High Density Polyethylene Foams. II. Elastic Modulus

Yaolin Zhang, Denis Rodrigue, Abdellatif Ait-Kadi

Department of Chemical Engineering and CERSIM, Laval University, Quebec City, Canada G1K 7P4

ABSTRACT: High density polyethylene (HDPE) foams (450–950 kg/m^3) were prepared by compression molding and their tensile moduli were measured in order to study the normalized elastic modulus as a function of the normalized density of closed-cell foams. The tensile data were then used to compare several models of cellular materials and polymer composites to determine which would fit our results. Of all models used, the simple empirical equation of Moore (square power-law) and the differential scheme predict the data very well in the range of voids volume fraction under study (0–55%). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2120–2129, 2003

Key words: polyethylene; modulus; mechanical properties; modeling

INTRODUCTION

It is known that polyolefins are tough, flexible, and resistant to chemicals and abrasion. Foams made from these polymers also exhibit these properties. Although classified as semi-rigid foams, polyolefin foams are generally firmer than flexible polyurethane foams.[1,2] Most polyolefin foams have a closed-cell structure, which makes them suitable for applications where buoyancy is important and provides resiliency for use in packaging applications. In addition, they are used in construction, transportation, insulation, sports and leisure, and agriculture.

Many attempts have been made to predict the overall mechanical behavior of cellular materials. In general, foams can be approximated as a two phase composite materials: a solid matrix enclosing gas "reinforcement." For example, Gibson and Ashby[3] developed a model based on unit cells and micromechanical considerations for both open and closed-cell low density materials. For most high density foams, Moore[4] found that an empirical square power-law relation is valid. Later, several methods were used in order to predict the mechanical properties of cellular materials, most of them being continuum approaches well known in the mechanics of composite materials. Hashin[5] introduced a model based on a gradation of sizes of spherical particles embedded in a continuous matrix for low inclusion concentration. Later, the development of the self-consistent and the generalized self-consistent schemes[6] for a wide range of inclusion concentrations was developed (also referred as the three-phase model). However powerful, the generalized self-consistent model is difficult to use because the parameters are rather complex functions of the inclusion and matrix elastic properties. Later, Mori and Tanaka[7] calculated the effective modulus of composite materials from the determination of the average internal stresses in the matrix consisting of spherical inclusions with determined eigenstrain or eigenstress, combined with the equivalent inclusion simplification introduced by Eshelby.[8] This approach was used in several studies related to the determination of the elastic stiffness of composites, including studies by Weng and co-workers,[9–11] Ju and Chen,[12–15] and Wong.[16]

Micromechanical analysis of a heterogeneous material can determine the overall behavior of a composite material from the properties of its individual constituents, including interaction, shape, and volume fraction. In the micromechanical approach, the heterogeneous microstructure is replaced by a homogeneous medium with isotropic or anisotropic properties. Since only the constituent properties are used, this approach avoids the difficulty of having to evaluate many material combinations, which makes it a powerful analysis that can be used for a variety of materials.

In the first part of this series of articles about polyethylene foams,[17] we showed that high density polyethylene (HDPE) foams have a closed-cell structure. It is thus possible to use the approaches described for this kind of composite consisting of a polymer matrix with gas inclusions. Based on the amount of data available in the literature, several different approaches were used to approximate the mechanical properties of polyethylene foams. In this study, HDPE foams were prepared using a compression molding technique.[17] This article reports the mechanical properties

TABLE I
Properties of Raw Materials

HDPE	Melt index	Manufacturer
J60-1700-173	16.0 g/10 min (190°C 2.16 kg)	Solvay Polymers
A60-70-162	0.72 g/10 min (190°C 2.16 kg)	Solvay Polymers
G60-110	11.0 g/10 min (190°C 21.6 kg)	Solvay Polymers
HBW555Ac	5.0 g/10 min (190°C 21.6 kg)	Nova Chemicals

of the foams. Comparisons are made among different models in terms of elastic modulus to determine which model best fits our measurements.

EXPERIMENTAL

Polymers and sample preparation

Four HDPE foams with different molecular weights were used in this study. Their suppliers and melt indices are given in Table I. Foam plates (60 × 60 × 2.8–3.4 mm) were obtained by a compression molding method. Further details on the molding procedure and the resulting foam morphology can be obtained from the first part of this study.[17]

Tensile measurements

Room-temperature uniaxial tension properties were evaluated as a function of foam density and molecular weight using an Instron 5565 tester with a 500 N load cell. The samples were cut in a type IV format according to ASTM D-638. The following conditions were

also used: a temperature of 25°C, an initial length between the clamps of 25 mm and a crosshead speed of 10 mm/min. The stress was determined from the ratio of the tensile load to the initial cross sectional area and the strain was obtained from the instantaneous length and the initial length of the sample. A minimum of eight specimens were tested for each condition. In each case, the results are reported as the average value plus/minus one standard deviation.

Elastic modulus models of two-phase materials

Elastic properties of isotropic materials

For homogeneous and linearly elastic materials, the constitutive relation that relates stress and strain through elasticity and/or compliance tensors is given by Hooke's law. The general relationship between stress and strain can be written:[18–22]

$$\boldsymbol{\sigma} \equiv \mathbf{C} : \boldsymbol{\varepsilon} \quad \text{or} \quad \sigma_{ij} = C_{ijkl}\varepsilon_{kl} \tag{1}$$

and

$$\boldsymbol{\varepsilon} \equiv \mathbf{D} : \boldsymbol{\sigma} \quad \text{or} \quad \varepsilon_{ij} = D_{ijkl}\sigma_{kl} \tag{2}$$

