

Effect of Rheological Behavior of Epoxy during Precuring on Foaming

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ABSTRACT: In this study, the effect of rheological behavior of epoxy during precuring on foaming was investigated. Dynamic time sweep test of epoxy/curing agent (100/1, w/w) was conducted. The viscosities as a function of time showed extremely rapid increase from the order of 10^2 – 10^3 to 10^6 Pa · s at a certain time, followed by slow increase of the viscosities. Dynamic frequency sweep test of precured epoxy with curing agent was conducted at 90°C. The critical gelation time was obtained by using rheological criterion proposed by Winter and Chambon. We found that the slopes of $G'(\omega)$ and $G''(\omega)$ decreased with increasing precuring time. Correspondingly, $\tan \delta$ showed a change from negative to positive slope at a critical time. By using the results, the critical gelation time was determined as $t = 895$ – 935 s. Samples of epoxy/curing

agent/blowing agent (100/1/0.5) were precured for 960–1620 s. And then precured samples were foamed at 230°C for 300 s to decompose chemical blowing agent. The formed bubble size distribution becomes sharp with increase of the precuring time. There are roughly two sizes of bubbles when precured for relatively short time ($t < 1080$ s) before foaming: large bubbles (>100 μm) and small ones ($\cong 30$ μm). On the other hand, foams precured for long time ($t > 1200$ s) before foaming, large bubbles disappear, and the average diameter of the bubble becomes small while the porosity is low. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 657–662, 2008

Key words: epoxy; foam; gelation point; rheology; chemical blowing agent

INTRODUCTION

Epoxy has outstanding characteristics in chemical resistance, heat resistance, electrical properties, etc. Therefore, epoxy has widely been used in applications of sealant of semiconductor, coating compositions, and so forth. Foaming is one of the potential applications of epoxy to improve electric properties such as low- k materials, thermal insulation properties, lightweight, and low cost. Homogeneous and small bubble is needed for electronic parts. However, an application of epoxy to foaming is quite difficult, since epoxy cures with rapid increase of viscosity. Some reports have been published on epoxy foam, but most of them focus on the composites and the mechanical properties.^{1–4} In some reports of epoxy foam, Stefani et al.⁵ reported the production of epoxy foam by changing the ratio of epoxy, curing agent, and blowing agent. They also evaluated the cure mechanism by measuring the gelation time. However, they measured the gelation time by a simple method. They used thin tubes containing epoxy-amine mixtures in an oil bath and took the gelation

time at which the whole tube was lifted up by pulling the wire. Moreover, the gelation time was very short (less than 10 s), and curing and foaming processes were carried out at the same time. Therefore, the relationship between the gelation time and characterization of epoxy foam is not obtained sufficiently. Rheology is one of the most precise and scientific evaluation methods to determine gelation. Winter and Chambon^{6–8} have reported the detailed relationship between rheology and gelation. They have reported storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ near gelation point by using polydimethylsiloxane. Then they suggested that $G'(\omega)$ and $G''(\omega)$ at critical gelation point were defined by⁷

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

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

where n is an exponent, and G'_c and G''_c are constants. Thus they found out that $G'(\omega)$ and $G''(\omega)$ are represented as power law relationship for wide range of frequency at the gelation point, and the exponent (called “critical exponent”) is the same. Many researchers have reported the gelation of epoxy by using this result and represented that the critical exponent of $G'(\omega)$ and $G''(\omega)$ at the gelation

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point is same.^{9–15} Adolf et al.^{9,10} used diglycidyl ether of bisphenol A (DGEBA) and amine-type curing agent, and found the critical exponent at about 0.7. Matejka¹¹ reported the details of the change in $G'(\omega)$, $G''(\omega)$, and $\tan \delta$ of epoxy near the gelation point. Other researchers reported for various combinations of epoxy and curing agent.^{12–15}

In the plastic foaming process, optimum viscosity should be required for stable growth of foaming cell. Low viscosity causes coalescence and rupture of bubbles due to the intensive growth, whereas high viscosity gives rise to low porosity. Epoxy has low viscosity at the initial state. Stefani et al.⁵ produced the epoxy foam by using epoxy, amine, and siloxane. They produced foam by hydrogen gas generated in reaction of siloxane with amine. However, the sizes of bubbles are relatively large and the size distribution of bubble is broad. One reason is the bubbles coalesce. So far little attention has been, however, given to the epoxy foaming process from the viewpoint of viscoelastic evolution during curing treatment. Although some studies have been made on the viscosity evolution with time for epoxy, little is known about the effect of enhanced viscoelasticity on the epoxy foaming.

