Young's Modulus of Transcrystallinities in Semicrystalline Thermoplastic Composites

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SYNOPSIS

In a fiber/semicrystalline polymer system, interphasial transcrystallinities might form between the fibers and the matrix bulk that is composed of spherulites. By using an analogy method, the Young's modulus E_T of transcrystallinities in their growth direction was predicted by a well-known composite modeling theory. It is shown that E_T is a function of the polymeric lamellar morphology and crystallinity. It is higher than the Young's modulus E_S of the bulk spherulites and positively affects the stiffness of the materials in which the transcrystallinities are formed. The study was focused on poly(ether ether ketone) (PEEK) but with polyethylene (PE) as a comparison. Also, it is demonstrated the various possibilities of the value E_T and the ratio E_T/E_S for different polymeric matrices depending on their lamellar moduli and the amorphous-phase ones. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The fiber–matrix interface or interphase plays a vital role in influencing the properties of fiber-reinforced composites. Strong interfacial adhesion can improve the stress transfer from the matrix to the fibers, whereas the presence of interphases or interlayers between the fibers with the matrix usually indicate composite toughness.[1-4] It is therefore very important to control the interfacial or interphasial structure in order to obtain final materials with optimum performance.

In composites based on a semicrystalline–thermoplastic polymer as the matrix, the representative interphase is characterized by the transcrystalline interlayers around the fibers. These crystalline interphases arise from the polymeric nucleation on the fibers and the following crystal growth. Their formation is related to the surfacial nature of the fibers and the processing condition. Crystalline fibers, such as aramic fiber and carbon fiber, were reported to be good nucleating substrates, whereas amorphous fibers, like glass fiber, to be the poor

ones.[5-8] The nucleating ability of crystalline fibers also depends on the crystalline morphology of the fibers. High-modulus carbon fiber with much larger graphite planes oriented along the fiber axis was believed to be better than the high-strength one with smaller graphite planes.[5-9] The conditions that may affect the formation of transcrystallinity are related to the melting and crystallization during the processing. High melting temperature, longer melting time, and higher crystallization temperature or slower cooling rate from the melt are all in favor of transcrystalline formation.[6,8,10,11]

As crystals that grow from the nucleating sites on fiber surfaces, transcrystallinities have a strong adhesion with the fibers. Early reports showed that a polymeric layer was left on the fiber surfaces after a composite was fractured, in the presence of transcrystallinities,[12,13] whereas a recent study showed that transcrystallinities can improve the interfacial bond strength.[14] One contribution of such strong fiber–matrix adhesion is its positive effect on the transverse tensile strength of an unidirectional composite.[10,15] Also, transcrystallinities were reported to possibly improve the composite tensile toughness and dynamic modulus.[16,17] However, the micromechanics of transcrystallinities is still unknown. Since the thickness of transcrystallinities might be large enough,[11] the properties of such an
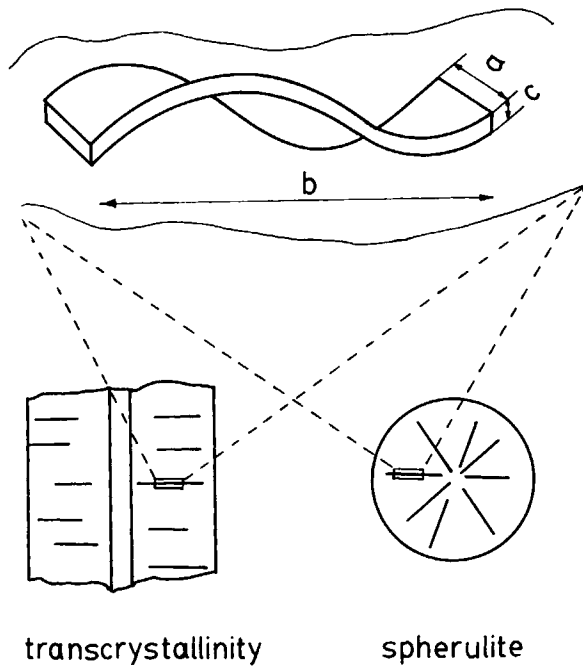

Figure 1 The lamellar organization models for transcrystallinity and spherulite.

interlayer and their role in the composite need to be investigated.

In this work, an attempt was made to predict the Young's modulus of transcrystallinities and its microstructure dependence, on the basis of the research on the spherulitic and transcrystalline structure of poly(ether ether ketone) (PEEK). The obtained results were analyzed by measuring the moduli of PEEK and the unidirectional composites of PEEK reinforced with carbon fiber. Also, a comparison between different polymeric systems was made.

