## *References*

1 Sperling, L. H. and Friedman, D. W. *J. Polym. Sci., Part A* 1969, **7**, 425
2 Grates, J. A., Thomas, D. A., Hickey, E. C. and Sperling, L. H. *J. Appl. Polym. Sci.* 1975, **19**, 1731
3 Akovali, G., Biliyar, K. and Shen, M. *J. Appl. Polym. Sci.* 1976, **20**, 2419
4 Kim, S. C., Klempner, D., Frisch, K. C., Radigan, W. and Frisch, H. L. *Macromolecules* 1976, **9**, 258
5 Touhsaent, R. E., Thomas, D. A. and Sperling, L. H. *J. Polym. Sci. (C)* 1974, **46**, 175
6 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites' Plenum Press, New York, 1976
7 Klempner, D. and Frisch, K. C. 'Polymer Alloys' Plenum Press, New York, 1977
8 Paul, D. R. and Newman, S. 'Polymer Blends' Academic Press, New York, 1978, Vol. 2, p 1
9 Kim, S. C., Klempner, D., Frisch, K. C., Frisch, H. L. and Ghiradella, H. *Polym. Eng. Sci.* 1975, **15**, 339
10 Donatelli, A. A., Thomas, D. A. and Sperling, L. H. 'Recent Advances in Polymer Blends, Grafts and Blocks' Plenum Press, New York, 1974
11 Huelk, V., Thomas, D. A. and Sperling, L. H. *Macromolecules* 1972, **5**, 340
12 Hourston, D. J. and Hughes, I. D. *J. Appl. Polym. Sci.* 1977, **21**, 3099
13 Williams, M. L. and Ferry, J. D. *J. Colloid Sci.* 1955, **10**, 474
14 Thurn, H. and Wolf, K. *Kolloid-Z.* 1958, **156**, 21
15 Heijboer, J. 'Physics of Non-Crystalline Solids' North Holland, Amsterdam, 1965, p 231
16 Read, B. E. *Polymer* 1964, **5**, 1
17 Mead, D. J. and Fuoss, R. M. *J. Am. Chem. Soc.* 1942, **64**, 2389
18 Mikhailov, G. P. *Zh. Tekh. Fiz.* 1951, **21**, 1395
19 Scheiber, D. J. Dissertation, University of Notre Dame, Indiana, 1957
20 Brouckere, L. and Offergeld, G. *J. Polym. Sci.* 1958, **30**, 105
21 Ishida, Y. *Kolloid-Z.* 1961, **174**, 124
22 Williams, G. *Trans. Faraday Soc.* 1964, **60**, 1548, 1556
23 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids' Wiley, London, 1967
24 Schmieder, K. and Wolf, K. *Kolloid-z* 1953, **134**, 149
25 Thurn, H. and Wolf, K. *Kolloid-Z.* 1956, **148**, 66

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# Modulus and strength of filled and crystalline polymers[*]

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### *Introduction*

When inclusions have a higher elastic modulus than the matrix, the chief effect of the filler is to increase the moduli of the composite. Theories of varying degrees of refinement have been reviewed[1,2] to account quantitatively for spherical filler particles and uniaxially oriented infinitely long fibres. For aligned chopped fibre composites, Halpin and Tsai[2] introduced a simple set of approximate equations which were later employed by Halpin and Kardos[3] to study the elastic moduli of partially crystalline polymers. Recently, Porter and his colleagues[4,5] have found that the Halpin–Tsai equation does not provide a correct estimation of the crystal shape in semicrystalline polyethylene.

Based on a recent model developed by the author[6,7], the relation of the modulus of semicrystalline polymers and the shape of crystallites will be discussed here. Because stress concentration factors are very critical parameters in the study of fracture and strength of heterogeneous materials, a relation is proposed for their determination which includes the effects of particle shape and volume concentration of fillers.

### *Modulus*

The modulus of a crystalline polymer has been considered by Takayanagi[8]. His series–parallel model gives the effective tensile modulus

$$E_{\parallel} = \left[ \frac{\psi}{\theta E_m + (1-\theta) E_f} + \frac{1-\psi}{E_f} \right] \qquad (1)$$

where the subscripts $f$ and $m$ identify the crystalline and amorphouse phases. The amorphous region is of volume $\psi\theta$ and the crystalline region $(1 - \psi\theta)$. The basic problem with the model is how to decide the values of $\psi$ and $\theta$.

