Semicrystalline Polyimide Matrices for Composites: Crystallization and Properties

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ABSTRACT: New semicrystalline polyimide/oligoimide blends, designated for matrices in carbon fiber-reinforced composites, were developed. A specific advantage of the proposed polyimides is their ability to crystallize from the melt, therein retaining their crystallinity throughout the manufacturing process. The generation of crystallinity after melting, referred to as recrystallization, was investigated here as affected by blending the polyimides with oligoimides of a similar chemical structure. Based on thermal analysis and enthalpy measurements, comparative X-ray diffraction analyses, and polarized light microscopy of hot-stage-controlled crystallization, the recrystallization ability was determined for five different oligoimides. In some cases, the addition of oligoimides, both amorphous and crystalline, resulted in complete recrystallization. The main contribution of the oligoimides is suggested to be through plasticization, allowing segmental chain mobility during crystallization, and not via nucleation. A similar effect was obtained by lowering the molecular weight of the polyimide; this, however, generates mechanical property reduction, rendering the polyimide irrelevant to composite materials. Finally, it was shown that crystallization was also enhanced by carbon fibers, serving as a nucleating agent and generating transcrystallization. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2873–2882, 2002; DOI 10.1002/app.10277

Key words: semicrystalline polyimide; oligoimides; recrystallization; transcrystallization; thermoplastics

INTRODUCTION

Of the many polymers used as matrices for composite materials, aromatic polyimides (PIs) are of particular interest as thermally stable binders,[1,2] primarily in aerospace, marine, and automotive applications. Thermoplastic PIs offer several advantages over conventional thermoset PIs,[3] the most notable being improved toughness and the ability to be thermally processed and shaped. However, demanding processing conditions prevent wide use of thermoplastic PIs for carbon fiber-reinforced composites (CFRCs) for high-temperature application. In this regard, great attention has been given to a family of thermoplastic PIs based on aromatic dianhydrides[4,5] or diamines.[6] These PIs were developed traditionally as an amorphous or mesomorphic class of high-temperature polymers,[1] whose reluctance to crystallize derives from the high viscosity of their melt.[7]

Another class of PI matrices for advanced composites, which can crystallize from the melt, was developed in the last years. These PI matrices are known by the names LARC–CPI,[8–10] LARC–CPI-2,[11,12] and PI-2.[13] They all exhibit attractive properties such as excellent thermal and oxidative stability, high mechanical properties, excellent resistance to solvents, and strong bases and high adhesive properties. A specific feature of these polymers is their ability to crystallize from the melt to form crystalline matrices for composite materials. This feature distinguishes them from other semicrystalline PI powders of the LARC–TPI type,[14] which melt in the temperature range 270–290°C and do not recrystallize upon cooling. LARC–TPI can crystallize after melting only in the presence of a residual solvent.[15]

The objective of this study was to investigate the crystallization behavior of a new PI semicrystalline polymer,[16] presented in Structure **(1)**, by considering various factors of potential influence on crystallization.

(1)
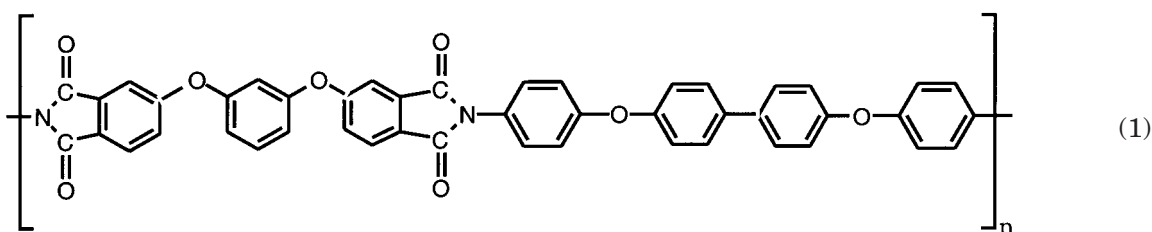
These factors include (i) variation of the processing conditions with emphasis on the melting and annealing temperature; (ii) addition of oligoimides (OIs) of related chemical structure to that of the PI molecules and of potential nucleating action; (iii) changing the molecular weight of the PI by shifting from the stoichiometric dianhydride/diamine ratio; and (iv) addition of carbon fibers with a potential nucleating ability. Because most of the manufacturing processes of thermoplastic matrix composites require matrix melting, crystallinity retention throughout the manufacturing process is a major advantage. The generation of PI crystallinity after melting, referred to as recrystallization, is therefore the main issue of this work.

It was intended to study the effect of each of these factors on the ability of the PI to recrystallize. The study was based on thermal analysis and calorimetry-based enthalpy measurements, comparative X-ray diffraction (XRD) analyses of the crystalline structure, and polarized light microscopy of hot-stage-controlled crystallization.

EXPERIMENTAL

Materials and Preparation

Poly(amic acid) (PAA) was obtained by polycondensation of 1,3-bis-(3,3′,4,4′-dicarboxyphenoxy)-benzene and 4,4′-bis-(4-aminophenoxy)biphenyl in a 25% solution of N-methyl-2-pyrrolidone (NMP) at 25°C and subsequent drying at 80°C for 20 h. A series of PI samples were synthesized in which the molecular mass was reduced by slightly increasing the dianhydride proportion in the monomer mixture above the stoichiometric ratio.