MECHANICAL MODELS OF TRANSCRYSTALLINITY AND SPHERULITE

Crystallized semicrystalline polymer is, in fact, a composite consisting of lamellae and an amorphous phase, in which the mechanical properties of the lamellae are different from those of the amorphous phase.[18,19] To predict its mechanical responses, various methods were used. An empirical two-phase model based on a combined series–parallel spring
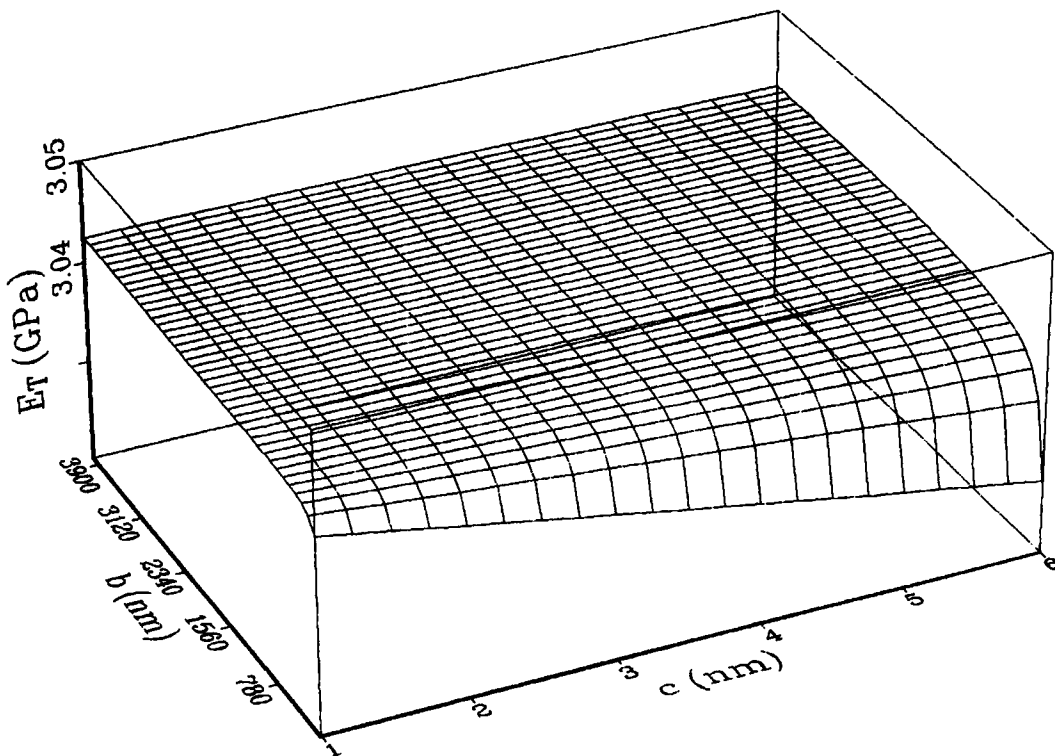

Figure 2 Transcrystalline Young's modulus of PEEK as the functions of b and c: $\alpha = 25$ vol %; $a = 15$ nm.
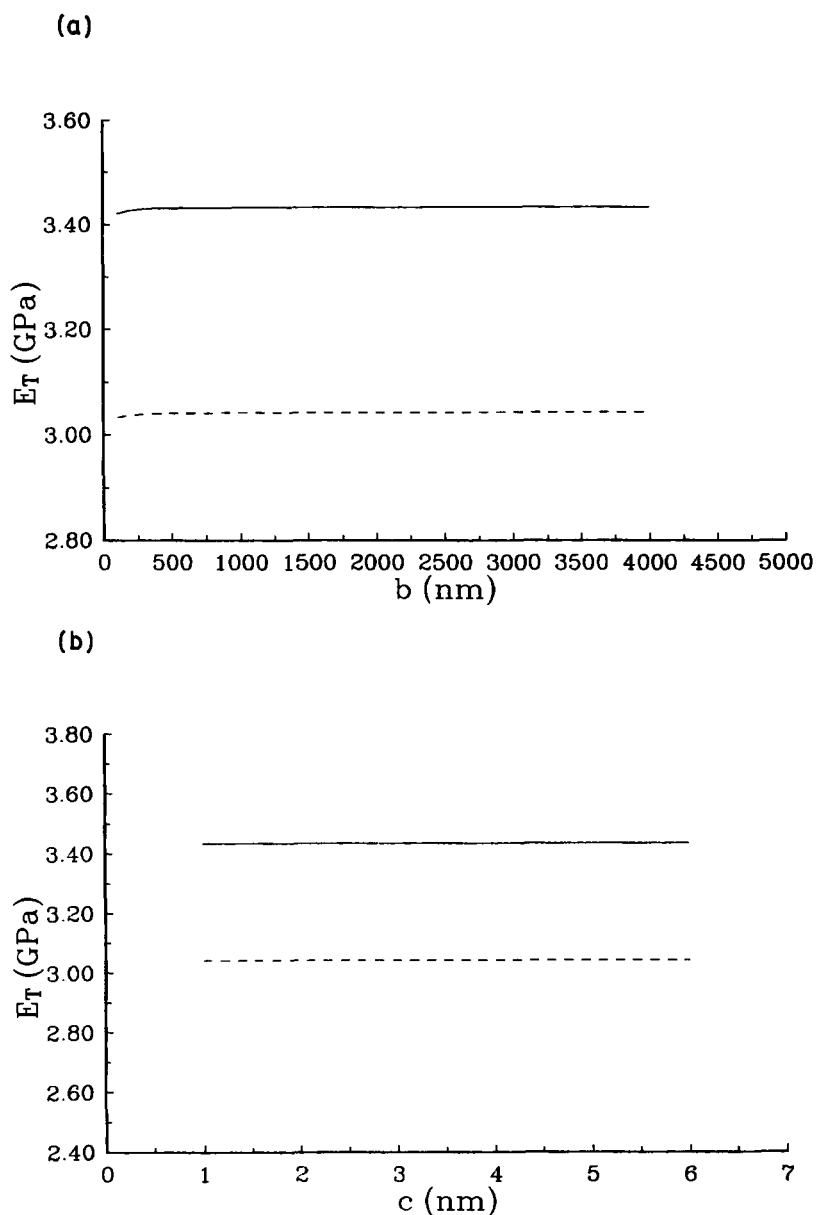
(a)

