In Situ Polymerization and Nano-Templating Phenomenon in Nylon Fiber/PMMA Composite Laminates

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ABSTRACT: Supercritical Carbon Dioxide (SC CO_2) is used as a reaction/processing medium in the fabrication of fiber-reinforced composite materials. SC CO_2 allows resin (reactive monomer), to penetrate inside the fibers themselves, partitioning into the amorphous regions of the fiber. The crystal structure then templates polymerization of matrix within the fiber. This process produces a composite that exhibits ultralong-range order from the nanoscale reinforcement of crystals to the macroscale fiber reinforcement of matrix. In addition, SC CO_2 lowers resin viscosity and aids in wetting out Nylon 6,6 fiber reinforcement in a process similar to reaction injection molding (RIM) or resin transfer molding (RTM). This article will discuss the fabrication technique in detail, including process parameters and the structure of resulting composites and morphology of modified fibers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1600–1607, 2003

Key words: composites; reinforcement; nylon

INTRODUCTION

Fiber-reinforced composite materials are an indispensable part of our modern world. With their high strength and low density they are steadily replacing heavier structural materials in applications from automobile engine components and state of the art fighter jet fuselages to civil infrastructure. The use of these materials has drastically increased fuel efficiencies and made possible structures that would not have been possible using conventional materials. As the demand for these materials increases, so does the need for improved fabrication techniques. To this end a great deal of academic and industrial work has focused on improving fabrication techniques as well as composite properties.

In recent years the most popular methods for composite fabrication are Resin Transfer Molding (RTM) and Structural Reaction Injection Molding[1] (SRIM). These techniques allow for the highest throughputs while still being flexible enough to accommodate relatively complicated pre-form geometries. The first step of a RTM process is the placement of a fiber pre-form in the mold cavity. The mold is then clamped shut and resin is injected into the mold where it flows through the reinforcing preform, expelling the air and wetting the fibers.[2] Optimal resin viscosity is in the range 200–300 cps. When the resin has completely filled the cavity, the flow is stopped and the cure begins. Cure schedules for RTM vary from several minutes to several hours.

In SRIM the mold and pre-form preparation are similar to RTM. The main difference is that the resin is injected into the mold very rapidly, and cure occurs in a matter of seconds.[3] Because of the need for rapid impregnation, SRIM requires lower viscosity resins and is more sensitive to pre-form construction.

Although there are distinct differences between RTM and SRIM, those differences are slowly being eroded. The need for faster cycle times in RTM and slower cures in SRIM to allow for larger parts is bringing the two techniques together. As mentioned, an important aspect of either technique is the viscosity of the resin. If the resin does not completely wet out the fiber reinforcement, voids will act as flaws, diminishing composite strength dramatically.

The true strength of any composite comes from its fiber reinforcement. Therefore, regardless of the composite fabrication technique employed, superior composite strength cannot be attained without excellent adhesion between fiber and matrix.[4] Without this adhesion, load cannot be efficiently transferred from matrix to fiber, and poor composite properties will result. Given that fiber and matrix are generally incompatible, fibers are always pretreated with compatibalizers called sizings to ensure adhesion between fiber and matrix. There are a wide variety of fiber sizing tech-

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niques. Glass fiber is most often treated with organosilanes, which form a covalent attachment to the glass and produce an organophilic surface for the matrix.[5] Although some organic fibers utilize small molecule sizings similar to the organosilanes, many require oxidative etching of the surface either by acid treatment or plasma.[6,7] The oxidized surface presents organic functionality to the resin, allowing for covalent bonding. Fiber sizing is expensive and utilizes environmentally toxic chemistry. Having the capacity to fabricate composites from unsized reinforcing fibers would simplify fiber processing and diminish the use of environmentally unfriendly processes.

