Long-range effects of carbon fiber on crystallization of semicrystalline thermoplastics

T.Q. Li[a,b,c], M.Q. Zhang[b,*], K. Zhang[b], H.M. Zeng[b]

[a]Department of Materials Science and Engineering, Guangdong University of Technology, Guangzhou 510090, People's Republic of China
[b]Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China
[c]Laboratory of Polymeric Composite and Functional Materials, The Ministry of Education of China, Zhongshan University, Guangzhou 510275, People's Republic of China

Abstract

Non-isothermal crystallization of carbon fiber reinforced polyetheretherketone composites was studied with differential scanning calorimetry and Fourier transform infrared spectroscopy. Composite prepregs prepared by a solution pre-impregnation method with the matrix of different molecular weights were employed in the present work as the main model materials. Analyses of the different dependencies of non-isothermal crystallization on melt residual time in these systems revealed that carbon fibers had long-range effects on bulk crystallization of matrix polymer, which is rooted in the fact that the fibers tend to promote strain-induced nucleation in polymer. Comparison of the crystallization behavior of prepregs with that of the composite laminates indicated the importance of wetting and absorption to the effects of fiber on matrix crystallization, coinciding with the mechanism that short-range interaction formed the boundary to the flow under thermal stress. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Semicrystalline thermoplastics; Interfacial interaction; Composites

1. Introduction

The effect of fibers on crystallization of semicrystalline thermoplastics is a major concern in polymer science because of the technical importance of fiber reinforced composites [1–3]. Knowledge has long been established that the competition between nucleation on the fiber surface and that in the bulk polymer controls the crystallization morphology [4–7]. In some cases, factors that facilitate interfacial nucleation can even result in transcrystallinity [1,2,8–10]. Efforts have been made to reveal the role of crystallographic matching [10] and short-range interfacial bonding [11] in determining the nucleation competition.

As for the other aspect of crystallization in fiber composites, namely the growth behavior, little information about the effects of fiber is now available. Although it was proposed that the thermal stress arising from the mismatch in thermal expansion between the reinforcements and the resins may contribute to the organized crystalline morphology [6,10,12], it was not clear how the factors decide the nucleation and growth mechanisms. This leads to difficulties in predicting crystalline morphology in practical composites.

In fact, the intrinsic character of semicrystalline polymers lies in the linear structure of molecular chains. Theoretical works suggested conformation change of coils on a heterogeneous surface [13,14], however, to our knowledge no experimental results about the long-range effects of fibers on chain dimension in fiber composites have been reported. If the prediction of the lowered chain dimension [13,14] is true, fibers should have long-range effects on chain conformation, provided there is strong anchorage of chains on fiber surfaces. Mismatched thermal properties may thus impose a force-field on the affected chains in the bulk resin phase because of the entanglement nature of polymers.

As a first step to probe into this aspect of crystallization mechanism, the present work studied crystallization of carbon fiber reinforced polyetheretherketon (PEEK) composites with different interfacial wetting levels as well as different polymer chain lengths. Non-isothermal crystallization was investigated using differential scanning calorimetry (DSC) to follow the whole crystallization process within a reasonable time scale. Also, conformation of the polymer was analyzed with Fourier transform infrared spectroscopy (FTIR). Emphasis was placed on the effects of melt residual

* Corresponding author. Tel.: +86-20-84036576; fax: +86-20-84036564.
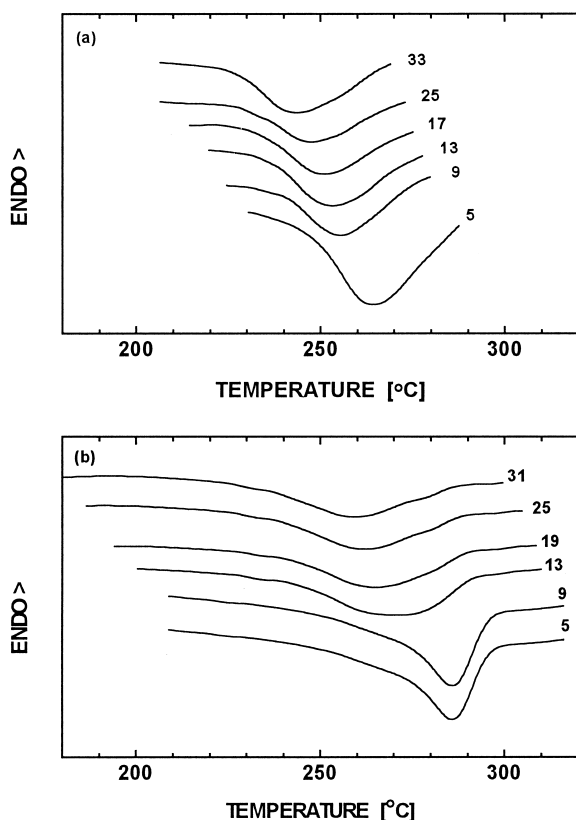E-mail address: ceszmq@zsulink.zsu.edu.cn (M.Q. Zhang)

Fig. 1. Non-isothermal crystallization curves of the solution pre-impregnated carbon fiber/PEEK prepregs made of ICI resins. The numerals denote MRT in minutes. Matrix molecular weights: (a) $N_v = 102$; (b) $N_v = 234$.

time (MRT) to reveal the nature of the long-range effects of carbon fiber on the bulk crystallization of the polymer.

