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Constitutive modeling for mechanical behavior of PMMA microcellular foams

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Abstract

Constitutive equations for nonlinear tensile behavior of PMMA foams were studied. Five viscoelastic models composed of elastic and viscous components were accounted for the modeling of the constitutive equations. The developed constitutive equations are expressed in terms of material properties and foam properties such as strain, strain rate, elastic modulus, relative density of foam, and relaxation time constant. It was found that the stress–strain behaviors by Generalized Maxwell model, Three Element model and Burgers model could be described by the constitutive equation obtained from the Maxwell model. For the verification of the constitutive model, poly(methyl methacrylate) (PMMA) microcellular foams were manufactured using batch process method, and then uniaxial tensile tests were performed. The stress–strain curves by experiment were compared with the theoretical results by the constitutive equation. It was demonstrated that nonlinear tensile stress–strain behaviors of PMMA foams were well described by the constitutive equation.

Keywords: Constitutive equation; Nonlinear viscoelastic model; PMMA microcellular foam

1. Introduction

Most polymers or polymeric foams have viscoelastic or viscoplastic behaviors [1–8]. To be able to describe a specific mechanical behavior of polymeric foams, the corresponding constitutive law is required for the specific deformation phenomena of the material.

The mechanical properties of microcellular foams have been of great interest to researchers in recent years because of their unique microstructure. Microcellular foams are usually defined as the foams having average cell sizes in the order of 10 μm and cell densities in the order of 10^9 to 10^{15} cells/cm^3 [9]. Compared to unfoamed polymers and conventional foams, microcellular foams have some superior mechanical properties such as high impact strength [10,11], high toughness [12], high stiffness-to-weight ratio [13], high fatigue life [14], and reduced material weight and cost. Therefore, microcellular foams have a great potential for applications such as packaging, insulation, automotive and aircraft industries, and structural components.

In order to describe the macroscopic nature of the materials in question, constitutive laws are used, so proper constitutive laws are necessary to govern the distinct types of macroscopic material behaviors. Schiessel et al. [15] derived fractional constitutive equations on the basis of viscoelastic models such as the Maxwell model and Kelvin-Voigt model, where each model was changed to generalized form using fractional elements. If a finite number of basic viscoelastic elements is used with a finite distribution of delay or relaxation times, the relationship between stress and strain can be obtained by a fractional model; Hernandez-Jimenez et al. [16] studied this method using the Maxwell model. A fractional viscoelastic constitutive equation using the three parameter model was studied by Schmidt and Gaul [17] and the adaptive capability of the equation to viscoelastic moduli by experiment was demonstrated. In search for a different method to express the nonlinear viscoelastic behavior of thermorheologically complex materials, Klompen and Govaert [18] considered stress-dependent viscosity in Generalized Maxwell model and applied it to PMMA. Also, nonlinear viscoelastic models based on free volume considerations were used as constitutive models [19], in which the effect of stress and

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strain on the free volume was considered and compared to tensile experimental data at various rates.

Convolution integral forms are sometimes used to describe the dynamic behavior of viscoelastic properties of foams [8,20] . Notably, the time-dependent response of a viscoelastic material has been expressed by convolution integral called Boltzmann superposition integral [21]. Lu and Zhang [22] showed a constitutive relation expressed in terms of relative density and strain, using the Boltzmann integral, and applied it for the tensile behavior of microcellular polycarbonate.

In this paper, constitutive equations for nonlinear tensile behavior of PMMA foams were studied. The modeling was presented in terms of foam parameters such as foam density and fraction of solid in the cell struts. The application of the constitutive model was confined to only tensile behavior of foams which show viscoelastic property. Also, experimental work to verify the constitutive model was performed; PMMA microcellular foams were manufactured using batch process method and tensile tests results of the foams were compared with the constitutive model.

2. Constitutive equations for nonlinear elastic behavior of PMMA foams

Several constitutive equations were derived from viscoelastic models to describe the tensile stress–strain behavior of PMMA foams.

2.1. Constitutive equation using Maxwell model

In the Maxwell model (Fig. 1(a)), the spring and dashpot represent the elastic response and the time-dependent response, respectively, where E is elastic modulus and η is defined as viscosity modulus. The equation of motion of the model is expressed as:

$$\dot{\sigma} + \frac{E}{\eta}\sigma = E\dot{\varepsilon} \tag{1}$$

where σ is the stress on both spring and dashpot, and ε is the total strain of the model. From Eq. (1), a constitutive equation is derived, providing strain rate is constant, as:

$$\sigma(t) = \eta\dot{\varepsilon}\left[1 - \exp\left(-\frac{E}{\eta}t\right)\right]. \tag{2}$$

The relationship between E and η is obtained from Fig. 1(a):

$$\eta = \frac{\varepsilon_s}{\dot{\varepsilon}_d}E \tag{3}$$

where ε_s and ε_d are the strains shown by the spring component and the dashpot component, respectively. In nonlinear behavior, the modulus of viscosity η is dependent on the stress during the deformation [18]. However, in this study, the strain and strain rate effects are assumed to be small and negligible. In other words, the constant value of the modulus of viscosity is used in the constitutive equation. Thus, the ratio of ε_s and $\dot{\varepsilon}_d$ could be considered as a constant and is represented using the relaxation time constant expressed as $\tau = \eta/E$, where τ is a material property determined experimentally. If the time variable is replaced by strain using the relationship $\varepsilon = \dot{\varepsilon}t$, the stress is expressed as a function of strain and strain rate:

$$\sigma = \eta\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right]. \tag{4}$$