In our work we explore the feasibility of employing supercritical carbon dioxide (SC CO_2) as a reaction/processing medium for the fabrication of fiber-reinforced composite materials. Although SC CO_2 is an excellent solvent for most small molecules, it is a nonsolvent for most polymers (notable exceptions being some siloxane and fluorinated polymers). SC CO_2 does, however, swell most polymers very efficiently. Swollen polymers exhibit a significant increase in free volume, and hence, a commensurate decrease in glass transition temperature and viscosity.[8] Several researchers have employed SC CO_2 in polymer and prepolymer melt flows and extrusion to take advantage of the reduced viscosity.[9] In addition, a significant amount of work has emerged elucidating the use of SC CO_2 as a unique solvent for polymer chemistry.[10] McCarthy et al.[11] have shown that monomer can be diffused into the amorphous regions of swollen host polymer and polymerized *in situ*. By this process they have made some very interesting kinetically trapped polymer blends. They have also shown that this polymerization is confined to the amorphous regions of semicrystalline polymers, and that in some cases, crystalline lamellae can actually template the polymerization in an ordered fashion.[12] Because SC CO_2 is a gas under ambient conditions, it can be completely removed after the reaction is complete.

In this article we investigate the use of SC CO_2 as a processing aid during composite fabrication. During this process the resin, dissolved in CO_2, can more effectively wet out the fiber surfaces. In addition, the CO_2 allows the resin to penetrate the fibers themselves, creating an interwoven structure between fiber and matrix. The processing parameters of this technique are explored as well as the resulting composite structure and fiber morphology. Given the interwoven fiber/matrix nature of these materials it is expected that fiber properties as well as overall composite mechanical response will be greatly affected. The mechanical testing of these composites is ongoing, and will not be addressed here.

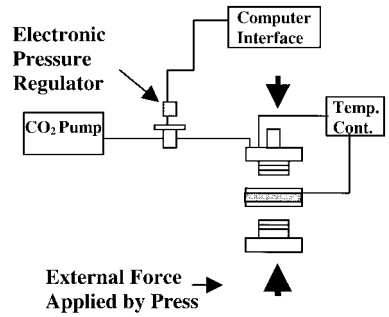

Figure 1 Schematic diagram of mold and SC CO_2 delivery system.

EXPERIMENTAL

Nylon 6,6 (Nylon) fiber was obtained in the form of a bidirectional fabric. The Nylon is 45% crystalline by Differential Scanning Calorimetry (DSC) and has an average fiber diameter of 28 microns. Methyl methacrylate (MMA) monomer, styrene monomer, and tertiary butyl-peroxybenzoate (TBPB) were obtained from Sigma–Aldrich and distilled over reduced pressure before use. Coleman grade Carbon Dioxide was purchased from Merriam Graves and used as received.

Composites were fabricated in a custom high-pressure apparatus specifically designed to allow the application of a compressive force to the samples while in the presence of SC CO_2 under controlled temperature and pressure as shown in Figure 1. The details of this experimental apparatus have been discussed elsewhere,[13] but for thoroughness, the main points will be reiterated here. The mold is mounted in a PHI 40,000 lb hydraulic press. CO_2 is supplied via an inlet port on the apparatus by a Thar Designs high-pressure carbon dioxide pump. The CO_2 pressure is controlled via a Tescom ER3000 electronic pressure regulator with a computer interface that allows for exact control of CO_2 pressure as well as rate of pressurization or depressurization. Thermocouples penetrate the body of the mold and allow for accurate monitoring and control of temperature.

The fiber reinforcement in the composites fabricated herein consisted of a Nylon 6,6 bidirectional fabric. Five layers of the Nylon fabric are stacked to form a flat plaque, then placed in the mold and sufficient MMA or styrene (with 300:1 ratio of TBPB initiator) is added to completely cover the fibers. The mold is then closed and placed in the PHI press with between 0 and 22 kN (5000 lbs) of compressive force. The mold is then pressurized to between 10 and 14 MPa (1500 and 2000 psi) of CO_2 at room temperature and the main valve is closed creating a closed system. The preform is then allowed to equilibrate at 60°C for 4 h and then the temperature is increased to 110°C for 6 h. After

reaction the temperature is allowed to drop and the mold is then reopened to dynamic pressure control from the ER3000. The pressure is then dropped slowly to 0 MPa over a 15 h period. Although this depressurization period is necessary to prevent foaming of the matrix material, it has not been optimized and may well be reduced to a few hours in the future.

Composite samples were potted in epoxy and polished on a polishing wheel for analysis on an optical microscope. Transmission electron microscopy (TEM) was done on a JEOL 100CX instrument at 100 kV to monitor changes in microscale fiber morphology. Samples fabricated with styrene as matrix resin were cryomicrotomed in a longitudinal direction on a Reichert-Jung FC4 Cryo-Ultramichrotome and stained with ruthenium tetroxide vapor for 30 min to provide contrast.