PI films, 30–40 μm thick, were prepared from PAA by casting onto soda lime glass plates and oven curing under air. The films were removed from the glass plates by soaking in water. They were cured for 20 min at 100°C, 20 min at 120°C, 20 min at 150°C, 15 min at 200°C, 30 min at 250°C, and 30 min at 280°C in the air. Films of PI/OI blends were prepared by adding 10 wt % of the OI in a fine powder form, to a stirred PAA solution described above. The film-casting procedure followed that of the pure PI.

Composite materials and single-fiber microcomposites were prepared with two types of carbon fibers, namely, a low modulus (200 GPa) polyacrylonitrile-based fiber (ELUR, NPO "Chimvolokno," Moscow, Russia) and a high modulus (770 GPa) pitch-based fiber (PRD-172, DuPont, Wilmington, DE). Carbon fiber prepregs were prepared by fiber impregnation with an NMP solution of PAA and subsequent drying of the resulting prepregs at 80°C for 20 h. The estimated weight content of the PI matrix in the prepregs after the imidization of the PAA was 34% (based on the respective densities of the fiber and the PI
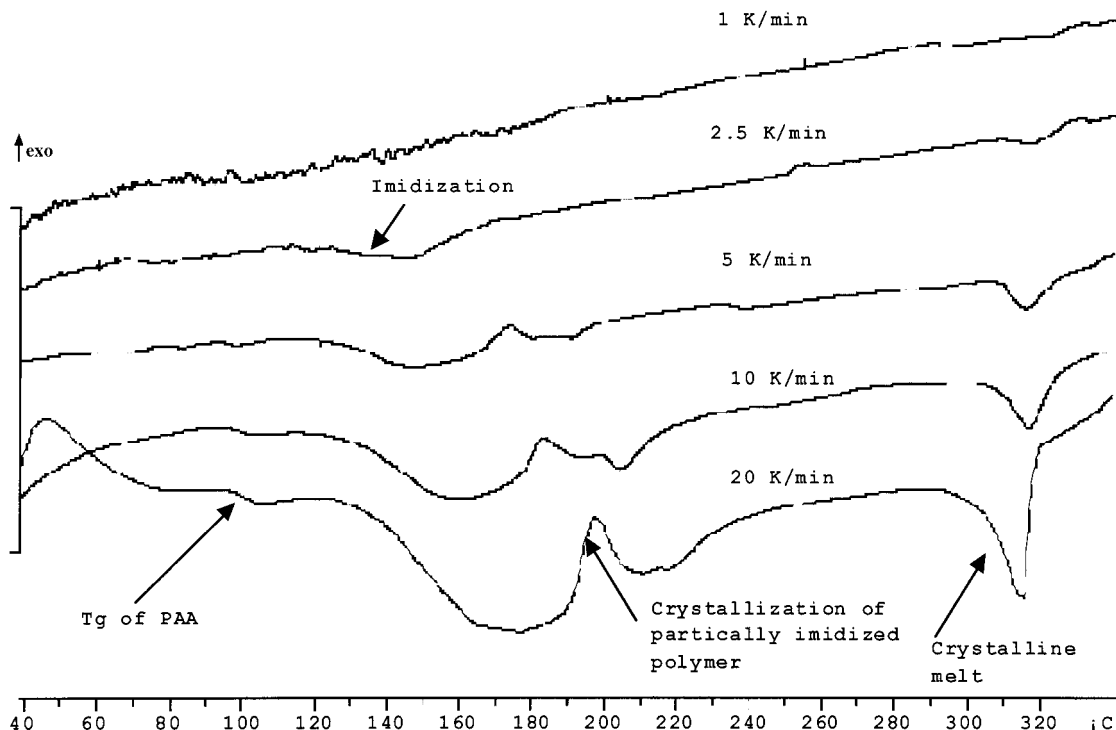
Figure 1   DSC traces of PAA at different heating rates, indicating its glass transition, with the imidization reaction followed by crystallization of the formed PI and by crystalline melting of the PI.

of 1.8 and 1.4 g/cm^3; the fiber volume fraction was about 60%).

Measurements

Intrinsic viscosity was measured in a 0.5% solution of PAA in NMP at 25°C. Differential scanning calorimetry (DSC) was performed using a Mettler DSC-30 Model on 5–10-mg samples contained in aluminum pans with a heating rate of 10–20°C/min under nitrogen. Thermogravimetric analysis (TGA) was conducted using 50-mg samples contained in a platinum crucible with a heating rate of 10°C/min under air. Crystallization studies were carried out on a hot-stage (FP82 HT, Mettler, Switzerland) under a polarizing optical microscope (Nikon Optophot-PDL) equipped with a video camera and monitor/color printer (Sony).

Wide-angle XRD measurements were conducted on a diffractometer with a Philips PW-1830 generator. A wavelength of 1.54 Å was generated from a CuKα source, with graphite as the monochromator. Samples were scanned in the angular range of 10–40°.