Therefore, in this study, we produced epoxy foam through two processes. In the first process, epoxy mixed with curing agent and blowing agent was precured at low temperature below the decomposition temperature of chemical blowing agent to obtain the optimum viscosity for foaming. Then this sample was foamed at high temperature. The purpose of this study is to investigate the effect of rheological behavior of epoxy during precuring on foaming.

EXPERIMENTAL

Materials

We used DGEBA as a starting material (EPIKOTE[®] 834, specific gravity is 1.18, molecular weight is about 470, manufactured by Japan Epoxy Resin, Japan). The curing agent is 2-ethyl-4-methylimidazole (2E4MZ) (Curezol[®] 2E4MZ, manufactured by Shikoku Chemicals, Japan) and the blowing agent is azodicarbonyl diamide (ADCA) (VINYFOR-AC#3C-K2, median particle diameter is 5 μm , specific gravity is 1.65, decomposition temperature is 208°C, amount of gas generated is 210 mL/g, manufactured by Eiwa Chemical Ind, Japan).

Time dependency of dynamic shear viscoelasticity

The sample was prepared as a weight ratio of DGEBA/2E4MZ of 100/1 without blowing agent. The dynamic shear measurement was performed by rotational rheometer (TA Instruments, ARES). 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 1.0 rad/s, strain of 1%, and temperatures of 90–140°C under nitrogen atmosphere. It was not possible to measure meaningful data at more than 150°C because curing reaction occurred intensely when reaching to the measurement temperature. The sample was set at 50°C to keep uncured state. The apparatus was set at a heating rate of 10°C/min when the temperature of the sample reached measurement condition. Then the isothermal measurement was started.

Frequency dependency of dynamic shear viscoelasticity

Frequency dependency of dynamic shear viscoelasticity was carried out to measure the gelation point of epoxy. The sample was prepared with the same as mentioned earlier. The dynamic shear measurement was performed by rotational rheometer (Anton Paar GmbH, Austria, Physica MCR301). The geometries of the test fixtures were parallel disks with a diameter of 12 mm for all measurements. The sample was precured at 90°C for a certain time, followed by dynamic tests ranging from 5 to 100 rad/s at 90°C.

Preparation of epoxy foams

The sample was prepared by a weight ratio of DGEBA/2E4MZ/ADCA of 100/1/0.5. It was applied for polyimide film at thickness of 300 μm . The samples before foaming were precured for 960, 1020, 1080, 1140, 1200, 1260, 1320, 1380, 1440, 1500, 1560, and 1620 s at 90°C. The samples treated with each precuring condition were foamed at 230°C for 300 s.

Scanning electron microscope observation

Scanning electron microscope (SEM) observation was performed with SEM (JEOL, Japan, JSM-5310). Fractured cross sections of foamed samples were observed. The samples were fractured with using an edged knife after immersed in liquid nitrogen for about 1 h. The samples were coated with gold before SEM observation. The average diameter of the bubble and the size distribution of bubble were calculated by image processing software (MOUNTECH). Porosity of foamed epoxy was calculated from SEM micrographs as follows:

$$p = (S_{\text{bubble}}/S_{\text{whole}}) \times 100 \quad (3)$$

where p is porosity, and S_{bubble} and S_{whole} are cross-sectional area of bubbles and whole, respectively.

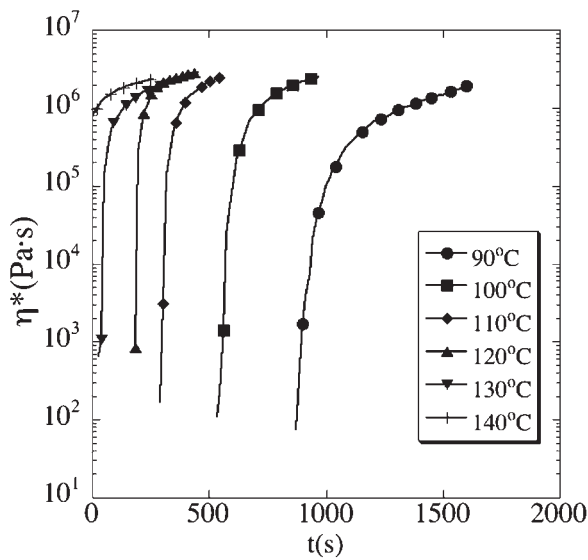


Figure 1 Complex viscosity η^* as a function of time, cured at temperature from 90 to 140°C.