Small-angle X-ray scattering was run on a Rigaku RU-H3R Rotating Anode Diffractometer with a multilayer focusing optic and evacuated Statton type camera to determine fiber long spacings. Differential Scanning Calorimetry (DSC) was conducted on a TA Instruments machine with a DuPont modulated DSC attachment. Gel permeation chromatography was run on a Polymer Laboratories LC1120 with a refractive index detector.

The weight percent of actual Nylon in the final composite is a crucial value that is necessary to determine the percent crystallinity of the modified Nylon via DSC. As the Nylon and matrix polymethyl methacrylate (PMMA) cannot be separated without destruction of morphology, they must be analyzed as a unit. To this end, a thermal cycling experiment was designed to extract the thermal properties of the Nylon from that of the overall composite. As a point of reference, Nylon fabric was placed in the DSC and heated to 280°C at 5° per min; (T_m = 258°C). The temperature was then held at 280°C for 10 min to completely erase the Nylon's initial thermal history. After the 10-min hold the sample was cooled at 5°C per min back to room temperature. After cooling, the sample was then reheated at 5°C per min to 280°C, and subsequently cooled again (Fig. 2). Nylon fiber crystallinity was then calculated based on the first heating cycle to be 45%. The 280°C hold and subsequent cooling then served to erase the initial thermal history and impose a known thermal history on the Nylon. When the second heating was undertaken, this known thermal history was seen to produce a percent crystallinity of 35% in the Nylon. Given that the percent crystallinity is a function of the crystallization kinetics and the thermal history, this standard thermal history will always produce the above stated 35% crystallinity.

Before employing the above-stated thermal experiment towards composite characterization, it is important to know how the PMMA will react to the temperatures involved. To determine this a thermal gravimetric analysis (TGA) was run with the same thermal conditions as the DSC specified above. Under these conditions the PMMA was found to lose 12.5% of its mass after the first heating run and 20% by the end of the second heating. This mass loss is not uncommon for PMMA, and is the result of a depolymerization reaction. The severity of the mass loss is proportional to the molecular weight of the PMMA as this depolymerization is initiated at chain ends. For the purposes of this experiment all calculations were modified to account for the loss of mass of the PMMA. Incidentally, although an energy exotherm may be expected for the depolymerization, this is not noticeable in the DSC data, and is therefore not considered a matter of concern.

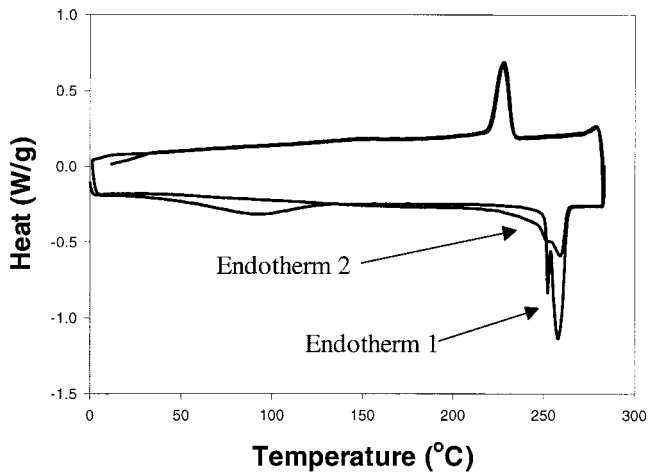

Figure 2 DSC thermal cycling experiment for Nylon 6,6 fiber.

DISCUSSION OF RESULTS

In the discussion that follows the details of a unique fiber reinforced composite fabrication technique involving the *in situ* polymerization of resin in and around fibers in a SC CO_2 environment will be discussed. The application of SC CO_2 as a reaction/processing medium in this fabrication process will be discussed as well as its effects on composite integrity and fiber morphology.

Fabrication process

The SC CO_2-assisted composite fabrication technique discussed in this work is very similar to that of a SRIM or a RTM process, with the obvious added condition that it is run under pressure. As SC CO_2 is known to decrease the viscosity of polymers and/or prepolymer during flow,[9] it is conceivable that with this apparatus,

more viscous resins could be employed in rapid infusion of pre-forms much like a SRIM process. However, the secondary effects of fiber impregnation requires long cure schedules, similar to an RTM process. Although MMA and styrene thermoplastic resins are used for these experiments, the technique is applicable to many resins that may be of higher viscosity or thermoset in nature.

