General paper

Rheological Behavior during Phase Separation Induced by UV Curing

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Abstract: The rheological changes during UV curing are examined for solutions of UV-reactive acrylic prepolymer and alkyd resin. To measure the dynamic viscoelasticity in the entire process of UV curing by a single run, a rheological program is developed, by which the storage modulus can be detected in the range of 10^0-10^8 Pa under linear conditions. The solutions containing alkyd resin at concentrations of 10-30wt% show phase separation in the course of curing. The storage modulus of such systems rapidly increases at first, goes through a maximum and then decreasingly approaches the equilibrium value. The microscopic observation of cured films clearly indicates that the droplets generated by phase separation can grow and migrate in the three-dimensional network. The growth of droplets accompanies the rupture of continuous network in a narrow range. The delicate balance between the local rupture of network by phase separation and formation of crosslinks by polymerization controls the appearance of peak in the time-dependent curve of storage modulus.

Key words: Dynamic viscoelasticity, UV curing, Phase separation, Network polymerization, Crosslinking, Gelation, Acrylic prepolymer, Alkyd resin

1. INTRODUCTION

Techniques of forming solid films by network polymerization of reactive monomers on exposure to ultraviolet (UV) light are widely used in various industrial applications, such as coating, printing, and adhesion. In the UV curing process, unbounded polymers with infinite molecular weights are developed over the system from discrete monomers with low molecular weights. The important properties required for the plastic materials are often the constant viscoelastic responses in a wide range of temperatures and insolubility in organic solvents. The three-dimensional network structures are essential to satisfy these requirements. Since the network polymerization uniformly proceeds in ordinary conditions, the gross structures of cured systems are homogeneous, in which the flexible chains are crosslinked.

Recently the composite films consisting of an insoluble phase embedded in a three-dimensional network of polymer matrix are of increasing interest in practice. For instance, liquid crystal/polymer composite (LCPC) films are very promising for information displays, optical shutters, and transmission-controlled windows. When placed between two transparent electrodes, the LCPC films can be switched from a light-scattering state to a highly transparent state by application of a suitable voltage. However, it is impossible to disperse the microdroplets of liquid crystal in the infinite network of polymer. The basic step in the preparation of such composite films is the phase separation in which the microdroplets of the insoluble phase are generated in the polymer matrix. The most frequently used method is the photopolymerization-induced phase separation[1-4]. When the molecular weight increases during curing, the microdroplets are produced as a result of a sharp decrease of solubility. After the phase separation, the continuous phase of unbounded polymer matrix is formed by network polymerization.

In the course of curing, the finite branched polymers combine with the infinite network, leading to an increase in the density of crosslinks. One can easily expect that the elasticity monotonously increases with the progress of curing. However, the distribution of crosslinks density becomes inhomogeneous in a long range, when the phase separation is induced. The physical properties strongly depend on the morphology of system and thus the phase separation makes the curing behavior very complex. In the present study, the dynamic viscoelasticity is measured during phase separation due to network polymerization. The rheological behavior will be discussed in relation to the morphology of cured systems.

2. EXPERIMENTAL

2.1. Materials

The samples were solutions of UV-reactive prepolymer (oligomers), alkyd resin, dryer, and photoinitiator. These UV-curable systems can be used as vehicles (medium) of printing inks. The UV-reactive prepolymer consisted of trimethylolpropanetriacrylate (TMPTA) (25% by weight), polyethyleneglycoldiacrylate (PEGDA) (25wt%), and epoxy acrylate (Ebecryl-600 from SK-ucb, Korea) (50wt%). The molecular weight of alkyd resin was about 3,000. The photoinitiator was 2,2-dimethoxy-2-phenylacetophenone and the concentra-
tion was 3.0 wt% based on the UV-reactive prepolymer. On the exposure to UV light, the decomposition of photoninitiator takes place and results in network polymerization of UV-reactive prepolymer. However, the chemical reaction is not induced for alkyd resin in the time scale of photopolymerization (2 hrs in this study). In application to printing technology, the flexible network with high density of crosslinks is desired. For this purpose, the dryer was used to activate the oxidation reaction of alkyd resin. Since the reaction is initiated by absorption of oxygen molecules, the network polymerization of alkyd resin is very slow and proceeds for several days. Although the samples contain a small amount of dryer, it is not a primarily important component in the present study. The concentration of UV-reactive prepolymer must be increased above some critical value to form the flexible matrix of unbounded polymer. The solutions of UV-reactive prepolymer and alkyd resin were prepared at alkyd resin concentrations of 40 wt% and below.