(b)

Figure 3   The effects of crystallinity on PEEK transcrystalline Young' modulus: (a) E_T
$\sim b$; (b) $E_T \sim c$. Crystallinity is (————), 40 vol % and (-----) 25 vol %.

model was suggested by Takayanagi,[20] and an analysis using micromechanics from the composite modeling theory was attempted by Kardos and Raison.[21] Unfortunately, in such approaches, all crystals were assumed to be oriented in one direction, and the results were not very satisfactory. By considering the lamellar organization in the polymer, these can be improved.[22] Since a calculationally simple format can be provided rapidly from the predicative methods developed for two-component composites based on the composite analogy,[21] this idea is used in the

work but with consideration of the lamellar organization.

Studies on the transcrystalline structure of PEEK on carbon fibers have shown that the lamellae in the transcrystallinities are oriented in the direction normal to the fibers.[23] But those in PEEK spherulites are radially arranged.[24] Since these lamellae are twisted,[23,25] their organization in transcrystallinities and spherulites in the case of two-dimensional growth can be illustrated (see Fig. 1). The two-dimensional transcrystalline or spherulitic plies can
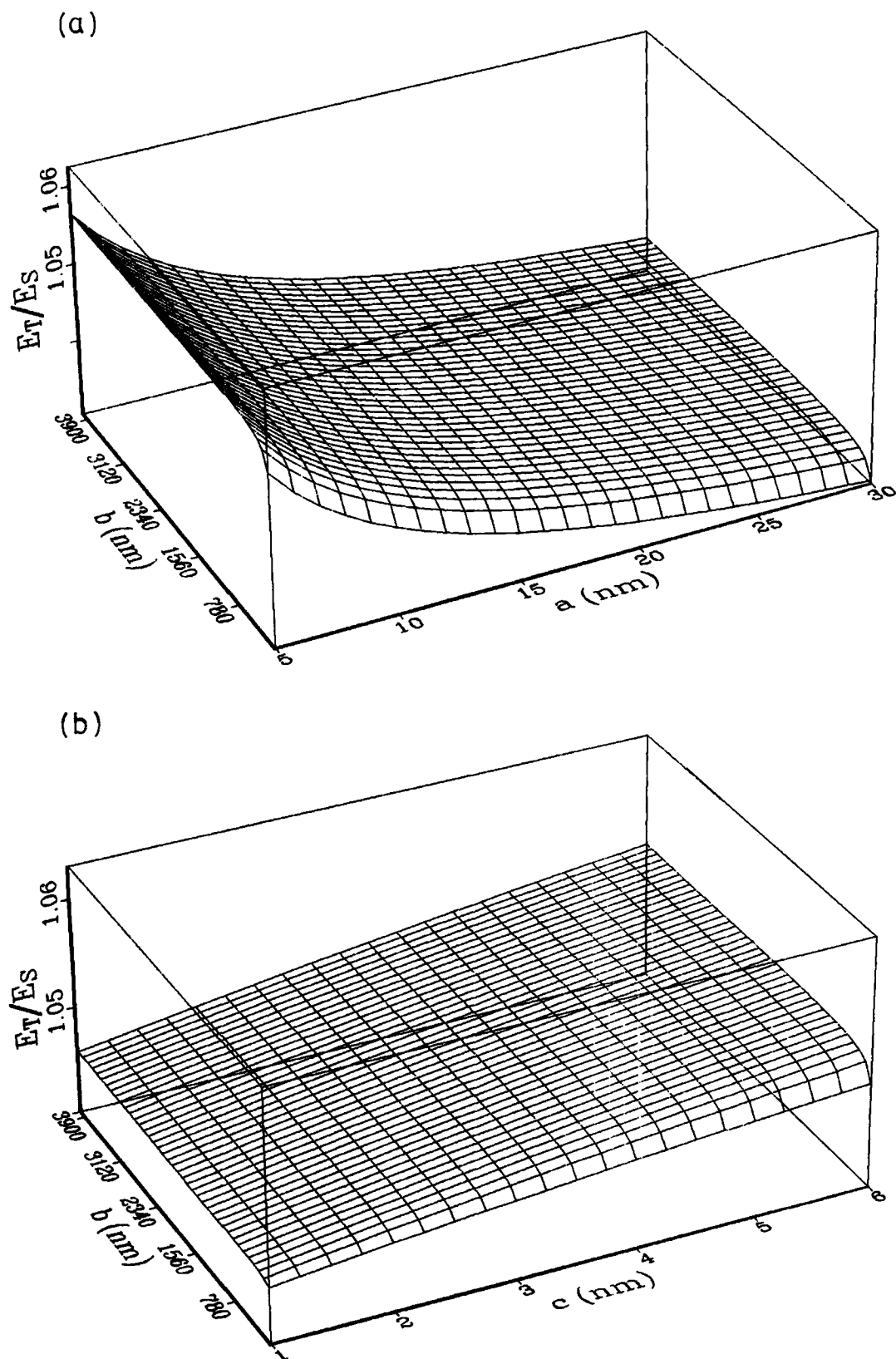
(a)

