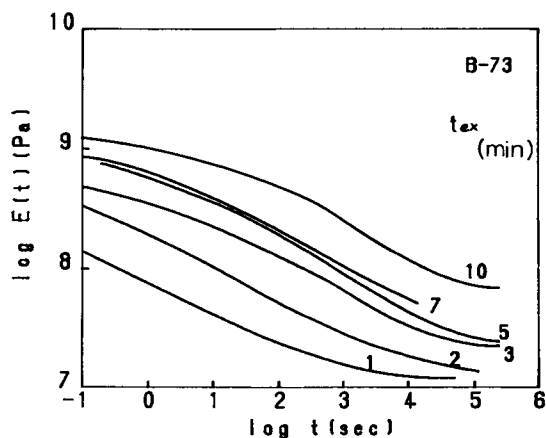


Fig. 4. Logarithmic plots of relaxation modulus against time for B-73 at various exposure times as indicated.

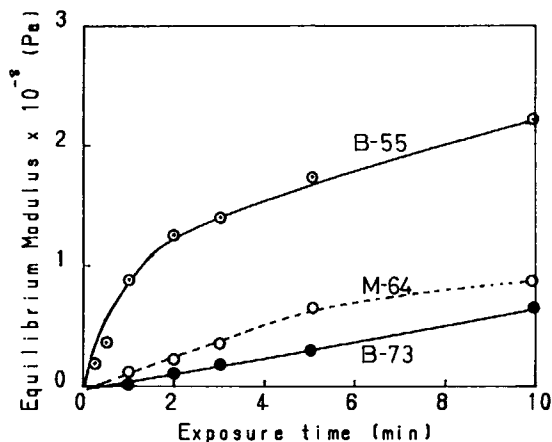


Fig. 5. The dependence of the equilibrium modulus on the exposure time at various binder systems as indicated.

ically estimate the relative crosslinked density from the magnitude of the equilibrium modulus.

Figure 5 shows the dependence of the equilibrium modulus on the exposure time for the specimens of B-55, M-64, and B-73. The equilibrium modulus for B-55 is largest of all and increases rapidly at short irradiation time. For B-55, the crosslinking process may be accelerated by the trifunctional monomer, and consequently, highly crosslinked network structures are formed at comparatively short irradiation times.

Creep and Recovery

Creep and creep recovery data are a powerful tool for the investigation of the structural change in the course of curing. Figures 6(a) and 6(b) show the

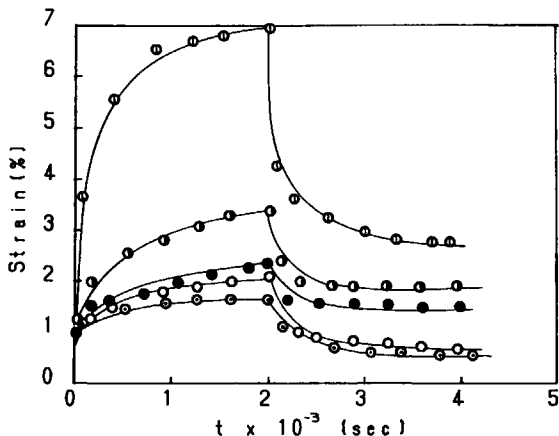


Fig. 6(a). Creep and recovery curves for B-55 at various exposure times. Exposure times (min); (⊙) 1, (●) 2, (●) 3, (○) 5, (⊙) 10.

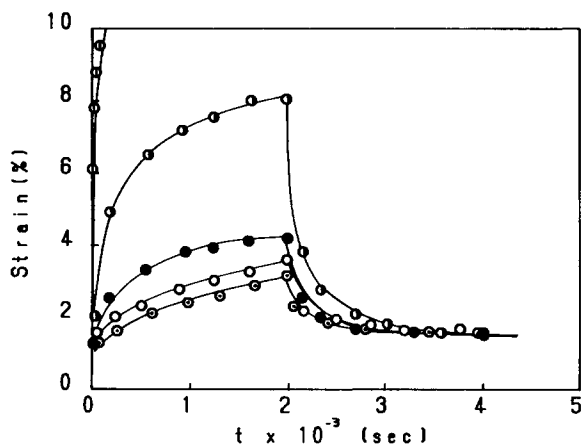


Fig. 6(b). Creep and recovery curves for B-73 at various exposure times. Exposure times (min); (⊕) 1, (●) 2, (●) 3, (○) 5, (⊙) 10.

creep and its recovery under a stress of 3.3×10^6 Pa at various irradiation times for B-55 and B-73, respectively. With increasing irradiation time both tensile strain and recoverable strain become smaller. Since the network density for B-55 is much higher than that for B-73 at a corresponding irradiation time, the magnitude of creep compliance for B-55 is smaller than that for B-73. From creep and recovery curves, B-73 seems to be more ductile and flexible compared with B-55.

