# Mechanical Moduli of Spherulitic Lamellar Semicrystalline Polymers

**Richard H. Boyd* and Wen-Bin Liau**

*Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112.* *Received April 1, 1986*

ABSTRACT: A treatment previously given for calculation of bounds on the moduli of lamellar semicrystalline polymers is extended to the case of the lamellae having spherulitic organization. The local elastic constant (**C**) and compliance constant (**S**) matrices that were previously constructed and that incorporate the interaction between the crystal and amorphous phases in lamellar structures are utilized. However, rather than directly three-dimensionally averaging these matrices to obtain bounds on engineering moduli, we first use these matrices to obtain the properties of a mechanically spherically isotropic inclusion. Then, following a procedure used by Wang, we use self-consistent embedding theory to calculate the moduli of a macroscopically isotropic aggregate of spherulites. Although the structure is determined to the extent that the lamellar ribbons point radially, the lamellar surfaces are randomly oriented normal to the radius and a two-dimensional averaging must still be carried out. Thus bounds are obtained from the two-dimensional averaging of **C** and **S**. Sample calculations show the bounds on the engineering moduli to be significantly, but not dramatically, tighter than the previous lamellar bounds for materials without further structural organization.

## Introduction

The modeling of a semicrystalline polymer as a macroscopic composite of its constituent crystal and amorphous phases is a subject of considerable and continuing interest (and has been reviewed on a number of occasions[1-7]). As might be expected, such modeling has proven to be difficult. The difficulties are largely of two kinds. First, at a local level there is the problem of the interaction between the two phases. That is, continuity conditions across the boundaries should be properly observed. Then, macroscopically, the material nearly always possesses a distribution of orientations of the crystals. Taking this into account has usually involved averaging over the orientations in some way. In the case of mechanical properties, averaging using a constant-strain assumption leads to an upper bound estimate of properties and constant-stress averaging leads to a lower bound. It is apparent that a really completely detailed model would incorporate various orientations as well as the local structure and thus be completely determinate. This stage, at least as far as analytical models are concerned, has not been reached. However, it would appear that progress can be made by incorporating larger more complex structures in the detailed modeling before the averaging takes place.

At the lowest level, the phase properties are *first* averaged separately and *then* combined, giving the Voigt upper bound equation

$$\langle E \rangle = v_1 E_1 + v_2 \langle E_2 \rangle \tag{1}$$

and the Reuss lower bound equation

$$\langle 1/E \rangle = v_1/E_1 + v_2 \langle 1/E_2 \rangle \tag{2}$$

where $v_1$ and $v_2$ are the volume fractions of the amorphous (1) and crystal (2) phases, respectively, and $E_1$ and $E_2$ are properties which, for the purposes of discussion, can be taken as the tensile moduli of the two phases and $E$ as that for the composite. It may be legitimate to regard the amorphous phase as isotropic and hence $E_1$ as a single specific number. However, the crystal is invariably highly anisotropic. $E_2$ depends on orientation and $\langle E_2 \rangle$ and $\langle 1/E_2 \rangle^{-1}$ are in general very different. The Voigt combining rule per se satisfies appropriate boundary conditions of continuous strains and additive forces appropriate only for a layered crystal/amorphous structure defomed in a direction within the layers. The Reuss combining rule per se incorporates appropriate boundary conditions of continuous stress and additive displacements only for a direction normal to the interface. Neither takes into account the effects of lateral contractions (Poisson's ratio). Averaging over orientation in the macroscopic material corresponds to averaging under constant strain for the Voigt equation and constant stress for the Reuss equation. The bounds afforded by the Voigt and Reuss equations are very poor.

Various attempts have been made to improve the above situation by first computing the local response of the two phases in contact and then averaging the response of the two phases, now represented locally as a single phase, over orientation. The "aggregate model"[2] accomplishes the local response description via experiments on oriented specimens of varying orientations. Other approaches use micromechanics from composite modeling theory[3,8-11] to effect the description. In previous work we have described local mechanical[12] and dielectric[13,14] response by setting up response matrices for lamellar structures. In the mechanical case, the combining rules were derived in such a way as to ensure simultaneous continuity of stress and additivity of displacements normal to the lamellar surfaces and continuity of strain and additivity of forces within the lamellar planes. In the dielectric case, matrices were set up that gave a continuous displacement field normal to the lamellar surfaces and continuous electric field within the planes. Averaging the elastic constant matrix and its inverse and averaging the dielectric constant matrix and its inverse led to much tighter bounds on the engineering moduli and the effective dielectric constant than the mixture equations embodied in eq 1 and 2.

