

Elongational Behavior of Epoxy During Curing

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ABSTRACT: Elongational behavior of epoxy (epoxy/curing agent = 100/0.5, w/w) cured at various conditions over the critical gelation time was investigated. Dynamic viscoelastic measurements of the epoxy system were performed and the critical gelation time of epoxy was determined according to the frequency dependence of G' and G'' proposed by Winter and Chambon. Elongational behavior of epoxy cured for various times were measured. Epoxy, cured over the critical gelation time, showed strain hardening and elongational behavior similar to a crosslinked rubber. Increase of elongational viscosity of the sample occurred early, and the sample broke at small strain as cur-

ing time increased. The effect of strain rate on the elongational stress of epoxy cured near the critical gelation time was measured at various strain rates. For epoxy cured for critical gelation time only, high stress at a small strain rate was represented as strain rate increased. When increasing curing time further, the tensile stress converged on a single curve regardless of strain rate, and samples broke at nearly the same stress and strain. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1018–1024, 2009

Key words: epoxy; critical gelation time; rheology; elongation

INTRODUCTION

Epoxy has been used widely in electrical parts such as cast articles, laminated plates, and semiconductor sealant because epoxy has excellent adhesion, mechanical, and electrical properties, etc. Recently, PCs, televisions, and cell phones have become downsized and thinned. Moreover, the speed of information processing is faster. Therefore, electronic information cannot be handled by the present electrical property of epoxy. In electrical properties, permittivity affects many electrical properties, and it is believed that this matter can be settled by lowering of permittivity. Foaming of epoxy is one effective method for lowering permittivity. Specific permittivity of air nearly equals 1.0. Therefore, lowering of permittivity becomes possible by foaming of epoxy. Carter et al.¹ reported that permittivity of polyamide lowers from 2.6 to 2.3 by introducing voids of ~ 20%.

There are some problems in epoxy foaming. Epoxy is thermoset, and viscosity rapidly increases at a certain time when curing. Few reports on epoxy foam have been published because it is difficult to keep the viscosity of epoxy at an optimal level during foaming.^{2–6} In these reports, we found that viscosity of epoxy rapidly increases around the critical gelation time with the curing time.^{5,6} The critical gelation time of epoxy was determined by the results

of rheological measurements through rheological criterion proposed by Winter and Chambon,^{7–9} who reported the detailed relationship between rheology and gelation. They reported storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ near gelation time by using polydimethylsiloxane. Then they suggested that $G'(\omega)$ and $G''(\omega)$ at critical gelation time were defined by⁸

$$G'(\omega) = G'_c \omega^n, G''(\omega) = G''_c \omega^n \quad (0 < \omega < \infty) \quad (1)$$

$$\tan \delta = \tan(n\pi/2) \quad (0 < n < 1) \quad (2)$$

where G'_c and G''_c are constant. They found that $G'(\omega)$ and $G''(\omega)$ represent the power law relationship for a wide range of frequency at the critical gelation time and that the values of exponents n of $G'(\omega)$ and $G''(\omega)$ (called “critical exponent”) are the same. The gelation of the sample denotes a change from viscoelastic liquids to viscoelastic solids. Sample in viscoelastic solid state deforms finitely under constant stress, whereas in the viscoelastic liquid state, it deforms infinitely. Thus, bubble (gas of blowing agent) is discharged out of the sample because stress of the deformed cell membrane in the viscoelastic liquid state relaxes easily. On the other hand, bubble is fixed in the sample of viscoelastic solid state because the stress induced by cell expansion is difficult to relax for crosslinked polymer due to the infinite extensibility of polymeric molecules. By using the method mentioned above, we reported the relationship between rheological behavior during precuring and foaming of epoxy.^{5,6} Epoxy foam was