In an alternative approach, Halpin and Kardos[3] employ the Halpin–Tsai equation[2] to determine the modulus of semicrystalline polymers from the crystal shape characterized by the aspect ratio $l/d$. For a uniaxially oriented morphology the tensile modulus is given by

$$E_{\parallel}/E_m = (1 + \epsilon\eta\phi)/(1 - \eta\phi) \qquad (2)$$

where $\eta = (E_f/E_m - 1)/(E_f/E_m + \epsilon)$, $\epsilon = 2(l/d)$ and $\phi$ is the volume fraction of crystals.

From electron diffraction measurements of ultradrawn polyethylene, Crystal and Southern[9] observed extended chain crystals approximately 200–250 Å in diameter and 5000 Å long. The properties of high-density polyethylene are[5]

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$$
\begin{aligned}
E_f &= 2.4 \times 10^{12}\ \text{dyn cm}^{-2}\\
E_m &= 1 \times 10^{9}\ \text{dyn cm}^{-2}\\
\phi &= 0.85
\end{aligned}
\tag{3}
$$

Mead, Porter, Southern and Weeks[4,5] found the crystal shape, calculated from equation (2), much greater than the measured aspect ratio $l/d = 20$–$25$. This conclusion is not entirely surprising because equation (2) was reduced from Hermans' solution[2] to a simple approximate form containing a geometric parameter $\epsilon$. The parameter is determined for ordinary short-fibre reinforced plastics with the ratio of $E_f/E_m$ rarely exceeding 1000. The ratio of moduli for semicrystalline polyethylene is 2400. Thus, the Halpin–Tsai equation originally proposed for composite materials may not be adequate for semicrystalline polymers.

A recent model by the author[7] has considered fully the effects of particle shape and concentration of two phase anisotropic heterogeneous materials. There is no fitting parameter in the model. Both the filler and matrix are assumed isotropic. Fillers are treated as identical spheroids

$$(x_1^2 + x_1^2)/a^2 + x_3^2/c^2 = 1 \tag{4}$$

When the corresponding axes are aligned and the spatial distribution of the fillers is random and homogeneous, the medium as a whole becomes transversely isotropic about the $x_3$ axis. The effective longitudinal Young's modulus $E_{\parallel}$ is given by

$$\frac{E_{\parallel}}{E_m} = 1 + \frac{(k_f/k_m - 1)G_1 + 2(\mu_f/\mu_m - 1)K_1}{2K_1G_3 + G_1K_3}\,\phi \tag{5}$$

where $k$ is the bulk modulus, $\mu$ is the shear modulus,

$$
\begin{aligned}
K_i &= 1 + (k_f/k_m - 1)(1-\phi)\alpha_i \quad (i = 1,3)\\
G_i &= 1 + (\mu_f/\mu_m - 1)(1-\phi)\beta_i \quad (i = 1,3)
\end{aligned}
\tag{6}
$$

$\alpha_i$ and $\beta_i$ are functions of the aspect ratio $\rho = c/a$ and Poisson's ratio $\nu_m$ of the matrix (see Appendix). Equation (5) compares well with experiments for reinforced plastics[7]. For spherical fillers ($\rho = 1$), $K_1 = K_3 = K$, $G_1 = G_3 = G$ and equation (5) reduces to the well known Kerner equation[7]. When the aspect ratio $\rho \to \infty$ equation (5) becomes the limiting upper bound for semicrystalline polymers[3]. Mead and Porter[4] measured the tensile modulus of ultraoriented high-density polyethylene: $E_{\parallel} = 50 \times 10^{10}$ dyn cm$^{-2}$. Using equation (3) and assuming $\nu_f = 0.25$ and $\nu_m = 0.45$, the calculated shape of crystallites from equation (5) is $\rho = 30$ which is very close to the measured aspect ratio ($l/d = 20 - 25$). This suggests the potential use of equation (5) in the structure–property estimation of a semicrystalline polymer.

### *Stress concentration*

The ratio of the maximum stress to the applied stress defines the stress concentration factor. Consider aligned prolate spheroids (see equation (4) with $c > a$) in a matrix of lower modulus under a uniform tensile stress parallel to the $x_3$ axis. The maximum stress occurs at $(x_1, x_2, x_3) = (0,0,c)$ where cohesive and/or adhesive failure takes place. Therefore, the determination of stress concentration factor is essential for heterogeneous materials.