## RESULTS AND DISCUSSION

Processing Conditions

PI can be obtained in the form of semicrystalline films, 30–40 μm thick, with a tensile strength of 90–110 MPa, tensile Young's modulus of 3.2 GPa, and breaking deformation of 5–8%. As follows from the experimental results, the possibility to obtain a semicrystalline PI film from the PAA precursor will depend on the heating rate. The results of the DSC investigation performed on the PAA film subjected to different heating rates is shown in Figure 1. The glass transition temperature, T_g, of the PAA was determined to be 100°C. Crystallization of the partially (30%) imidized polymer occurs in the temperature region of 180–190°C, followed by further imidization and possibly additional crystallization. The endotherm at 315°C is attributed to the melting of the crystalline phase. The TGA results in Figure 2 indicate that the imidization reaction begins at 130°C; about 80% of the reaction occurs between 130 and 220°C and it ends completely at about 300°C. A fully imidized PI film shows the beginning of
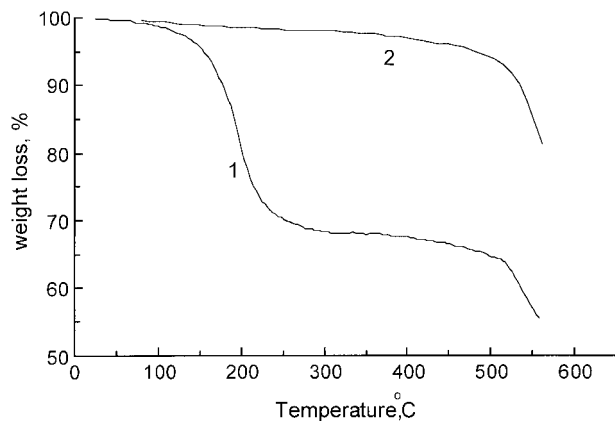
Figure 2 TGA traces at a heating rate of 10 k/min: (1) PAA, showing a major weight loss in the temperature range of 130–220°C due to water loss associated with the imidization; (2) fully imidized PI, showing a significant thermal stability above 500°C.

weight loss in air at ~500°C. The existence of a crystalline phase is proved also by the XRD results in Figure 3, showing a series of distinctive crystallinity peaks.

As shown in Figure 1, both the possibilities to create an initial crystalline phase and the melting enthalpy, ΔH_m, depend on the heating rate. For example, for 1°C/min, no crystallization of the PAA film occurred. Also, based on the melting peaks, increasing of the heating rate from 2.5 to 20°C/min increased ΔH_m from 18 to 32 J/g. Ac-
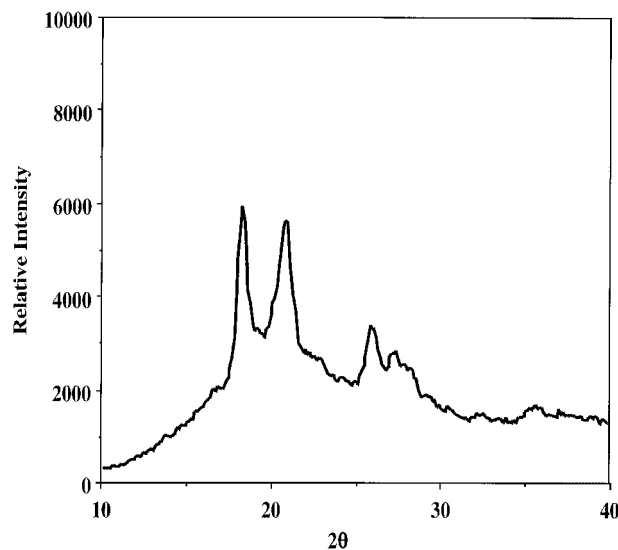
Figure 3 Wide-angle XRD pattern of a fully imidized PI film.

Table I   DSC Data of the PI Film After Thermal Treatment at T_x

T_x (°C)	T_m (°C)	ΔH_m (J/g)	T_g (°C)
Initial film	317	38.6	198
310	324	24.5	199
320	314	7.8	200
330	Not detectable	Not detectable	200
350	Not detectable	Not detectable	200

cordingly, the properties of PI films in the first step of the PAA–PI transformation will depend strongly on the conditions of their temperature treatment. For this reason, a uniform curing treatment of PAA (prescribed in the Experimental section above) was maintained throughout the experiments. The ability of PI to recrystallize was studied by DSC performed on crystalline PI (T_m = 315°C, ΔH_m = 44 J/g) obtained from PAA by imidization on a glass plate up to 280°C. The PI film was melted in the DSC crucible for 5 min at a temperature T_x (Table I) above the melting point and subsequently cooled to 300°C and maintained isothermally for 40 min, followed by cooling to room temperature. After this thermal cycle, the sample underwent a second DSC scan during which the melting temperature, T_m, and enthalpy were recorded again.

