

Dynamic Mechanical Properties of Functionally Graded Syntactic Epoxy Foam

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Abstract We investigated dynamic mechanical properties in functionally graded (FG) syntactic foams which had graded distribution of Acrylonitrile micro-balloons in epoxy resin matrix. The density distributions in the FG syntactic epoxy foams were graded by floating phenomenon of the micro-balloons in the matrix resin during curing process. Dynamic viscoelastic measurements and compression tests were conducted to evaluate distributions of mechanical properties in the foams. The dynamic viscoelastic measurements revealed that the thermo-viscoelastic properties of the foams were determined by the properties of the epoxy matrix resin. The static and dynamic compression tests provided relations between the mechanical properties: the compressive Young's modulus and yield stress, and the density in the foams.

1 Introduction

Functionally graded materials (FGMs) [1, 2] were first suggested as materials for relaxing thermal stress in structures. The FGMs can be designed and manufactured to have excellent properties or to suit required conditions of applications by controlling distributions of the phases [2]. Recently, some numerical studies [3–5] have suggested that functionally graded (FG) foams having density distribution are effective for impact energy absorption.

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Concurrently with those numerical studies, syntactic foam [6] having density distribution have been produced for the purpose of impact energy absorption [6–10]. The syntactic foams easily fabricated by filling matrix material with small hollow spherical particles (micro-balloons) have light weight and high absorption of mechanical energy [6]. The mechanical properties of the syntactic foams can be adjusted by the volume fraction of the micro-balloons in the matrix material, namely density of foam as well as properties of the matrix material and the micro-balloons. The authors have developed fabrication process of FG syntactic foams [9–11]. In order to control the distributions of the mechanical properties, the density distributions in the foams are graded by floating phenomenon of the micro-balloons in the matrix resin during curing process [9–11].

In the present study, we investigated distributions of mechanical properties in the FG syntactic epoxy foams which have graded distribution of Acrylonitrile micro-balloons in epoxy resin matrix to apply for impact energy absorption. Dynamic viscoelastic measurements were conducted out to clarify the effect of filling the micro-balloons into the epoxy resin on viscoelastic properties of the FG syntactic epoxy foams. Static and dynamic compression tests were performed to obtain relation between density and mechanical properties including the strain rate effect due to the viscoelastic properties.

2 Fabrication of FG Syntactic Epoxy Foam

Figure 1 shows fabrication process to produce FG syntactic epoxy foams [9–11]. A mixture of micro-balloons and matrix resin was heated up to constant temperature T_F to decrease viscosity of the matrix resin. Then the micro-balloons were floated easily during a retaining time t_F due to density difference between the matrix resin and the micro-balloons, that is, graded distribution of micro-balloons occurs. Here, the distribution of the micro-balloons can be controlled by constant temperature T_F and a retaining time t_F based on temperature dependency on the viscosity of the matrix resin until the gelation of the resin. After the gradating micro-balloons, the mixture was cured based on a standard curing process. In the paper, FG syntactic epoxy foams were produced by adding Acrylonitrile copolymer micro-balloons coated by calcium carbonate powder (MFL-100CA, Matsumoto Yushi-Seiyaku) into epoxy resin. The average diameter of the micro-balloons was 80–110 μm and the density was $130 \pm 30 \text{ kg m}^{-3}$. The matrix epoxy resin was bisphenol-A-type epoxide resin (AER2603, Asahi Kasei E-materials) with a curing agent (RIKACID MH-700, New Japan Chemical) which was an ad-mixture of 4-methyl hexahydrophthalic anhydride (4-methyl HHPA) and hexahydrophthalic anhydride (HHPA) and an accelerator (BMI12, Mitsubishi Chemical) which was 1-benzil-2-methylimidazoles. The weight ratio of the main agent, the curing agent and the accelerator was determined as 100:86:0.5 according to stoichiometry. The curing condition for the epoxy resin system was composed of the pre-curing at 373 K for 2 h for the gelling and the post-curing at 403 K for 15 h for cross-linking