where $\boldsymbol{\sigma}$ is the stress vector, $\boldsymbol{\varepsilon}$ is the strain vector, $\mathbf{C}$ is the elastic tensor, and $\mathbf{D}$ is the compliance tensor. Because the stress and strain tensors are symmetrical, out of the eighty-one components of $\mathbf{C}$ or $\mathbf{D}$, only thirty-six are independent. It is thus convenient to express the stress-strain relations in terms of a six by six matrix:

$$
\begin{bmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \\ \tau_4 \\ \tau_5 \\ \tau_6 \end{bmatrix}
=
\begin{bmatrix}
C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1131} & C_{1112} \\
C_{2211} & C_{2222} & C_{2233} & C_{2223} & C_{2231} & C_{2212} \\
C_{3311} & C_{3322} & C_{3333} & C_{3323} & C_{3331} & C_{3312} \\
C_{2311} & C_{2322} & C_{2333} & C_{2323} & C_{2331} & C_{2312} \\
C_{3111} & C_{3122} & C_{3133} & C_{3123} & C_{3131} & C_{3112} \\
C_{1211} & C_{1222} & C_{1233} & C_{1223} & C_{1231} & C_{1212}
\end{bmatrix}
\begin{bmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ \gamma_4 \\ \gamma_5 \\ \gamma_6 \end{bmatrix}
\tag{3}
$$

in which

$$
\begin{array}{lll}
\tau_1 = \sigma_{11}, & \tau_2 = \sigma_{22}, & \tau_3 = \sigma_{33}, \\
\tau_4 = \sigma_{23} = \sigma_{32}, & \tau_5 = \sigma_{31} = \sigma_{13}, & \tau_6 = \sigma_{12} = \sigma_{21} \\
\gamma_1 = \varepsilon_{11}, & \gamma_2 = \varepsilon_{22}, & \gamma_3 = \varepsilon_{33}, \\
\gamma_4 = 2\varepsilon_{23} = 2\varepsilon_{32}, & \gamma_5 = 2\varepsilon_{31} = 2\varepsilon_{13}, & \gamma_6 = 2\varepsilon_{12} = 2\varepsilon_{21}
\end{array}
$$

For isotropic materials, there are only two independent elastic parameters. The elasticity tensor becomes

$$
\begin{bmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \\ \tau_4 \\ \tau_5 \\ \tau_6 \end{bmatrix}
=
\begin{bmatrix}
C_{1111} & C_{1122} & C_{1122} & 0 & 0 & 0 \\
C_{1122} & C_{1111} & C_{1122} & 0 & 0 & 0 \\
C_{1122} & C_{1122} & C_{1111} & 0 & 0 & 0 \\
0 & 0 & 0 & (C_{1111} - C_{1122})/2 & 0 & 0 \\
0 & 0 & 0 & 0 & (C_{1111} - C_{1122})/2 & 0 \\
0 & 0 & 0 & 0 & 0 & (C_{1111} - C_{1122})/2
\end{bmatrix}
\begin{bmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ \gamma_4 \\ \gamma_5 \\ \gamma_6 \end{bmatrix}
\tag{4}
$$

The engineering elastic constants such as bulk (K), shear (μ), tensile moduli (E), and Poisson's ratio (ν) have the following relationships with the above equation:

$$E = C_{1111} - \frac{2C_{1122}^2}{C_{1111} + C_{1122}} \quad \text{or} \quad E = \frac{9K\mu}{3K + \mu} \quad (5)$$

$$\nu = \frac{C_{1122}}{C_{1111} + C_{1122}} \quad \text{or} \quad \nu = \frac{3K - 2\mu}{2(3K + \mu)} \quad (6)$$

$$\mu = \frac{C_{1111} - C_{1122}}{2} \quad \text{or} \quad \mu = \frac{E}{2(1 + \nu)} \quad (7)$$

$$K = \frac{C_{1111} + 2C_{1122}}{3} \quad \text{or} \quad K = \frac{E}{3(1 - 2\nu)} \quad (8)$$

In our case, high density foams can be approximated as composites constituted by a polymer matrix filled with gas voids that can be analyzed by micromechanical models.

General equations of composite effective properties

Mori and Tanaka[7] introduced the idea of a representative volume element (RVE), which consists of a uniform elastic matrix with elasticity and compliance tensors $\mathbf{C}$ and $\mathbf{D}$, containing elastic micro-inclusions consisting of the same material (Ω) with elasticity and compliance tensors $\mathbf{C}^1$ and $\mathbf{D}^1$. The micro-inclusions are perfectly bonded to the matrix, all constituents of the RVE are assumed to be linearly elastic, and the matrix and each inclusion are assumed to be uniform. The overall elasticity and compliance are denoted by $\mathbf{C}_c$ and $\mathbf{D}_c$, respectively. For constant macro-stress and micro-inclusions made of the same homogeneous materials they obtained[23]

$$(\mathbf{D} - \mathbf{D}_c) : \boldsymbol{\sigma}^0 = f(\mathbf{D} - \mathbf{D}^1) : \bar{\boldsymbol{\sigma}}^1 \quad (9)$$

where f is the volume fraction of the inclusions and $\bar{\boldsymbol{\sigma}}^1$ is the average stress in the inclusions. For constant macro-strain with micro-inclusions made of the same homogeneous material, a similar relationship was obtained:

$$(\mathbf{C} - \mathbf{C}_c) : \boldsymbol{\varepsilon}^0 = f(\mathbf{C} - \mathbf{C}^1) : \bar{\boldsymbol{\varepsilon}}^I \quad (10)$$

where $\bar{\boldsymbol{\varepsilon}}^I$ is the inclusions' average strain.

