AIAA JOURNAL
Vol. 32, No. 5, May 1994

Development of Free-Edge Effect During Processing of Semicrystalline Thermoplastic Composites

Moshe M. Domb* and Jorn S. Hansen†
University of Toronto, Downsview, Ontario M3H 5T6, Canada

The residual thermal stresses developed during processing of fiber-reinforced semicrystalline thermoplastic composites are strongly affected by variations in temperature and degree of crystallinity within a laminate. A model which enables the prediction of the temperature and volume fraction crystallinity distributions over the cross-sectional area of these laminates during processing from the melt is presented. In this study, emphasis is on the prediction of temperature and crystallinity gradients in the vicinity of free edges. Results are shown for the case of unidirectional APC-2 laminates for different surface cooling rates.

Introduction

FIBER-REINFORCED composite materials have gained widespread applicability in high-performance aerospace structures as a result of their superior specific strength and stiffness. This superiority, however, does not come without tradeoffs, which are mainly associated with the matrix and matrix/fiber interfaces. Among fiber-reinforced composites, thermoplastic-based composites possess many advantages over thermoset composites, including among others, impact resistance, improved fatigue life, increased toughness, higher service temperatures, unlimited prepreg shelf life, and the ability to be remelted and reprocessed.

One characteristic of fiber-reinforced composite laminates is their tendency to delaminate under service loading, with failure typically initiating in the vicinity of traction-free edges.[1-5] Delamination is associated with high interlaminar stresses due to property and geometric discontinuities through the thickness at the free edge. This failure mode can be partially controlled by the selection of tougher matrices, by the stacking sequence, and by fiber orientation.[6] Thermoplastic-based composites have given an order of magnitude increase in interlaminar toughness compared to existing epoxy resin composites,[7] increasing their resistance to the initiation of delamination and free-edge failures. However, substantial residual thermal stresses may be developed in thermoplastic composites due to the elevated processing temperatures and the high matrix/fiber thermal expansion mismatch. These thermally induced residual stresses may represent a significant fraction of the failure stress of the material, possibly leading to premature failure in the form of delamination and transverse cracking.[8,9]

Within the class of thermoplastic composites, it is important to distinguish between amorphous and semicrystalline matrices. The high-stiffness crystalline phase in semicrystalline resins contributes to enhanced mechanical properties when compared to those of the amorphous phase. The buildup of residual stresses during processing for amorphous resins begins only below the glass transition temperature, whereas for semicrystalline matrices it begins during the crystallization process.[10] In semicrystalline thermoplastics, crystallization causes a large volumetric shrinkage in addition to the usual thermal contraction[11] and causes the buildup of additional residual stresses. As the composite's mechanical properties are dependent on the matrix constituents and the reinforcing phase,[12,13] the development of thermal stresses is directly affected by the variations in temperature and degree of crystallinity occuring during processing.[9] As a result, the study of residual thermal stresses in semicrystalline thermoplastic composites is directly related to the determination of the temperature, temperature rates, and crystallization kinetic profiles as function of time in the laminate, and especially in the vicinity of traction-free edges.

Several studies have been performed to determine the temperature distribution and crystallization kinetics during the processing of thermoplastic-based composites. The majority of these studies model the thermal process using a one-dimensional heat conduction energy equation through the thickness of the composite,[9,14] and include a prediction of the degree of crystallinity profile using a crystallization kinetics model coupled to the heat transfer analysis. The aforementioned models emphasize the skin/core (through-the-thickness) distributions, without being able to address the free-edge effect developing during processing. A two-dimensional model that can predict both temperature distribution and crystallization kinetics in thermoplastic composites is presented in Ref. 15. This model accommodates two-dimensional complex shapes in the plane of the laminate, but again, does not address the free-edge effect problem.