(b)

Figure 4 E_T/E_S of PEEK as the functions of a, b, and c: α = 25 vol %; (a) $E_T/E_S \sim a$, b (c = 4 nm); (b) $E_T/E_S \sim b$, c (a = 15 nm); (c) $E_T/E_S \sim a$, c (b = 2100 nm).
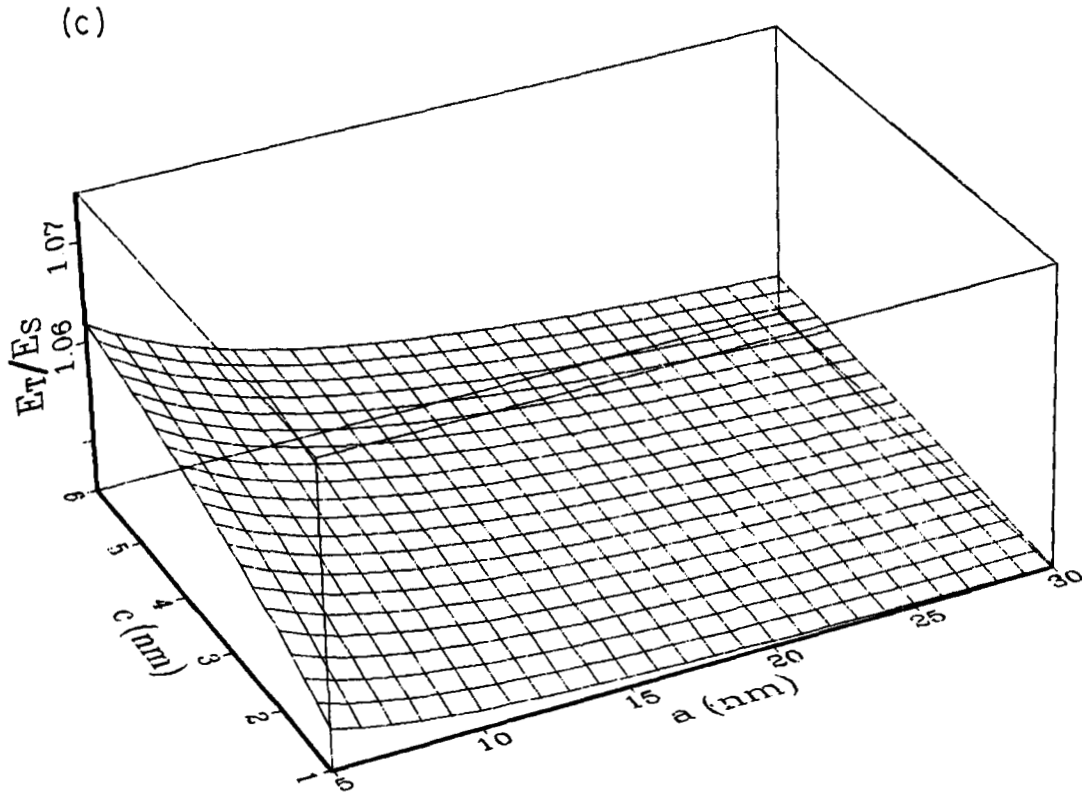
(c)

Figure 4   (*Continued from the previous page*)

be considered to stack up to form one-directional laminate and an isotropic one, respectively, according to the lamellar organization in them. If the lamellae are treated as short fibers and the amorphous phase as a matrix in composite laminates, an analogy can be drawn between the polymeric laminates with the composite laminates.[21] The unidirectionally composite laminate with oriented fibers is similar to the transcrystalline laminate, whereas that with a randomly oriented fiber is similar to the spherulitic one. Based on the analogy, the elastic modulus of transcrystallinity and the spherulite can be predicted by the composite modeling theory.

It is known that the mechanical response of an unidirectionally oriented short-fiber composite laminate is given as[26]

$$M_c/M_m = (1 + \xi\eta V_f)/(1 - \eta V_f) \qquad (1)$$

and

$$\eta = (M_f/M_m - 1)/(M_f/M_m + \xi) \qquad (1.1)$$

$$\xi = 2l/d \qquad (1.2)$$

where M is the elastic modulus, and V, the volume fraction, subscripts c, m, and f refer to composite, matrix, and fibers, respectively, whereas l and d represent the fiber length and fiber diameter, respectively. From the above analysis, the transcrystalline Young's modulus in the direction perpendicular to the fiber can be expressed as $E_T = M_c$; the modulus of the amorphous phase in the transcrystallinity, as $E_u = M_m$; the modulus of individual lamella in its length direction (**b** axis), as $E_b = M_f$; crystallinity, as $\alpha = V_f$; and $\xi = 2 \, b/c$ with b, as the lamellar length and c as its thickness. The modulus E_T can thus be calculated with eq. (1), when E_u, E_b, α, b, and c are given.