The results, which are presented in Table I, show that the maximum temperature which allows recrystallization is 320°C, namely, 5–10°C above the melting temperature. According to polarized light microscopy, in this temperature range, a residual structural organization in the molten PI is still retained, which, upon cooling, initiates recrystallization. Otherwise, by transforming to a fully isotropic state, the molten PI loses its ability to recrystallize as a result of its high melt viscosity. This has been reported previously for other semicrystalline PIs.[10,12,17] Obviously, a narrow window of 5–10°C is insufficient for practical operations such as melt impregnation of fibers; hence, the use of pure PI for composite materials is not feasible if crystallinity is to be retained.

Effect of OIs on Recrystallization

The idea to blend thermoplastic PI with OIs of similar chemical structure to nucleate recrystallization has been suggested in the litera-
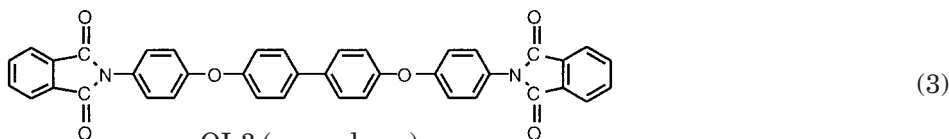
ture.[5,10,12] In this study, five OIs of chemical resemblance to the PI repeating unit, the dianhydride segment, or the diamine segment, as suggested in refs. 5 and 12, were tested. The chemical structures of these OIs are presented in Structures **(2)–(6)** below:
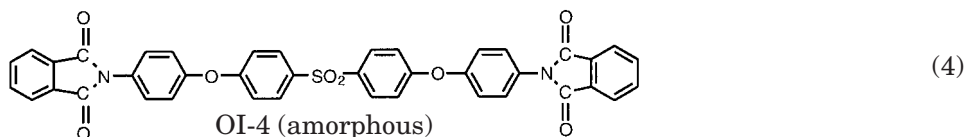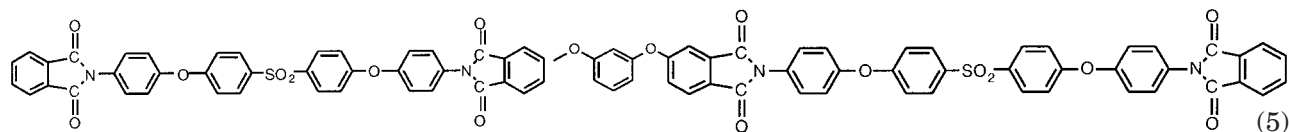
OI-1 (T_m = 294.4 °C)

(2)

OI-2 (T_m = 288.9 °C)

(3)
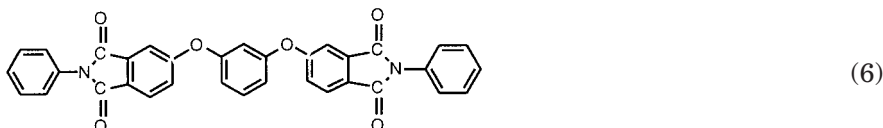
OI-3 (amorphous)

(4)

OI-4 (amorphous)

(5)

OI-5 (T_m = 277.5 °C)

(6)
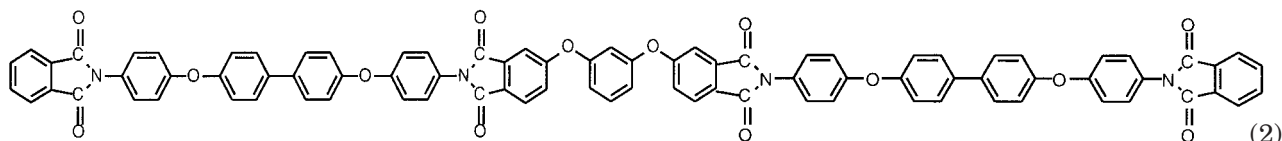
The PI/OI blends were subjected to the following thermal treatment in the DSC: Each sample was heated at 10°C/min to 340°C, that is, to a temperature from which the pure PI cannot recrystallize upon cooling (Table I); the melting enthalpy of the first scan, ΔH_{m1}, was determined. The sample was maintained at 340°C for 1 min to ensure complete melting and then cooled at a rate of 10°C/min to a given crystallization temperature for a 40-min isothermal treatment. This was followed by cooling at 10°C/min to 30°C. A second DSC scan was performed subsequently at a heating rate of 10°C/min, to obtain the melting enthalpy of the recrystallized phase, ΔH_{m2}. The ratio of $(\Delta H_{m2}/\Delta H_{m1}) \times 100\%$, denoted as the recrystallization percentage (RP) and the treatment temperature that gave the maximum crystallinity, was determined for each PI/OI sample, as displayed in Table II.
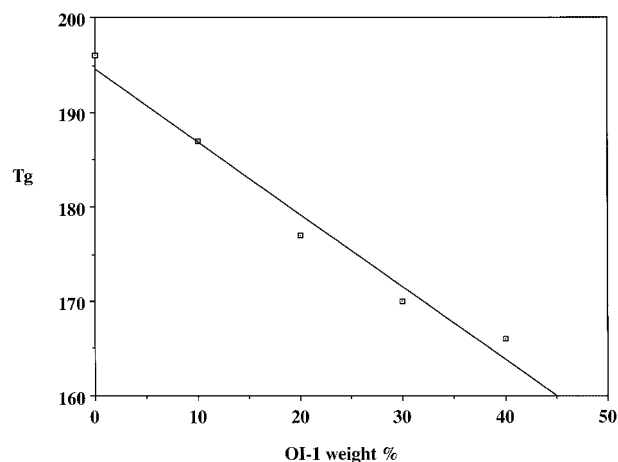
It is seen that the maximum values of RP were obtained with the lower molecular mass OI-2, OI-3, and OI-5 rather than with OI-1 and OI-4. It is also noted that the amorphous OI-3 generated the maximum ΔH_{m2} and the crystalline OI-5 generated the maximum RP. Because crystallinity of the OI additive is not a prerequisite for PI recrys-