The model presented in this study is based on a thermal analysis over the cross-sectional area of a composite laminate coupled to a crystallization kinetics analysis. The model enables the prediction of the time-dependent temperature and crystallinity profiles during the nonisothermal processing from the melt. To elucidate the development of the free-edge effect, results are shown for the case of unidirectional APC-2 [graphite/polyetheretherketone (PEEK)] laminates. These results emphasize the importance of predicting free-edge gradients developing during processing of fiber-reinforced semicrystalline thermoplastic composites.

Model Description

Thermal Analysis

The composite laminate considered for the thermal analysis is a long (infinite) composite strip with finite width and finite thickness. Consequently, the domain modeled is the cross-sectional area of the laminate (Fig. 1), where the heat transfer due to conduction and the release of heat caused by the nucleation and growth of crystals are taken into consideration. The analysis requires the simultaneous modeling of temperature and crystallization histories, while the purpose is to determine the complete temperature and crystallinity profiles as a function of position and time.

Presented as Paper 93-1348 at the AIAA/ASME/ASCE/AHS/ASC 34th Structures, Structural Dynamics, and Materials Conference, La Jolla, CA, April 19-21, 1993; received May 7, 1993; revision received Nov. 8, 1993; accepted for publication Nov. 16, 1993.

*Research Assistant, Institute for Aerospace Studies. Student Member AIAA.

†Professor, Institute for Aerospace Studies.

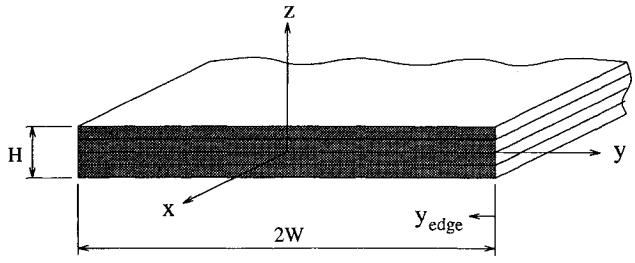

Fig. 1 Two-dimensional space domain of the problem.

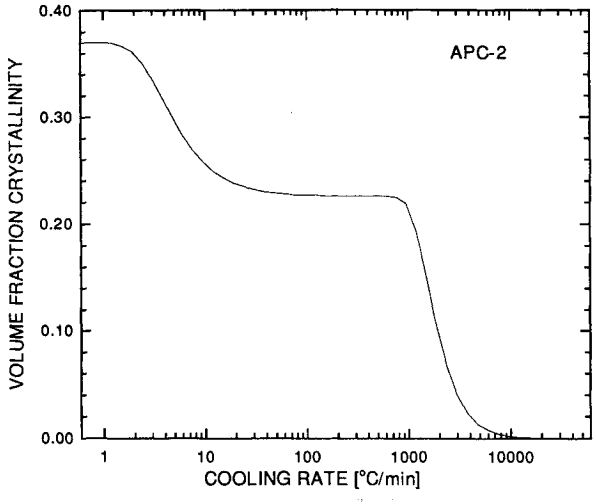

Fig. 2 Volume fraction crystallinity vs cooling rate for APC-2 (model of Velisaris and Seferis[17]).

The thermal analysis is governed by the following two-dimensional heat conduction equation, subjected to the appropriate boundary and initial conditions:

$$\frac{\partial}{\partial t}[\rho(T)C(T)T] = \nabla \cdot \{K(T)\nabla T\} + U(\dot{X}_{vc}(T)) \qquad (1)$$

where t, ρ, T, C, K, U, and X_{vc} are the time, density, temperature, specific heat, conductivity matrix, heat release rate per unit volume due to crystallization, and volume fraction crystallinity, respectively. The overdot on X_{vc} implies a derivative with respect to time. The coupling between the temperature and crystallinity via the term U was found to be relatively weak.[14,15] Therefore, the temperature distribution can be explicitly calculated from the heat conduction equation.