In the dielectric case above, a further improvement was possible in the case where the lamellae are further organized into spherulites (Figure 1).[13] These structures are effectively isotropic transversely about the spherulite radius but have different radial and tangential response. The response to an electric field of such a sphere embedded in an isotropic medium could be calculated. Then it could be shown that for a particular organization of spherulites, the dielectric constant of the isotropic medium could be made exactly self-consistent with that of the sphere itself. Because the lamellar normals are oriented effectively randomly about the radial direction, the computation of the tangential dielectric constant of the sphere requires averaging. Thus bounds still result when constant electric field and constant displacement field averages are taken. However, the averaging is now two-dimensional, rather than three-dimensional, and tighter bounds than obtained for lamellar structures not invoking spherulitic organization result. Although the improvement in bounds effected

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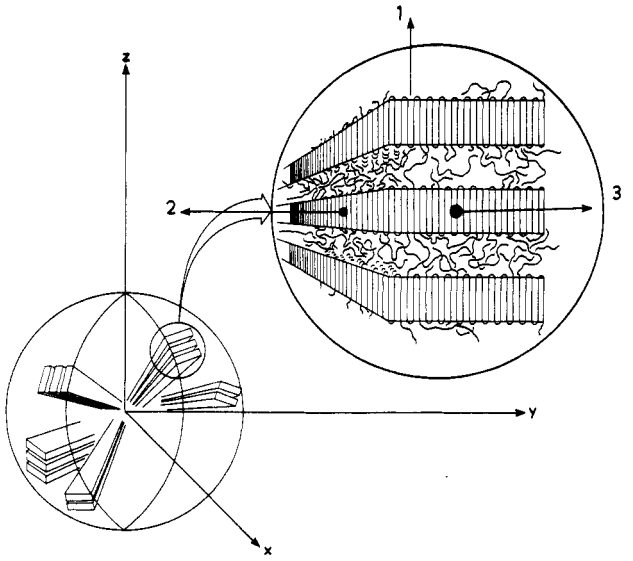


**Figure 1.** Schematic representation of a lamellar semicrystalline polymer with spherulitic superstructure. The orientation of the coordinate system in the local region is also shown.

via recognizing this higher structure is not dramatic it does suggest investigating the same question in the mechanical case. The purpose of the present work was to carry this out.

## Calculation

Fortunately much of the required machinery for carrying out the calculation of the response of a spherulitic structure using lamellar micromechanics is already available. Wang[10] has carried out such a calculation but with use of a different specific composite model for the local response and a specific averaging rule for the crystal properties about the radial direction. His calculation made use of the solution presented by Chen[15] to the mechanical response of a "spherically isotropic" (i.e., different radial and tangential response but transversely isotropic about the sphere radius) inclusion in a continuous isotropic elastic medium. This solution was used in conjunction with self-consistent embedding theory[16-19] to match the inclusion response to that of the isotopic continuous medium.

**Mechanical Properties of the Sphere (Step 1).** The local elastic constant matrix, **C**, and the compliance constant matrix, **S**, are set up in a Cartesian system such that the 3 axis is along the spherulite radius, the 2 axis is in the lamellar planes normal to the 3 axis, and the 1 axis is normal to the lamellar planes (see Figure 1). The **C** matrix is constructed from the elastic constant matrices **C**(1) and **C**(2) of the separate amorphous (1) and crystal (2) phases, respectively, using equations for the individual elements already given.[20] Equations for formulating **S** from the separate phase matrices **S**(1) and **S**(2) are also given in the previous work. The amorphous phase is assumed to be isotropic so that the elements of **C**(1) and **S**(1) are given in terms of just two parameters, the shear modulus, $G_1$, and the Poisson ratio, $\nu_1$, as