The equivalent elastic modulus E_{eq} is obtained from Eq. (4) and it can be counted as the elastic modulus of foams, E^*:

$$E_{eq}(= E^*) = \left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon\to 0} = E \tag{5}$$

Eventually, the constitutive equation is expressed as a function of strain, elastic modulus of foams, time constant τ, and strain rate:

$$\sigma = E^*\tau\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right]. \tag{6}$$

By expressing E^* and τ as function of foam properties, the constitutive equation can be represented in terms of foam properties such as the relative density of foams.

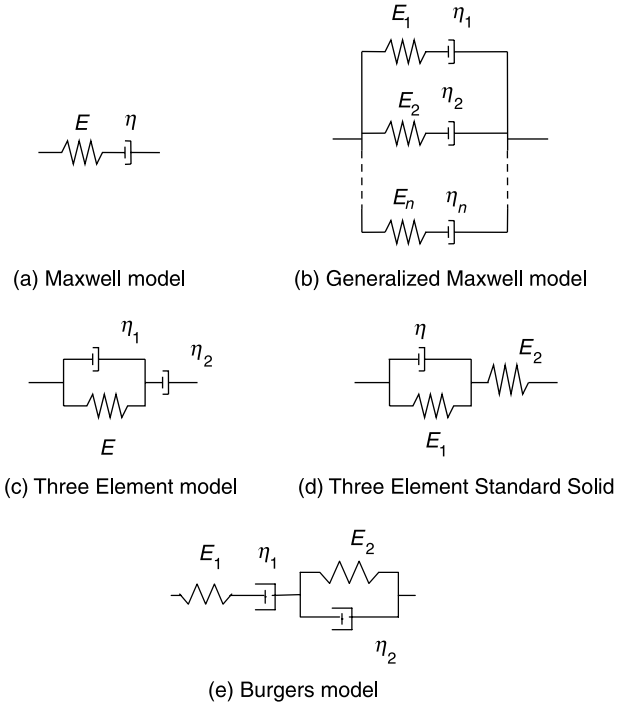


Fig. 1. Viscoelastic models.

2.2. Constitutive equation using Generalized Maxwell model

Using the Riesz representation theorem [23], the stress tensor expressed by strain history can be changed to the Stieltjes integral form, and from the integral the stress constitutive equation is obtained with variable changes [21]:

$$\sigma(t) = \int_0^t E(t-t')\dot{\varepsilon}(t')\mathrm{d}t'. \tag{7}$$

E is defined as a relaxation function which represents modulus. Since the force on each value of Generalized Maxwell model (Fig. 1(b)) relaxes exponentially, the modulus is expressed as [5]:

$$E(t-t') = \sum_{i=1}^{n} E_i \exp\left(-\frac{(t-t')}{\tau_i}\right) \tag{8}$$

in which the relaxation time constant τ_i is defined as $\tau_i = \eta_i/E_i$. Accordingly, the constitutive equation is obtained providing $\dot{\varepsilon} =$ constant and $t = \varepsilon/\dot{\varepsilon}$ as:

$$\sigma = \sum_{i=1}^{n} E_i \tau_i \dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau_i \dot{\varepsilon}}\right)\right]. \tag{9}$$

Eq. (9) contains the concepts of convolution integral and fractional model. Since the stress in Generalized Maxwell Model is the sum of the stresses of each Maxwell model component, the stress in Eq. (9) can also be obtained from Eq. (4) by summation of each stress component:

$$\sigma = \sum_{i=1}^{n} \sigma_i = \sum_{i=1}^{n} \eta_i \dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau_i \dot{\varepsilon}}\right)\right]. \tag{10}$$

The equivalent elastic modulus of the Generalized Maxwell model is obtained from Eq. (9);

$$E_{\mathrm{eq}}(= E^*) = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon}\right|_{\varepsilon \to 0} = \sum_{i=1}^{n} E_i \tag{11}$$

If $\eta_i = \eta$ and $E_i = E$, as a special case of the Generalized Maxwell model, $E^* = nE$ and $\tau_i = (\eta/E)(=\tau)$. Then, Eq. (9) becomes

$$\sigma = nE\tau\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right] = E^*\tau\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right]. \tag{12}$$