2.2. Rheological Measurements

Dynamic viscoelasticity during UV curing was measured by the use of a parallel plate geometry on a stress-controlled rheometer (Haake Rheo-Stress RS150). The diameter of plates was 20 mm and the gap between two plates was 0.1 mm. The sample thickness was controlled within an accuracy of 1.0 μm. The lower plate was made of quartz glass to transmit the UV irradiation. For all runs, the temperature was 25°C and the angular frequency was kept at ω = 6.28 s^-1 (1 Hz).

When irradiated with UV light, the systems undergo transition from viscous liquids to elastic solids. In general procedure, the time dependence of dynamic viscoelasticity is measured at a fixed strain or stress, depending on the material and limitation of instrument. However, it is difficult to carry out the measurements under the constant conditions, because the curing is accompanied by drastic and complex changes of rheological properties. In addition, the internal structures are easily broken down under large deformation [5-7]. The structural formation processes such as gelation and flocculation in suspensions are often influenced by the strain amplitude. The dynamic viscoelastic measurements at small strains are required especially for phase separation processes. For accurate measurements of the entire process of curing by a single run in a linear viscoelasticity range, the stress amplitude was increased stepwise according to the progress of curing. Figure 1 shows a typical measuring procedure. The strain amplitude is about 0.2 at the beginning and decreases below 0.01 at the end of curing. By using this technique, the storage modulus during curing can be detected in the range of 10^2-10^8 Pa.

3. RESULTS AND DISCUSSION

In the absence of UV irradiation, the solutions used in this study exhibit phase separation when the temperature is decreased. Figure 2 shows the phase diagram of the initial solutions before UV irradiation. The phase separation was determined in a polarizing microscope equipped with a heating stage and by observation of the turbidity of the samples in sealed glasses. Since the solution is phase-separated at low temperatures, this is characterized as the upper critical solution temperature (UCST) behavior. The maximum temperature where the phase separation occurs is about 20°C, which is achieved at an alkyd resin concentration of 20 wt%. Above 20°C, the solutions are homogeneous, irrespective of alkyd resin concentration. The research interests are focused on the phase separation induced by network polymerization. Therefore, the UV curing experiments were carried out at 25°C for all solutions. The UV energy fed into the solutions did not have a significant effect on the sample temperature, owing to the relatively low intensity of UV lamp.
Figure 3 shows the time dependence of storage modulus $G'$ and loss modulus $G''$ during UV curing of solution containing 40wt% alkyd resin. Once the curing reaction starts, both moduli rapidly increase. Because the principal ingredients of initial systems are multifunctional reactive oligomers, the viscosity component ($G''$) is much higher than the elasticity ($G'$) at the early stage of curing. The polymerization of multifunctional oligomers includes crosslinking that forms randomly branched polymers. The average size of the branched polymers rapidly increases until a critical threshold is reached where the average sizes diverges to infinity. Above this threshold the systems are composed of an infinite network and many finite branched polymers. In the network, the diffusion of segments is possible in a short range, whereas the long-range motion (flow) of crosslinks never takes place. Therefore, the systems containing three-dimensional network of unbounded polymers can be regarded as solids. The network polymerization leads to the development of elasticity at very low frequencies.

Figure 4 shows the time dependence of storage and loss moduli during UV curing of solution containing 20wt% alkyd resin. Both moduli rapidly increase at first, go through a maximum, and then decreasingly approach the equilibrium value. Beyond the gel point, the discrete polymers which could migrate freely to some extent are incorporated into the network and immobilized. Since the viscous effect decreases, the loss modulus often shows a maximum around the gel point [8-11]. On the other hand, the storage modulus monotonously increases with time in the whole process of curing, because the network polymerization always causes an increase in the density of crosslinks. Hence, it seems difficult to explain the appearance of peak in time-dependent curve of storage modulus on the basis of the simple pictures of network polymerization.

Figure 5 shows the effect of alkyd resin concentration on the time dependence of storage modulus during UV curing. The sharp peaks appear in the time-dependent curves of storage modulus for solutions with alkyd resin at concentrations from 10 to 30wt%. The peak heights are of the order of $10^8$ Pa. The exposure time at the peak increases with increasing alkyd resin concentration. Since the alkyd resin can be considered to be inert in the photochemical reaction, the cure rate is faster for solutions with alkyd resin at lower concentrations.