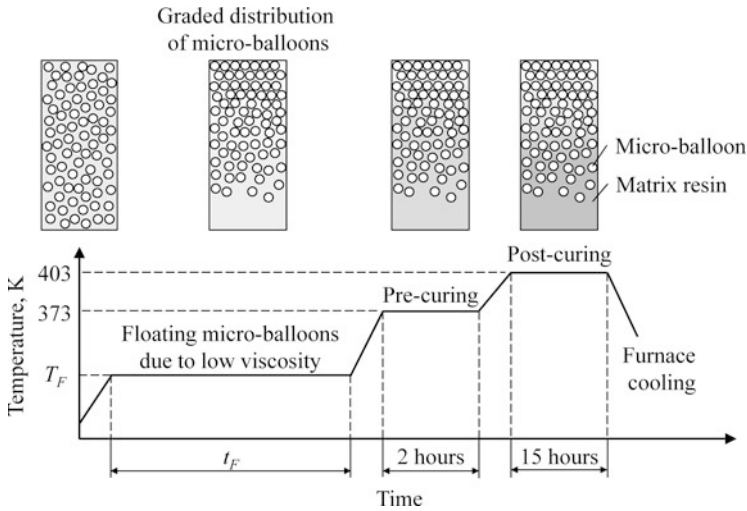


Fig. 1 Fabrication process for FG syntactic epoxy foam

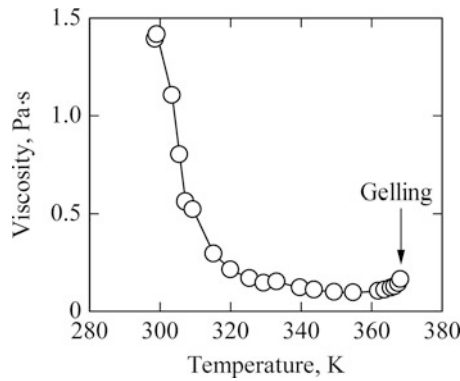
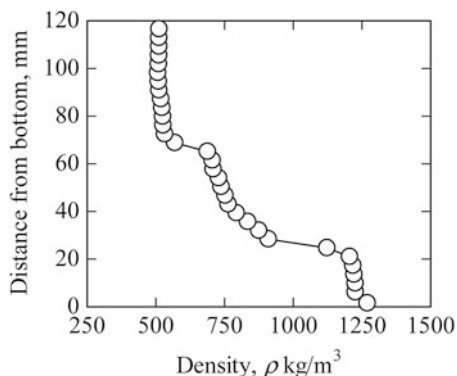


Fig. 2 Relation between viscosity and temperature for epoxy resin

reaction. Figure 2 shows temperature dependency of the viscosity for the epoxy resin before curing measured by a rotational viscometer (DV-1+, Brookfield). The viscosity decreased drastically with temperature increase from room temperature to 330 K. The viscosity maintained nearly constant value above 330 K. After that, gelling of the resin occurred at 370 K. After the mixture of the epoxy resin and the micro-balloons was stored in a vacuum vessel to remove voids, the mixture was poured into an aluminum mold. The mold was 260mm long, 10mm wide and 130mm deep. The mixture was kept at $T_F = 323\text{ K}$ for $t_F = 2\text{ h}$ to grade the distribution of the micro-balloons as shown in Fig. 1. Then the mixture was cured according to above mentioned curing conditions. After curing, densities ρ

Fig. 3 Density distribution of FG syntactic epoxy foam



at different positions in the foams were measured by the Archimedes method according to JIS Z8807 to obtain the density distributions.

The density distribution of the fabricated FG syntactic epoxy foam having average density 710 kg m^{-3} is shown in Fig. 3. The density in the fabricated FG foam was distributed from minimum density of 500 kg m^{-3} to maximum density of $1,200 \text{ kg m}^{-3}$ (density of neat epoxy resin).