Solution of the heat conduction equation is based on a discretization of the space domain using the finite element method, whereas the time domain is discretized using a time-marching procedure (recurrence relation) based on a finite difference scheme. The time-marching procedure chosen is the unconditionally stable implicit algorithm of Crank-Nicolson.[16]

Crystallization Kinetics Analysis

Crystallization kinetics is modeled because it influences the development of residual stresses and the free-edge effect through the mechanical properties of the material. Calculation of the time-dependent crystallinity profile is based on the crystallization kinetics model of Velisaris and Seferis.[17] The model is based on a linear combination of two crystal nucleation and growth processes (dual mechanism) observed experimentally and occurring in parallel. This model has showed good agreement with measurements of crystallinities for both neat and carbon-fiber reinforced PEEK samples for a wide range of cooling rates from the melt.

The expression for the aforementioned crystallization kinetics model is given by

$$\frac{X_{vc}}{X_{vc}^{\infty}} = w_1 F_{vc1} + w_2 F_{vc2} \qquad (2)$$

where

$$F_{vci} = \left\{1 - \exp\left[-C1_i \int_0^t T \exp\left\{-\left[\frac{C2_i}{T - T_g + 51.6} + \frac{C3_i}{T(T_{mi} - T)^2}\right]\right\} n_i t^{n_i - 1}\, dt\right]\right\} \quad ; \quad i = 1, 2 \qquad (3)$$

Here X_{vc}^{∞} is the equilibrium volume fraction crystallinity; w_i are weighting factors; $C1_i$, $C2_i$, and $C3_i$ are model constants (material-dependent); T_g is the glass transition temperature; T_{mi} are crystal melt temperatures for the dual mechanism; and n_i are Avrami exponents for the dual mechanism. The values used in the present study are reported in Ref. 17.

The crystallization kinetics in semicrystalline thermoplastics has been shown to be directly related to the cooling rates experienced within the material.[17,18] As the laminate undergoes large gradients in cooling rates in the vicinity of free edges, variations in degree of crystallinity are expected within this region. Figure 2 presents the dependence of the volume fraction crystallinity on the cooling rate applied from the melt for APC-2 based on the model of Velisaris and Seferis.

Mechanical Properties Determination

The lamina's mechanical properties required for the stress analysis are strongly dependent on the individual constituent properties, that is, on the reinforcing fibers, the matrix crystalline phase, and the matrix amorphous phase. Ply properties in both longitudinal and transverse directions are calculated using micromechanics models, and take into consideration the contribution of the different constituents.

The mechanical properties of the carbon fibers and the crystalline phase of the PEEK matrix are assumed to exhibit no temperature dependence. The amorphous phase in the PEEK matrix, however, does exhibit a strong dependence on temperature, as illustrated in Fig. 3 for the elastic modulus.[9] Consequently, the determination of the time-dependent temperature and crystallinity profiles in the laminate, as calculated from the preceding sections, directly influence the development of residual thermal stresses and the free-edge effect through the mechanical properties of the material in both longitudinal and transverse directions.

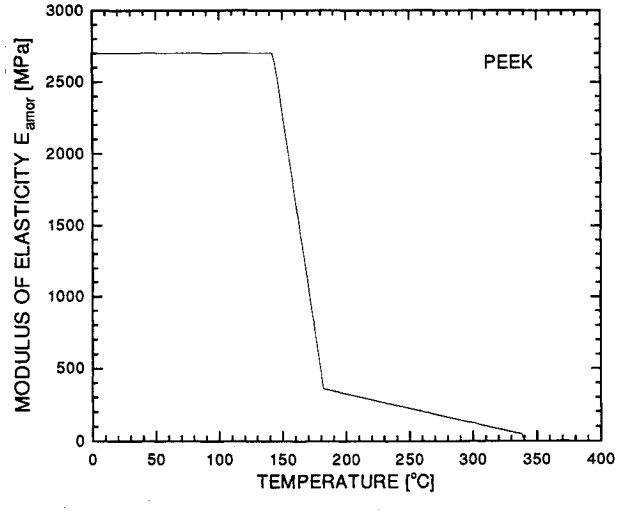

Fig. 3 Elastic modulus of PEEK amorphous phase vs temperature (calculated[9]).