For a randomly oriented short-fiber composite laminate, its isotropic Young's modulus is[26]

$$M_R = 3/8 \, M_{\parallel} + 5/8 \, M_{\perp} \qquad (2)$$

where $M_{\parallel}$ represents the fiber-axial Young's modulus of an unidirectionally oriented short-fiber laminate, whereas $M_{\perp}$ is its transverse one. The isotropic spherulitic Young's modulus can be expressed as $E_S = M_R$, where $M_{\parallel}$ is equal to E_T mentioned above, and $M_{\perp}$ can be obtained with eq. (2) with $E_a = M_f$, $E_u = M_m$, $\alpha = V_f$, and $\xi = 2a/c$ (a as lamellar width).
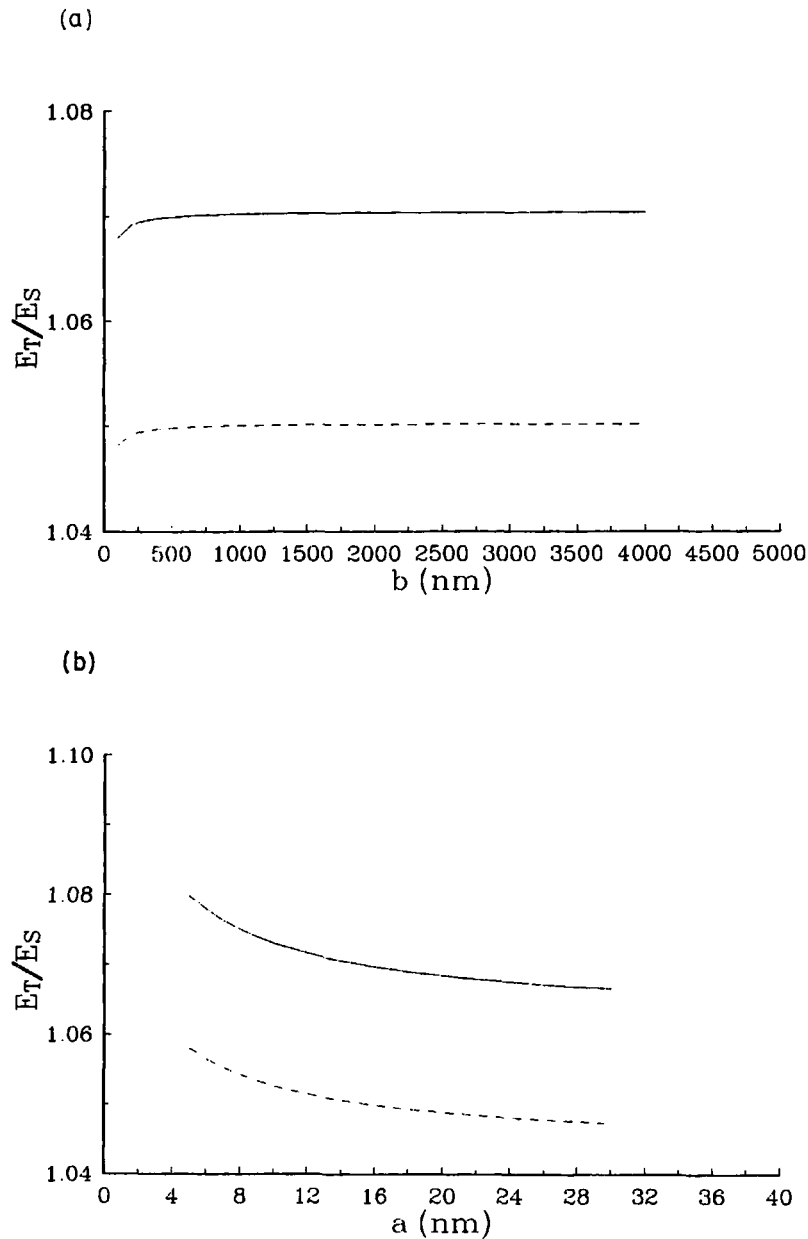
(a)

(b)

Figure 5 The effect of crystallinity on the E_T/E_S of PEEK: (a) $E_T/E_S \sim b$ (a = 15 nm, c = 4 nm); (b) $E_T/E_S \sim a$ (b = 2100 nm, c = 4 nm); (c) $E_T/E_S \sim c$ (a = 15 nm, b = 2100 nm). Crystallinity is (————) 40 vol %; (- - - - -) 25 vol %.

Whenever E_u, E_a, E_b, α, a, b, and c are obtained, E_S can be calculated. Because the lamellar organization in spherulite has been considered here, the obtained formulas for predicating E_S should be more accurate than that[21] used previously.

THEORETICAL PREDICATION OF TRANSCRYSTALLINE YOUNG'S MODULUS

To calculate the transcrystalline Young's modulus of a semicrystalline polymeric matrix and compare