3 Dynamic Thermo-Viscoelasticity Measurements

The dynamic thermo-viscoelasticity measurements were conducted out to clarify the effect of filling the micro-balloons into the epoxy resin on the viscoelastic properties in the FG syntactic epoxy foams by using a dynamic viscoelastometer (Rheogel-E4000, UBM) with a non-resonance tensile method. The specimens were 2 mm in thick, 40 mm long and 5 mm wide, which were cut from the fabricated foam (Fig. 3) not to have density distribution in the longitudinal direction of the specimens. The densities of the specimens were 510 , 800 and $1,200 \text{ kg m}^{-3}$ (epoxy resin density). Storage modulus E' , loss modulus E'' and loss factor, $\tan \delta (= E'/E'')$ for tensile oscillation with frequency of 10 Hz were measured at each 5 K in the temperature range from 233 to 493 K. The heating rate was 1 K min^{-1} .

Figure 4 shows temperature dependencies of storage modulus E' , loss modulus E'' . Regardless of the densities of the specimens, the storage modulus decreased gradually with the temperature increase up to 420 K. After that, the storage modulus decreased rapidly in the temperature range from 420 to 460 K, namely the glass transition occurred. Additionally, the storage and loss moduli in whole temperature range were reduced with decreasing the density from the epoxy resin density to lower densities. In contrast, temperature dependencies of the loss factor defined by $\tan \delta (= E'/E'')$ shown in Fig. 5 were not affected by the densities, and the loss factors showed peak values at temperature of 440 K for all densities. Regardless of the specimen density (namely the volume fraction of the micro-balloons), the glass

Fig. 4 Temperature dependencies of storage modulus E' and loss modulus E''

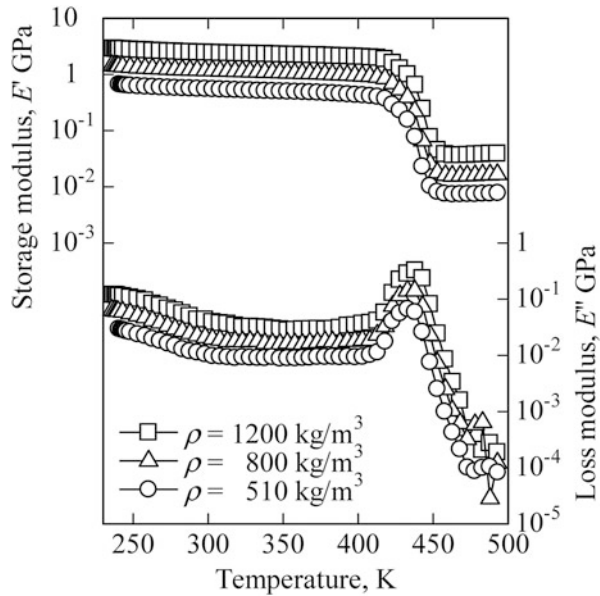
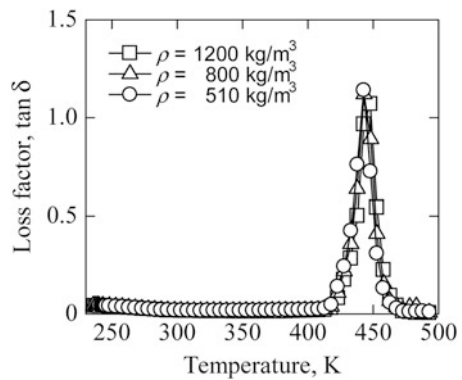


Fig. 5 Temperature dependencies of loss factor $\tan \delta$



transition temperatures were identified to be 440 K. Therefore, absolute values of the viscoelastic properties of the FG syntactic foams depended on the volume fraction of the micro-balloons, meanwhile the temperature dependencies of the viscoelastic properties were found to be governed by the epoxy matrix.

4 Static and Dynamic Compression Tests

Static and dynamic compression tests were performed to evaluate the mechanical properties of the FG syntactic epoxy foams. The specimens were 10 mm long, 10 mm wide and 5 mm high. The average densities of the specimens were 510, 690, 780, 920 and 1,200 kg m⁻³.