RESULTS AND DISCUSSION

Dynamic shear viscoelasticity of DGEBA/2E4MZ

Figure 1 shows curves of complex viscosity η^* as a function of time for sample, cured at temperature from 90 to 140°C. It was impossible to detect the instrument torque at the onset of each test, since viscosities were too low. When viscosities reached about 2×10^6 Pa · s at all conditions, the measurements were stopped so that it did not exceed the instrument capabilities. The samples showed an extremely rapid increasing in viscosities after a critical time and then presented a slow increase beyond the viscosities of 10^6 Pa · s. This tendency was similar at all temperatures tested here. The time up to the onset of the rapid increase of viscosity were found to be about 870, 540, 240, 180, and 20 s at 90, 100, 110, 120, and 130°C, respectively. The start-up viscosity cured at 140°C was not observed. It is clear

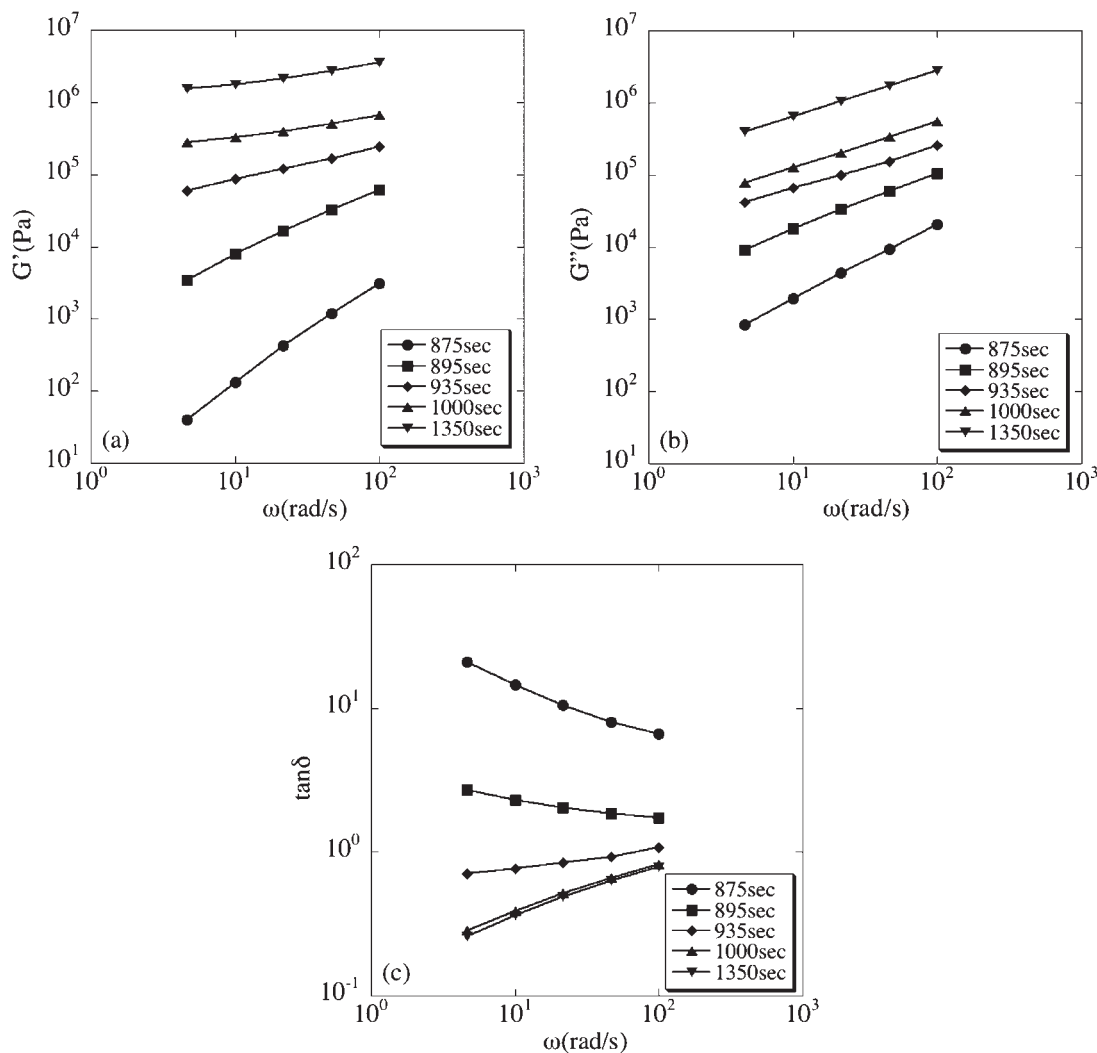


Figure 2 (a) Storage modulus G' ; (b) loss modulus G'' ; (c) $\tan \delta$ as a function of angular frequency with different curing times at 90°C.