it with a spherulitic one, the lamellar and amorphous moduli and the lamellar morphology of the polymer should be provided. The early detailed studies on poly(ether ether ketone) (PEEK) have made the predication possible. Also, because of the increased attraction on fiber/PEEK composites, this polymer is chosen in the attempt. The Young's modulus of amorphous PEEK E_u was reported to be 2.39 GPa,[27] and those of PEEK lamellae, 5.00 GPa (E_b), in the lamellar length direction (**b** axis) and 4.20 GPa (E_a) in the width direction (**a** axis).[28] By summarizing
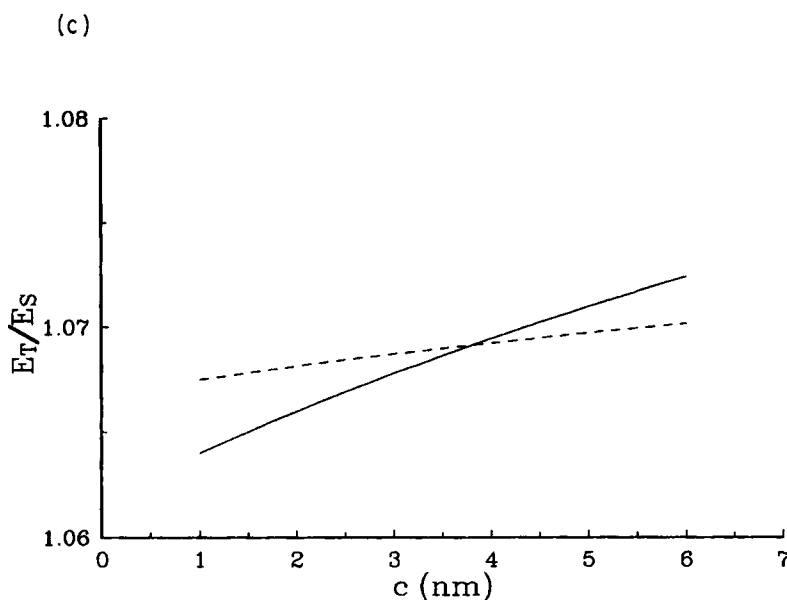
(c)

Figure 5   *(Continued from the previous page)*

the lamellar-morphological studies on PEEK[24,29,30] and extending the value ranges, a range of 1–6 nm is given to the lamellar thickness of PEEK c; 5–30 nm, to the width a; 100–4100 nm, to the length b; and 25–40 vol %, to the crystallinity α. The transcrystalline modulus can then be calculated using eqs. (1), (1-1), and (1-2).

In Figure 2, the Young's modulus E_T of PEEK transcrystallinities in their growth direction, as a function of lamellar length b and thickness c when $\alpha = 25\%$, is illustrated. It is seen that E_T increases with increasing b, but decreases with c. The crystallinity dependence of E_T is shown in Figure 3. A higher value of E_T is obtained at higher crystallinity.

Since PEEK spherulites will form in the matrix bulk when PEEK is nucleated on fibers and forms transcrystallinities between the fibers with the bulk,[8,11] it is very important to compare the moduli of the transcrystallinities with those of the spherulites in the same composites. Fortunately, previous studies have shown that the growth characteristics of transcrystallinities is identical to that of its nearby spherulites[11,31] and the lamellar morphology in the transcrystallinities is the same as that in the spherulites.[5] It is thus reasonable to make the modulus comparison between transcrystallinities with spherulites, with the same a, b, c, and α. From eq. (2) with $E_S = M_R$ and $M_{\parallel} = E_T$, the ratio of the transcrystalline modulus in the direction perpendicular to fiber or in the transcrystalline growth direction (E_T) to the isotropic spherulitic modulus (E_S) is expressed as

$$E_T/E_S = 1/(3/8 + 5/8\ M_{\perp}/E_T) \qquad (3)$$

where E_T and $M_{\perp}$ can be calculated in the way described above.

Figure 4 shows the ratio E_T/E_S as a function of a, b, and c, where $c = 4$ nm is assumed in Figure 4(a); $a = 15$ nm, in Figure 4(b); and $b = 2100$ nm, in Figure 4(c). It is seen that E_T/E_S is larger than 1 independent of a, b, and c. The reason is that the lamellar Young's modulus of PEEK in the direction of the b axis is higher than that in the direction of the a axis. Besides, it is known that the ratio E_T/E_S tends to increase with increasing b or c, but to decrease with increasing a. Also, the relationship between E_T/E_S with one of value a, b, or c is dependent on the others. For example, the variation