Model Flow Chart

A simple flow chart illustrating the interaction between the various sections in the model is presented in Fig. 4.

Results

To elucidate the development of the free-edge effect during processing from the melt of semicrystalline thermoplastic composites, some results describing the transient temperature and crystallinity profiles are presented for the case of unidirectional 16-ply APC-2 (graphite/PEEK) laminates. The specimen under discussion is shown schematically in Fig. 5, where the laminate's half cross section and the designated distribution lines are depicted. Results are presented for three different regions: horizontal distribution (measured from the free edge), vertical distribution (measured from the midsurface in the through-the-thickness direction), and contour distribution (isoparametric representation in the half-cross-sectional area).

The temperature and crystallinity profiles in the different regions of the specimen are presented in Figs. 6–10 for a surface cooling rate of 2100°C/min. As expected, slower cooling rates are experienced at locations away from the surfaces

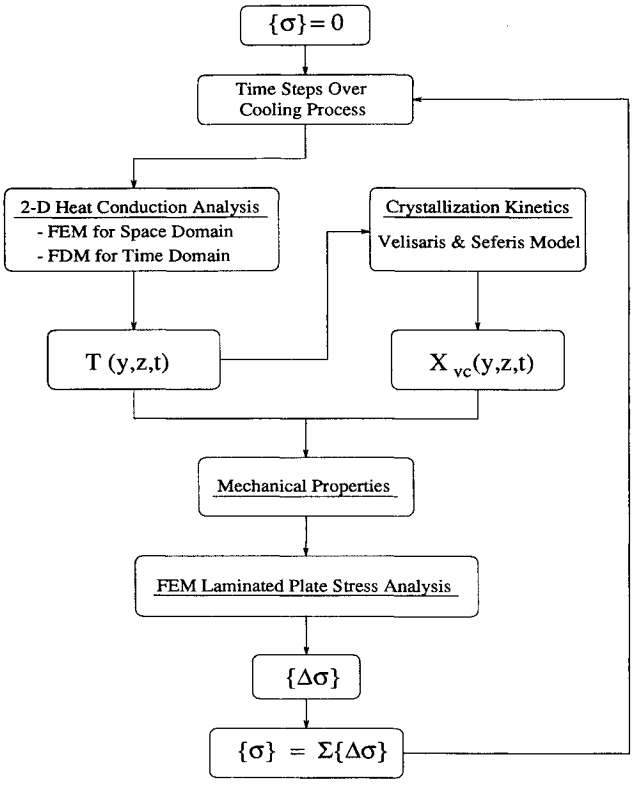

Fig. 4 Model flow chart.

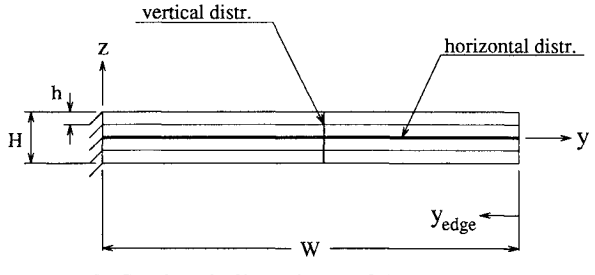

Fig. 5 Specimen's dimensions and distribution lines.

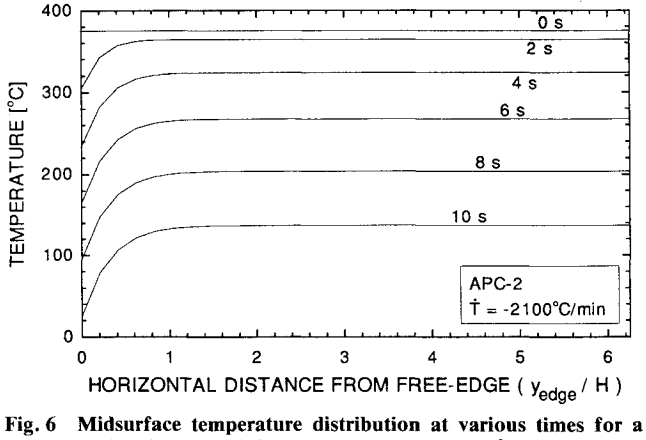

Fig. 6 Midsurface temperature distribution at various times for a 16-ply unidirectional APC-2 laminate cooled at 2100°C/min.