2. Experimental

The polymers employed in the present work are molded plates of ICI Victrex PEEK and PEEK powders kindly supplied by Jilin University, China. The average degree of polymerization, N_v, by viscosity method of the three ICI specimens is 102 and 234, respectively. The domestic PEEK powder is similar to ICI 150P PEEK resin. The PAN-based carbon fiber, AS4, is a size-free product of Hercules.

Two sorts of AS4/PEEK prepregs were used. One was a home-made solution pre-impregnated by immersing the AS4 fibers, which was hand-wound on a polytetrafluoro-ethylene (PTFE) fixture, in a 2 g/100 ml chlorophenol solution [15] of PEEK from ICI and Jilin University, respectively, and then degassed at 60 mm Hg vacuum. The amount of the solution was controlled to ensure the highest possible fiber volume content, calculated to be 66% by assuming random dense packing of the fibers in the unidirectional fiber preforms. Solvent in the system was subsequently evaporated in a vacuum at 150°C. All the solution prepregs were compressed with contact pressure in a hot-press at

400°C and cooled at 20°C/min prior to the DSC study so as to further remove the residual solvent. As the element analysis demonstrated that the amount of chlorophenol in the prepregs became negligible after the aforementioned treatment [16], the possible effect of residual solvent could be ruled out during the subsequent DSC measurement. The other sort of prepreg was prepared by the Aeromaterial Research Institute, Beijing, using the AS4 carbon fiber and the resin from Jilin University through a powder pre-impregnation technique (fiber fraction: 60% by weight).

The 16-ply (2 mm thick) unidirectional laminates were prepared by compressing the solution prepregs and the powder ones from the domestic resin at 400°C under 10 MPa with a matched mold in a hot-press for a specified MRT. The temperature of the mold was registered directly through a hole located about 1 mm away from the cavity of the mold. The time required to heat the mold from 340 to 400°C was measured to be shorter than 5 min, ensuring the resolution of the MRT at 400°C to be better than at 2 min. The cooling rate of the mold was kept at 20°C/min unless otherwise specified.

Non-isothermal crystallization of the solution prepregs from the ICI resins with different N_v was studied with a Perkin–Elmer DSC-7 equipment at −10°C/min. Variation in MRT was achieved by repeatedly heating a specimen quickly to 400°C and keeping it at that temperature for a predetermined time. The accumulated holding time at 400°C was referred to as MRT. In the case of laminates with different MRT, their non-isothermal crystallization was studied with a Perkin–Elmer DSC-2 calorimeter by cooling the specimens from 400°C at −10°C/min. DSC crystallinities of the specimens were obtained from the endotherms on the 20°C/min heating traces.

FTIR spectra were collected by a Bio-Rad FTS 600 spectrometer using gold film as a background with a reflective geometry. Each spectrum was the average of 200 scanning results with 4 cm^{-1} resolution. Unlike the defuse reflective spectra of AS4/PEEK prepregs [17], the present spectra showed almost no distortion except for the strongest bands at around 1300 and 1600 cm^{-1}. A recorded spectrum was transformed to absorbance prior to the procedure of quantitative analysis.

3. Results and discussion

3.1. Effect of melt residual time on the non-isothermal crystallization of the prepregs

Fig. 1 illustrates the DSC cooling traces of the solution prepregs from the ICI resins with different degrees of polymerization. Shifting of the non-isothermal crystallization peaks with a rise in MRT towards lower temperature can be found for both sorts of prepregs. When the data were translated into time dependence of conversion (i.e. crystalline fraction developed at a given time and obtained by the
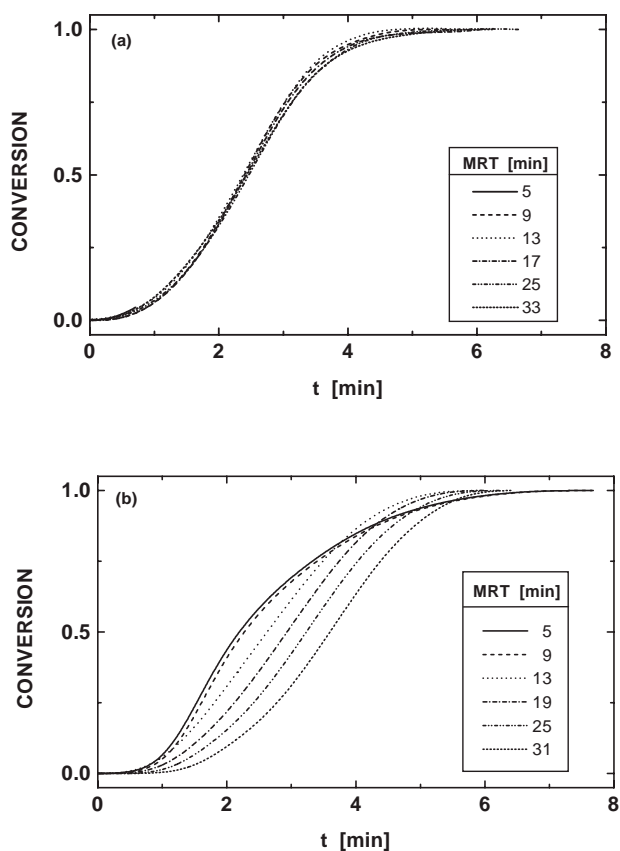
Fig. 2. Conversion as a function of time, *t*, calculated from Fig. 1. Material: solution pre-impregnated carbon fiber/PEEK prepregs made of ICI resins. Matrix molecular weights: (a) $N_v = 102$; (b) $N_v = 234$.