Table II   DSC Data of the PI/OI Blends

Materials	Annealing Temperature (°C)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)	RP (%)
PI/OI-1	270	199	317.6	317.6	44.0	13.0	29.5
PI/OI-2	280	190	316.6	316.4	36.4	36.0	98.9
PI/OI-3	270	192	312.5	313.0	40.6	38.5	94.8
PI/OI-4	270	194	317.8	315.2	33.1	27.2	82.2
PI/OI-5	250	—	313.1	310.7	25.5	30.0	117.6

tallization, it is implied that the contribution of the OI additive to recrystallization is by plasticization of the PI. This is supported by another observation that the T_g of the PI/OI blend decreases with the OI content as demonstrated in Figure 4 for OI-1 blends, showing a linear decrease (with a correlation coefficient of 0.97) from about 200°C for pure PI to 167°C in a 60:40 wt % mixture. Concomitantly, the T_m of this mixture changes only slightly from 317 to 308°C. These effects, which are typical of plasticizers,[18] reflect a larger free volume and an easier chain segmental mobility needed for the crystallization process.

The idea that the contribution of the OI is by plasticization, and not necessarily by nucleation, is supported further by the XRD results. Figure 5 presents the diffraction results of PI, OI-2, and the PI/OI-2 blend. For a qualitative impression, Figure 6 presents polarized light photomicrographs of OI-2 and the PI/OI-2 blend, respectively, crystallized on a glass plate. While the photos in Figure 6 confirm the crystalline struc-
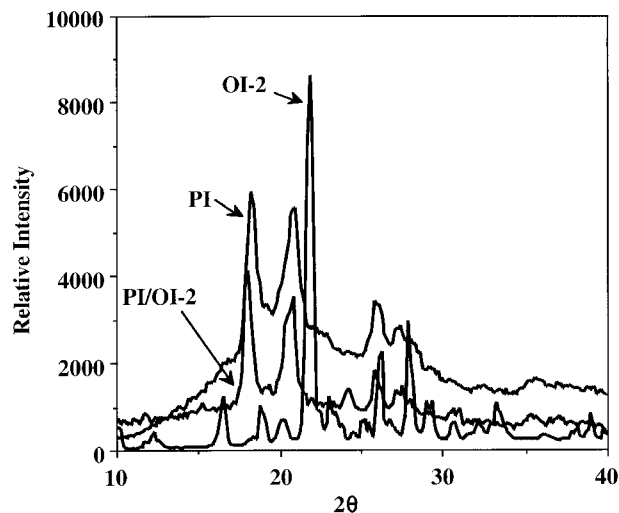
ture of the three materials, the important observation is that the typical diffraction lines of the OI disappear completely from the diffraction pattern of the blend, which is identical to that of the original PI. In other words, the XRD results contradict the anticipated mechanism of PI nucleation on OI crystals.

Because OI-3 is soluble in NMP and therefore can be readily mixed with PAA, it becomes the material of choice for fiber preimpregnation in composite material manufacturing. This OI was also selected for the second part of this study.

Effect of Molecular Mass on Recrystallization

To test the suggestion that chain mobility is a dominant factor in the recrystallization capability, and because chain mobility is affected by the molecular mass, the effect of the molecular mass

Figure 4   Dependence of the glass transition temperature of PI/OI-1 blends on the weight fraction of OI-1.