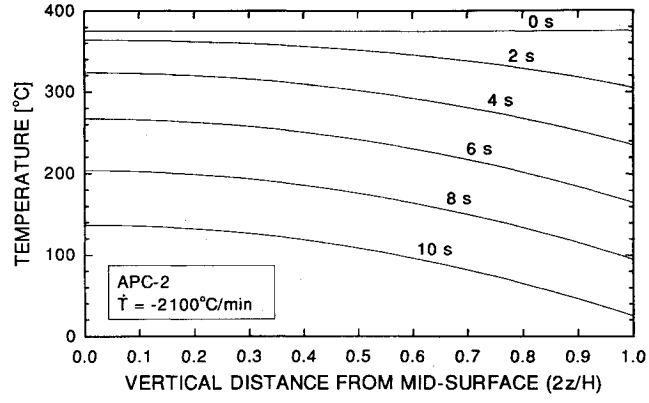

Fig. 7 Through-the-thickness temperature distribution at various times for a 16-ply unidirectional APC-2 laminate cooled at 2100°C/min.

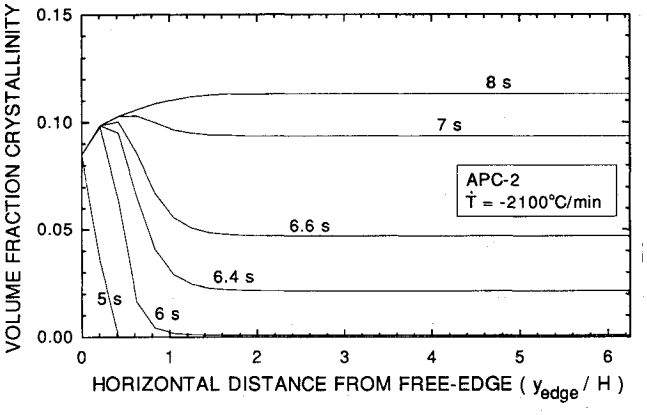

Fig. 8 Midsurface crystallinity distribution at various times for a 16-ply unidirectional APC-2 laminate cooled at 2100°C/min.

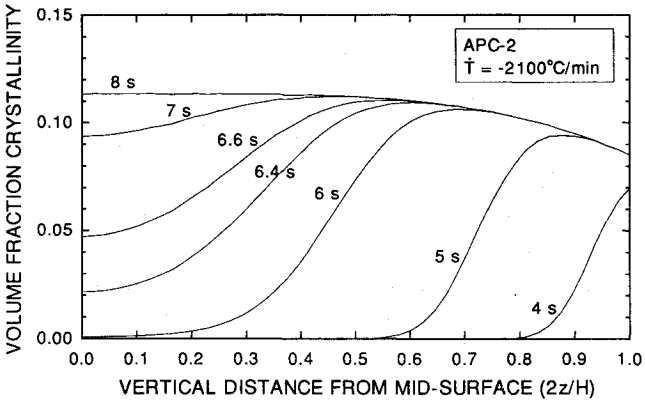

Fig. 9 Through-the-thickness crystallinity distribution at various times for a 16-ply unidirectional APC-2 laminate cooled at 2100°C/min.