ratio of the crystallization area at a given time over the total area of the exothermic peak), however, the effect of MRT is completely different for the two specimens (Fig. 2). Crystallization of the prepreg with a higher molecular weight matrix was affected more significantly by the increase in MRT. Figs. 3 and 4 show this difference clearly. As the MRT dependencies of non-isothermal crystallization of neat PEEK with different molecular weights make no distinct difference within the molecular weight range of the current work [18], the incorporation of carbon fiber should be responsible for the observed disparity.

In the case of crystallization of a higher molecular system ($N_v = 234$), peak conversion (i.e. crystalline fraction developed at the time corresponding to the exothermic peak temperature and obtained by the ratio of the crystallization area at the same time over the total area of the exothermic peak) increases from a lower level to a higher one as MRT increases from 9 to 19 min (Fig. 3(a)). The result seems to reveal a rise in heterogeneous nucleation, as suggested by Lee and Porter in their isothermal crystallization investigation of AS4/PEEK prepregs prepared by a film-stacking method [3]. However, the corresponding maximum crystallization rate, characterized by the maximum of the first derivative of conversion with respect to time, decreases in

this MRT range (Fig. 3(b)), manifesting other factors may have contributed to the increase in bulk crystalline conversion.

From Fig. 4, it can be seen that the bulk crystallization rate, as represented by the inverse time for half conversion, $t_{1/2}^{-1}$, decreases with increasing values of MRT. Obviously, the crystallization was slowed down owing to the prolonged treatment at 400°C. A similar effect of melt treatment on isothermal crystallization of neat PEEK has been attributed to a decrease in residual nuclei in the melt [19]. Besides, an increase in the molecular weight [20] and possible chain branching would also lead to a decrease in the isothermal crystallization rate of PEEK. Therefore, the aforesaid reduced non-isothermal crystallization rate might result from these mechanisms.

On the contrary, the low molecular weight system shows much weaker dependence on MRT. Both the maximum and the overall crystallization rate drop slightly with an increase in MRT (Figs. 3(b) and 4), while peak conversion remains almost unchanged (Fig. 3(a)). Such an evident difference between the MRT dependencies of the prepregs with PEEK of $N_v = 102$ and 234 implies that the effect of prolonged MRT in destroying residual nuclei and promoting chain branching could not be applicable.

As a first-order approximation, kinetics of non-isothermal crystallization can be analyzed in terms of the Avrami equation. Fig. 5 illustrates typical Avrami plots of conversion, *C*, against non-isothermal crystallization time, *t*. A linear relationship between $\log[-\ln(1 - C)]$ and $\log t$ is found in the major part of the plots for most specimens. In general, the predominant deviation of the non-isothermal crystallization process from the Avrami model results in the non-simultaneous nucleation of the non-isothermal process [21]. As a result, the linearity between $\log[-\ln(1 - C)]$ and $\log t$ implies that the time-dependent nucleation has either reached a saturated level or has been compensated by a decrease in linear growth rate of the crystals. The apparent Avrami exponent, n_a, and rate constant, K_a, as shown in Fig. 6, can thus be used to estimate the growth dimension and crystallization rate of the corresponding growth process.