This corresponds to the constitutive equation by the Maxwell model (Eq. (6)). As another case, when $n = 2$, Eq. (9) is expanded to:

$$\sigma = E_1\tau_1\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau_1\dot{\varepsilon}}\right)\right] + E_2\tau_2\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau_2\dot{\varepsilon}}\right)\right] \tag{13}$$

where $E^* = E_1 + E_2$, $\tau_1 = \eta_1/E_1$ and $\tau_2 = \eta_2/E_2$. For more simplicity, if E_1 is assumed equal to E_2, then Eq. (13) is:

$$\sigma = \frac{E^*}{2}\tau_1\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau_1\dot{\varepsilon}}\right)\right] + \frac{E^*}{2}\tau_2\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau_2\dot{\varepsilon}}\right)\right] \tag{14}$$

in which $E^* = E_1 + E_1 = 2E_1$. Eq. (14) becomes the constitutive equation obtained from the Maxwell model when $\tau_1 = \tau_2$. Despite $\tau_1 \neq \tau_2$, it was proved that by choosing proper value of τ_1 and τ_2 in Eq. (14), the same stress–strains curves as those by the Maxwell model (Eq. (6)) are made; where $\tau_1 + \tau_2 \geq \tau$ is always maintained. This rule is applied to all n in the Generalized Maxwell model. For the cases of $n = 2$ and $n = 3$, the stress–strain curves of Eq. (9) are plotted and compared with the one by the Maxwell model (Eq. (6)) in Fig. 2. For the plot of Eq. (6) in Fig. 2, the value of τ was determined so that the theoretical curve can fit to the experimental data. Also, the values of E^* and $\dot{\varepsilon}$ were obtained from experimental data and Eq. (30). In order to match to the stress–strain curve by Maxwell model, the Generalized Maxwell model ($n = 2$) can have many values of τ_1 and τ_2, however, only one value ($\tau_1 = 47$ and $\tau_2 = 100$) was specified in Fig. 2. The Generalized Maxwell model with $n = 3$ was also used by the same method as $n = 2$. From Fig. 2, it is clear that the constitutive equation by the Generalized Maxwell model created the same stress–strain behavior as the Maxwell model with only different time constants. Fig. 3 shows the stress–strain curves by the Generalized Maxwell model with each different E_i and τ_i. It was also proved in the Figure that if the same equivalent elastic modulus is used in both models, any form of the constitutive equation by the Generalized Maxwell model can describe the stress–strain behavior made by the Maxwell model. In other

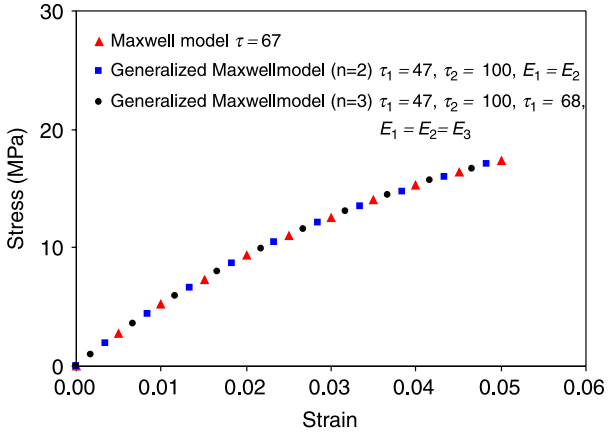


Fig. 2. Comparison of the constitutive equations by Generalized Maxwell model with that by Maxwell model (E^* are the same in all three models).

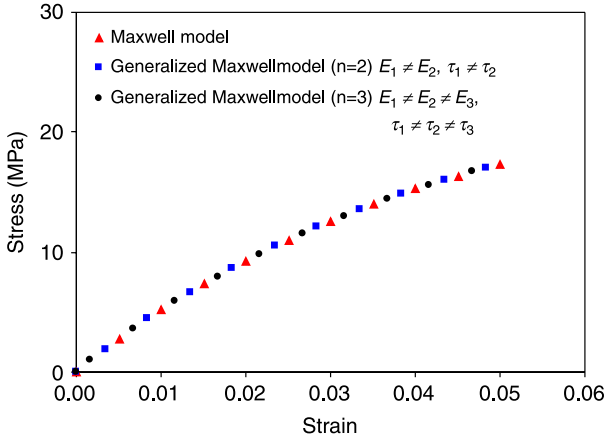


Fig. 3. Comparison of the constitutive equations by Generalized Maxwell model with that by Maxwell model (E^* are the same in all three models).

words, the behavior of Eq. (9) almost coincides with that of Eq. (6) if proper combinations of E_i and τ_i are used in Eq. (9).

2.3. Constitutive equation using Three Element model

The equation of motion of the Three Element model (Fig. 1(c)) is:

$$\dot{\sigma} + \frac{E}{\eta_1 + \eta_2}\sigma = \frac{E\eta_2}{\eta_1 + \eta_2}\dot{\varepsilon} + \frac{\eta_1\eta_2}{\eta_1 + \eta_2}\ddot{\varepsilon}. \tag{15}$$

Assuming that $\dot{\varepsilon} = \text{constant}$ and $\ddot{\varepsilon} = 0$, a constitutive equation is derived using the similar procedures as in Section 2.1:

$$\sigma = \eta_2\dot{\varepsilon}\left[1 - \exp\left(-\frac{E}{\eta_1 + \eta_2}\frac{\varepsilon}{\dot{\varepsilon}}\right)\right]. \tag{16}$$

If the relaxation time constant is set as $\tau = (\eta_1 + \eta_2)/E$,

$$\sigma = \eta_2\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right]. \tag{17}$$

The equivalent elastic modulus is calculated in the same method:

$$E_{\text{eq}}(= E^*) = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon}\right|_{\varepsilon\to 0} = \frac{\eta_2}{\eta_1 + \eta_2}E \tag{18}$$

From Eqs. (17) and (18), the constitutive equation by the Three Element model is:

$$\sigma = E^*\tau\dot{\varepsilon}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right] \tag{19}$$

which is identical to the constitutive equation by the Maxwell model. This means that even if the values of the components E and η are different between the Maxwell model and the Three Element model, the stress–strain behaviors by both models are coincident with each other if and only if E^* and τ are the same in both models. The expressions of E and η are also summarized in Table 1.