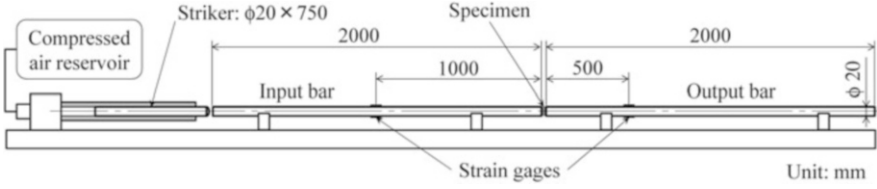


Fig. 6 Schematic diagram of split Hopkinson pressure bar equipment

The static compression tests were carried out under a constant displacement rate of 1 or 10 mm min⁻¹ with a universal testing machine (Autograph DSC-25T, Shimadzu). The corresponding strain rates were 3.3×10^{-3} and 3.3×10^{-2} s⁻¹, respectively. The dynamic compression tests were conducted to obtain stress-strain curves under high strain rates by using a split Hopkinson pressure bar (SHPB) equipment. A schematic diagram of the SHPB equipment is shown in Fig. 6. The striker, input and output bars were made of aluminum alloy (JIS A7075-T6) to accurately measure stress-strain response of the low mechanical impedance specimen. The histories of the nominal strain $\varepsilon(t)$, strain rate $\dot{\varepsilon}(t)$ and stress $\sigma(t)$ in the specimen under assumption of force equilibrium between both side of the specimen were determined by the following equations:

$$\begin{aligned}\varepsilon(t) &= \frac{2c_0}{h_s} \int_0^t [\varepsilon_I(t') - \varepsilon_T(t')] dt', \\ \dot{\varepsilon}(t) &= \frac{2c_0}{h_s} [\dot{\varepsilon}_I(t) - \dot{\varepsilon}_T(t)], \\ \sigma(t) &= \frac{A_0}{A_s} E_0 \varepsilon_T(t),\end{aligned}\quad (1)$$

where $\varepsilon_I(t)$ and $\varepsilon_T(t)$ denote the incident and transmitted strain pulse, c_0 , E_0 and A_0 are the longitudinal elastic wave velocity ($= 5.1 \times 10^3$ ms⁻¹), Young's modulus ($= 73.2$ GPa) and the cross-sectional area of the input and output bars, and h_s and A_s are the height and cross-sectional area of the specimen. The strain rates in the dynamic tests were approximate 2×10^3 ms⁻¹. Figure 7 shows compressive stress-strain curves obtained by the static and dynamic tests for the specimens with the densities of 510 and 920 kg m⁻³. The static test curves showed typical behavior of conventional foam material; elastic deformation, deformation in plateau region after the yielding, and densitification. The compressive stress-strain relations were found to strongly depend on the density. In the dynamic tests, although the densitification did not occur due to the brittleness of the epoxy resin in high strain rates, the Young's modulus and yield stress increased compared with those of static tests due to the viscoelastic properties of the epoxy matrix as show in Fig. 4. In general, mechanical properties of foam materials depend on the relative density to the one of matrix [12]. Consequently, the relative Young's modulus, $E(\rho, \dot{\varepsilon})/E_0(\dot{\varepsilon})$ and relative yield stress,