As shown in Fig. 6(a), n_a varies from 1.66 to 3.50 and is much lower than the literature value of 5.1 of neat PEEK [22]. For the higher molecular weight system, the quantity remains unchanged when MRT increases from 5 to 9 min, and then increases significantly with a further rise in MRT. For the prepreg with lower molecular weight resin, much less changes can be found though n_a maximizes at 9 min and decreases slightly at longer MRT regime. As the Avrami exponent of the isothermal crystallization of a neat Victrex PEEK specimen at 309°C has been found to decrease monotonously from 3.87 to 2.54 when the holding time at 400°C increases from 0 to 25 min [21], the present dependence of n_a on MRT for the prepregs, that is completely different from the case of the neat resin, reveals the specific influence of carbon fiber on the non-isothermal crystallization of the polymer.
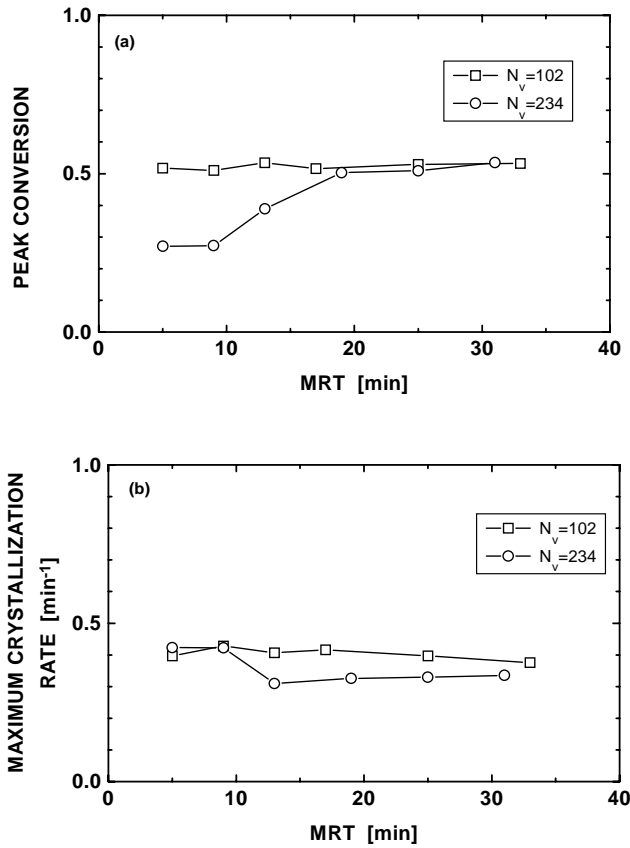
Fig. 3. Peak conversion and maximum crystallization rate of the non-isotherms in Fig. 1 as a function of MRT. Material: solution pre-impregnated carbon fiber/PEEK prepregs made of ICI resins.

To our knowledge, only two kinds of growth morphology have been found for the bulk crystallization of PEEK, namely transcrystallinity near a heterogeneous surface [6,8–10] and self-seeded, cart-wheel spherullites [6], both of which are spherullitic in nature and grow preferentially along the b crystallographic axis [23]. The large magnitude of changes in n_a implies that impingement of crystallites played an important role in the process. In fact, two-stage
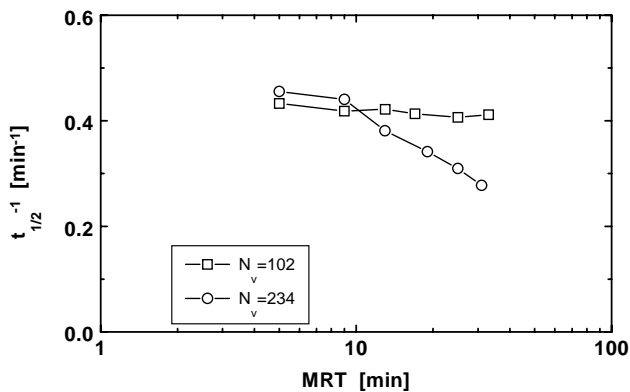

Fig. 4. Bulk crystallization rate in terms of the time for half conversion, $t_{1/2}^{-1}$, as a function of MRT. Material: solution pre-impregnated carbon fiber/PEEK prepregs made of ICI resins.
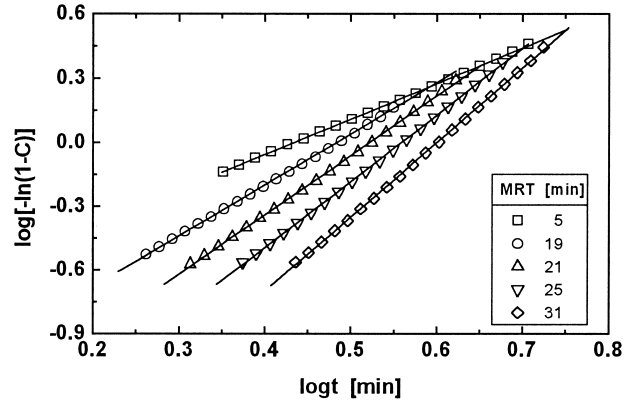

Fig. 5. Typical Avrami plots of non-isothermal crystallization against MRT of solution pre-impregnated carbon fiber/PEEK prepregs made of ICI resins. Matrix molecular weight: $N_v = 234$.