Voigt model

Voigt[24] assumed that the average strain on both inclusion and matrix is equal to the applied strain. The overall elasticity tensor from eq. (10) becomes

$$(\mathbf{C} - \mathbf{C}_c) = f(\mathbf{C} - \mathbf{C}^1) \quad (11)$$

For foams, the void's elastic modulus tensor is negligible. This means that $\mathbf{C}^1 \rightarrow 0$ and the foam's elastic modulus is reduced to

$$\mathbf{C}_c = (1 - f)\mathbf{C} \quad (12)$$

Young's modulus it thus given by:

$$E_f = (1 - f)C_{1111} - \frac{2((1 - f)C_{1122})^2}{(1 - f)C_{1111} + (1 + f)C_{1122}}$$
$$= (1 - f)E_m \quad (13)$$

where E_f and E_m are the foam and matrix moduli, respectively.

Modulus models with continuum approach

Because the inclusion's properties are different from the polymer matrix, there is a mismatch between matrix and inclusion. In order to account for this mismatch in material properties, the eigenstrain and eigenstress simplifications of Eshelby[8] are introduced for the inclusions and homogenization.

Dilute distribution with constant macro-stress

For a dilute distribution of micro-inclusions embedded in an unbounded homogeneous solid, the interactions between the inclusions and the matrix, as well as the interactions among inclusions, are not considered. For spherical micro-inclusions, the elastic modulus of the composite is[23]

$$\frac{K_c}{K} = \left\{ 1 + f \left(\frac{K}{K - K^1} - \frac{1 + \nu}{3(1 - \nu)} \right)^{-1} \right\}^{-1} \quad (14)$$

$$\frac{\mu_c}{\mu} = \left\{ 1 + f \left(\frac{\mu}{\mu - \mu^1} - \frac{2(4 - 5\nu)}{15(1 - \nu)} \right)^{-1} \right\}^{-1} \quad (15)$$

For foams, eqs. (14) and (15) simplify to

$$\frac{K_f}{K} = \left\{ 1 + f \left(1 - \frac{1 + \nu}{3(1 - \nu)} \right)^{-1} \right\}^{-1}$$
$$= \frac{2(1 - 2\nu)}{2(1 - 2\nu) + 3(1 - \nu)f} \quad (16)$$

$$\frac{\mu_f}{\mu} = \left\{ 1 + f \left(1 - \frac{2(4 - 5\nu)}{15(1 - \nu)} \right)^{-1} \right\}^{-1}$$
$$= \frac{7 - 5\nu}{7 - 5\nu + 15(1 - \nu)f} \quad (17)$$

Substitution of eqs. (16) and (17) into eqs. (7) and (8) gives the elastic modulus as

$$\frac{E_f}{E} = \frac{2(7-5\nu)}{2(7-5\nu)+3(9-4\nu-5\nu^2)f} \quad (18)$$

Because this model is based on very low inclusion concentration ($f \ll 1$), the overall elastic modulus predicted by this model is valid only for high density foams.

Dilute distribution with constant macro-strain

For a dilute distribution of micro-inclusions embedded in an unbounded homogeneous solid, inclusion/matrix and inclusion/inclusion interactions are not considered. For spherical micro-inclusions, the elastic modulus of the composite with constant macro-strain is[23]

$$\frac{K_c}{K} = 1 - f\left(\frac{K}{K-K^1} - \frac{1+\nu}{3(1-\nu)}\right)^{-1} \quad (19)$$

$$\frac{\mu_c}{\mu} = 1 - f\left(\frac{\mu}{\mu-\mu^1} - \frac{2(4-5\nu)}{15(1-\nu)}\right)^{-1} \quad (20)$$

For foams, eqs. (19) and (20) become

$$\frac{K_f}{K} = 1 - f\left(1 - \frac{1+\nu}{3(1-\nu)}\right)^{-1} = 1 - \frac{3(1-\nu)}{2(1-2\nu)}f \quad (21)$$

$$\frac{\mu_f}{\mu} = 1 - f\left(1 - \frac{2(4-5\nu)}{15(1-\nu)}\right)^{-1} = 1 - \frac{15(1-\nu)}{7-5\nu}f \quad (22)$$

Substitution of eqs. (21) and (22) into eqs. (7) and (8) gives the elastic modulus as

$$\frac{E_f}{E} = \frac{1}{2}\frac{(45\nu^2+45-90\nu)f^2 + (126\nu-51-75\nu^2)f + 20\nu^2-38\nu+14}{(-12+30\nu+15\nu^3-33\nu^2)f+7-19\nu+10\nu^2} \quad (23)$$

Mori-Tanaka method for two phase spherical inclusion composites

Mori and Tanaka[7] proposed that the perturbed stress was in equilibrium with the constrained stress. Based on the Mori-Tanaka method, Weng[9] developed the normalized modulus for a two phase composite of spherical inclusions as:

$$\frac{K_c}{K} = 1 - \frac{3(1-\nu)(K-K^1)f}{3(1-\nu)K + (1-f)(1+\nu)(K^1-K)} \quad (29)$$

Because this model is based on the dilute inclusion concentration ($f \ll 1$), it is valid only for high density foams.

Self-consistent approximation

For a random distribution of spherical micro-inclusions at higher concentrations, some degree of interaction among the inclusions has to be included. The overall elasticity is now given by[23]

$$\frac{K_c}{K} = 1 - f\frac{K_c(K-K^1)}{K(K_c-K^1)}\left(\frac{K_c}{K_c-K^1} - \frac{1+\nu_c}{3(1-\nu_c)}\right)^{-1} \quad (24)$$

$$\frac{\mu_c}{\mu} = 1 - f\frac{\mu_c(\mu-\mu^1)}{\mu(\mu_c-\mu^1)}\left(\frac{\mu_c}{\mu_c-\mu^1} - \frac{2(4-5\nu_c)}{15(1-\nu_c)}\right)^{-1} \quad (25)$$