Figure 5   Comparison of wide-angle XRD patterns of the PI film, the oligoimide OI-2, and their 90/10 PI/OI-2 blend. The typical features of the blend are identical to those of pure PI.
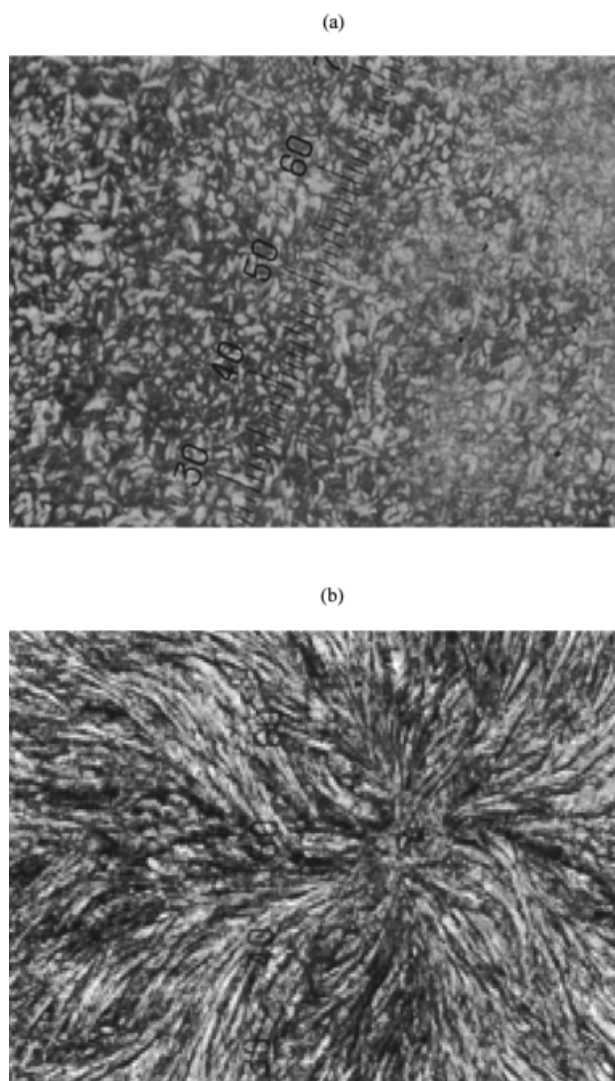
Figure 6 Polarized light micrographs of the crystalline structures of the PI/OI-2 blend (a) and the OI-2 (b).

of the PI was studied next. The molecular mass of the PI was reduced by slightly increasing the dianhydride proportion in the monomer mixture above the stoichiometric ratio, reflected in the intrinsic viscosity $[\eta]$ of the PAA in NMP. The PI films were obtained by thermal imidization of PAA. The mechanical properties of these films and the RP value in comparison with OI-1, which marks the minimum molecular mass of the PI molecule, are shown in Table III. The recrystallization treatment was identical to that described in the section above on the effect of OIs. The treatment temperatures which gave the maximum crystallinity for the PI-2 and PI-3 films were 310 and 300°C, respectively.

The results in Table III show that the gradual reduction in the molecular mass, as reflected by the intrinsic viscosity, results in a gradual decrease of the glass transition and melting temperature and in a corresponding increase of the RP value. Again, the ability of PI to recrystallize seems to depend on the extent of the segmental chain mobility. At strength, σ and the modulus, E, retention is also observed; however, the elongation to break, ε, is lowered significantly and the PI becomes brittle, so that decreasing the intrinsic viscosity of PAA below 0.8 dL/g seems impractical.
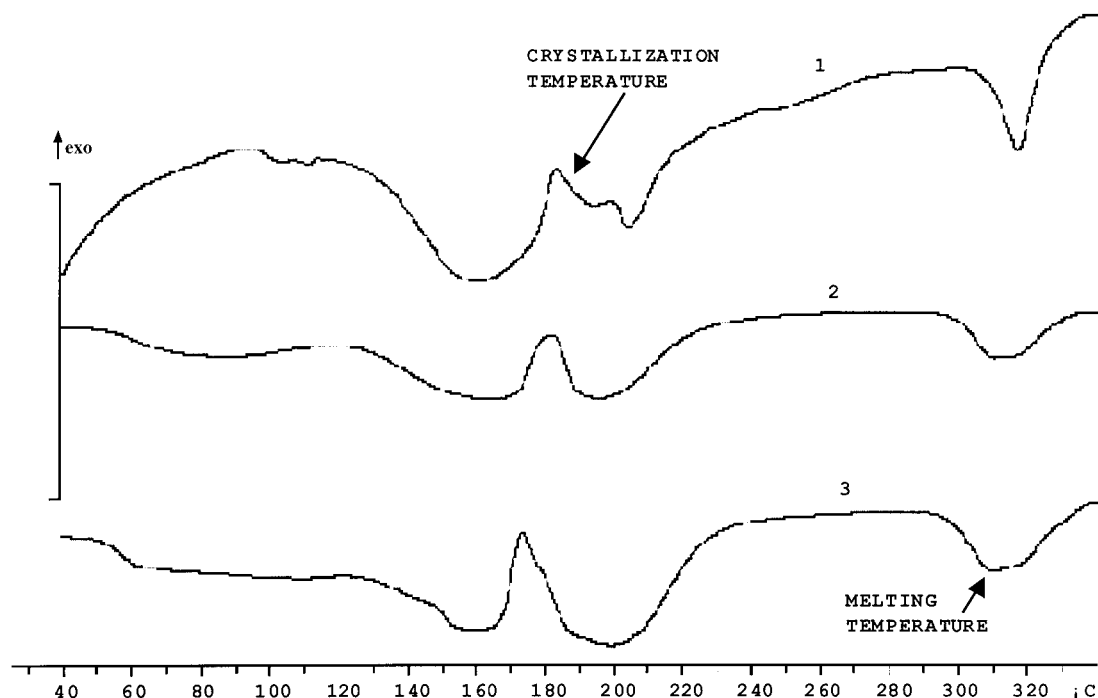
Effect of Carbon Fibers on Recrystallization