growth kinetics was frequently observed in this polymer by means of DSC [24], thermo-mechanical analysis [25], and microscopy [6,8]. The corresponding morphology explanation relies on secondary crystallization with lower growth dimension filling the space left by the primary one [6,23–25]. An increased portion of the secondary crystallization was considered to be responsible for the lower final crystallinity of PEEK in its carbon-fiber laminates [23]. The same reason should also account for the changes in n_a with MRT.
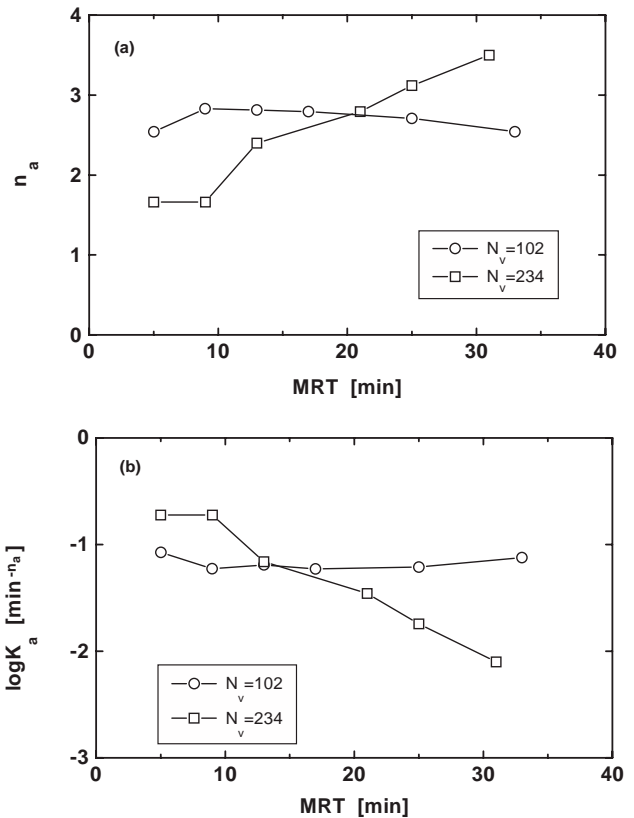

Fig. 6. Apparent Avrami exponent, n_a, and rate constants, K_a, as a function of MRT.
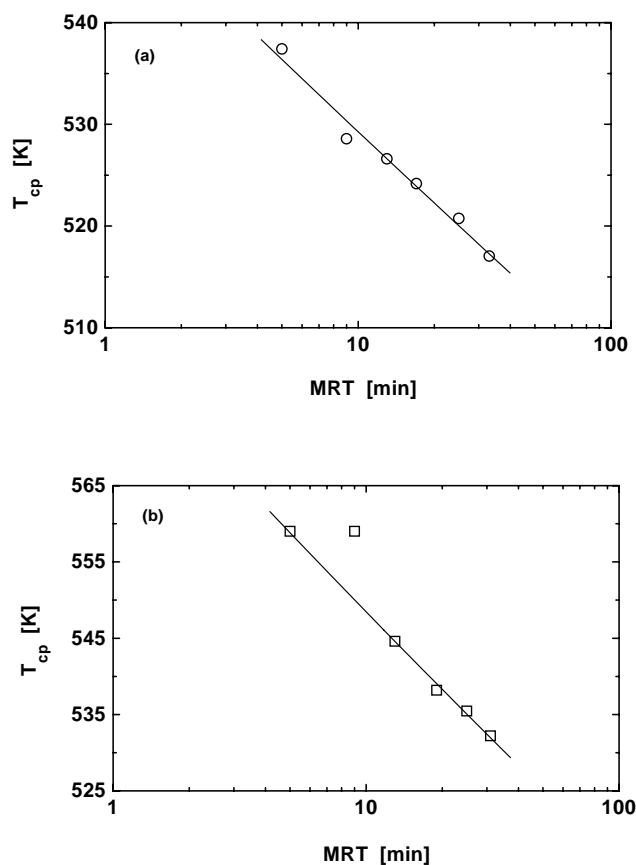
Fig. 7. Exothermic peak temperature during non-isothermal crystallization, T_{cp}, as a function of MRT obtained from Fig. 1. Material: solution pre-impregnated carbon fiber/PEEK prepregs made of ICI resins. Matrix molecular weights: (a) $N_v = 102$; (b) $N_v = 234$.

With a prolonged melt treatment, more nucleation sites formed during the early period of the DSC scan. Consequently, the higher density of primary crystallites impinged earlier and resulted in an increased contribution from the secondary mechanism. This should be reflected as a decrease in the measure of growth dimension, n_a, as observed for the prepreg with lower molecular weight and for longer MRT.

However, the exponent n_a increases profoundly with increasing MRT for the other system ($N_v = 234$). Such an increase is even perceivable for the prepreg with lower molecular weight when MRT rises from 5 to 9 min. Considering the fact that there is a competition between the nucleation from the fiber surface and that in the bulk polymer, the increase in n_a is assumed to originate from an increase in bulk nucleation if a decrease in this quantity is due to the increased contribution made by the secondary crystallization. Therefore, there must be a factor that facilitates the bulk nucleation, rather than the nucleation on fiber surface. As an increase in MRT can only destroy the residual nuclei in the bulk polymer, the factor must be the orientation caused by the mismatched thermal properties of the components in the prepreg. With the strong anchorage of molecular

chains on the carbon fiber surface in AS4/PEEK composites [11], the thermal stress would induce orientation of segments in the bulk polymer, which in turn nucleated the crystallization, as observed in the case of strain-induced crystallization of the same polymer [12]. In other words, it is the strain-induced bulk nucleation that caused an increased contribution from the primary crystallization, and thus an increase in the growth dimension, n_a, and a decrease in the apparent rate constant, K_a (Fig. 6).