2.4. Constitutive equation using Three Element Standard solid

The equation of motion of the Three Element Standard Solid (Fig. 1(d)) is:

$$\dot{\sigma} + \frac{E_1 + E_2}{\eta}\sigma = \frac{E_1E_2}{\eta}\varepsilon + E_2\dot{\varepsilon}. \tag{20}$$

The corresponding constitutive relation is obtained from Eq. (20) as:

$$\sigma = \frac{E_1E_2}{E_1 + E_2}\varepsilon - \frac{E_2}{E_1 + E_2}\eta\dot{\varepsilon}\left(\frac{E_1}{E_1 + E_2} - 1\right)\left[1 - \exp\left(-\frac{E_1 + E_2}{\eta}\frac{\varepsilon}{\dot{\varepsilon}}\right)\right]. \tag{21}$$

The equivalent elastic modulus is:

$$E_{\text{eq}}(= E^*) = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon}\right|_{\varepsilon\to 0} = E_2. \tag{22}$$

If the relaxation time constant is set as $\tau = \eta/(E_1 + E_2)$, then

$$\sigma = \frac{E_1E_2}{\eta}\tau\varepsilon - E_2\tau\dot{\varepsilon}\left(\frac{E_1}{\eta}\tau - 1\right)\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right]. \tag{23}$$

Using the relationship, $E_1 = (\eta/\tau) - E_2$ and $E^* = E_2$, the constitutive equation is expressed as:

$$\sigma = E^*\varepsilon - \frac{E^{*2}\tau}{\eta}\varepsilon + \frac{E^{*2}\tau^2\dot{\varepsilon}}{\eta}\left[1 - \exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right]. \tag{24}$$

As shown in Fig. 4, the stress–strain curves by Eq. (24) are getting closer to that made by the Maxwell model as E_1 becomes small. The three curves ($\tau = 45$, $\tau = 25$, and $\tau = 10$) in Fig. 4 were made so that they have the same tensile strength as the curve by the Maxwell model. Under this condition τ is always smaller than that of Maxwell model provided E_1 is positive. To the given τ, numerous values of η and E_1 exist.

Table 1
Summary of constitutive equations and equivalent elastic modulus for foams

Type of model	Equivalent elastic modulus of foams	Relaxation time constant	Constitutive equations
Maxwell	$E^* = E$	$\tau = \eta/E$	$\sigma = E^*\tau\dot{\varepsilon}[1 - \exp(-(\varepsilon/\tau\dot{\varepsilon}))]$
Generalized Maxwell ($E_i = E$, $\eta_i = \eta$)	$E^* = nE$	$\tau = \eta/E$	$\sigma = E^*\tau\dot{\varepsilon}[1 - \exp(-(\varepsilon/\tau\dot{\varepsilon}))]$
Three Element (E, η_1, η_2)	$E^* = (\eta_2/(\eta_1 + \eta_2))E$	$\tau = (\eta_1 + \eta_2)/E$	$\sigma = E^*\tau\dot{\varepsilon}[1 - \exp(-(\varepsilon/\tau\dot{\varepsilon}))]$
Generalized Maxwell	$E^* = \sum_{i=1}^{n} E_i$	$\tau_i = \eta_i/E_i$	$\sigma = \sum_{i=1}^{n} E_i\tau_i\dot{\varepsilon}[1 - \exp(-(\varepsilon/\tau_i\dot{\varepsilon}))]$
Burgers	$E^* = -(\eta_1^2/(\eta_1 + \eta_2))\lambda_1 - ((\eta_1\eta_2)/(\eta_1 + \eta_2))\lambda_2$ where $\lambda_{1,2} = (1/2\eta_1\eta_2)(-B \pm \sqrt{B^2 - 4AC})$		$\sigma = \eta_1\dot{\varepsilon} + [-\eta_1\dot{\varepsilon} + (1/(\lambda_1 - \lambda_2))(E^* + ((E_1E_2)/(\lambda_2\eta_2\dot{\varepsilon})))]$ $e^{\lambda_1\varepsilon} - (1/(\lambda_1 - \lambda_2))(E^* + ((E_1E_2)/(\lambda_2\eta_2\dot{\varepsilon})))e^{\lambda_2\varepsilon}$ where $\lambda_{1,2} = (1/2\eta_1\eta_2\dot{\varepsilon})(-B \pm \sqrt{B^2 - 4AC})$, $A = \eta_1\eta_2$, $B = E_2\eta_1 + E_1(\eta_1 + \eta_2)$, $C = E_1E_2$ or $\sigma = \eta_1\dot{\varepsilon}[1 - (\eta_1/(\eta_1 + \eta_2))\exp(\lambda_1(\varepsilon/\dot{\varepsilon})) - (\eta_2/(\eta_1 + \eta_2))\exp(\lambda_2(\varepsilon/\dot{\varepsilon}))]$ where $\lambda_{1,2} = (1/(2\eta_1\eta_2))(-B \pm \sqrt{B^2 - 4AC})$
Three Element Standard Solid (E_1, E_2, η)	$E^* = E_2$	$\tau = \eta/(E_1 + E_2)$	$\sigma = E^*\varepsilon - ((E^{*2}\tau)/\eta)\varepsilon + ((E^{*2}\tau^2\dot{\varepsilon})/\eta)[1 - \exp(-(\varepsilon/\tau\dot{\varepsilon}))]$