For foams, eqs. (24) and (25) become

$$\frac{K_f}{K} = 1 - f\left(1 - \frac{1+\nu_f}{3(1-\nu_f)}\right)^{-1} = 1 - \frac{3(1-\nu_f)}{2(1-2\nu_f)}f \quad (26)$$

$$\frac{\mu_f}{\mu} = 1 - f\left(1 - \frac{2(4-5\nu_f)}{15(1-\nu_f)}\right)^{-1} = 1 - \frac{15(1-\nu_f)}{7-5\nu_f}f \quad (27)$$

Substituting eqs. (26) and (27) into eqs. (7) and (8) gives the elastic modulus of the foams as

$$\frac{E_f}{E} = \frac{1}{2}\frac{-8+f-15\nu f^2+3f^2-20\nu+37\nu f+\Delta}{10-7f-20\nu+13\nu f+2\nu^2 f} \quad (28)$$

where

$$\Delta = \left(\begin{array}{c} 784 - 3000f + 400\nu^2 - 7830\nu f^2 + 4752\nu f^3 - 1026\nu f^4 - 1336\nu^2 f + 81\nu^2 f^4 \\ + 1473\nu^2 f^2 - 630\nu^2 f^3 + 5264\nu f - 1120\nu + 4089f^2 - 2394f^3 + 513f^4 \end{array}\right)^{1/2}$$

$$\frac{\mu_c}{\mu} = 1 - \frac{15(1-\nu)(\mu-\mu^1)f}{15(1-\nu)\mu + (1-f)(8-10\nu)(\mu^1-\mu)} \quad (30)$$

These equations do not consider inclusion interaction but are similar to the analytical results of Ju and Chen.[13] For foams, eqs. (29) and (30) become

$$\frac{K_f}{K} = 1 - \frac{3(1-\nu)f}{3(1-\nu) - (1-f)(1+\nu)} \quad (31)$$

ν_m	0.02	0.06	0.10	0.12	0.16	0.20	0.22	0.26
n	1.94	1.96	1.97	1.98	1.99	2.00	2.00	2.01
ν_m	0.30	0.32	0.36	0.40	0.42	0.46	0.49	0.495
n	2.01	2.00	2.00	1.98	1.97	1.95	1.93	1.93

$$\frac{\mu_f}{\mu} = 1 - \frac{15(1 - \nu)f}{15(1 - \nu) - (1 - f)(8 - 10\nu)} \quad (32)$$

Substituting eqs. (31) and (32) into eqs. (7) and (8) gives the elastic modulus of the foams as

$$\frac{E_f}{E} = \frac{2(7 - 5\nu)(1 - f)}{(1 + \nu)(13 - 15\nu)f + 2(7 - 5\nu)} \quad (33)$$

Differential scheme for two phase spherical inclusion composites

McLaughlin[25] developed a differential scheme based on Boucher's work. Later, Farber and Farris[26] developed a differential scheme using a different approach but obtained exactly the same differential equations for the shear and bulk moduli of a two-phase composite with spherical inclusions:

$$\frac{d\mu_c}{df} = \frac{15\mu_c(1 - \nu_c)(1 - \mu^1/\mu_c)}{[7 - 5\nu_c + 2(4 - 5\nu_c)\mu^1/\mu_c](1 - f)} \quad (34)$$

$$\frac{dK_c}{df} = \frac{K^1 - K_c}{(1 + \{(K^1 - K_c)/[K_c + (4/3)\mu_c]\})(1 - f)} \quad (35)$$

These equations constitute a coupled system that can be solved by numerical methods with the following boundary conditions:

$f = 0, \mu_c = \mu_m$ (matrix shear modulus)
$K_c = K_m$ (matrix bulk modulus)
$f = 1, \mu_c = \mu^1$ (inclusion shear modulus)
$K_c = K^1$ (inclusion bulk modulus)

For foams, $\mu^1 \to 0$ and $K^1 \to 0$. Eqs. (34) and (35) become

$$\frac{d\mu_f}{df} = \frac{15\mu_f(1 - \nu_f)}{(7 - 5\nu_f)(1 - f)} = \frac{5\mu_f(3K_f + 4\mu_f)}{(9K_f + 8\mu_f)(-1 + f)} \quad (36)$$

$$\frac{dK_f}{df} = \frac{-K_f}{\{1 - K_f/[K_f + (4/3)\mu_f]\}(1 - f)} = \frac{K_f(3K_f + 4\mu_f)}{4\mu_f(-1 + f)} \quad (37)$$

where

$f = 0, \mu_f = \mu_m$ (matrix shear modulus)

$K_f = K_m$ (matrix bulk modulus)
$f = 1, \mu_f = 0$ (voids shear modulus)
$K_f = 0$ (voids bulk modulus)

To solve the differential system of equations, Euler's method was used:[27]

$$\frac{dy}{dt} = f(t, y) \quad \text{subject to } y = y_0 \text{ when } t = t_0 \quad (38)$$

For each subinterval $[t_i, t_{i+1}]$, a small step size ($h = t_{i+1} - t_i$) is used to discretize the equations:

$$y(t_{i+1}) \approx y_i + (t_{i+1} - t_i)f_i \quad (39)$$

Eqs. (36) and (37) can now be written as

$$\mu_{i+1} \approx \mu_i + (f_{i+1} - f_i)\frac{5\mu_i(3K_i + 4\mu_i)}{(9K_i + 8\mu_i)(-1 + f_i)}$$
$$(0 \leq f_i \leq 1) \quad (40)$$

$$K_{i+1} \approx K_i + (f_{i+1} - f_i)\frac{K_i(3K_i + 4\mu_i)}{4\mu_i(-1 + f_i)} \quad (0 \leq f_i \leq 1) \quad (41)$$

The Young modulus and the Poisson ratio can be obtained from the shear modulus and the bulk modulus. Using a small step size (10^{-5}), the Young modulus was found to follow a power-law relation:

$$\frac{E_f}{E_m} \approx (1 - f)^n \quad (1.93 \leq n \leq 2.01) \quad (42)$$

where n is the power-law index. The results are presented in Table II.