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successfully produced through two processes. In the first process, epoxy mixed with curing agent and blowing agent was precured above the critical gelation time at low temperature below the decomposition temperature of the chemical blowing agent to obtain the optimum condition for foaming. This sample was then foamed at high temperature. It was reported that roughly two sizes of bubbles, large bubbles ($>100\ \mu\text{m}$) and small ones ($\cong 30\ \mu\text{m}$), were observed when the sample was precured for a relatively short time before foaming. This phenomenon is shown in other reports of epoxy foaming.²⁻⁴ The clarification of this phenomenon is very important to produce epoxy foam with homogeneous bubbles. Almost all of the reports of rheological behavior of epoxy were discussed in terms of dynamic shear viscoelasticity. Foaming cells undergo elongational and nonlinear deformation. In particular, strain hardening in elongational flow plays an important role to stabilize expanding cell deformation. Many researchers have reported the relationship between strain hardening and foaming for thermoplastics and represented that control of strain hardening is extremely important to stabilize foaming structure.^{10,11} Yamaguchi and Suzuki¹⁰ blended linear low-density polyethylene (LLDPE) with crosslinked LLDPE (cLLDPE) to enhance strain hardening in elongational behavior and compared foaming behavior of pure LLDPE with a blended sample. They reported that the cell size of foam of the blended sample became homogeneous, whereas the cell size of foam of pure LLDPE became heterogeneous. Spitael and Macosko¹¹ studied the effects of rheological behavior on foamability of polypropylene (PP). They reported that linear PP mixed with branched PP represented better foamability than that of linear PP. On the other hand, the elongational behavior of epoxy of thermosetting polymer during curing has never been published as far as the authors know, whereas many papers of the dynamic shear viscoelasticity have been reported.¹²⁻¹⁶

Therefore, in this study, we investigated elongational behavior of epoxy curing at various conditions over the critical gelation time. To accomplish the purpose of this study, first we needed to measure the accurate critical gelation time. Usually, viscosity of epoxy with the general composition of the epoxy/curing agent used in industry increases with increasing time. In many reports about rheology of epoxy,¹²⁻¹⁶ to measure the accurate critical gelation time, epoxy cures slowly for a long time (1 h to more than 1 day) by using a slow-curing type of agent or lowering the temperature. We used catalytic curing agent and, in this case, slowing of the curing rate was possible by decreasing the weight ratio of the curing agent. Therefore, we measured the variation of viscosity with time for various weight ratios

of epoxy/curing agent and determined the condition of the weight ratio of them to measure the critical gelation time. We then obtained the critical gelation time by the results of rheological measurements and using rheological criterion proposed by Winter and Chambon. Second, we needed to produce the elongational measurement sample by using the results described above. The elongational measurement sample is generally prepared by using metal mold. However, epoxy adheres to metal mold. Therefore, we coated the metal mold with Teflon film. Finally, elongational measurement was accurately carried out for cured samples. If elongational measurement temperature is the same as curing temperature, the sample cures very quickly and the state of the sample changes while setting the sample. Therefore, we measured elongational behavior at a low temperature, at which the effect of crosslinking reaction is negligible.

EXPERIMENTAL

Materials

We used diglycidyl ether of the bisphenol A (DGEBA) as a starting material (jER®828, specific gravity is 1.17, molecular weight is about 370, manufactured by Japan Epoxy Resin, Tokyo, Japan). The curing agent is 2-ethyl-4-methylimidazole (2E4MZ) (Curezol®2E4MZ, melting point [T_m] is 41°C , manufactured by Shikoku Chemicals Corporation, Marugame, Japan). In reaction to 2E4MZ with DGEBA, only the epoxy group has ring-opening addition reaction and is polymerized anionically. Therefore, 2E4MZ in itself is not incorporated in the chemical structure. Thus, the increase or decrease of the additive amount only contributes increase or decrease of reaction rate. Epoxy was heated to 80°C and dried to remove water in vacuo overnight before use. The curing agent was used as received. Epoxy and curing agent were mixed for 5 min at a constant speed of 720 rpm and temperature of 50°C . Then, after the mixed sample was degassed in vacuum for 10 min at room temperature, it was immediately used for measurement.