$$\lambda_1 = 2\nu_1 G_1/(1 - 2\nu_1) \quad (3)$$

$$E_1 = 2(1 + \nu_1)G_1 \quad (4)$$

$$C_{11}(1) = C_{22}(1) = C_{33}(1) = \lambda_1 + 2G_1 \quad (5)$$

$$C_{12}(1) = C_{13}(1) = C_{23}(1) = \lambda_1 \quad (6)$$

$$C_{44}(1) = C_{55}(1) = C_{66}(1) = G_1 \quad (7)$$

$$S_{11}(1) = S_{22}(1) = S_{33}(1) = 1/E_1 \quad (8)$$

$$S_{12}(1) = S_{13}(1) = S_{23}(1) = -\nu_1/E_1 \quad (9)$$

$$S_{44}(1) = S_{55}(1) = S_{66}(1) = 1/G_1 \quad (10)$$

The crystal is assumed to have orthorhombic or higher symmetry to conform to the orthotropic material for which averaging will be carried out. The nine elastic constants for the crystal are assumed to be known. With the local response **C** and **S** (=$\mathbf{C}^{-1}$) matrices set up, they are next averaged about the spherulite radius direction (axis 3, Figure 1) assuming random distribution of lamellar normals about the radius. The averaging procedure has been described and formulas have been listed for representing the elements of $\langle\mathbf{C}\rangle$ and $\langle\mathbf{S}\rangle$ in terms of those of **C** and **S**.[6,12] The averaging reduces the number of independent constants in $\langle\mathbf{C}\rangle$ and $\langle\mathbf{S}\rangle$ from nine to five. Averaging of **C** implies constant strain, and the elements, $C_{ij}^{U} = \langle C_{ij}\rangle$, of $\langle\mathbf{C}\rangle$ are upper bound estimates of the true values. The averaged compliance matrix, which implies constant-stress averaging, may be inverted to $\langle\mathbf{S}\rangle^{-1}$. The elements of the inverted averaged compliance matrix, $C_{ij}^{L} = \langle S_{ij}\rangle^{-1}$, are lower bound estimates of the true elastic constants.

**Mechanical Response of the Embedded Sphere (Step 2).** The response of the spherically isotropic inclusion requires the five independent elastic constants, $C_{ij}$ ($ij$ = 11, 12, 13, 33, and 44), of $C_{ij}^{U}$ (for an upper bound calculation) or the corresponding elements of $C_{ij}^{L}$ (for a lower bound calculation). The sphere is embedded as an inclusion in a homogeneous isotropic medium which is subjected to a uniform stress or strain at a large distance from the inclusion. Using the solution of Chen[15] one may calculate the medium and inclusion stresses and strains. Then under self-consistent embedding theory, the volume-average inclusion stresses and strains are made equal to those of the homogeneous isotropic medium. This process, as reported by Wang,[10] for the effective bulk modulus, $K$, gives the result

$$K = [C_{33}(\nu_{01} - \tfrac{1}{2}) + 2C_{13}]/3 \quad (11)$$

where

$$\nu_{01} = [\tfrac{1}{4} + 2(C_{11} + C_{12} - C_{13})/C_{33}]^{1/2}$$

and the effective shear modulus, $G$, is given by the solution to the quadratic equation

$$16G^2(K_{23} - K_{21}) + 2G\{2C_{44}[(K_{23} + \nu_{23} - \tfrac{3}{2})(K_{21} - 3) - (K_{21} + \nu_{21} - \tfrac{3}{2})(K_{23} - 3)] + C_{33}[K_{23}(\nu_{23} - \tfrac{1}{2})(K_{21} - 1) - K_{21}(\nu_{21} - \tfrac{1}{2})(K_{23} - 1)] + 4C_{13}(K_{23} - K_{21})\} + 2C_{13}C_{44}[(K_{23} + \nu_{23} - \tfrac{3}{2})(K_{21} - 3) - (K_{21} + \nu_{21} - \tfrac{3}{2}) \times (K_{23} - 3)] + C_{33}C_{44}[K_{21}(K_{23} + \nu_{23} - \tfrac{3}{2})(\nu_{21} - \tfrac{1}{2}) - K_{23}(K_{21} + \nu_{21} - \tfrac{3}{2})(\nu_{23} - \tfrac{1}{2})] = 0 \quad (12)$$