Traditionally, the stress concentration calculation has been limited to a single isolated inclusion[11–13] which does not include the concentration dependence. The analysis, to include the filler–filler interaction, follows exactly the mean field theory developed for elastic moduli[7] (see equation (5)) and thermal expansion[14].

The spheroids are assumed to be firmly bonded to the matrix and the composite as a whole is macroscopically homogeneous. The volume average of internal stresses, $\langle\sigma_{pq}\rangle$, inside prolate spheroids due to uniform applied stress $\sigma_{ij}^A$ can be determined from[7]

$$
\begin{aligned}
&(1-\phi)[(\lambda_f - \lambda_m)S_{kkpq}\delta_{ij} + 2(\mu_f - \mu_m)S_{ijpq}]\langle\sigma_{pq}\rangle\\
&+ \lambda_m\langle\sigma\rangle\delta_{ij} + 2\mu_m\langle\sigma_{ij}\rangle = \lambda_f\sigma^A\delta_{ij} + 2\mu_f\sigma_{ij}^A
\end{aligned}
\tag{7}
$$

where $\lambda = k - 2\mu/3$ is the Lame constant, $\delta_{ij}$ is the Kronecker delta, $S_{ijpq}$ is Eshelby's tensor[7,15] and $e$ is the dilatation. There are five independent equations with $\langle\sigma_{23}\rangle = \langle\sigma_{13}\rangle$.

Consider a uniform tensile stress $\sigma_{33}^A$ as the only nontrivial stress applied to the system. The stress concentration factor is

$$S \equiv \frac{\langle\sigma_{33}\rangle}{\sigma_{33}^A} = \frac{(k_f/k_m)G_1 + 2(\mu_f/\mu_m)K_1}{2K_1G_3 + G_1K_3} \tag{8}$$

where $K_i$ and $G_i$ ($i = 1,3$) are given in equation (6). The above equation contains both shape and concentration effects of fillers. When $\phi \to 0$ and $\rho = 1$, equation (8) becomes

$$S = [(k_f/k_m)/K + 2(\mu_f/\mu_m)/G]/3 \tag{9}$$

which is the classical Goodier Equation[11]. For illustration, consider glass-filled poly(phenylene oxide) (PPO) possessing the following properties:

$$
\begin{aligned}
E_f &= 73.1 \times 10^{10}\ \text{dyn cm}^{-2}, \quad \mu_f = 0.22\\
E_m &= 2.6 \times 10^{10}\ \text{dyn cm}^{-2}, \quad \mu_m = 0.35
\end{aligned}
\tag{10}
$$

The stress concentration factor is calculated from equation (8) as a function of $\rho$ and $\phi$. The general behaviour is shown in *Figure 1*. It reveals that the concentration dependence diminishes for large values of the aspect ratio.

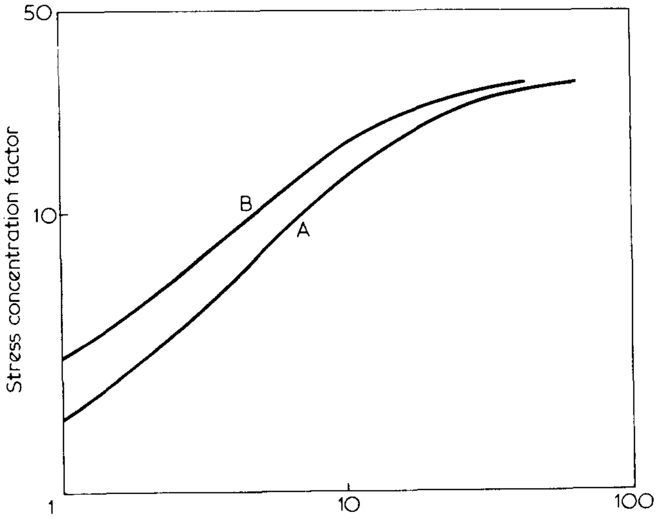

*Figure 1* Effects of $\rho$ and $\phi$ on the stress concentration factor. A, $\phi \to 0$; B, $\phi = 0.4$