Time dependency of dynamic shear viscoelasticity

The sample was prepared as a weight ratio of epoxy/curing agent of 100/1, 100/0.75, and 100/0.5 (hereinafter called EP-1, EP-0.75, and EP-0.5, respectively). The dynamic shear measurement was performed by rotational rheometer (Anton Paar GmbH, Graz, Austria, Physica MCR301). The geometries of the test fixtures were parallel disks with a diameter of 25 mm for all measurements. The isothermal measurement was performed until the sample was

cured. The measurement was carried out at constant angular frequency of 10 rad/s, strain of 3%, and temperature of 90°C under nitrogen atmosphere. The measurement temperature of 90°C is the lowest at the range of reaction temperatures between epoxy and curing agent. The sample was set at 50°C to maintain the uncured state. The apparatus was set at a heating rate of 10°C/min until the temperature of the sample increased from 50 to 90°C. The isothermal measurement was then started. As for EP-0.5, the time sweep tests were carried out at angular frequencies of 1, 3.16, 10, 31.6, and 100 rad/s, strain of 3%, and temperature of 90°C under nitrogen atmosphere.

Frequency dependency of dynamic shear viscoelasticity

The measurement of frequency dependency of dynamic shear viscoelasticity was carried out to measure the critical gelation time of EP-0.5. The sample was prepared with the same as mentioned before. Preparation of sample, rotational rheometer, and test fixtures are the same as mentioned before. EP-0.5 was cured for a determined time, followed by dynamic tests ranging from 3 to 100 rad/s at 90°C.

Elongational behavior

The measurement of elongational behavior was performed by elongational rheometer (Melten Rheometer, Toyo Seiki Seisaku-sho, Tokyo, Japan). We used EP-0.5 as an elongational measurement sample because EP-0.5 cured slowly, and the critical gelation time could be obtained accurately. Square rod-like samples (5 mm × 5 mm × 140 mm long) were prepared by Teflon-coated mold. EP-0.5 was cast into the mold and was cured for 103, 108, 113, 123, 133, 143, 153, and 163 min at 90°C. Elongational measurement was performed at low temperature, that the effect of crosslinking reaction is negligible because setting of the sample to the elongational rheometer took time (3 to 5 min), the sample cured more, and the state of the sample changed. The cured samples were elongated in 50°C oil bath until break at strain rate of 0.1/s. Additionally, the measurements of samples cured for 103, 108, and 113 min were carried out at strain rates of 0.1, 0.3, 1/s and 50°C in oil bath.

RESULTS AND DISCUSSION

Dynamic shear viscoelasticity of EP-1, EP-0.75, and EP-0.5

Figure 1 shows curves of complex viscosity η^* as a function of time for EP-1, EP-0.75, and EP-0.5, cured at a temperature of 90°C. It was impossible to detect the instrument torque at the onset of each test because viscosities were too low. When viscosities

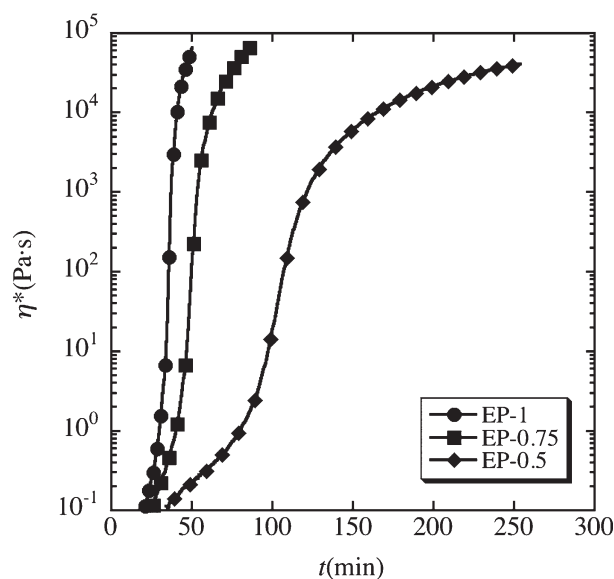


Figure 1 Complex viscosity η^* as a function of time for EP-1, EP-0.75, and EP-0.5, cured at 90°C.