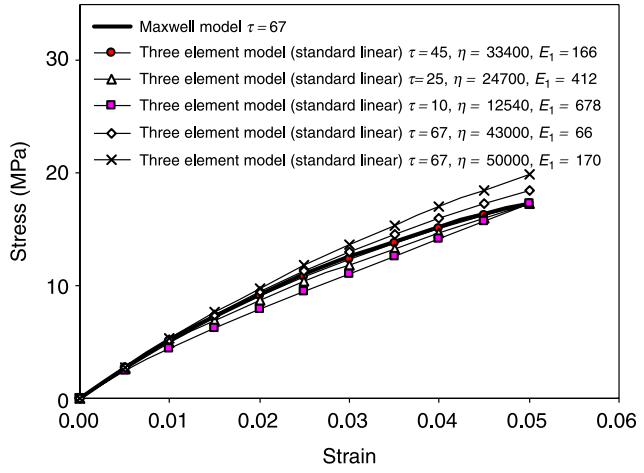


Fig. 4. Comparison of the constitutive equations of foams by Three Element Standard Solid ($E^* = E_2 = 576$ MPa) with that by Maxwell model ($E^* = 576$ MPa).

In Fig. 4, one of those was chosen and specified for each τ. If one value of η or E_1 is determined, the other is calculated by $E_1 = (\eta/\tau) - E_2$ or $\tau = \eta/(E_1 + E_2)$. If the same τ $(=67)$ is used, the stresses by the Three Element Standard Solid model are always greater than that by the Maxwell model unless E_1 is negative. In other words, the stress–strain behavior by the Three Element Standard Solid has more strain hardening phenomenon than the Maxwell model.

2.5. Constitutive equation using Burgers model

The equation of motion of the Burgers model (Fig. 1(e)) is:

$$\eta_1\eta_2\ddot{\sigma} + [E_2\eta_1 + E_1(\eta_1 + \eta_2)]\dot{\sigma} + E_1E_2\sigma = E_1E_2\eta_1\dot{\varepsilon} + E_1\eta_1\eta_2\ddot{\varepsilon}. \quad (25)$$

If the strain rate is considered as a constant during the tensile deformation, the constitutive equation is expressed as:

$$\sigma = -\frac{\eta_1^2}{\eta_1 + \eta_2}\dot{\varepsilon}e^{\lambda_1(\varepsilon/\dot{\varepsilon})} - \frac{\eta_1\eta_2}{\eta_1 + \eta_2}\dot{\varepsilon}e^{\lambda_2(\varepsilon/\dot{\varepsilon})} + \eta_1\dot{\varepsilon} \quad (26)$$

where, $\lambda_{1,2} = (1/2\eta_1\eta_1)(-B \pm \sqrt{B^2 - 4AC})$, $A = \eta_1\eta_2$, $B = E_2\eta_1 + E_1(\eta_1 + \eta_2)$, $C = E_1E_2$ and $D = E_1E_2\eta_1$.

The equivalent elastic modulus is

$$E_{eq}(= E^*) = \left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon\to 0} = -\frac{\eta_1^2}{\eta_1 + \eta_2}\lambda_1 - \frac{\eta_1\eta_2}{\eta_1 + \eta_2}\lambda_2. \quad (27)$$

In order to E^* be shown in the constitutive equation, Eq. (25) can be solved by the Laplace transformation method with initial conditions $\sigma(0) = 0$ and $\dot{\sigma}(0) = E_{eq}$.

$$\sigma = \eta_1\dot{\varepsilon} + \left[-\eta_1\dot{\varepsilon} + \frac{1}{\lambda_1 - \lambda_2}\left(E^* + \frac{E_1E_2}{\lambda_2\eta_2\dot{\varepsilon}}\right)\right]e^{\lambda_1\varepsilon} - \frac{1}{\lambda_1 - \lambda_2}\left(E^* + \frac{E_1E_2}{\lambda_2\eta_2\dot{\varepsilon}}\right)e^{\lambda_2\varepsilon} \quad (28)$$

where $\lambda_{1,2} = (1/2\eta_1\eta_2\dot{\varepsilon})(-B \pm \sqrt{B^2 - 4AC})$.