Figure 6 shows the stress-strain curves for cured films prepared from solutions with alkyd resin at different concentrations. The sample solutions were sandwiched between two glass plates and exposed to UV light. After the curing was completed, the solid films were torn from the plates. For solutions containing alkyd resin at concentrations of 40wt% and above, the solid films were not obtained. The structural buildup of three-dimensional network was impossible in such systems. The measurements were carried out at a constant extensional rate until the solid films ruptured. For all cured films, the yielding behavior is not observed, but the stress monotonously increases with strain. As the alkyd resin concentration is increased, the tensile strength (maximum stress)
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Fig. 6. Stress-strain curves for cured films prepared from solutions with alkyd resin at different concentrations.

decreases and the strain at rupture increases. If the plots for each film are approximated by a straight line, the slope gives the elastic modulus in extension (Young's modulus). Reflecting the density of crosslinks, the elastic modulus of cured film decreases with increasing alkyd resin concentration.

Figure 7 shows the microphotograph of cured film from solution with alkyd resin at a concentration of 20wt%. The UV light was applied for 15 min. It must be stressed that the initial solution before UV irradiation is homogeneous. The cured film consists of small droplets dispersed in the polymer matrix. The compositions of dispersed droplets and continuous phase are alkyd resin and crosslinked polymer of acrylic resins, respectively. The intrinsic mechanism to generate highly heterogeneous structure is phase separation induced by UV curing. Since the solubility is decreased with the progress of curing, the alkyd resin is separated from the solution as droplets. However, the fraction of dispersed droplets in cured film is lower than that predicted from the initial composition of solution. Imaging analysis of microphotograph implies that some part of alkyd resin remain in continuous phase. The polymer matrix may be composed of crosslinked polymer of acrylic resins and dissolved alkyd resin.

Microscopic observations were repeated for films prepared from solutions at different alkyd resin concentrations. At concentrations from 10 to 30wt%, the cured films show the phase-separated structure consisting of a collection of many small droplets. Although the fraction of dispersed droplets generated by phase separation increases with increasing alkyd resin concentration, the continuous structures of alkyd resin like a sponge can not be constructed. At 40wt% no droplets are observed and the film structure is optically homogeneous. The phase separation does not occur at concentrations above 40wt%. Referring back to Fig. 5, interesting correspondence can be seen that the peaks in time-dependent curve of storage modulus during UV curing appear for the systems having the phase-separated structures.

Let us now consider the relation between the rheological behavior and structural changes. As a simplified model, we can assume that the phase separation occurs at the time where the storage modulus shows the maximum. However, this approach is not acceptable. Figure 7 clearly indicates that the cured film already has the phase-separated structures before the storage modulus reaches the maximum. From the detailed microscopic observations, it is confirmed that the phase separation starts at the early stage of curing. The droplets must be separated from the liquid state prior to the development of three-dimensional network. Presumably the storage modulus may be less than $10^4$ Pa for phase separation.

The solution with alkyd resin at a concentration of 20wt% was UV-cured for 50 min. Figure 8 shows the microphotograph of completely cured film. Both cured films shown in Figs. 7 and 8 are phase-separated, the continuous phase of which may be composed of three-dimensional network of acrylic resin. The general agreement with respect to mechanical properties of three-dimensional network is that the macroscopic flow is not allowed and the deformation reaches the equilibrium after a long time under a constant stress. The gels have a
certain shape and behave as elastic solids. However, the comparison of two microphotographs shows that the average size of droplets is increased during curing. The droplets can grow and migrate in the gels. This process inevitably accompanies the rupture of network in a short range, especially in a boundary layer of polymer matrix surrounding the droplets. The rearrangement of phase-separated structures may be driven by a combination effect of growth of droplets and local rupture of network. The overall effect of chemical reaction is to increase the density of crosslinks in the whole system, but at the same time the reduction of elasticity can take place due to the local rupture of crosslinks. When the phase separation is induced, the polymerization reaction contributes to the storage modulus in two opposing ways. Although further definitive experiments are required to establish the quantitative explanation, the primary factor controlling the appearance of peak in the time-dependent curves of storage modulus during UV curing may be a delicate balance between the local rupture of network by droplet growth and formation of crosslinks by polymerization.

4. CONCLUSIONS

(1) A rheological program is developed to measure the dynamic viscoelasticity in the entire process of UV curing by a single run. By increasing the stress amplitude stepwise according to the progress of curing, the storage modulus can be accurately determined in the range of $10^7$ to $10^8$ Pa.

(2) The solutions of UV-curable prepolymer containing alkyd resin at concentrations of 10-30wt% show phase separation in the course of curing. The storage modulus of such systems rapidly increases at first, goes through a maximum, and then decreasingly approach the equilibrium value.

(3) From the microscopic observations of cured films, the droplets generated by phase separation can grow and migrate in the three-dimensional network. The growth of droplets accompanies the rupture of continuous network in a short range. The delicate balance between the local rupture of network by phase separation and formation of crosslinks by polymerization controls the appearance of peak in the time-dependent curves of storage modulus.

REFERENCES