reached about $5 \cdot 10^4$ Pa/s at all conditions, the measurements were stopped so that it did not exceed the instrument capabilities. Curing time took longer with decreasing curing agent, as shown in Figure 1. The samples showed an extremely rapid increasing beyond the viscosities of 5×10^{-1} Pa·s and then presented a slow increase when the viscosities exceeded $\sim 2 \times 10^4$ Pa·s. This tendency was similar in all measurements tested. The time of EP-1, EP-0.75, and EP-0.5 when the viscosities reached to 5×10^{-1} Pa·s were 28, 37, and 69 min, respectively. The time of EP-1, EP-0.75, and EP-0.5 when the viscosities reached to 2×10^4 Pa·s were 43, 69, and 197 min, respectively. Therefore, the period of EP-1, EP-0.75, and EP-0.5 when viscosities reached from 5×10^{-1} Pa·s to 2×10^4 Pa·s were 15, 32, and 128 min, respectively. These times represent the times that viscosity increased extremely rapidly for EP-1, EP-0.75, and EP-0.5, and the time was long at EP-0.5, whereas others were short at EP-1 and EP-0.75. Slow curing behavior of epoxy is required to closely measure the critical gelation time. For example, the measurement time of frequency dependency of dynamic shear viscoelasticity is about 60 s. When the measurement of frequency dependency of dynamic shear viscoelasticity was carried out at a certain curing state, epoxy cures during this measurement. Therefore, the crosslinked structure at the start is different from that at the end of this measurement if viscosity of epoxy rapidly increases. However, the effect of the variation of the crosslinked structure becomes negligibly small by slowing of epoxy curing, and the critical gelation time of epoxy can be closely measured. From the result of Figure 1, EP-0.5 represented slow increase of viscosity in comparison

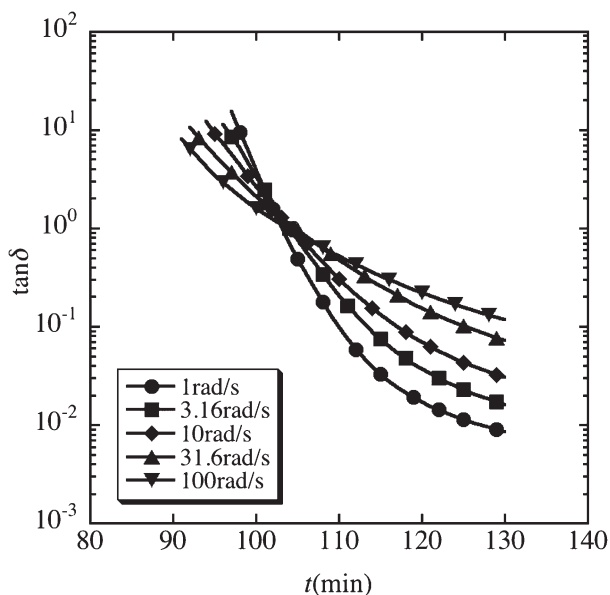


Figure 2 $\tan \delta$ as a function of time for EP-0.5 at angular frequencies of 1, 3.16, 10, 31.6, and 100 rad/s, cured at 90°C.

with EP-1 and EP-0.75. The variation of η^* of EP-0.5 in 60 s was very small at the range of rapidly increasing of η^* . Moreover, Matejka¹² closely measured the critical gelation time of epoxy at about the same curing time scale with that of EP-0.5. Therefore, the dynamic shear viscoelasticity in our study is also possible to measure by using EP-0.5. In the following measurements, we used only EP-0.5 to measure the critical gelation time.