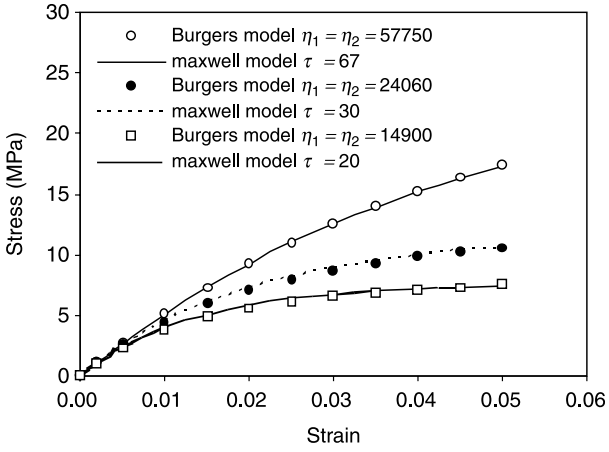


Fig. 5. Comparison of the constitutive equations of foams by Burgers model with that by Maxwell model: (equivalent elastic moduli in both models are the same).

If the value of η_1 is chosen equal to η_2 in the model, the magnitude of the equivalent elastic modulus is determined only by E_1 and E_2:

$$E_{eq}(= E^*) = \left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon\to 0} = \frac{E_2}{2} + E_1 \quad (\text{when } \eta_1 = \eta_2). \quad (29)$$

The shape of the stress–strain curves are dependent on $\eta_1(=\eta_2)$ providing the equivalent elastic modulus is not changed. The stress–strain curves in this case are plotted in Fig. 5 and compared with those of the Maxwell model. As shown in Fig. 5, the stress–strain curves by Burgers model are almost identical to the Maxwell model's even though there are slight differences at low time constant τ.

Summary of the constitutive equations studied in this paper and their equivalent elastic moduli for foams are listed in Table 1. The characteristics of those equations are that the relaxation time constant and the equivalent elastic modulus play important roles in every constitutive equation. By comparing the constitutive equations studied in this paper, it is proved that the constitutive equation by the Maxwell model could be a representative one. To verify the relevance of the constitutive equation, experimental work has been performed to compare with the theoretical results.

3. Experimentation

In order to obtain the stress–strain curves by experiment, PMMA closed cell microcellular foams were manufactured in a batch process method [24] and then uniaxial tensile tests were performed.

3.1. Materials

PMMA with a $M_w = 108{,}500$ and a $M_n = 56{,}700$ was supplied by Canus Plastics. Before use the samples were dried at a temperature of 90 °C for at least 24 h. With the use of a hydraulic, heated, press (Carver, Inc) machine, PMMA resins were molded into 1.5 mm thick panels by hot compression

molding, where 5 tons of pressure were applied for four minutes. The temperature of the hot pressing plates was 180 °C. Rectangular strips were obtained from the mold with dimensions of 6 mm × 50 mm. The blowing agent used in this study was carbon dioxide obtained from Praxair-Inc.

3.2. Foaming experiment

The foaming experiments were performed by a batch process. First, the polymer samples were saturated in a high pressure CO_2 chamber at a pressure of 3.8–5.8 MPa and at room temperature (21–23 °C). The saturation time, which varies from 1 day to 2 weeks, was calculated according to the diffusion coefficient of the carbon dioxide in PMMA [25]. In the next stage, the saturated samples were put in a water bath with selected temperature for 5–20 s. The rapid change in temperature and pressure induced cell nucleation and cell growth [26,27]. Afterwards, the samples were put in cold water to fix the foam morphology.

3.3. Sample characterization

The samples were air dried for 7 days before testing. The foam density was measured by a buoyancy method using a density determination kit supplied by Denver Instrument. The gravity of the solid was measured in distilled water and in the air. The Archimedean principle was applied for determining the specific gravity of the foams. The relative foam density is defined as the ratio of the foam density and the unfoamed polymer density. The expansion ratio is defined as the ratio of the unfoamed polymer density to the foam density.

3.4. Mechanical testing

The tensile mechanical properties were tested with an Instron 4202 machine with a 10 kN load cell at room temperature. Rectangular strip samples with thicknesses from 1.5 to 3 mm, depending on their expansion ratios, were used for tensile testing. A crosshead speed of 1.0 mm/min was used and the strain was calculated from the displacement of the crosshead of the machine. The elastic moduli were obtained by calculating the slope of the stress–strain curves at the initial linear portions. The experimental results of tensile strength and elongation at break were also reported. A minimum of five specimens were tested for each sample and the average data were used in this study.

4. Results and discussion

4.1. Mechanical properties of PMMA microcellular foams

Mechanical behaviors of PMMA microcellular foams were determined by tensile experiments. Different densities of the PMMA foams were obtained by changing the processing parameters such as foaming time, foaming temperature and saturation pressure. The engineering stress–strain curves of the PMMA microcellular foams are presented in Fig. 6 at different relative densities. As shown in the figure, the tensile

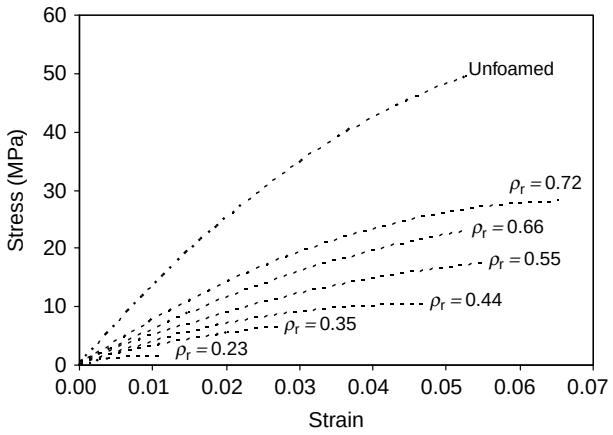


Fig. 6. Experimental tensile behaviors of PMMA microcellular foams.