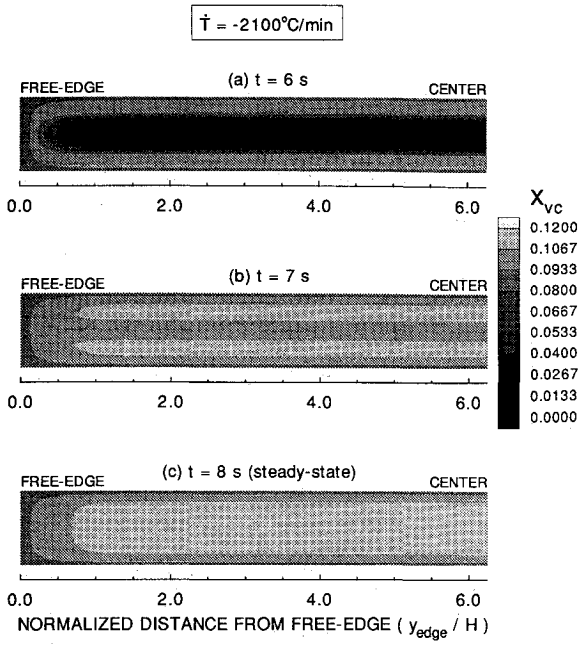

Fig. 10 Overall crystallinity distribution for a 16-ply unidirectional APC-2 laminate cooled at 2100°C/min at a) t = 6 s, b) t = 7 s, and c) t = 8 s.

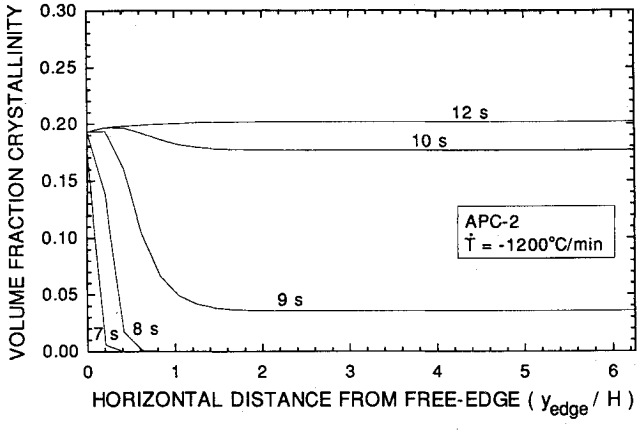

Fig. 11 Midsurface crystallinity distribution at various times for a 16-ply unidirectional APC-2 laminate cooled at 1200°C/min.

(Figs. 6 and 7). Significant gradients in degree of crystallinity are obtained during processing in both horizontal and through-the-thickness directions (Figs. 8 and 9, respectively) as a result of different cooling rates in the surfaces and in the core of the laminate. These substantial gradients are especially significant in the horizontal direction, where the influence of the free edge can be readily identified (Fig. 8). An overall picture of the volume fraction crystallinity distribution in the cross-sectional area of the laminate at various times is presented in Fig. 10. This figure elucidates the existence of the free-edge effect during different stages in the processing and qualitatively emphasizes its magnitude.

The free-edge effect is very localized and appears to vanish at a distance of approximately two times the thickness of the laminate measured inward from the free edge. The region where the free-edge effect takes place can also be seen in Figs. 11 and 12 for surface cooling rates of 1200°C/min and 600°C/min applied during processing. This important observation regarding the size of the free-edge zone is compatible with experimental measurements reported by Unger[19] and depicted in Fig. 13 for an APC-2 laminate. Unger developed a thermal

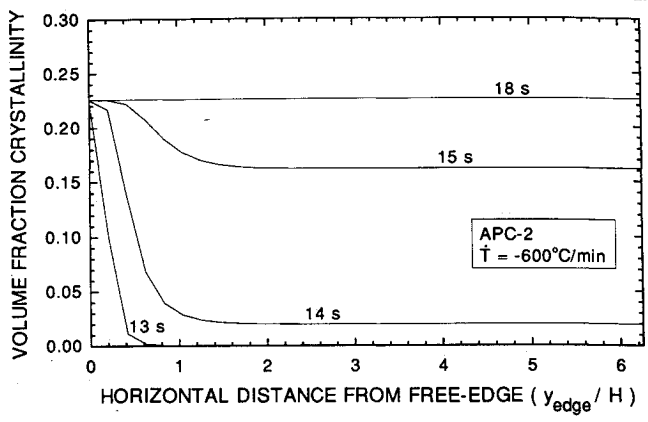

Fig. 12 Midsurface crystallinity distribution at various times for a 16-ply unidirectional APC-2 laminate cooled at 600°C/min.