Figure 2 shows curves of $\tan \delta$ as a function of time for EP-0.5 at angular frequencies of 1, 3.16, 10, 31.6, and 100 rad/s, cured at 90°C. $\tan \delta$ decreased with time at all curves. It is considered that the elasticity of epoxy increased with time by curing. All curves converged at a single point, $t = 103$ min. Since $\tan \delta$ becomes constant at a wide range of frequency at critical gelation time, in the eq. (2) it was considered that 103 min was the critical gelation time. The critical exponent at this point was 0.67.

Figure 3 shows the variation of (a) storage modulus $G'(\omega)$, (b) loss modulus $G''(\omega)$, and (c) $\tan \delta$ with frequencies for cured epoxy. Frequency dependency of dynamic shear viscoelasticity was measured for samples cured at 90°C for 97, 100, 103, 106, 109, and 112 min, which were the times around the critical gelation time of 103 min obtained in Figure 2. In Figure 3, the values in the legends denote the time of cure treatment before measurement. In Figure 3(a), the curves of $G'(\omega)$ at 97 and 100 min represented a large slope at small ω . The slope of $G'(\omega)$ decreased with increasing curing time. Above 103 min, $G'(\omega)$ tended to level off. The variation in $G'(\omega)$ denotes the change from viscoelastic liquids to viscoelastic

solids. Moreover, $G'(\omega)$ and $G''(\omega)$ were represented as power law relationship for this frequency range at 103 min, and the critical exponent was 0.68. The $\tan \delta$ curves at 106, 109, and 112 min represent the

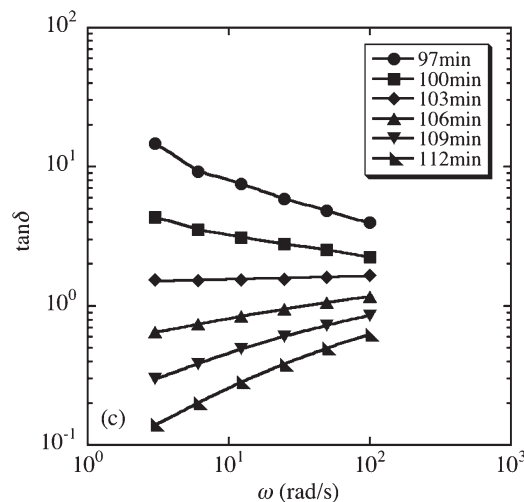
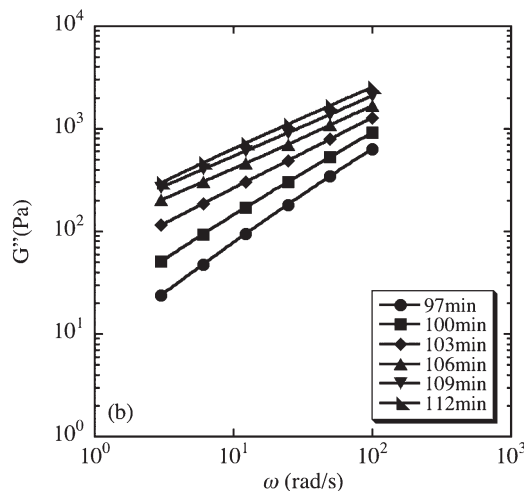
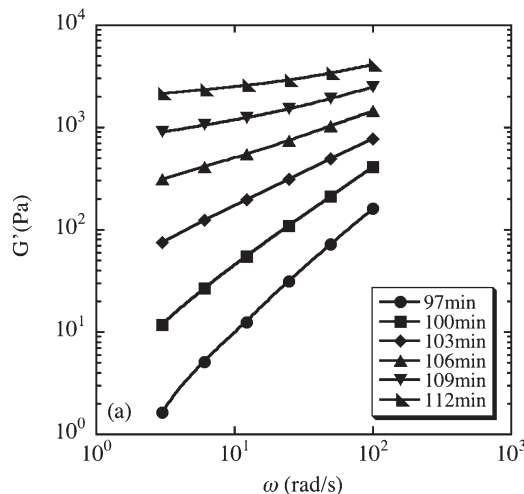


Figure 3 (a) Storage modulus G' ; (b) loss modulus G'' ; (c) $\tan \delta$ as a function of angular frequency for 97, 100, 103, 106, 109, and 112 min at 90°C.