mechanical properties of the PMMA microcellular foams were closely related to the foam density, which is controlled by the foaming conditions. The elastic modulus, tensile strength and the elongation at break were studied as functions of foam relative density. The experimental correlation between the modulus and the relative density matched Gibson's equation on the whole. The tensile strength and elongation at break both decreased when decreasing foam density. For some of the foaming conditions which resulted in higher foam density, higher elongation at break of the microcellular PMMA foam was observed compared with the unfoamed PMMA [24].

4.2. Parametric verification of the constitutive equation

The constitutive equation obtained from the Maxwell model was used for validation with experimental results. The elastic modulus of foams E^* under the tensile loading can be represented in terms of the relative density of foams using Gibson and Ashby's prediction [28] for closed cell foams;

$$\frac{E^*}{E_s} \approx \phi^2 \rho_r^2 + (1-\phi)\rho_r \tag{30}$$

where E_s is Young's modulus of the unfoamed solid and ρ_r is the relative density of foams and ϕ is the fraction of solid in the cell struts. Using Eq. (30), Eq. (6) is expressed as a function of the relative density of foams;

$$\sigma = \tau\dot{\varepsilon}E_s[\phi^2\rho_r^2 + (1-\phi)\rho_r]\left[1-\exp\left(-\frac{\varepsilon}{\tau\dot{\varepsilon}}\right)\right] \tag{31}$$

This constitutive equation can be applied for nonlinear elastic tensile behavior of foams. The parametric studies to Eq. (31) are shown in Fig. 7. As expected, the stresses increased with increasing strain rate, elastic modulus, time constant, and relative density, though this stress decreases as ϕ increases, which implies that the cells are approached to open-celled form.

4.3. Validation of the constitutive equation for PMMA microcellular foams

In Fig. 8, the stress–strain curves plotted by Eq. (31) were compared with uniaxial tensile test data. It was demonstrated

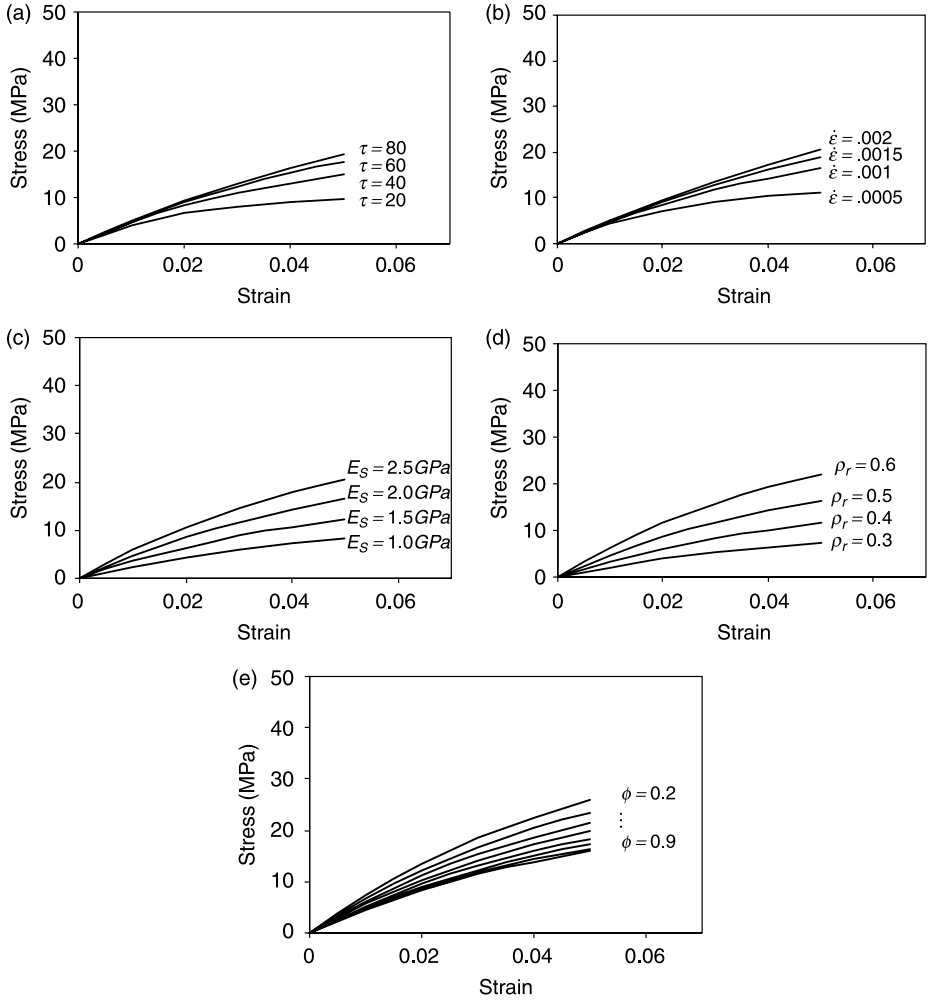


Fig. 7. Parametric verification of the constitutive equation (a) relaxation time constant, (b) strain rate, (c) elastic modulus, (d) relative density of foams, and (e) fraction of solid in the cell struts.