Semi-empirical and empirical models for two-phase composites

Halpin-Tsai model. Halpin and co-workers[28–33] evaluated the elastic properties of unidirectional and randomly distributed short fiber composites using Hill's generalized self-consistent model. For unidirectional short fiber composites, the following equations were obtained:

$$E_{11} = \frac{1 + 2(l_f/d_f)\eta_L f}{1 - \eta_L f} E_m \quad (43)$$

$$E_{22} = \frac{1 + 2\eta_T f}{1 - \eta_T f} E_m \qquad (44)$$

where E_{11} is the tensile modulus in the longitudinal direction, and E_{22} is the tensile modulus in the transverse direction. The subscript f refers to the fiber phase, and f is the volume fraction of the fibers. The other parameters are defined by

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l_f/d_f)}$$

$$\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2}$$

$$l_f/d_f = \text{fiber aspect ratio}$$

Halpin et al. also developed some semi-empirical equations for the calculation of the in-plane tensile modulus of composites containing a two-dimensional random orientation of short fibers:

$$E_c = \frac{3}{8} E_{11} + \frac{5}{8} E_{22} \qquad (45)$$

For a three-dimensional random orientation of fibers, Nielsen and Landel[34–35] modified eq. (45) for the tensile modulus as

$$E_c = \frac{1}{5} E_{11} + \frac{4}{5} E_{22} \qquad (46)$$

Equations (45) and (46) can be used to approximate the foam's tensile properties ($E_f/E_m \rightarrow 0$ and $l_f/d_f \rightarrow \xi$: the aspect ratio) for in-plane randomly distributed voids as

$$E_f = \frac{3}{8} \frac{1 - f}{1 + \dfrac{f}{2\xi}} E_m + \frac{5}{8} \frac{1 - f}{1 + \dfrac{f}{2}} E_m \qquad (47)$$

and for three-dimensional foams as

$$E_f = \frac{1}{5} \frac{1 - f}{1 + \dfrac{f}{2\xi}} E_m + \frac{4}{5} \frac{1 - f}{1 + \dfrac{f}{2}} E_m \qquad (48)$$

If all of the bubbles in the foam are spherical ($\xi \rightarrow 1$), eqs. (47) and (48) reduce to the same equation:

$$\frac{E_f}{E_m} = \frac{1 - f}{1 + 0.5f} \qquad (49)$$

Kerner model. Kerner[36] developed a widely used model for predicting the mechanical properties of par-

ticle-reinforced composites. The Young modulus was given as

$$\frac{E_c}{E_m} = \frac{1 + ABf}{1 - Bf} \qquad (50)$$

where

$$A = \frac{7 - 5v_m}{8 - 10v_m}$$

v_m is the Poisson ratio of the matrix and

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A}$$

E_f is the modulus of the filler. For foams ($E_f/E_m \rightarrow 0$) eq. (50) becomes

$$\frac{E_f}{E_m} = \frac{1 - f}{1 + \dfrac{8 - 10v_m}{7 - 5v_m} f} \qquad (51)$$

Modified Kerner model. Nielsen[34,35,37] modified the Kerner model as follows:

$$\frac{E_c}{E_m} = \frac{1 + ABf}{1 - B\phi f} \qquad (52)$$

with

$$A = k_E - 1$$

where k_E is an empirical constant related to the Poisson ratio of the matrix[35] and

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A}$$

$$\phi \cong 1 + \frac{(1 - v_{fm})f}{v_{fm}^2}$$

v_{fm} is related to the inclusion shape and the state of the inclusion in the matrix.[35] For closed and spherical cell foams ($E_f/E_m \rightarrow 0$ and $v_{mf} = 0.7405$ for face centered cubic packing), eq. (52) becomes

$$\frac{E_f}{E_m} = \frac{1 - f}{1 + \dfrac{f}{k_E - 1} (1 + 0.4732f)} \qquad (53)$$

Moore empirical equation. Moore and Iremonger[4] developed an empirical relationship between the modulus and the density of high density foamed thermo-

plastics, which can be very closely approximated by a square power-law relationship:

$$E_f/E_m = (\rho_f/\rho_m)^2 \qquad (54)$$

This simple equation has been found to be in agreement for several polymer foams.

Gibson and Ashby model. Gibson and Ashby[38] assumed that a unit cell consists of a cubic array of plates (cell walls) connected by struts (cell edges) to form a single cell. They derived the normalized Young modulus of low density closed-cell foams as

$$\frac{E_f}{E_m} \approx \phi^2\left(\frac{\rho_f}{\rho_m}\right)^2 + (1 - \phi)\,\frac{\rho_f}{\rho_m} + \frac{p_0}{E_m}\frac{1 - 2\nu_f}{1 - \rho_f/\rho_m} \quad (55)$$

where ϕ is the fraction of solid material in the cell struts and p_0 is the internal gas pressure. The foam modulus is composed of three terms: the first term gives the contribution of the cell struts, the second term accounts for the cell walls, and the third term is the contribution from the internal gas pressure. In order to predict the normalized modulus, three variables (ϕ, p_0, and ν_f) need to be determined. Usually, when the foam is left at atmospheric pressure after manufacture, the internal gas pressure and the surrounding pressure reach equilibrium. Since the internal gas pressure is much less than the Young modulus of the matrix, the third term is negligible. Eq. (55) becomes

$$\frac{E_f}{E_m} \approx \phi^2\left(\frac{\rho_f}{\rho_m}\right)^2 + (1 - \phi)\,\frac{\rho_f}{\rho_m} \qquad (56)$$