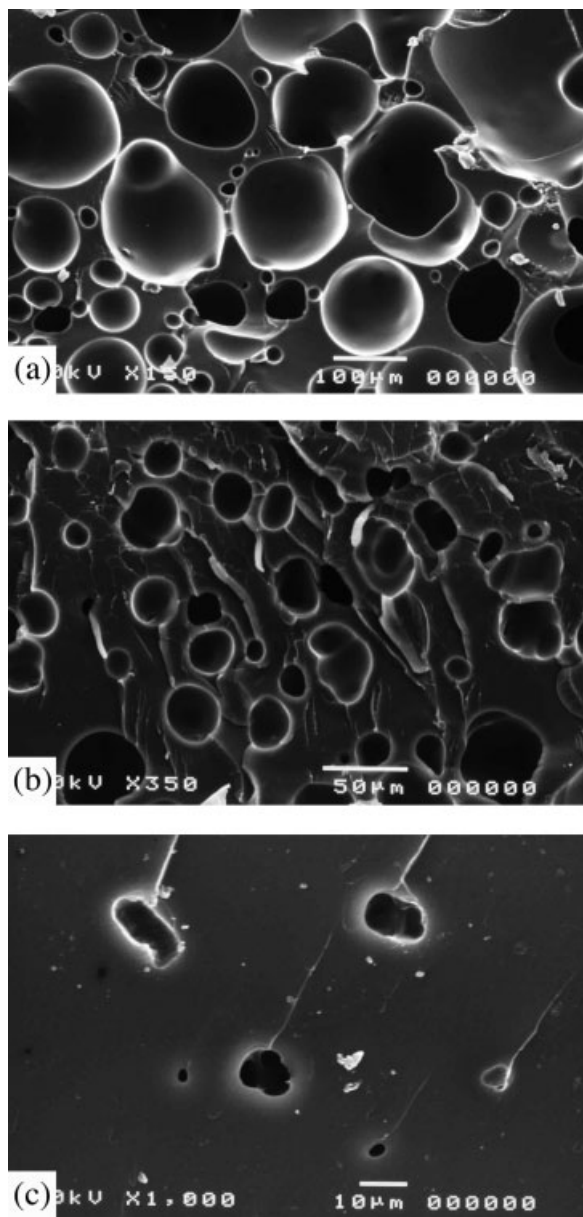


Figure 3 SEM micrographs of fracture cross sections of the foamed samples at 230°C for 300 s after precuring for (a) 960, (b) 1200, (c) 1620 s at 90°C.

that the crosslinking reaction already occurred before the start of measurement at 140°C.

Figure 2 shows the variation of storage modulus $G'(\omega)$, loss modulus $G''(\omega)$, and $\tan \delta$ with precuring time at 90°C. This temperature was determined in terms of stability of epoxy since the precure rate was slowest as shown in Figure 1. Frequency dependency of dynamic shear viscoelasticity was measured for samples precured at 90°C for 875, 895, 935, 1000, and 1350 s, which correspond to values when the viscosity reached at 10^2 , 10^3 , 10^4 , 10^5 , and 10^6 Pa · s, respectively, (see Fig. 1). The values in the legends denote the time to run each dynamic test during the precure treatment. The time to require the dynamic

test was within 100 s. As the time to fully cure epoxy is longer than that of other temperature, we chose this condition to study a relationship between rheological behavior near the gelation point and foaming processability.

In Figure 2(a), the curves of $G'(\omega)$ at 875 and 895 s represent the rapid lowering of $G'(\omega)$ at small ω . The slope of $G'(\omega)$ decrease with increasing precuring time. At 935 s and longer, $G'(\omega)$ and $G''(\omega)$ tend to level off. The change in $G'(\omega)$ denotes the change from viscoelastic liquids to viscoelastic solids. Furthermore, the $\tan \delta$ curves at 935, 1000, and 1350 s represent the positive gradient, whereas $\tan \delta$ of 875 and 895 s represent the negative gradient in Figure 2(c). Matejka has particularly reported about the rheological behavior of epoxy near the gelation point and obtained a gelation point as with our procedure.¹¹ As shown in Figure 2(c), $\tan \delta$ changed from negative to positive gradient as increasing precure time. It is considered that ω -independent $\tan \delta$ exists in 895–935 s and the gradient leveled off at around $\tan \delta = 2$. The exponent for critical gelation point is obtained by eq. (2) and the value nearly equals 0.7. This value is consistent with other reports.^{9–15} Therefore, we determined the gelation point to be in the range of time $t = 895$ – 935 s according to eqs. (1) and (2).