that theoretical curves closely represent the experimental data. Chen's experiments [29] have yield like behaviors on quasi-static tensile tests of PMMA, however, there was little yield phenomenon observed in the current experiment as shown in Fig. 8. The macroscopic responses of the PMMA foams appeared quite brittle. The tensile strengths of the analytical curves in Fig. 8(a) were calculated by the formula proposed for PMMA microcellular foams [24]:

$$\frac{\sigma^*_{\mathrm{TS}}}{\sigma_{\mathrm{TS}}} \approx \rho_{\mathrm{r}}^2 \tag{32}$$

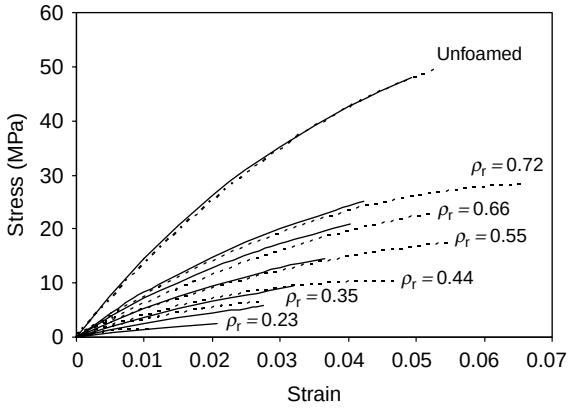
where σ^*_{TS} and σ_{TS} are the tensile strengths of the foam and unfoamed solid, respectively. For the value of ϕ, 0.8 was chosen in Eq. (31) because the magnitude of the elastic modulus of foams, E^*, (Eq. (30)) was close to the experimental data when $\phi = 0.8$. If the percent elongation is used for the determination of the failure strain, the stress–strain curves from Eq. (31) fit the experimental data more closely as shown in Fig. 8(b).

The same strain rate ($=0.000667\ \mathrm{s}^{-1}$) was applied to both Eq. (31) and experimental results, and the relaxation time constant $\tau = 65$ was used for plotting of Eq. (31) in Fig. 8. Also the Young's modulus of unfoamed PMMA $E_s = 1940$ was used in Eq. (31). The time constant $\tau = 65$ is valid only at the strain rate used in this experiments. Therefore, if the test condition is changed, τ would be changed too.

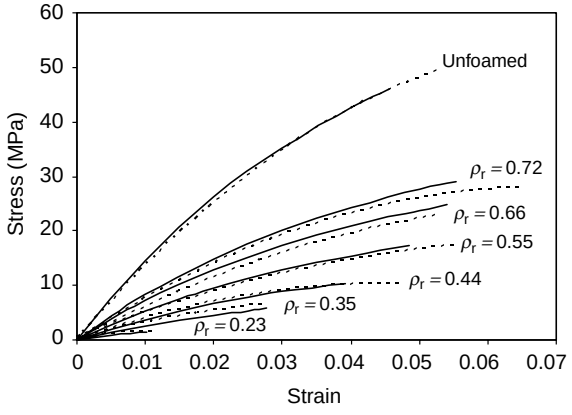
In this study, only one relaxation time constant was used for comparison with experimental results, however, the rate of the change of the time constant τ to the change of the strain rate or time should be defined with more experimental data. Therefore, for generalized expression of the constitutive equation, the time constant τ should be represented in terms of test conditions or foam properties, such as strain rate, and requires the effect of varying strain rate during loading to be taken into account. Also, the effects of cell morphology such as cell size, cell distribution, cell type and cell wall thickness are recommended to be considered in formulating the constitutive equations.

5. Conclusion

Constitutive equations for PMMA foams subjected to tensile loading were studied, where viscoelastic components were used to model the nonlinear tensile behavior of foams.



(a) tensile strength was used for break point in Eq.(31).



(b) failure strain was used for break point in Eq.(31).

Fig. 8. Comparison of the engineering tensile stress–strain curves of PMMA foams; (solid lines: Eq. (31), dotted lines: experimental results).

Results indicated that the constitutive equation obtained from the Maxwell model could be representative of all the constitutive equations based on different types of viscoelastic models such as: the Generalized Maxwell model, the Three Element model and the Burgers model. In other words, any stress–strain curve made by the Generalized Maxwell model, Three Element model and Burgers model could also be generated by the constitutive equation using the Maxwell model; provided the relaxation time constant is chosen properly.

The proposed constitutive equations are expressed as functions of strain, strain rate, relaxation time constant and elastic modulus, where foam properties such as equivalent elastic modulus, fraction of solid in the cell struts, and relative density of foams are used. With these parameters, the constitutive model could describe the nonlinear elastic tensile behavior of foams. Without considering the temperature effect, this constitutive model has an advantage in that it can be applied to practice with only a few foam properties. For verification of the constitutive model, microcellular foams were prepared from PMMA using the batch method and tensile test results of the foams were compared with the model. The theoretical model demonstrates a fit quite similar to test data.

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