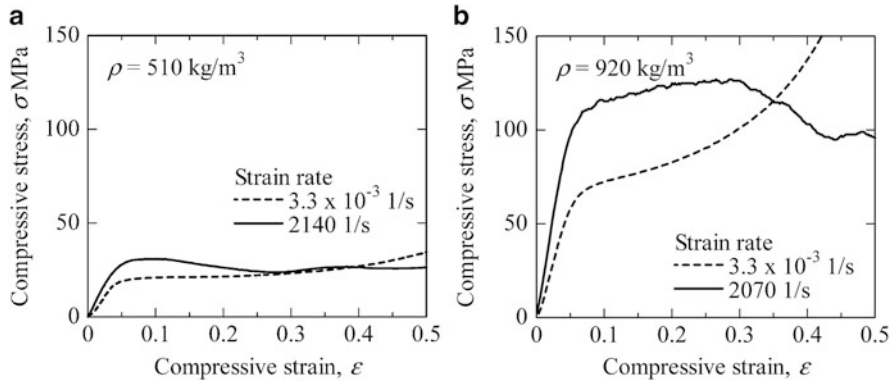


Fig. 7 Compressive stress-strain curves obtained by static and dynamic tests. (a) Density, $\rho = 510 \text{ kg m}^{-3}$. (b) Density, $\rho = 920 \text{ kg m}^{-3}$

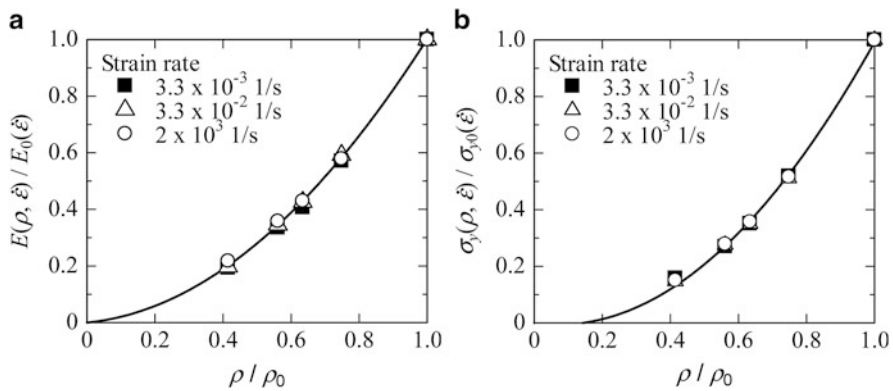


Fig. 8 Relation between viscosity and temperature for epoxy resin. (a) Relative Young's modulus. (b) Relative yield stress

$\sigma_y(\rho, \dot{\epsilon})/\sigma_{y0}(\dot{\epsilon})$ for various strain rates are plotted against the relative density, ρ/ρ_0 in Fig. 8. Here, ρ_0 is the density of the epoxy matrix, $E_0(\dot{\epsilon})$, and $\sigma_{y0}(\dot{\epsilon})$ denote the Young's modulus and yield stress including strain rate effect for the epoxy matrix. From Fig. 8, the compressive Young's modulus $E(\rho, \dot{\epsilon})$ and yield stress $\sigma_y(\rho, \dot{\epsilon})$ could be expressed in the separation variables composed of the quadratic function of the relative density and the Young's modulus or yield stress for the epoxy matrix including the strain rate effect:

$$E(\rho, \dot{\epsilon}) = \left[0.89 \left(\frac{\rho}{\rho_0} \right)^2 + 0.11 \frac{\rho}{\rho_0} \right] E_0(\dot{\epsilon}),$$

$$\sigma_y(\rho, \dot{\epsilon}) = \left[1.15 \left(\frac{\rho}{\rho_0} \right)^2 - 0.15 \frac{\rho}{\rho_0} \right] \sigma_{y0}(\dot{\epsilon}). \quad (2)$$

Therefore, the graded distributions of the compressive Young's modulus and yield stress can be identified from the density distribution with the relations of Eq. (2).

5 Conclusion

We investigated the dynamic mechanical properties in the FG syntactic foams which have graded distribution of the Acrylonitrile micro-balloons in the epoxy resin matrix. The dynamic viscoelastic measurements and compression tests for low and high strain rates were conducted to evaluate the distributions of mechanical properties in the FG syntactic foams. Because temperature dependences of the FG syntactic epoxy foams are determined by the ones of the epoxy matrix, the compressive Young's modulus and yield stress were expressed in the separation of variables composed of the quadratic function of the relative density and the Young's modulus or yield stress for the epoxy matrix including strain rate effect.

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