Table I   The Processing and Properties of Unidirectional CF/PEEK Composites

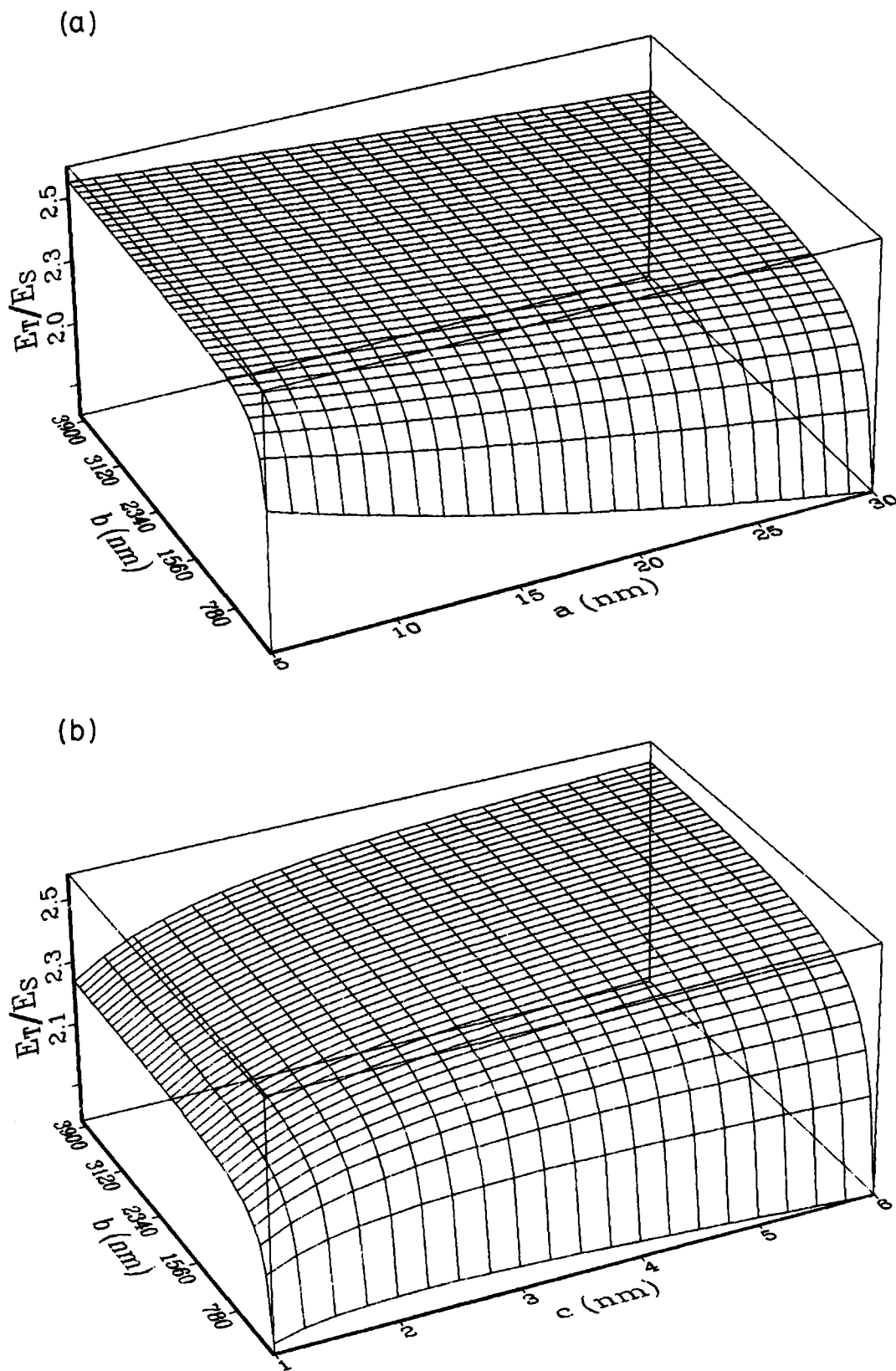|	Composite A	Composite B
Processing	Held at 310°C for 1 h after melted at 420°C[a]	Naturally cooled after melted at 420°C[a]
Postannealing	250°C, 12 h	250°C, 12 h
V_f (vol %)	58	58
$E_{\perp}$ (GPa)	7.44	6.94

[a] The pressure is 70 GPa.

(a)

(b)

Figure 6 E_T/E_S of PEEK as the functions of a, b, and c: $\alpha = 25$ vol %; (a) $E_T/E_S \sim a, b$ ($c = 4$ nm); (b) $E_T/E_S \sim b, c$ ($a = 15$ nm); (c) $E_T/E_S \sim a, c$ ($b = 2100$ nm).
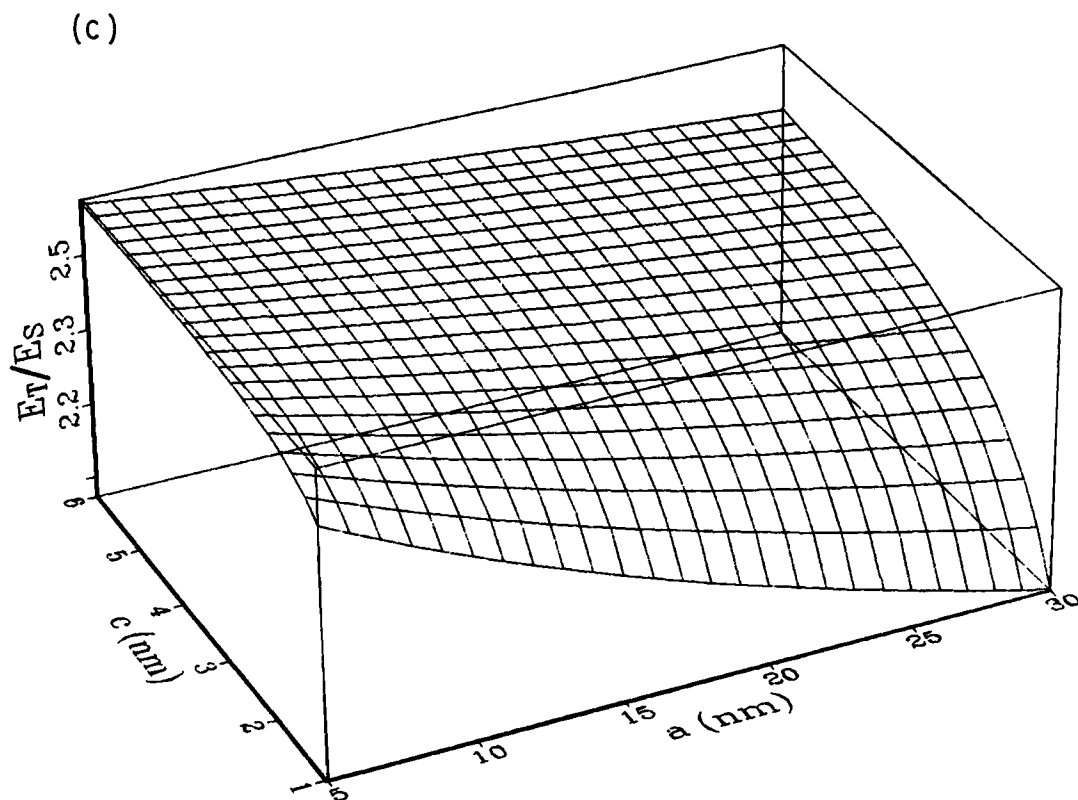
Figure 6   (*Continued from the previous page*)

of E_T/E_S with b is greater when a or c is higher, as found in Figure 4(a) and (b). Also, E_T/E_S is affected by the crystallinity α, as shown in Figure 5. Due to the depression of E_S with increasing c, E_T/E_S increases with a rise in c differing from the variation of E_T [refer to Figs. 3(b) and 4(c)].