In the above two equations, the five elastic constants $C_{ij}$ ($ij$ = 11, 12, 13, 33, and 44) are determined as above and the constants $K_{21}$, $K_{23}$, $\nu_{21}$, and $\nu_{23}$ are given by the following relations:

$$\nu_{21} = [a_2 + (a_2^2 - b_2)^{1/2}]^{1/2}$$

$$\nu_{23} = [a_2 - (a_2^2 - b_2)^{1/2}]^{1/2}$$

$$K_{2m} = [5C_{11} + C_{12} - C_{44}(\nu_{2m}^2 - \tfrac{9}{4})]/[(C_{13} + C_{44}) \times (\nu_{2m} - \tfrac{1}{2}) + (2C_{44} + C_{11} + C_{12})] \quad (m = 1, 3)$$

where

$$2C_{33}C_{44}a_2 = 6[C_{44}^2 + C_{11}C_{33} - (C_{13} + C_{44})^2] + C_{33}(2C_{44} + C_{12} - C_{11}) + 2C_{44}(C_{11} + C_{12} - C_{13}) + \tfrac{1}{2}C_{33}C_{44}$$

and

$$C_{33}C_{44}b_2 = [6C_{44} + 2(C_{11} + C_{12} - C_{13}) + \tfrac{1}{4}C_{33}][6C_{11} + 2C_{44} + C_{12} - C_{11} + \tfrac{1}{4}C_{44}] - 6[2C_{44} + C_{12} + C_{11} - \tfrac{1}{2}(C_{13} + C_{44})]^2$$

**Table I**
**Elastic and Compliance Constants of Polyethylene[a,b]**

| elastic constant, GPa | compliance constant, $GPa^{-1}$ |
|---|---|
| $C_{11} = 4.83$ | $S_{11} = 0.2144$ |
| $C_{12} = 2.55$ | $S_{12} = -0.0015$ |
| $C_{13} = 1.16$ | $S_{13} = -0.02755$ |
| $C_{22} = 257.1$ | $S_{22} = 0.00396$ |
| $C_{23} = 5.84$ | $S_{23} = -0.002455$ |
| $C_{33} = 8.71$ | $S_{33} = 0.1201$ |
| $C_{44} = 2.83$ | $S_{44} = 0.3533$ |
| $C_{55} = 3.54$ | $S_{55} = 0.2825$ |
| $C_{66} = 0.78$ | $S_{66} = 1.282$ |

[a] Odajima and Maeda.[21] [b] 1 = $a$ axis, 2 = $c$ axis, 3 = $b$ axis.

The effective tensile modulus is given by the familiar isotropic relation

$$E = 9KG/(3K + G) \tag{13}$$

and, similarly, Poisson's ratio by

$$\nu = \tfrac{1}{2}E/G - 1 \tag{14}$$

## Results and Discussion

In examining the bounds formulated above, it is most expeditious to present illustrative calculations. To accomplish this, we have chosen polyethylene, as the crystal-phase elastic constant matrix is fairly well-known from empirical energy calculations. The values reported by Odajima and Maeda,[21] as listed in Table I, were used in our calculations. The $b$ axis of the crystal has been taken as the radial direction of the spherulite. The properties of the amorphous phase were regarded as a free parameter. A series of calculations at two values of the shear modulus, $G_1$, were carried out. The amorphous-phase Poisson's ratio, $\nu_1$, was kept fixed at 0.4 in all of the examples.