For this model, the normalized modulus reaches $1 - \phi + \phi^2$ when the normalized density reaches unity. This makes E_f less than E_m because ϕ is less than 1. Even
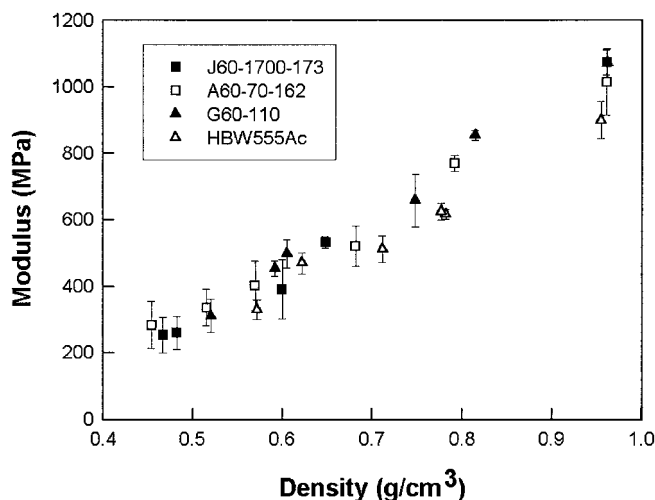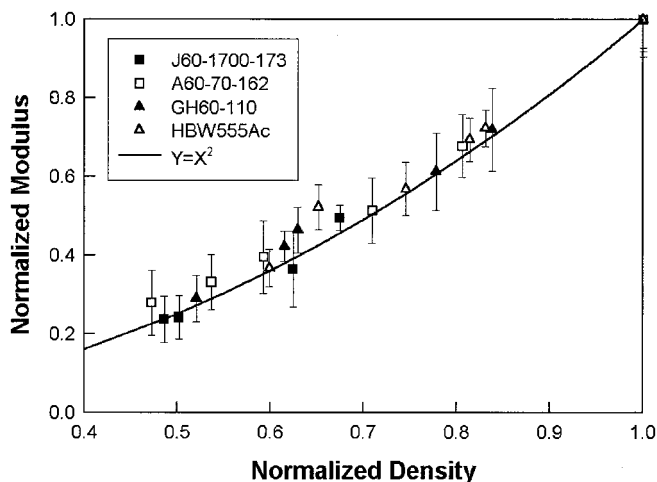

Figure 2 Normalized modulus as a function of normalized density. The solid line traces the square power-law.

though this equation is valid for low density foams, it will be used to compare with our lower limit of foam density.

RESULTS AND DISCUSSION

Mechanical properties

The moduli of our foams as a function of foam density are shown in Figure 1. Because the foam modulus is related to the modulus of the parent polymer, we use the normalized modulus (ratio of foam's modulus to modulus of unfoamed polymer matrix), and normalized density (ratio of foam density to density of unfoamed polymer matrix) to analyze the relationship between modulus and density. This is done to eliminate the effect of the unfoamed polymer matrix on the foam properties. The normalized modulus as a function of normalized density is shown in Figure 2. It can be seen that the normalized modulus exhibits a square power-law dependence with respect to the normalized density of the foam.

Comparison of models

All the models described contain simplifying assumptions on the structure and the distribution of the inclusions that are most likely unrealistic. Their validity must be judged, at least partially, in terms of how closely they predict the experimental data between the relative modulus and density. For the sake of comparison, all calculations have been made using a ν_m value of 0.34 for polyethylene.[39]

Continuum approach

Figure 3 shows a comparison of the normalized modulus as function of the normalized density using the

Figure 1 Foam modulus as a function of foam density.

continuum approach. The Mori-Tanaka model and the differential scheme show good agreement with the experimental data. The macro-stress model is based on a constant macro-stress, which is not the case in our study because the measurements were performed under tension at a constant strain rate. Furthermore, this model is valid only for very low inclusion concentration. This is why the predictions of the model are not in agreement with the experimental data even at a very low inclusion concentration (higher foam density). The constant macro-strain model does not consider the matrix/inclusion interactions. It does however do a better job at very low inclusion concentrations, but the normalized elastic modulus becomes negative at $f = 0.323$, which is clearly impossible. Even though the self-consistent model considers some matrix/inclusion interaction, it still does not consider the inclusion/inclusion interaction. However, the effect of inclusion interaction is important only at high inclusion concentrations. From these results, we can conclude that the constant macro-strain model and the self-consistent model could be used at very low inclusion concentrations ($f < 10\%$). The average deviations of the predictions were found to be 9.4% and 7.9% for the Mori-Tanaka model and the differential scheme that considers the change in the overall modulus when a small amount of the inclusion is introduced in the system. However, the Mori-Tanaka model does not consider the interactions among inclusions. This could be the reason Mori-Tanaka overestimates the normalized modulus at high inclusion concentrations. Therefore the differential scheme seems best to predict the foam behavior over the range of inclusion concentrations studied.
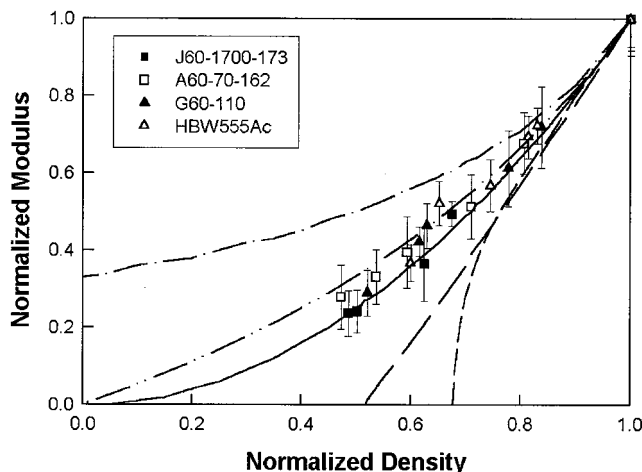