DISCUSSION

To analyze the theoretically predicated results, two kinds of unidirectional composites of PEEK reinforced by carbon fiber were prepared. The processing condition and the volume fraction of carbon fibers in the composites are shown in Table I. The processing condition for composite A is believed to favor the transcrystalline formation, whereas that for composite B, to result in spherulites only.[8] Their transverse Young's moduli measured by the ultrasonic immersion technique[32] are illustrated in Table I. It is seen that the value of composite A is higher. By using this result, the interphasial contribution to the composites stiffness can be discussed as the following:

It is considered that the transverse Young's modulus of unidirectionally fiber-reinforced material can be written as

$$1/E_{\perp,B} = V_m/E_m + V_f/E_f$$
$$= (V_m - V_i)/E_m + V_i/E_i + V_f/E_f \quad (4)$$

and

$$1/E_{\perp,A} = (V_m - V_i)/E_m + V_i/E_i + V_f/E_f \quad (5)$$

where E is the Young's modulus, and V, the volume fraction. The subscripts f, m, and i indicate the fiber, the matrix bulk phase, and the interphase, respectively. In this system, eq. (5) is suitable for composite A due to the formation of interphasial PEEK transcrystallinities on fibers, and eq. (4), for composite B because only PEEK spherulites are formed in the matrix. Also, the Young's moduli of transcrystallinities are distinctive from the bulk PEEK spherulites (matrix bulk phase) in the same composites according to the above analysis. Comparison of eq. (4) and eq. (5) can easily conform the above predicted result of $E_T/E_S > 1$.

The Young's modulus difference between PEEK transcrystallinities and spherulites arises from their distinct lamellar organization. This will result in an increased transverse stiffness in an unidirectional composite when transcrystallinities form, as implied by the above analysis. Meanwhile, it is emphasized that the values of E_T and E_T/E_S and their dependence on a, b, and c are dominated mainly by the values E_b/E_u and E_a/E_u. As illustrated in Figure 6, E_T/E_S is higher, exceeding 1.60, than the identical value of α and similar ranges of a, b, and c as those in Figure 5 when polyethylene (PE) with E_b = 4.00, E_a = 3.20, and E_u = 0.01 GPa[21] is chosen. By varying E_b/E_u and E_a/E_u in a wide range and calculating the moduli and the ratio, E_T and E_T/E_S were concluded to increase, and the effects of values a, b, and c on E_T/E_S become stronger with increasing E_b/E_u and E_a/E_u. Since the lamellar moduli and the amorphous-phase modulus of one polymer differ from those of others, various transcrystalline Young's moduli and their contribution to composite stiffness are expected for different systems. Obviously, a good stress-transfer and stiffness-improvement effect might be obtained for the system with higher values of E_b/E_u and E_a/E_u.

As noticed, a higher ratio E_T/E_S is obtained when the values of b, a, and crystallinity α are increased. Although the lamellar length b does not represent spherulitic radius R in a spherulite due to its branching growth, larger b is probably associated with larger R.[24,31] Also, b was treated as R in previous work.[21] Therefore, transcrystalline thickness, whose average value is identical to the radius of the bulk spherulites,[11] is thought to affect the moduli in a similar way to b. It means that transcrystallinities might have an increased positive influence on the composite stiffness with their increasing thickness. Because a high value of transcrystalline thickness can be obtained when the composite experiences a high melting temperature or a high crystallization temperature,[11] and high crystallization temperature and prolonged crystallization time or a slow cooling rate from the polymeric melt will lead to high values of lamellar thickness c and crystallinity α, as is well known, these processing conditions should be recommended if an optimum composite stiffness is needed.

CONCLUSION

Transcrystallinities are the interphase formed in the fiber-reinforced composites with semicrystalline polymer as the matrix. They are structurally differ-

ent from the bulk spherulites formed in the same composite and positively affect the adhesion between the fibers with the matrix. In this article, an attempt was made with the composite modeling theory to predicate the transcrystalline Young's modulus E_T of poly(ether ether ketone) (PEEK) on the basis of the analogy between the polymer matrix and short-fiber reinforced composites. E_T was shown to depend on the lamellar morphology and crystallinity, and, also, the ratio of E_T, to the bulk spherulitic Young's modulus E_S (E_T/E_S). The theoretical predication of $E_T/E_S > 1$ was confirmed by experiment and indicates the positive contribution of the transcrystallinities to the composites' stiffness. By comparing the predicated results of PEEK with those of polyethylene (PE), it was demonstrated that E_T and E_T/E_S depend on the difference between lamellar moduli with the amorphous-phase ones.

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