Moreover, it is important to note that the increase in n_a and the decrease in K_a were observed for both the prepregs. Evidently, the strain-induced crystallization is a general feature of the bulk crystallization in the thermoplastic composites. As the trend is more significant for the prepreg with higher molecular weight at longer MRT region, it can be deduced that this long-range effect of the fibers on matrix crystallization is viscoelastic in nature.

It must be pointed out that the MRT has factually affected the non-isotherms of both the systems (Fig. 1), although it did not change the conversion plot of the lower molecular system. The constant peak conversion (Fig. 3(a)) allows one to use the expression of non-isothermal crystallization by Ozawa [26,27], Flynn and Wall [28]:

$$\ln q = 1.052\, E_a/(RT_{cp}),\tag{1}$$

where q, E_a, R and T_{cp} denote the cooling rate, the activation energy of the crystallization process, the gas constant, and the peak temperature of the corresponding exotherm [29], respectively. This equation implies that T_{cp} can also be a measure of the activation energy in the case of non-isothermal crystallization of the same type of crystallization at the same cooling rate. Owing to the fact that the results in Fig. 1(a) reveal a semi-logarithmic dependence of T_{cp} in Kelvin on MRT (Fig. 7(a)):

$$T_{cp} = 552.6 - 23.33\log \text{MRT}\tag{2}$$

an increase in MRT corresponded to a decrease in the apparent activation energy of the bulk crystallization. Clearly, a reduced E_a suggests easier formation of crystalline entities from melt or rubbery state. Therefore, an increase in MRT enhanced either bulk nucleation or primary growth or both, in agreement with the observed MRT dependence of the apparent growth dimension. The result further demonstrates that prolonged MRT facilitated the effect of fibers on nucleating bulk crystallization with increasing thermal strain in the polymer, even though the molecular weight is lower.

A similar phenomenon can also be found for the system with higher molecular weight

$$T_{cp} = 588.8 - 38.06\log \text{MRT}\tag{3}$$

although the requirement of Eq. (1) is not satisfied for a few specimens (Fig. 7(b)). The stronger dependency on MRT of the prepreg with higher N_v resin further proves the important role of thermal stress in non-isothermal crystallization. In addition, the difference in the MRT effects on the two kinds of prepregs reflects just another aspect of fiber/matrix
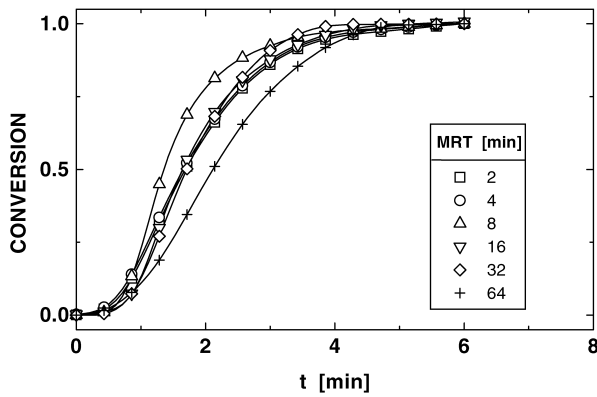
Fig. 8. Non-isothermal crystallization conversion as a function of time, *t*, of the in-mold processed laminates made from solution pre-impregnated prepregs with domestic PEEK as matrix resin.

interfacial interaction, i.e. a different time is required for the fibers to affect the conformation of matrix chain coils with different molecular weight. In other words, the effect of the reinforcing fibers on polymer structure is not limited to a relatively short range, for example, a few tenths of microns as in thermosetting composites. Given enough time for melt treatment, it can affect the conformation of all chains in the composite, as can be deduced from the theoretical prediction of chain dimension near a heterogeneous surface [13,14].

3.2. Effects of melt residual time on the non-isothermal crystallization of the in-mold processed laminates

As the long-range effects of fibers on bulk crystallization of AS4/PEEK prepregs have been related to their role in inducing thermal strain, hence constraints from the fiber/polymer interface must play a very important part. Consolidation of the prepregs should thus exert significant influence on the long-range interfacial interaction, and the MRT dependence of non-isothermal crystallization behavior
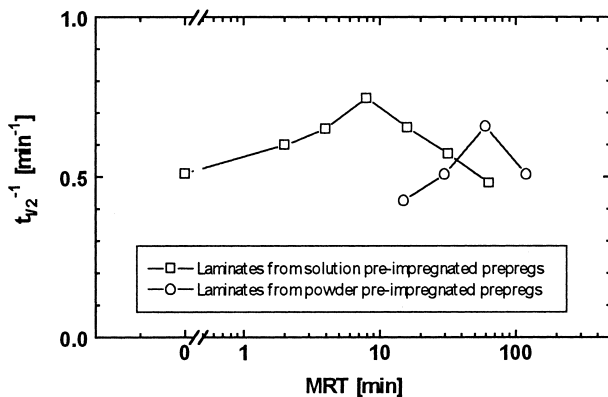