Comparisons of the spherulitic lamellar bounds for the tensile modulus as a function of degree of crystallinity were made with three other approaches. These approaches are the previous lamellar bounds for materials without further organization,[12] the Voigt and Reuss bounds for spherulitic structures, and the calculations of Wang for spherulites. The Voigt bounds were calculated by formulating, in step 1 in the calculation above, the averaged elastic constant matrix, $\langle \mathbf{C} \rangle$, by *preaveraging* the separate phase matrices, $\mathbf{C}(1)$ and $\mathbf{C}(2)$, and *then* combining according to the Voigt rules (eq 1). Then the response matrix thus found was used in step 2 above to find the response of the spherulitic aggregate. Similarly, the Reuss bounds were found by preaveraging $\mathbf{S}(1)$ and $\mathbf{S}(2)$ and combining according to the Reuss rules (eq 2) and then using the inverted response matrix in step 2. In Wang's calculation[9,10] a fiber composite equation due to Hill[22] and Hermans[23] was used to calculate the local response in step 1. This equation assumes transverse isotropy about the fiber axes. In setting an input for the transverse fiber response, a Voigt upper bound preaveraged value of the crystal constants ($a$ and $c$ directions) was used. This is in contrast to the lamellar mechanics approach where the transverse averaging is done on the already combined crystal and amorphous response matrices. In addition, in the lamellar mechanics approach we have investigated the effects of both upper and lower bound averaging rather than precommitting to one or the other. McCullough[6] has pointed out that the Hermans fiber composite equation used in the Wang method is a lower bound equation and thus the calculation has both upper and lower bound elements in it.

In Figure 2 the tensile modulus vs. crystallinity is shown, for an assumed amorphous-phase $G_1$ of 1.0 GPa, for the spherulitic lamellar bounds and for the previous lamellar

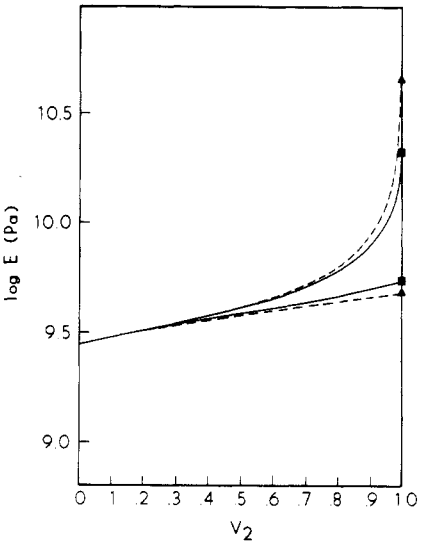


**Figure 2.** Comarison of spherulitic lamellar bounds (solid curves) with previously presented lamellar bounds for a material without the higher spherulitic structure (dashed curves). Tensile modulus vs. crystallinity (amorphous-phase shear modulus $G_1$ = 1.0 GPa).

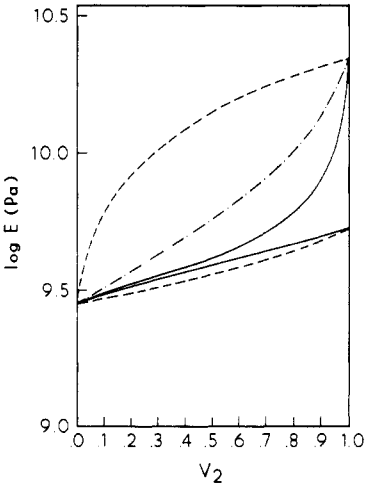


**Figure 3.** Comparison of spherulitic lamellar bounds (solid curves) with spherulitic Voigt upper and Reuss lower bounds (dashed curves) and also with Wang's fiber composite spherulitic model (dashed-dot curve). Tensile modulus vs. crystallinity (amorphous-phase shear modulus $G_1$ = 1.0 GPa).

bounds. In Figure 3 a similar comparison is made for the spherulitic lamellar bounds, the Voigt and Reuss spherulitic bounds, and the Wang fiber composite calculation. The calculations shown in Figures 2 and 3 are repeated for an amorphous-phase shear modulus of 0.1 GPa, and the results are displayed in Figures 4 and 5. Several conclusions seem to be warranted. The spherulitic lamellar bounds are immensely better than the Voigt–Reuss spherulitic bounds. Bounds must diverge at high crystallinity because of the severe crystal-phase anisotropy as discussed in the Introduction. The divergence is delayed to high crystallinity in the lamellar mechanics approach. This result is not unexpected on the basis of the previous comparisons of lamellar bounds with Voigt–Reuss bounds for materials without spherulites.[12] The Wang calculation follows the upper bound divergence at high crystallinity. This, of course, results from the averaging used for the crystal $a$ and $c$ constants as discussed above. This calculation falls outside of the spherulitic lamellar bounds for the $G_1$ = 1.0 GPa examples but lies largely inside them for the lower value of $G_1$ = 0.1 GPa. At high values of $G_1$ (where the amorphous-phase stiffness is fairly close to the