Figure 3 Comparison of normalized modulus as a function of normalized density for the continuum approach. Lines show predictions of different models: (– · – · –) constant macro-stress, (– ·· – ·· –) Mori-Tanaka model, (———) differential scheme, (– – –) self-consistent model, (- - - - - - -) constant macro-strain.
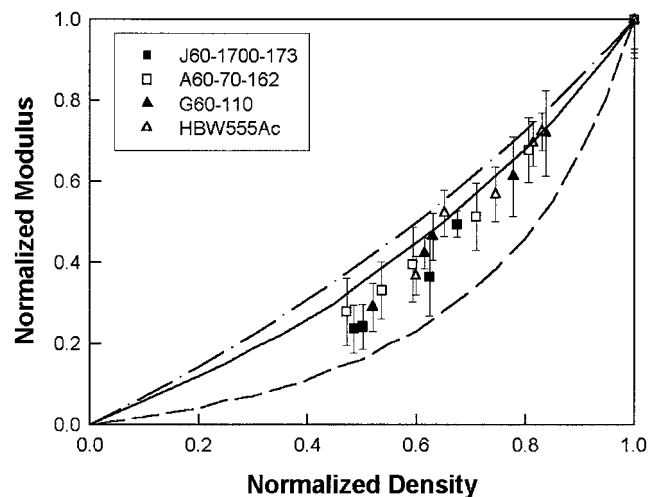

Figure 4 Comparison of normalized modulus as a function of normalized density for semi-empirical models. Lines show predictions of different models: (– · – · –) Halpin-Tsai, (———) Kerner, (– – – –) modified Kerner models.

Semi-empirical approach

Figure 4 compares the normalized modulus as function of the normalized density of the semi-empirical models. It can be seen that these models do not produce good agreement. Among them, the Kerner model gives the most reasonable prediction, even though this model still overestimates the elastic modulus when the inclusion volume fraction is larger than 20%. The average deviations were found to be 21%, 12%, and 35% for the Halpin-Tsai, Kerner, and modified Kerner models, respectively. Halpin-Tsai developed a model for discontinued oriented fiber composites and an empirical equation for an in-plane random distribution. The inclusion shape and properties affect the final moduli of the composites. In this model, the shape of the inclusion is cylindrical, but the shape for our closed cell foam is mostly spherical. This explains why the Kerner model gives a more reasonable prediction than the Halpin-Tsai model. The modified Kerner model considers a particle state (aggregation or not), which is not the case for our closed-cell foams. If two cells come in contact, they could coalesce to become a larger void during foaming. This model thus underestimates the modulus of the composites for all inclusion concentration.[5]

Other models

Figure 5 compares the predictions from the other models discussed. For the Gibson-Ashby model, one needs to determine the value of ϕ. In their book,[38] the value of ϕ for polyurethane is around 0.8–0.9. Closed-cell foams usually have similar morphological structures. In our case, a value of 0.85 is used for ϕ. Because the Gibson-Ashby model was developed for low den-

sity foams, this model will be in error when applied to high density foams. Using this model, the normalized modulus does not reach unity when the void fraction reaches zero, but the model gives reasonable predictions at higher void fractions ($f > 0.4$). From Figure 5, we can see that the Voigt model, which represents the simple linear law of mixture, substantially overestimates the elastic modulus. On the other hand, the experimental data are in good agreement with the predictions of Moore's empirical model. The average deviations are 39%, 13%, and 7.9% for the Voigt, Gibson-Ashby, and Moore empirical models, respectively. This means that Moore's empirical model seems to work best in our case. The following section compares the models that gave the best predictions for our HDPE foams.

Best models

Figure 6 compares the models that gave the most reasonable predictions. The average deviations of the predictions were found to be 12%, 7.9%, and 7.9% for Kerner's model, the differential scheme, and Moore's empirical model, respectively. We could not differentiate between the differential scheme and Moore's empirical model, so both are believed to be equal. Nevertheless, from the trend observed in the curves, we expect that Kerner's model will not give good results at void fractions higher than the ones studied here.

CONCLUSIONS

Even though several mechanical models are available to predict the properties of two phase materials, most of them were found to be inapplicable to polymer foamed materials. The question of which model is best
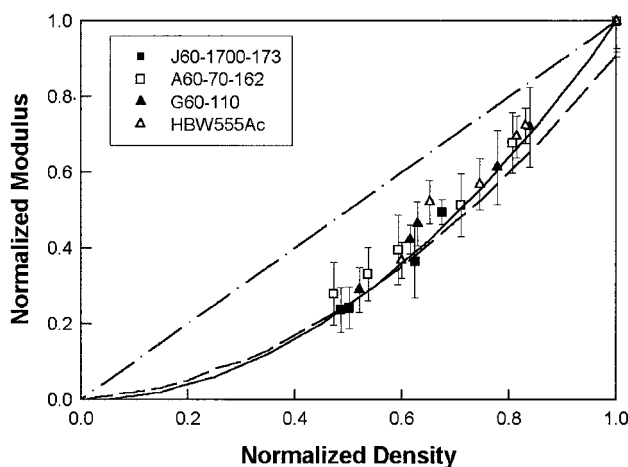
Figure 5 Comparison of normalized modulus as a function of normalized density for general models. Lines show predictions of different models: (– · – · –) Voigt, (- - - - - - -) Gibson-Ashby, (———) Moore.
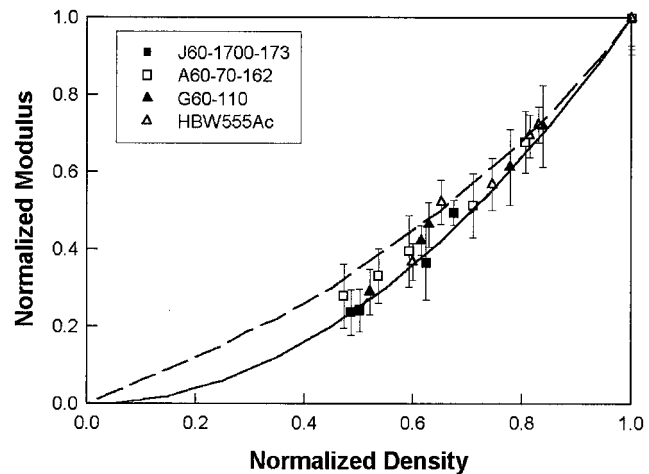
Figure 6 Comparison of normalized modulus as a function of normalized density for the best models. Lines show predictions of different models: (– – – –) Kerner, (———) differential scheme and Moore's empirical model.

to predict the properties of foamed polymers over a wide range of void fractions thus arises.