Fig. 9. Half conversion time, $t_{1/2}^{-1}$, of non-isothermal crystallization as a function of MRT. Materials: laminates made from solution and powder pre-impregnated prepregs with domestic PEEK as matrix resin.
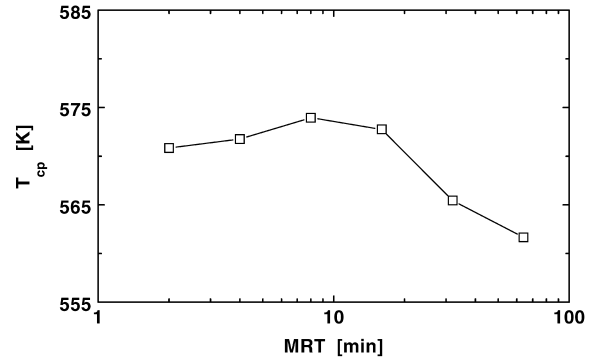

Fig. 10. Exothermic peak temperature during non-isothermal crystallization, T_{cp}, as a function of MRT. Material: laminates made from solution pre-impregnated prepregs with domestic PEEK as matrix resin.

of the molded laminates should be different in the case of different wetting levels in the prepregs.

Fig. 8 shows the non-isothermal crystallization of a solution pre-impregnated laminates with different MRT at 400°C. It can be seen that crystalline conversion is accelerated when MRT rises from 2 to 8 min and then slows down at longer MRT. With increasing MRT, the bulk crystallization rate as revealed by $t_{1/2}^{-1}$, increases when MRT is shorter than 8 min and decreases when MRT becomes longer (Fig. 9). The difference in the MRT dependencies at the two MRT ranges is further revealed by the peak temperature of the non-isothermal crystallization, the measure of apparent activation energy of the bulk crystallization (Fig. 10). While the decrease in $t_{1/2}^{-1}$ at longer MRT is consistent with the result of the prepreg with higher molecular weight ($N_v = 234$), the increase in $t_{1/2}^{-1}$ at shorter MRT reveals the nature of consolidation. With a rise in MRT, interfacial wetting and adhesion tended to be improved, the voids in the composite system vanished, and more residual nuclei were destroyed. Chain mobility was thus decreased and heterogeneous nucleation enhanced, resulting in a simultaneous increase in $t_{1/2}^{-1}$ and T_{cp} at shorter MRT.

It would be interesting to note that similar dependence of $t_{1/2}^{-1}$ on MRT can also be found for the laminates from powder prepreg (Fig. 9). The fact that $t_{1/2}^{-1}$ peaks at longer time coincide with the non-fully wetted nature [16] of the prepreg, indicates again the important role of intimately interfacial contact. It is the interfacial wetting and absorption that was widely understood as the structure nature of this AS4/PEEK system. The results here clearly manifest that the interfacial interaction is not necessarily limited to chains near the fiber surface. Instead, these short-range interactions form the boundary of the flow under thermal stress and further affect the bulk crystallization. This is believed to be an intrinsic reason for the strong dependence [16,30–33] of composite properties on processing conditions.

3.3. Ordering of polyetheretherketon chains

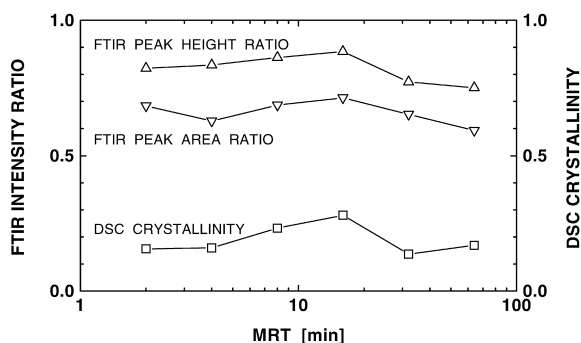The important role of thermal strain in determining the

Fig. 11. Ordering of PEEK as a function of MRT. Material: laminates made from solution pre-impregnated prepregs with domestic PEEK as matrix resin.

long-range effects of fibers on bulk crystallization should also be reflected in the change of chain conformation. As the ratio of IR intensity of the 962 cm^{-1} band to that of the 955 cm^{-1} band characterizes the ordering of both neat PEEK [34,35] and its carbon fiber laminates [36], it can be deduced that ordering of PEEK is strongly dependent on MRT, as illustrated by the peak height ratio and integrated intensity ratio (Fig. 11). While the peak height ratio increases with MRT up to 16 min, and then decreases with a further increase in MRT, the integrated area ratio changes with the variable in a more complex manner. Considering that the peak intensity describes the content of corresponding conformation of segments predominant in the specimen and peak area reflects the total content of the conformer, the difference between the two FTIR intensity ratios reveal that the ordering of PEEK segments is not necessarily related to crystallinity. With the similar MRT dependence of FTIR peak height ratio and DSC crystallinity (Fig. 11), the aforementioned two-stage effects of fibers on bulk crystallization is further proved. However, the decrease in integrated intensity ratio with a rise in MRT from 2 to 4 min directly indicates the loss in ordering caused by the enhanced interfacial wetting and absorption.