## *References*

1 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum Press, N.Y., 1976, Ch. 12
2 Ashton, J. E., Halpin, J. C. and Petit, P. H. 'Primer on Composite Materials: Analysis', Technomic, Stamford, Conn., 1969, p 77
3 Halpin, J. C. and Kardos, J. L. *J. Appl. Phys.* 1972, **43**, 2235
4 Mead, W. T. and Porter, R. S. *J. Appl. Phys.* 1976, **47**, 4278
5 Porter, R. S., Southern, J. H. and Weeks, N. *Polym. Eng. Sci.* 1975, **15**, 213
6 Chow, T. S. *J. Appl. Phys.* 1977, **48**, 4072
7 Chow, T. S. *J. Polym. Sci. (Polym. Phys. Edn.)* 1978, **16**, 959
8 Takayanagi, M., Harima, H. and Iwata, Y. *Rep. Prog. Polym. Phys. Jpn* 1963, **6**, 121
9 Crystal, R. C. and Southern, J. H. *J. Polym. Sci.* A2, 1971, **9**, 1641
10 Hermans, J. J. *Proc. R. Acad. Amsterdam* 1967, **B70**, 1
11 Goodier, J. N. *J. Appl. Mech.* 1933, **1**, 39
12 Edwards, R. H. *J. Appl. Mech.* 1951, **18**, 19
13 Argon, A. S. Fibre Sci. Technol. 1976, **9**, 265
14 Chow, T. S. *J. Polym. Sci. (Polym. Phys. Edn.)* 1978, **16**, 967
15 Eshelby, J. D. *Proc. R. Soc. London Ser. A.* 1957, **241**, 376

## *Appendix*

The parameters for equation (6) are listed in the following:

$$\alpha_1 = 4\pi Q/3 - 2(2\pi - I)R$$

$$\alpha_3 = 4\pi Q/3 + 4(I - \pi)R$$

$$\beta_1 = \left(4\pi/3 - \frac{4\pi - 3I}{1 - \rho^2}\right) Q - 4(I - 2\pi)R$$

$$\beta_3 = [4\pi/3 - (4\pi - 3I)\rho^2/(1 - \rho^2)]\,Q + (4\pi - I)R$$

where

$$Q = \frac{3}{8\pi}\,\frac{1}{1 - \nu_m}\,,\quad R = \frac{1}{8\pi}\,\frac{1 - 2\nu_m}{1 - \nu_m}$$

and

$$r = \begin{cases} \dfrac{2\pi\rho}{(1 - \rho^2)^{3/2}}\,[\cos^{-1}\rho - \rho(1 - \rho^2)^{1/2}] & \text{for } \rho < 1, \\[2ex] \dfrac{2\pi\rho}{(\rho^2 - 1)^{3/2}}\,[\rho(\rho^2 - 1)^{1/2} - \cosh^{-1}\rho] & \text{for } \rho > 1 \end{cases}$$

When $\rho \to 1$, we have

$$\alpha_1 = \alpha_3 = \alpha = \frac{1}{3}\left(\frac{1 + \nu_m}{1 - \nu_m}\right)$$

$$\beta_1 = \beta_3 = \beta = \frac{2}{15}\left(\frac{4 - 5\nu_m}{1 - \nu_m}\right)$$

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# ERRATUM

## 'Proton spin-lattice relaxation in vinyl polymers and an application of a solvable model of polymer dynamics'

F. Heatley* and J. T. Bendler†

There is an error in the definition of the relaxation coefficients in equation (3) of reference 1, concerned with coupled proton spin-lattice relaxation in vinyl polymers. The equation defining the cross-relaxation coefficients $T_{AX}$ and $T_{XA}$ is in error by a factor of 2, and should read

$$\frac{1}{T_{AX}} = \frac{1}{2T_{XA}} = K\,\frac{12J(\omega_A + \omega_X) - 2J(\omega_A - \omega_X)}{R_{AX}^6}$$

This error is solely a transcription error. Relaxation parameters reported in reference 1 were evaluated using the correct form.

Unfortunately, the incorrect expression was employed in a subsequent application of a jump model of polymer motion[2]. As a consequence of the correction above, calculated nuclear Overhauser enhancements given in *Table III* of reference 2 should be multiplied by 2. The agreement with experiment is much improved. (Note also that the entry for the parameter $N_A$ at 10°C in the fourteenth column of *Table III* has been incorrectly printed as –0.9 instead of –0.09.)

## *References*

1 Heatley, F. and Cox, M. K. *Polymer* 1977, **18**, 225
2 Bendler, J. T. and Yaris, R. *Macromolecules* 1978, **11**, 650

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