Since the PI blends are destined for CFRC materials, the effect of the fiber must be evaluated in addition to the effects of the OI and molecular mass. The fiber is expected to nucleate crystallization on its surface and to induce a highly ordered transcrystallinity, which may result in improved mechanical properties of the composite material in the fiber direction.[19]

Below, the transcrystallization ability of a pitch-based carbon fiber is compared with that of a polyacrylonitrile-based fiber. As indicated above, because OI-3 is soluble in NMP and therefore can be readily mixed with PAA, it becomes the material of choice for fiber preimpregnation in composite material manufacturing and its blend was studied with the carbon fibers. The influence

Table III Properties of OI-1 and PI Films with Different Intrinsic Viscosity of PAA

Sample	$[\eta]$ (dL/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	RP (%)	σ (MPa)	E (GPa)	ε (%)
PI-1	1.3	213	Not determined	Not determined	—	101	2.86	13.4
PI-2	0.8	205	325	40	42	92	3.70	3.1
PI-3	0.5	198	322	44	53			
OI-1	0.1	154	294	45	100	Very brittle powder		

Figure 7 DSC scans at a heating rate of 10 K/min of PAA: (1) neat; (2) with polyacrylonitrile-based carbon fibers; (3) with pitch-based carbon fibers.

of the fibers on the crystallization process in PAA is expressed in the DSC results shown in Figure 7 and Table IV. It is seen that the crystallization temperature shifts by 5–10°C to lower values for PAA/carbon fiber prepregs compared with the pure PAA film. Also, the carbon fibers increase the melting enthalpy of the PI matrix (taking into account a 34% weight fraction of the matrix in the composite). Moreover, the nucleating ability of the high modulus pitch-based fiber is stronger than that of the other fiber, which is expressed in the lower crystallization temperature and the higher melting enthalpy of the first.
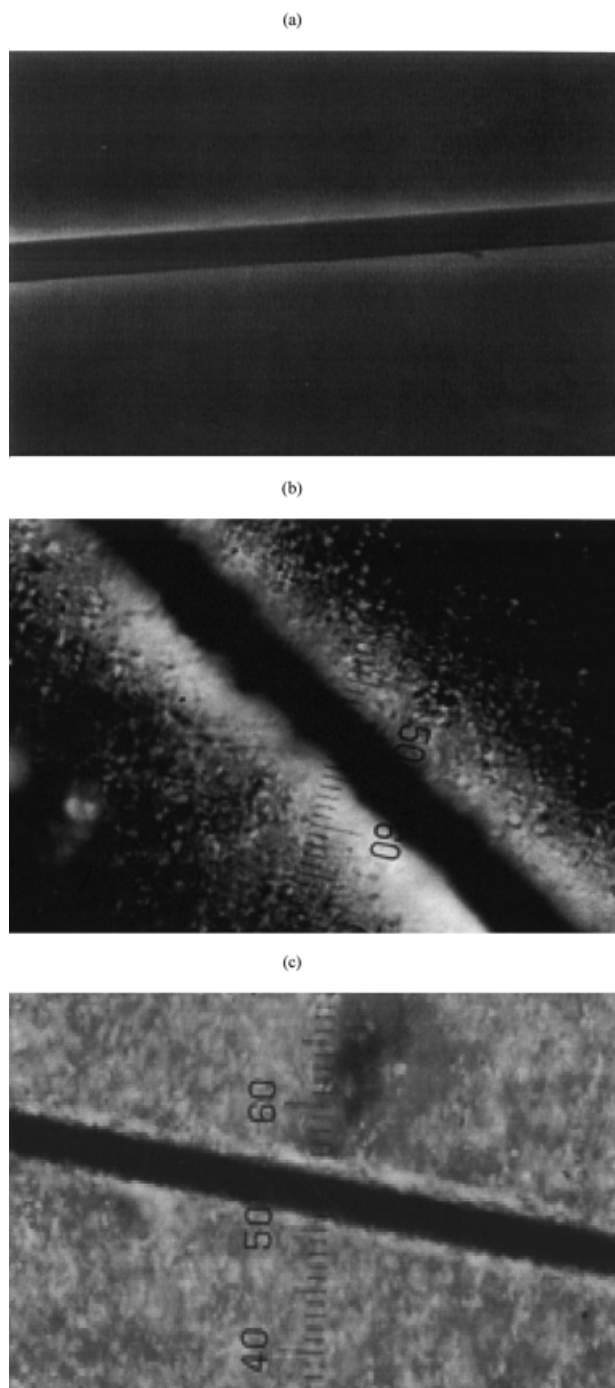
The question of the possibility to recrystallize the PI matrix after its melting in the presence of carbon fibers was investigated with single-fiber

Table IV DSC Data for the Imidization of PAA at 10 K/min in the Presence of Carbon Fibers