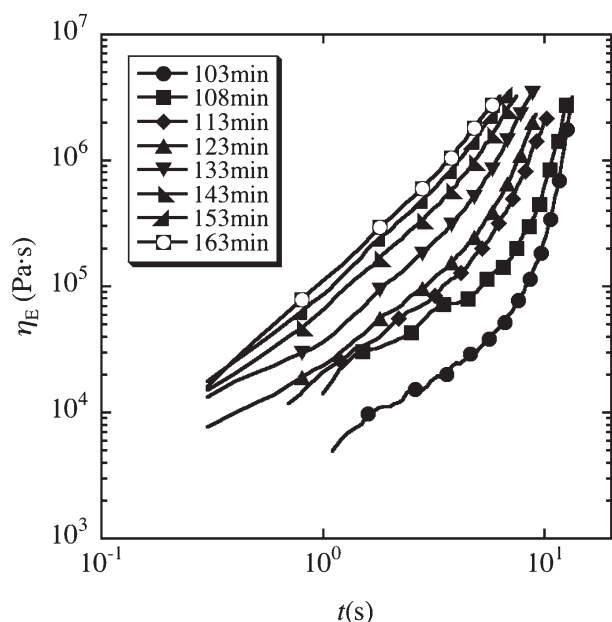


Figure 4 η_E as a function of time for the samples of EP-0.5 elongated at 50°C in oil bath after curing for 103, 108, 113, 123, 133, 143, 153, and 163 min at 90°C.

positive gradient, whereas $\tan \delta$ of 97 and 100 min represent the negative gradient in Figure 3(c). At 103 min, $\tan \delta$ became constant in a wide range of frequency. We should note that these results correspond to that of Figure 2. Therefore, we determined that the time of 103 min is critical gelation time according to eqs. (1) and (2).

Elongational behavior

Figure 4 shows curves of η_E as a function of time for samples elongated at 50°C in oil bath after curing for 103, 108, 113, 123, 133, 143, 153, and 163 min at 90°C. All the samples were at or above the critical gelation time (103 min). Samples were elongated until break at strain rate of 0.1/s and 50°C in oil bath. In addition, samples that did not fulfill the criteria for the critical gelation were impossible to homogeneously elongate because samples immediately became droplet state in oil bath. The maximum strain of samples became smaller with increasing curing time, and elongated strain of EP-0.5 cured for 163 min was less than half of EP-0.5 cured for 103 min. It is considered that samples represented rigidity because crosslink density of epoxy increased as the curing time became longer. All curves represented that η_E slowly increased in a short time area and rapidly increased in long time range. These shapes of curves are similar to that of crosslinked rubber. In the classical theory of rubber elasticity, chemical crosslinks deform affinely, and the molecular chains between the crosslinks stretch according

to the relative displacement of the crosslinks in the small strain. Crosslinked rubber shows the sharp upturn in the stress–strain curve in the large strain regime by the finite extensibility of the molecular chains. Epoxy is a chemically crosslinked material, and all conditions of samples for elongational measurements were at the critical gelation time (103 min) and above. Therefore, we understand that epoxy deformed similarly to rubber. For EP-0.5 cured for 103 min, the η_E curve represented very low value in comparison with other curves in short time ranges. This is considered the effect of the viscous component of short relaxation time, such as low molecular weight in the sample. When relaxation time is short, elongational viscosity becomes low at small strain (short time) since the effect of relaxation becomes large in deformation. For the viscous component, $G'(\omega)$ decreases with lowering of ω , and this represents the existence of the viscous component in Figure 3(a). The viscous component then becomes small as curing time becomes long. To clarify this consideration, we elongated the samples of 103, 108, and 113 min at various strain rates. The effect of strain rate on stress–strain curve was then investigated.