Foaming processability

Without precuring process, epoxy foams could not be observed since the gas of chemical blowing agent was discharged out of epoxy. Figure 3 shows SEM micrographs of fractured cross section of the foamed samples at 230°C for 300 s after precuring at 90°C.

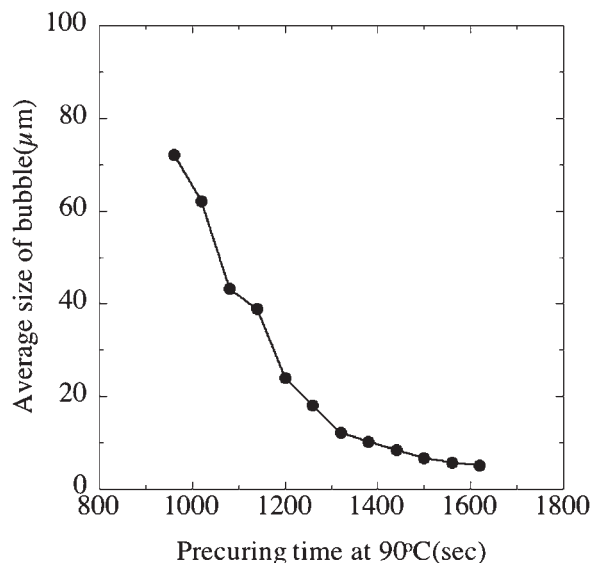


Figure 4 The average diameter of the bubble of fracture cross sections of the foamed samples at 230°C for 300 s after precuring at all conditions.

Figure 4 shows the average diameter of the bubble of fracture cross section of the foamed samples at 230°C for 300 s after precuring for 960, 1020, 1080, 1140, 1200, 1260, 1320, 1380, 1440, 1500, 1560, and 1620 s at 90°C. All conditions were above the gelation point ($t = 895\text{--}935$ s). The average diameter of the bubble became small as the precuring time before foaming became long. Finally, the average diameter of the bubble was almost the same with median size of ADCA powder. Figure 5 shows the porosity of foams calculated from SEM micrographs for different precuring time at 90°C. The porosity decreased with increasing the precuring time. Figure 6 shows the size distribution of bubble for different precuring time at 90°C before foaming. The large bubbles ($>100\ \mu\text{m}$) were gradually decreased as the precuring time became longer and the bubble size was below $50\ \mu\text{m}$ over 1200 s of precuring time.

From the results of Figures 3–6, we found to be able to produce epoxy foams through precuring process before foaming. The average diameter of the bubble and porosity decreased with increasing the precuring time. This is due to the high viscosity, which prevents further expansion and coalesce of the cell. On the other hand, the size distribution of bubble represented characteristic behavior. We should note that peaks of frequency were less than $50\ \mu\text{m}$ at all conditions, but large-sized bubbles over $100\ \mu\text{m}$ existed only when the precuring time was short such as 960 and 1080 s. Foam precured for 1200 s did not have large size bubbles over $100\ \mu\text{m}$ but sharp size distribution. Foams precured for 1320 s had small size bubbles less than $30\ \mu\text{m}$.

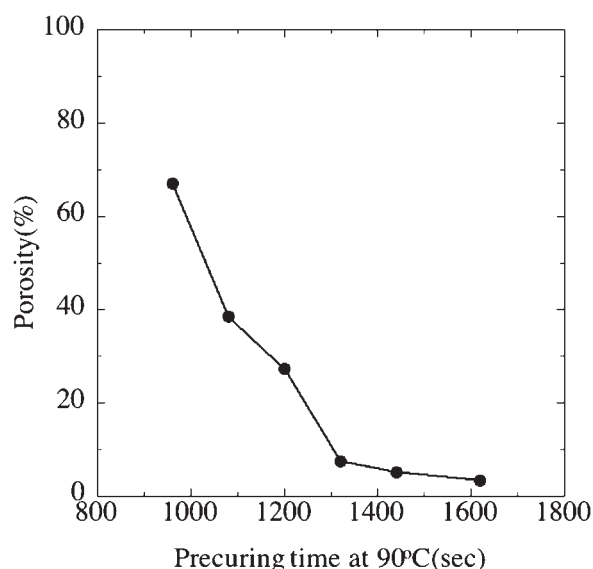


Figure 5 The porosity of foams calculated from SEM micrographs for different precuring time at 90°C.