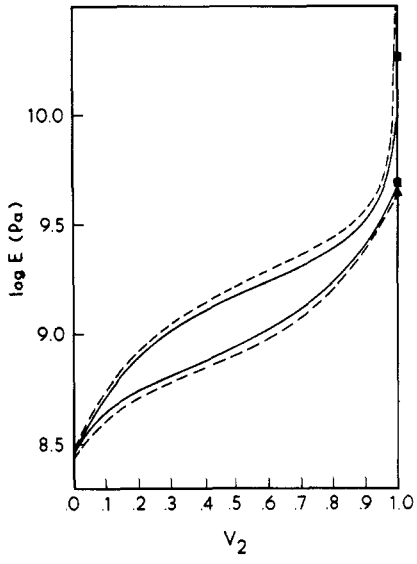


**Figure 4.** Comparison of spherulitic lamellar bounds (solid curves) with prevously presented lamellar bounds for a material without the higher spherulitic structure (dashed curves). Tensile modulus vs. crystallinity (amorphous-phase shear modulus $G_1$ = 0.1 GPa).

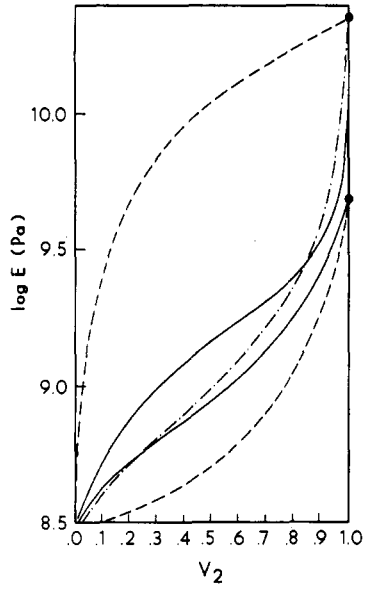


**Figure 5.** Comparison of spherulitic lamellar bounds (solid curves) with spherulitic Voigt upper and Reuss lower bounds (dashed curves) and also with Wang's fiber composite spherulitic model (dashed-dot curve). Tensile modulus vs. crystallinity (amorphous-phase shear modulus $G_1$ = 0.1 GPa).

average crystal-phase stiffness) the Wang results are dominated by the *a,c* crystal averaging element of the calculation and are thus more upper bound like. At low values of $G_1$ the calculation is dominated by the fiber equation element and the results are predominantly lower bound in character.

From comparison of the spherulitic lamellar bounds with the previous lamellar bounds for materials without these higher structures (from Figures 2 and 4) it appears that the spherulitic ones are noticeably, but not dramatically, better. This, based on similar results for the dielectric constant,[13] is not surprising. In summary, it may be fair to conclude that, due to the crystal anisotropy and the considerable differences between the amorphous- and crystal-phase stiffnesses typically encountered, any model that requires spatial averaging will lead to a somewhat imprecise description. The degree of imprecision is such that calculation of a phase property (such as, for example, $G_1$) from measured specimen values (and known elastic constants) could be rather inaccurate (the application of the simple lamellar bounds to experimental data has been discussed by us previously[7,24,25]). However, it is also probably true that in the reverse sense, a useful engineering description of the stiffness of semicrystalline polymers in terms of a single (temperature dependent) parameter ($G_1$) already exists if the crystal elastic constants are available.

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(20) The equations of ref 12 must be modified to accommodate a different numbering of the axes. To utilize the notation for averaging under axial symmetry, the symmetry axis must be numbered as 3. In the original work, 3 was taken as the lamellar normal; here it is in the spherulite radius direction and in the plane of the lamellae. All of the equations for combining the separate phase elastic constants and compliance constants into **C** and **S** respectively should have the indices changed according to 3(old) → 2(here), 2(old) → 3(here), 1 unchanged. Then the axial averaging procedure and notation can be used unchanged for averaging around 3.
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