Material	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PAA	182.8	31.1	317.0	26.7
PAA + ELUR	180.9	33.3	309.6	44.7
PAA + PRD-172	172.8	42	309.7	56.5

microcomposites by polarized light microscopy coupled with a temperature-controlled hot stage. A single carbon filament was first incorporated into the PI/OI-3 (90/10) matrix melt at 340°C, followed by treatment at 270°C until the appearance of the first crystallites on the fiber surface. To prevent bulk crystallization, this system was then quenched to room temperature. The results of the polarized light microscopy in Figure 8 show that the pitch-based fiber generated a significantly thick transcrystalline layer, while the polyacrylonitrile-based fiber under the same conditions hardly generated any. The nucleation ability of the fiber depends on its crystalline structure and on the crystalline lattice match with the matrix structure. It has been shown that, due to a number of reasons, which are beyond the scope of this article, the nucleation ability of a pitch-based carbon fiber is significantly higher than that of a polyacrylonitrile-based carbon fiber (for comparison, a glass fiber, which is amorphous, does not initiate transcrystallization spontaneously).[20] Figure 8 shows also that if, instead of quenching, the first sample was left longer on the hot stage significant bulk crystallinity would also develop, as expected. It is noted that the ability of the pitch-

Figure 8 Polarized light micrographs of single carbon fiber microcomposites in a 90/10 PI/OI-3 matrix recrystallized from the melt at 280°C for 1–2 min: (a) a polyacrylonitrile-based fiber; (b) a pitch-based fiber; (c) a pitch-based fiber after 30 min at 280°C.

based carbon fiber to enhance significant transcrystallization enhances, in turn, the operating temperature window for fiber impregnation.

CONCLUSIONS

New semicrystalline PI matrices for carbon fiber-reinforced composites were developed. In the process of thermal imidization of PAA, which occurs during the fiber-impregnation stage, a semicrystalline structure can form in the matrix. The ability of this crystallinity to regenerate through the molding process of composite laminates from the original prepregs, that is, the capability of the PI matrix to recrystallize after melting, can be enhanced by the addition of OIs and by fiber-driven transcrystallization.

The mechanism by which the OIs enhance recrystallization is most probably plasticization of the matrix, allowing the PI to crystallize by increasing its chain mobility. A similar effect was recorded for the decreasing of the molecular mass of the PI. Transcrystallization, which is favored for pitch-based carbon fibers, also results in a higher level of recrystallization.

REFERENCES

1. Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. Polyimides—Thermally Stable Polymers; Plenum: New York, 1987.
2. Sroog, C. E. Prog Polym Sci 1991, 16, 561.
3. Pilato, L. A.; Michno, M. J. Advanced Composite Materials: Springer-Verlag: Berlin, Heidelberg, 1994; pp 10–15.
4. Anonymous. Chem Eng 1983, 90, 61.
5. Takekoshi, T.; Anderson, P. P. U.S. Patent 4 906 730, 1990.
6. Svetlichnyi, V. M.; Zhukova, T. I.; Kudryavtsev, V. V.; Yudin, V. E.; Gubanova, G. N.; Leksovskii, A. M. Polym Eng Sci 1995, 35, 1321.
7. Sroog, C. E. In Proceedings of 4th European Technical Symposium on Polyimides and High Performance Polymers, LEMP/MAO, University Montpellier, 1996; Vol. 2, p 266.
8. Hergenrother, P. M.; Havens, S. J. SAMPE J 1988, 24(4), 13.
9. Wilkes, G. L.; Muellerleile, J. T.; Risch, B. G.; Brandom, D. K. Abstr Am Chem Soc 1992, 203, 256-poly Part 3.
10. Muellerleile, J. T.; Risch, B. G.; Rodrigues, D. E.; Wilkes, G. L.; Jones, D. M. Polymer 1993, 34, 789.

11. Brandom, D. K.; Wilkes, G. L. In Proceedings of 5th Conference on Polyimides, Nov. 2–4, Ellenville, NY, 1994; p 133.
12. Brandom, D. K.; Wilkes, G. L. Polymer 1994, 35, 5672.
13. Cheng, S. Z. D.; Mittleman, M. L.; Janimak, J. J.; Shen, D.; Chalmers, T. M.; Lien, H.-S.; Tso, C. C.; Gabori, P. A.; Harris, F. W. Polym Int 1992, 29, 201.
14. Bell, V. L.; Stump, B. L.; Gager, H. J Polym Sci 1976, 14, 2275.
15. Wang, J.; DiBenedetto, A. T.; Johnson, J. F.; Huang, S. J.; Cercena, J. L. Polymer 1989, 30, 718.

16. Yudin, V. E.; Svetlichnyi, V. M.; Gubanova, G. N.; Kudryavtsev, V. V.; Ivanova, I. G. In Proceedings of 4th European Technical Symposium on Polyimides and High Performance Polymers, LEMP/MAO, University Montpellier, 1996; Vol. 2, p 318.
17. Hsieh, A. J.; Desper, C. R.; Schneider, N. S. Polymer 1992, 33, 306.
18. Nielsen, L. E. Mechanical Properties of Polymers and Composites; Marcel Dekker: New York, 1974.
19. Nuriel, H.; Klein, N.; Marom, G. Compos Sci Tech 1999, 59, 1685.
20. Incardona, S.; Migliaresi, C.; Wagner, H. D.; Gilbert, A. H.; Marom, G. Compos Sci Tech 1993, 47, 43.