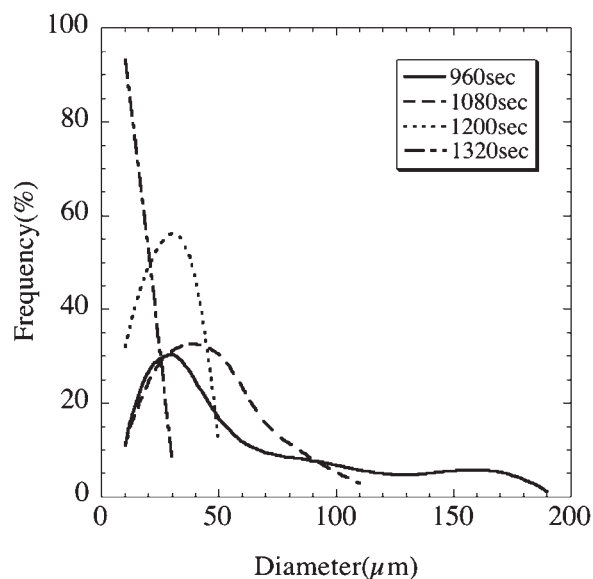


Figure 6 The size distribution of bubble for different precuring time at 90°C.

From the result of dynamic shear viscoelasticity, all the samples after precuring have already gelled, i.e., the samples changed from sol to gel-state, in which the three-dimensional network was formed. In addition, η^* becomes higher as the precuring time is longer. Therefore, we can understand that bubble size and porosity become smaller and lower as precuring time is longer. But, at present, we cannot explain the reason why the size distribution of bubbles is roughly bimodal in Figure 3(a), though the phenomenon was also confirmed by other reports.^{4,5} However, the bubble size of our report is smaller than that of other reports^{3–5} by precuring process and we found that precuring process is an effective method to control bubble size, size distribution, and porosity.

In near future, we will further study the elongational rheology of precured epoxy to clarify the phenomenon mentioned earlier. The cell size and shape would be affected by elongational flow at foaming. In addition, growth of bubble at foaming has a relationship with elongational flow behavior. In particular, control of strain hardening of elongational viscosity is needed to stabilize deformation of the bubbles. In many papers, researchers report the relationship between a strain hardening and foaming for thermoplastic and find that control of strain hardening is extremely important to stabilize the bubbles.^{16,17} Yamaguchi and Suzuki¹⁶ blended linear low-density polyethylene (LLDPE) and crosslinked LLDPE (cLLDPE) to enhance strain hardening of elongational viscosity and compared foaming behavior of pure LLDPE with blended sample. They represented that cell size of foam of blended sample became homogeneous, whereas cell size of foam of

pure LLDPE became heterogeneous. Spitael and Macosko¹⁷ used pure and blend polypropylene (PP) and compared foamability of PP. They reported that linear PP mixed with branched PP represented better foamability than linear PP.

CONCLUSIONS

Dynamic shear viscoelasticities of DGEBA/2E4MZ (100/1, w/w) were measured as a function of time. We found that the sample showed an extremely rapid increasing in viscosities after a critical time and then showed a slow increasing after the viscosities reached about 10^6 Pa · s. Dynamic frequency sweep test was conducted at 90°C. The critical gelation time was obtained by using rheological criterion proposed by Winter and Chambon. We found that the slopes of $G'(\omega)$ and $G''(\omega)$ decreased with increasing curing time. Correspondingly, $\tan \delta$ showed a change from negative to positive slope at a critical time. By using the results, the critical gelation time was determined as $t = 895\text{--}935$ s.

The curing treatment at 90°C enabled foaming of DGEBA/2E4MZ/ADCA (100/1/0.5, w/w). The curing time is an important factor for epoxy foam and affected the cell size and the size distribution. We confirmed that the size distribution of bubbles is roughly bimodal when the curing time was short. And this phenomenon disappeared when

the curing time became over 1080 s. In future, we need to clarify this phenomenon to produce homogeneous and high-porosity foams.

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