Using our measurements, several very well known models were compared. The Voigt model, which is actually the linear law of mixture for composites, was not valid in our case for all void volume fractions. The constant macro-stress model was not suitable in our case because our measurements were made using a constant strain rate. The constant macro-strain and the self-consistent models are valid only at very low void volume fractions (less than 0.1) because of the simplifications made in their development. The Kerner and the Mori-Tanaka models have similar limitations. The Halpin-Tsai model overestimates the modulus, while the modified Kerner model underestimates the modulus for all void fractions. Finally, the Gibson-Ashby model seems to give reasonable predictions only for very high void fractions ($f > 0.4$).

Of all models tested, it was found that the differential scheme and Moore's empirical square power-law were the best models to approximate the tensile moduli of our closed-cell HDPE foams. Each one gave similar results that could not be differentiated, their average deviation being 7.9%.

References

1. Burillo, G. In Polymeric Materials Encyclopedia, Salamonde, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 8, 6015.
2. Mark, H. F.; Kroschwitz, J. I. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; John Wiley & Sons: Hoboken, NJ, 1985; Vol. 3, 1–59.
3. Gibson, L. J.; Ashby, M. F. Proc Roy Soc London 1982, A382, 43.
4. Moore, D. R.; Iremonger, M. J. J Cell Plast 1974, 10, 230.
5. Hashin, Z. J Appl Mech 1962, 29, 143.
6. Aboudi, J. Studies in Applied Mechanics 29: Mechanics of Composite Materials; Elsevier: Amsterdam, 1991.
7. Mori, T.; Tanaka, K. Acta Metall 1973, 21, 571.
8. Eshelby, G. J. Proc Roy Soc 1957, A241, 376.
9. Weng, G. J. Inter J Eng Sci 1984, 22, 845.
10. Li, J.; Weng, G. J. J Eng Mat Tech 1994, 116, 495.
11. Wang, Y. M.; Weng, G. J. J Appl Mech 1992, 59, 510.
12. Ju, J. W.; Chen, T. M. Acta Mech 1994, 103, 103.
13. Ju, J. W.; Chen, T. M. Acta Mech 1994, 103, 123.
14. Ju, J. W.; Chen, T. M. J Appl Mech 1994, 61, 349.
15. Ju, J. W.; Chen, T. M. J Appl Mech 1994, 61, 359.
16. Wong, F. Ph.D. Dissertation, University Laval, 1997.
17. Zhang, Y.; Rodrigue, D.; Aït-Kadi, A. J Appl Polym Sci, submitted.
18. Sokolnikoff, I. S. Mathematical Theory of Elasticity; McGraw-Hill: Toronto, ON, 1956.
19. Lekhnitskii, S. G. Theory of Elasticity of an Anisotropic Elastic Body; Holden-Day: San Francisco, 1963.
20. Jone, R. M. Mechanics of Composite Materials; McGraw-Hill: New York, 1975.
21. Kaw, A. K. Mechanics of Composite Materials; CRC Press: Boca Raton, FL, 1997.
22. Mase, G. E. Theory and Problems of Continuum Mechanics: Schaum's Outline Series; McGraw-Hill: New York, 1970.
23. Nemat-Nasser, S.; Hori, M. Micromechanics: Overall Properties of Heterogeneous Materials, 2nd ed.; Elsevier: Amsterdam, 1999.
24. Voigt, W. Wied Ann Physik 1889, 38, 573.
25. McLaughlin, R. Inter J Eng Sci 1977, 15, 237.
26. Farber, J. N.; Farris, R. J. J Appl Polym Sci 1987, 34, 2093.
27. Maron, M. J. Numerical Analysis: A Practical Approach, 2nd ed.; Macmillan: New York, 1982.
28. Halpin, J. C.; Tsai, S. W. US Air Force Materials Laboratory Report, AFML-TR-67-423, 1969.
29. Halpin, J. C.; Pagano, N. J. J Composite Mater 1969, 3, 720.
30. Halpin, J. C.; Kardos, J. L. Polym Eng Sci 1976, 16(5), 344.
31. Kardos, J. L.; Piccarolo, S.; Halpin, J. C. Polym Eng Sci 1976, 16(5), 344.
32. Halpin, J. C.; Kardos, J. L. Polym Eng Sci 1978, 18(6), 496.
33. Kardos, J. L.; Piccarolo, S.; Halpin, J. C. Polym Eng Sci 1978, 18(6), 505.
34. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites; Marcel Dekker, Inc: New York, 1994.
35. Mallick, P. K. In Particulate and Short Fibre Reinforced Polymer Composites in Comprehensive Composite Materials; Elsevier: Amsterdam, 2000; Vol. 2, p. 291.
36. Kerner, E. H. Proc Phys Soc London 1956, B69, 808.
37. Nielsen, L. E. J Appl Phys 1970, 41(11), 4626.
38. Gibson, L. J.; Ashby, M. F. Cellular Solid, Structure and Properties, 2nd ed.; Cambridge Solid State Science Series, 1997.
39. Wong, F. C.; Ait-Kadi, A. J Appl Polym Sci 1995, 55, 263.