4. Conclusions

Effects of reinforcing carbon fiber on bulk crystallization of PEEK are characterized by using solution pre-impregnated composites as experimental materials. A careful examination of the non-isothermal crystallization of prepregs with different molecular weights reveals that the bulk crystallization of the matrix polymer depends on the strain-induced nucleation originating from the thermal stress in the composite. A comparison with the crystallization of the molded laminates suggests that strong short-range interaction between the fiber and the polymer is the pre-requisite for this long-range effect. The result is further proved through a study on the segment ordering by means of FTIR spectroscopy. Considering our previous analysis of interfacial structure of the composite, it can be concluded

that carbon fiber affects the non-isothermal crystallization of the matrix PEEK through the following two-stage mechanism:

1. forming strong interaction with the neighboring PEEK segments, and thus restricting chain movements during the cooling process;
2. inducing thermal strain in bulk polymer, and thus accelerating its crystallization through strain-nucleation.

In other words, the fibers exert long-range effect on bulk crystallization of the matrix polymer. The higher the molecular weight, the stronger the effect will be. It is believed that the present result directly reveals the different nature of consolidation of thermoplastic composites in comparison with their thermosetting counterparts. A full consolidation of the thermoplastic composites required changes in chain conformation to be completed in the whole matrix. A matrix polymer of higher molecular weight needs a longer processing time and a higher processing temperature. This aspect of interfacial interaction factually leaves space for tailoring the structure and properties of a composite with pre-determined composition.

Moreover, the result raises a question about the relationship between the thermal stress and crystallization. It is not enough to estimate the residual thermal strain of the composite merely by considering the dependence of the matrix modulus on crystallinity and using the kinetics data of the neat polymer for thermal strain facilitates crystallization of the matrix polymer. The nature of the interdependence between thermal strain and crystallization should be further studied by attempting to understand the contribution of strain-induced crystallization in a composite.

References

[1] Bessel T, Shortall JB. J Mater Sci 1975;10:2035.
[2] Zeng H, Ho G. Angew Makromol Chem 1984;127:103.
[3] Lee Y, Porter RS. Polym Engng Sci 1986;26:633.
[4] Gray DJ. J Polym Sci, Polym Lett Ed 1974;12:509.
[5] Campbell D, Qayyum MM. J Polym Sci, Polym Phys Ed 1980;18:83.
[6] Blundell DJ, Crick RA, Fife B, Peacock J, Keller A, Waddon A. J Mater Sci 1989;24:2057.
[7] Lustiger A. SAMPE J 1989;12(6):39.

[8] Zeng H, Zhang Z, Zhang M, Xu J, Jian N, Mai K. J Appl Polym Sci 1994;54:541.

[9] Zeng H, Zhang Z, Peng W, Pu T. Eur Polym J 1994;30:235.

[10] Chen EJH, Hsiao BS. Polym Engng Sci 1992;32:280.

[11] Li TQ, Zhang MQ, Zeng HM. Polymer 1999;40:4307.

[12] Chien MC, Weiss RA. Polym Eng Sci 1988;28:6.

[13] de Gennes P-G. Scaling concept in ploymer physics. Ithaca, NY: Cornell University, 1979. p. 219.

[14] Wu DC, Du P, Kang J. Sci China Ser B 1996;26:409.

[15] Xu J, Zhang Z, Xiong X, Zeng H. Polymer 1992;33:4432.

[16] Li TQ. PhD thesis. Zhongshan University, China, 1997.

[17] Cole KC, Noel D, Hechler JJ. Polym Compos 1988;9:395.

[18] Zhang Z, Yang C, Zeng H. Aerospace Mater Technol 1989;(6):37.

[19] Lee Y, Porter RS. Macromolecules 1988;21:2170.

[20] Day M, Deslandes Y, Roovers J, Suprunchuk T. Polymer 1991;32:1258.

[21] Zhang ZY. PhD thesis. Zhongshan University, China, 1990.

[22] Cebe P, Hong SD. Polymer 1986;27:1183.

[23] Lovinger AL, Hudson SD, Davis DD. Macromolecules 1992;25:1752.

[24] Velisaris CN, Seferis JC. Polym Eng Sci 1986;26:1574.

[25] Chen HL, Porter RS. Polymer 1993;34:4576.

[26] Ozawa T. Bull Chem Soc Jpn 1965;38:1881.

[27] Ozawa T. J Thermal Anal 1970;2:301.

[28] Flynn JH, Wall LA. J Res N B S Phys Chem 1968;70A:487.

[29] Denault J, Vu-khanh T. Polym Compos 1992;13:361.

[30] Xiao XR, Denault J, Vu-khanh TJ. Thermoplast Compos Mater 1992;5:64.

[31] Tregun A, Harel H, Marom GJ. Mater Sci Lett 1994;13(5):329.

[32] Talbot M, Springer GS, Berglund LA. J Compos Mater 1987;21:1056.

[33] Jar PY, Cantwell WJ, Kausch HH. Compos Sci Technol 1992;43:299.

[34] Cebe P, Chung SY, Hong SD. J Appl Polym Sci 1987;33:487.

[35] Chalmers JM, Gaskin WF, Mackenzie MW. Polym Bull 1984;11:433.

[36] Blundell A, Chalmers JM, Mackenzie MW, Gaskin WF. SAMPE Q 1985;16(4):22.