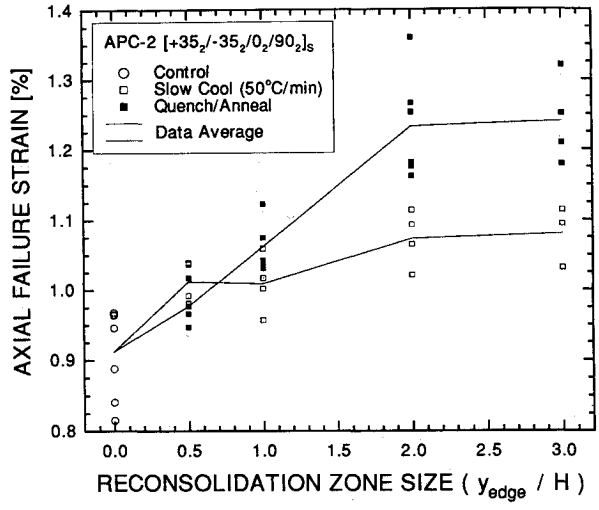

Fig. 13 Effect of reconsolidation zone size on failure strain for APC-2 (Unger[19]).

process for fiber-reinforced semicrystalline thermoplastic laminates which reduces the free-edge effect and improves static strength and fatigue life. In this process, referred to as localized reconsolidation, heat and pressure are applied to a laminate's free edge to locally melt the matrix, followed by cooling at a specified rate. A zone of reduced residual stresses was found to be formed, causing a significant improvement in the overall static and fatigue strength. Figure 13 shows the influence of the size of the melt zone on the axial failure strain of a $[+35_2/-35_2/0_2/90_2]_S$ APC-2 laminate. Unger's experimental results confirm the observation regarding the size of the free-edge effect region, as no additional improvement was achieved when the free edge was melted beyond a distance of two times the laminate's thickness.

Conclusions

A model which predicts the temperature and volume fraction crystallinity distributions in the cross-sectional area of a semicrystalline thermoplastic laminate during processing from the melt is presented. The model enables the prediction of free-edge gradients developing during processing.

Application of fast cooling rates may lead to significant temperature and crystallinity gradients in the vicinity of free edges. This effect is very localized, and it seems to vanish at a distance of two laminate thicknesses measured inward from the free edge. Moreover, existence of large free-edge gradients during the processing is evident for any surface cooling rate applied.

The residual stress state is strongly affected by the temperature and crystallinity gradients occurring during processing (and not only by the steady-state levels) through changes in mechanical properties. Therefore, the results emphasize the importance of the prediction of the free-edge effect developing during processing from the melt of fiber-reinforced thermoplastic composites in general, and semicrystalline thermoplastics in particular.

Acknowledgment

The authors would like to acknowledge the financial support provided by the Ontario Government through the Ontario Centre for Materials Research.

References

[1]Pipes, R. B., and Pagano, N. J., "Interlaminar Stresses in Composite Laminates Under Uniform Axial Extension," *Journal of Composite Materials,* Vol. 4, Oct. 1970, pp. 538–548.

[2]Pagano, N. J., "On the Calculation of Interlaminar Normal Stress in Composite Laminates," *Journal of Composite Materials,* Vol. 8, Jan. 1974, pp. 65–81.

[3]Wang, A. S. D., and Crossman, F. W., "Edge Effects on Thermally Induced Stresses in Composite Laminates," *Journal of Composite Materials,* Vol. 11, July 1977, pp. 300–312.

[4]Hsu, P. W., and Herakovich, C. T., "Edge Effects in Angle-Ply Composite Laminates," *Journal of Composite Materials,* Vol. 11, Oct. 1977, pp. 422–428.