Figure 5 shows the stress–strain curves of the samples of EP-0.5 cured for (a)103, (b)108, and (c)113 min at strain rates of 0.1, 0.3, and 1/s, respectively. Preparation of the samples and measurement temperature were the same as mentioned before. High stress was represented as strain rate increased at small strain in Figure 5(a). Stress then converged regardless of strain rate as strain increased and samples broke at about the same stress and strain. Strain rate dependence on stress at small strain became smaller for cured EP-0.5 for 108 min, as shown in Figure 5(b), and finally disappeared for cured EP-0.5 for 113 min in Figure 5(c).

Stress depends on strain rate because the effect of the viscous component is large at the viscoelastic body, such as in thermoplastic. On the other hand, in the case of an elastic body such as crosslinked rubber, stress does not depend on strain rate. The molecular weight of epoxy increases by chemical crosslinking. Therefore, epoxy represents a property of the elastic body when curing time becomes long. As mentioned above, we understand that the large amount of viscous component with short relaxation time exists because stress greatly depends on strain rate, as in Figure 5(a). We then find that the viscous component becomes small by lowering of strain dependence on stress, as in Figure 5(b). In Figure 5(c), we understand that the sample represents the elastic body because stress does not depend on strain rate. The change to the elastic body of epoxy is confirmed in Figure 3(a). If the measurement of frequency dependency of dynamic shear viscoelasticity was carried out for the elastic body, $G'(\omega)$ becomes constant

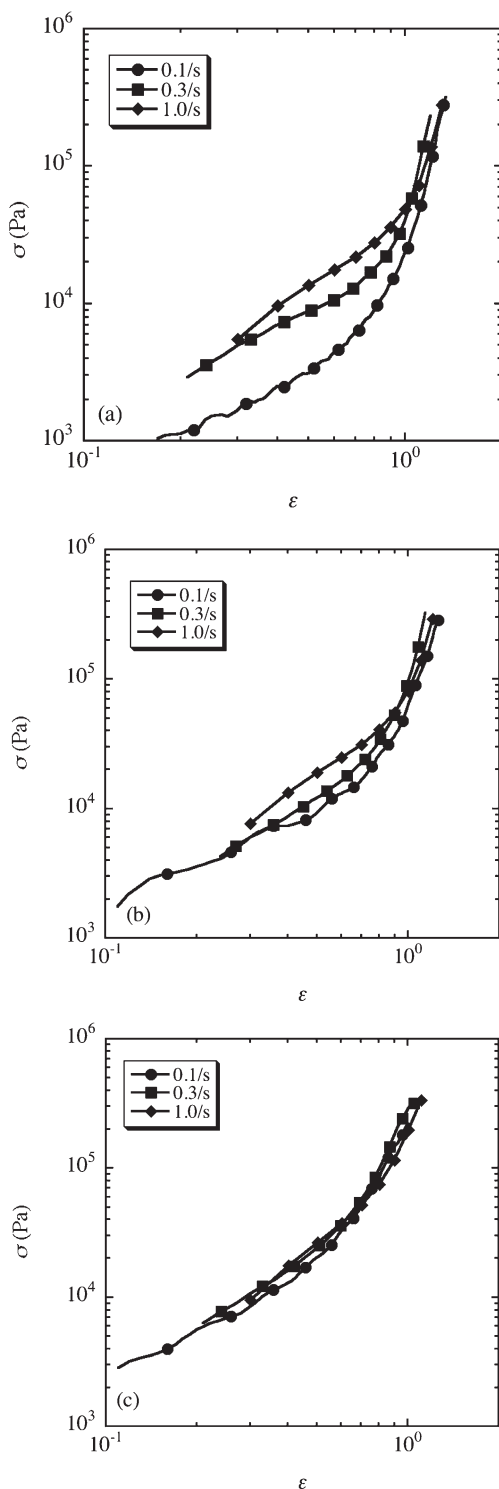


Figure 5 Stress–strain curves of the samples of EP-0.5 cured for (a)103, (b)108, and (c)113 min at strain rates of 0.1, 0.3, and 1/s, respectively.