Residual strain corresponding to an irreversible flow deformation is observed for all creep recovery curves. The creep viscosity can be evaluated from the strain increasing rate in the long time region of the creep curve and also from the magnitude of the residual strain. In Figure 7 the values of creep viscosity calculated from each method for B-55 and B-73 are plotted against the irradiation time. In the region of linear viscoelastic behavior, both viscosity values coincide with each other irrespective of the method of calculation. When a structural change occurs in the course of creep measurement, the values of the creep viscosity obtained from the rate of strain may differ from that obtained from the residual strain. For cured films the physical meaning of viscosity is rather vague. However, we can deduce a deformability of the specimen from the value of creep viscosity. The value of creep viscosity of cured films increases with increasing irradiation time. For B-55 the dependence of viscosity on the irradiation time is more remarkable than that for B-73. In B-55 the viscosity values determined from the increasing rate of strain in the creep curve are larger than those determined from the residual strain in the creep recovery curve, whereas in B-73 both values of viscosity show the same order of magnitude. This phenomenon may be attributable to the difference in the structural network for both specimens. For B-55, the rate of film curing is so fast that the distribution of chain length between crosslinking points becomes much broader. Therefore, in B-55 each polymeric chain between crosslinking points is subject to uneven loading in the creep measurement and the crosslinking points which receive unexpected huge stress may be broken down. Consequently,

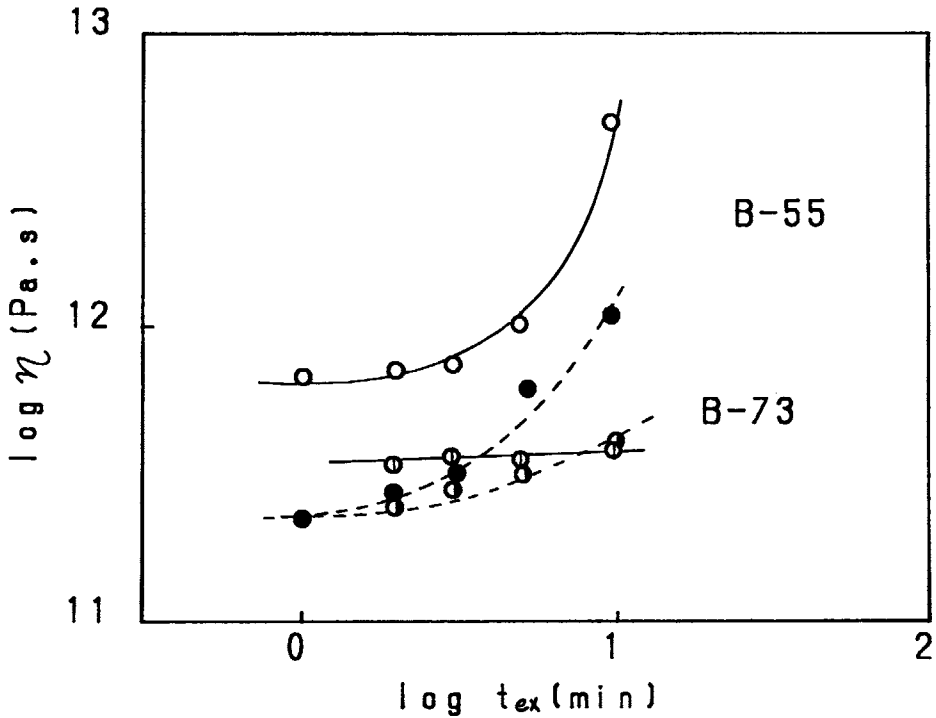


Fig. 7. Plots of creep viscosity obtained from the strain increasing rate (—) and the residual strain (---) for B-55 (O, ●) and B-73 (O, ●) against the exposure time.

the specimens containing irregular network strands are not so tough and non-linear creep behavior is observed.

Storage and Loss Moduli

Temperature sweep experiments for storage and loss moduli over a sufficiently wide temperature range is one of the most effective and practical methods for investigating the structural change in polymeric materials. Figures 8(a) and 8(b) show the temperature dependences of G' and G'' at various curing stages of B-55 and B-73, respectively. The value of G' changes drastically and that of G'' reaches a maximum in the temperature range corresponding to viscoelastic transition. The transition region shifts to higher temperature with increasing irradiation time.