[5]Daniel, I. M., "Behavior of Graphite-Epoxy Plates with Holes Under Biaxial Loading," *Experimental Mechanics,* Vol. 20, No. 1, 1980, pp. 1–8.

[6]Rybicki, E. F., and Schmueser, D. W., "Effect of Stacking Sequence and Lay-Up Angle on Free Edge Stresses Around a Hole in a Laminated Plate Under Tension," *Journal of Composite Materials,* Vol. 12, July 1978, pp. 300–313.

[7]Leach, D. C., Curtis, D. C., and Tamlin, D. R., "Delamination Behavior of Carbon-Fiber/PEEK Composites," *Toughened Composites,* edited by N. J. Johnston, ASTM STP 937, American Society for Testing and Materials, Philadelphia, PA, 1987, pp. 358–380.

[8]Jeronimidis, G., and Parkyn, A. T., "Residual Stresses in Carbon Fibre-Thermoplastic Matrix Laminates," *Journal of Composite Materials,* Vol. 22, No. 5, 1988, pp. 401–415.

[9]Chapman, T. J., Gillespie, J. W., Jr., Pipes, R. B., Manson, J.-A. E., and Seferis, J. C., "Prediction of Process-Induced Residual Stresses in Thermoplastic Composites," *Journal of Composite Materials,* Vol. 24, No. 6, 1990, pp. 616–643.

[10]Nairn, J. A., and Zoller, P., "Matrix Solidification and the Resulting Residual Thermal Stresses in Composites," *Journal of Materials Science,* Vol. 20, 1985, pp. 355–367.

[11]Schulte, K. J., and Hahn, H. T., "Prediction and Control of Processing-Induced Residual Stresses in Composites. Part II : AS4/PEEK Composites," Final Report for the Air Force Office of Scientific Research, AFOSR Grant 87-0242, Oct. 1989, pp. 1–76.

[12]Lee, W. I., Talbott, M. F., Springer, G. S., and Berglund, L. A., "Effects of Cooling Rate on the Crystallinity and Mechanical Properties of Thermoplastic Composites," *Journal of Reinforced Plastics and Composites,* Vol. 6, Jan. 1987, pp. 2–12.

[13]Talbott, M. F., Springer, G. S., and Berglund, L. A., "The Effects of Crystallinity on the Mechanical Properties of PEEK Polymer and Graphite Fiber Reinforced PEEK," *Journal of Composite Materials,* Vol. 21, No. 11, 1987, pp. 1056–1081.

[14]Velisaris, C. N., and Seferis, J. C., "Heat Transfer Effects on the Processing-Structure Relationships of Polyetheretherketone (PEEK) Based Composites," *Polymer Engineering and Science,* Vol. 28, No. 9, 1988, pp. 583–591.

[15]Saliba, T. E., Anderson, D. P., and Servais, R. A., "Process Modelling of Heat Transfer and Crystallization in Complex Shapes Thermoplastic Composites," *Journal of Thermoplastic Composite Materials,* Vol. 2, April 1989, pp. 91–104.

[16]Huebner, K. H., and Thornton, E. A., *The Finite Element Method for Engineers,* Wiley Interscience Publications, Wiley, New York, 1982, pp. 423–426.

[17]Velisaris, C. N., and Seferis, J. C., "Crystallization Kinetics of Polyetheretherketone (PEEK) Matrices," *Polymer Engineering and Science,* Vol. 26, No. 22, 1986, pp. 1574–1581.

[18]Blundell, D. J., and Willmouth, F. M., "Crystalline Morphology of the Matrix of PEEK-Carbon Fiber Aromatic Polymer Composites," *SAMPE Quarterly,* Vol. 17, No. 2, 1986, pp. 50–57.

[19]Unger, W. J., "Reduction of the Free-Edge Effect in Fibre-Reinforced Thermoplastic Laminates by Localized Reconsolidation," Ph.D. Thesis, Univ. of Toronto Inst. for Aerospace Studies, Toronto, Ontario, Canada, 1993.