for frequency. As shown in the curve of 112 min in Figure 3(a), the curing time is nearly equal to 113 min [Fig.5(c)], and $G'(\omega)$ is nearly constant for frequency. This shows the change to the elastic body of epoxy. From the results of Figures 4 and 5, we

understand that epoxy changes from a viscoelastic liquid state to a viscoelastic solid state by gelating and changes to an elastic body as curing time becomes longer above the critical gelation time.

This study was performed to clarify the mechanism of epoxy foaming, since the sample undergoes elongational flow at the foaming process. Therefore, we need additional consideration of mechanism of epoxy foaming by using the results of this study. We reported the effect of rheological behavior of epoxy during precuring on foaming in a previous report.⁶ We understood epoxy foam as follows. (i) Epoxy foam can be produced by precuring at more than the critical gelation time before foaming. (ii) Average diameter of bubble and porosity of epoxy foam became smaller as precuring time became longer. (iii) Size distribution of bubbles of epoxy foam is roughly bimodal when epoxy was precured for a relatively short time before foaming: large bubbles ($>100\ \mu\text{m}$) and small ones ($\cong 30\ \mu\text{m}$). The number of large bubbles then became small and finally disappeared as precuring time became longer. Using the relationship between the results above and this study, we understand that bubbles can be kept in epoxy foam, since strain hardening in elongational behavior appeared by gelating (i). Then, as in (ii), growth of bubbles was constricted due to high elongational viscosity at low strain with increasing curing time. As in (iii), when curing time was nearly equal to critical gelation time, elongational stress depended on strain rate. Strain rate dependence on stress means that the existence of viscous component and elastic component with finite deformation and viscous component exist in epoxy cured near the critical gelation time. Therefore, it is considered that the gel structure of epoxy was heterogeneous and that bubbles could easily coalesce at near the critical gelation time. On the other hand, when curing time becomes long enough, the gel structure of epoxy develops into a fully crosslinked structure extending through epoxy. Therefore, we understand that large bubbles disappeared because the coalescence of bubbles was prevented by formation of the homogeneous gel structure by changing to an elastic body.

CONCLUSIONS

We measured the elongational behavior of epoxy cured by various conditions over the critical gelation time. To obtain the optimal condition of epoxy for elongating, measurement of dynamic shear viscoelasticity was performed. The optimal weight ratio of epoxy/curing agent for elongation was obtained by the measurement of time dependency of shear viscosity. The critical gelation time of the sample at the optimal weight ratio was then determined by the results of time dependency of loss tangent and

frequency dependency of storage modulus, loss modulus, and loss tangent and using the rheological criterion proposed by Winter and Chambon.

Elongational viscosity was able to measure the appearance of strain hardening by gelating epoxy, and elongational behavior was similar to crosslinked rubber. For the relationship between elongational viscosity and curing time, elongational viscosity became higher as curing time increased at low strain. We confirmed that strain rate dependence on stress at small strain was small as curing time became longer and finally disappeared by the measurement of stress-strain curves at various strain rates. Moreover, we considered the relationship between elongational behavior of epoxy and foaming by using the result of this study and previous report of epoxy foaming. Then, for the reason that the size distribution of bubbles was roughly bimodal when the precuring time was short, we found that large bubbles existed, since the gel structure of epoxy was heterogeneous and bubbles could easily coalesce at short precuring time.

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