The network density in B-55 is so high that the width of the transition region seems to be rather broad compared with that in B-73. Shibayama and Suzuki reported that the transition region for unsaturated polyester becomes broader with increasing crosslinked density.⁸

The structural density in the B-73 cured by 1 min irradiation of UV light is not so high that values of moduli show some scatter at higher temperatures. However, for the specimen irradiated over 5 min, G' at higher temperature shows a constant value at the order of 10^8 Pa irrespective of the irradiation time and composition of the binder system. From the magnitude of the equi-

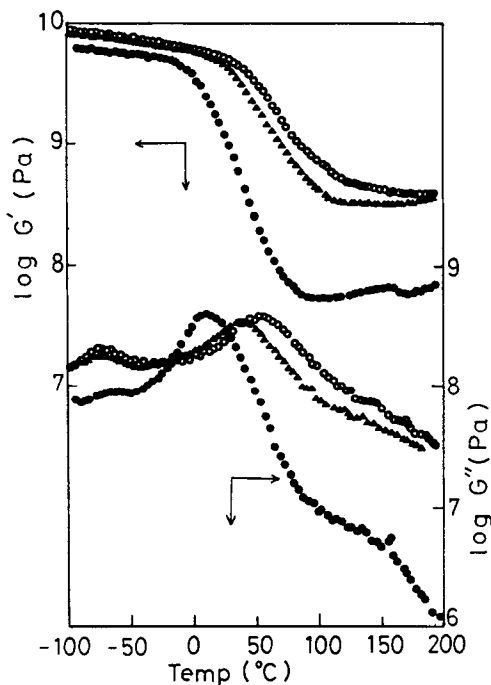


Fig. 8(a). Temperature dependence of G' and G'' at various exposure times for B-55. Exposure times (min); (●) 1, (▲) 5, (○) 10.

librium storage modulus, the network density of cured films is deduced to be extremely high.

The transition in G'' is observed at -70°C for all specimens irrespective of the irradiation time, but the height of the G'' peak seems to increase with increasing irradiation time. The low temperature transition in G'' may be associated with a relaxation in the crosslinking couplings. As pointed out by Kaelble⁹ and Gerberich,¹⁰ the height of the G'' peak at lower temperature can be related to the toughness and bond failure strength.

CONCLUSIONS

The mechanical properties of UV-cured films obtained from different binder systems were measured using various kinds of rheometers and the following conclusions were obtained:

For the UV-cured binder systems, the crosslinking process may be accelerated by trifunctional monomer and highly crosslinked network structures are finally formed at a comparatively short time of irradiation.

The network structure is markedly affected by the rate of reaction. Faster curing reaction causes a local increase in network density and irregular network structures are formed. The specimen containing the irregular network strands is not so tough, even though the network density is quite high and nonlinear viscoelastic behavior is observed.

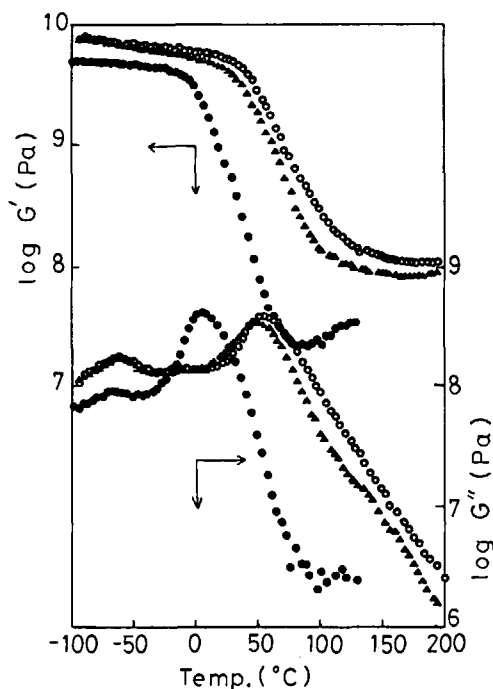


Fig. 8(b). Temperature dependence of G' and G'' at various exposure times for B-73. Exposure times (min); (●) 1, (▲) 5, (○) 10.

On the other hand, for the specimen containing a large amount of epoxy prepolymer, the rate of curing is not so fast, however a regular network structure is formed. The network chains having uniform length behave as elastically effective strands and the ultimate strength becomes larger with growing network structure.

In the temperature sweep experiments for G' and G'' , the transition region shifts to higher temperature and becomes broader with increasing network density. Since the magnitude of the equilibrium storage modulus at higher temperature is the order of 10^8 Pa, the network density of UV-cured films is deduced to be extremely high.

The low temperature transition in G'' which is associated with a relaxation in the crosslinking couplings is observed at -70°C and the height of the G'' peak which is related to the bond failure strength increases with increasing irradiation time.

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