In the first step of this process resin and thermal initiator are injected into the mold with the fiber preform. In the case of low viscosity resins like MMA or styrene, excellent wetting occurs almost immediately. With higher viscosity resins the initial injection may not wet all surfaces. The second step of the process is the pressurization with CO_2 and equilibration at 60°C. When the mold is filled with SC CO_2 the resin is partially dissolved in the organophilic solvent. The almost zero surface tension of SC CO_2 allows it to carry the resin throughout the mold, wetting all surfaces. The CO_2 also swells the Nylon fibers, carrying resin and initiator in with it. Resin partitions itself only in the amorphous regions, shying away from the denser crystalline regions.[11]

After equilibration, the cure process begins by increasing the temperature to 110°C. The radical chain polymerization that ensues is heterogeneous in nature owing to the fact that although most small molecules are soluble in CO_2, polymers are not. Therefore, as the growing chain reaches a critical molecular weight, it crashes out of solution, and although the polymerization continues, the kinetics are significantly altered. The PMMA polymerized in this manner was analyzed via gel permeation chromatography (GPC) and determined to have an M_w, of 493,000 with a PDI of 2.24.

Because the resin is polymerized within the fiber as well as without, it is assumed that some portion of the resin polymer crosses the fiber/matrix interface. This would, in theory, lead to excellent adhesion between the fiber and the matrix without the need for chemically specific and expensive sizing agents. The mechanical ramifications of this crossboundary polymerization as well as the effects on fiber and overall composite strength are the focus of future work and will not be discussed here. Instead, the focus of this work is on the effects of processing conditions on composite structure and morphology.

Optical microscopy and SAXS

After fabrication, samples were cross-sectioned on a wafering saw and analyzed via optical microscopy. For purposes of comparison a control was fabricated as described previously with a minimal compressive force (sufficient for intimate fabric contact), and no CO_2 was employed.

In the control composite (CC) (Fig. 3A), integrity is good, with excellent wetting of the fabric and no obvious voids. This is not surprising given the low viscosity of the MMA. The fibers themselves are unchanged with an average diameter of 28 microns and a long spacing as measured by SAXS of 73A, both identical to the unmodified Nylon fabric (Fig. 4). The volume fraction of fiber in this sample is 75% as measured optically by cross section (Table I).

The next composite (C1) (Fig. 3B), was fabricated with the use of SC CO_2 at 14 MPa (2000 psi) CO_2 pressure and 2.8 MPa (5000 lbf) of compressive force. In this sample we see a pronounced increase in the average fiber diameter from 28 to 37 microns, and the long spacing is increased to 75A from 73A. The percent fiber volume has also increased significantly to 85%. This increase in fiber diameter and corresponding increase in long spacing are attributable to a swelling of the fiber with MMA monomer and ultimately with polymerized MMA. It is important to note that no void formation is apparent within the fibers.

It is also apparent in composite C1 that the fibers have grown to the extent that they have impinged on each other. The growth in these fibers was apparently inhibited by the volume constraint put on the fibers by the initial compressive force.

To verify this relationship between initial compressive force and fiber swelling, a third composite (C2) (Fig. 3C) was fabricated, in the presence of SC CO_2 with minimal compressive force. Under these unconstrained conditions, the fiber diameter increases to 103 microns, with an increase in long spacing to 83A. Although the fibers in composite C2 have grown to touch each other, they have not deformed to completely fill volume as composite C1 did; this is observed in the drop in fiber volume to 81% from the 85% of composite C1.

These results indicate a degree of control over both resin uptake in the fiber, as well as overall fiber volume in the composite (Table I). This control is important, given that fiber volume is an important factor in the final mechanical properties of the composite. The control over resin uptake is also very important, as this will certainly affect the mechanical characteristics of the fibers themselves.

Thermal analysis

As discussed in the previous section, the long spacing as measured by SAXS is seen to increase with the increase in fiber diameter. In fibers like these the long spacing is a measure of the thickness of crystalline lamellae plus amorphous region. Except in the case of extremely high-performance fibers like Kevlar or Dynema, the amorphous region is generally significantly larger than the crystalline region. Given that

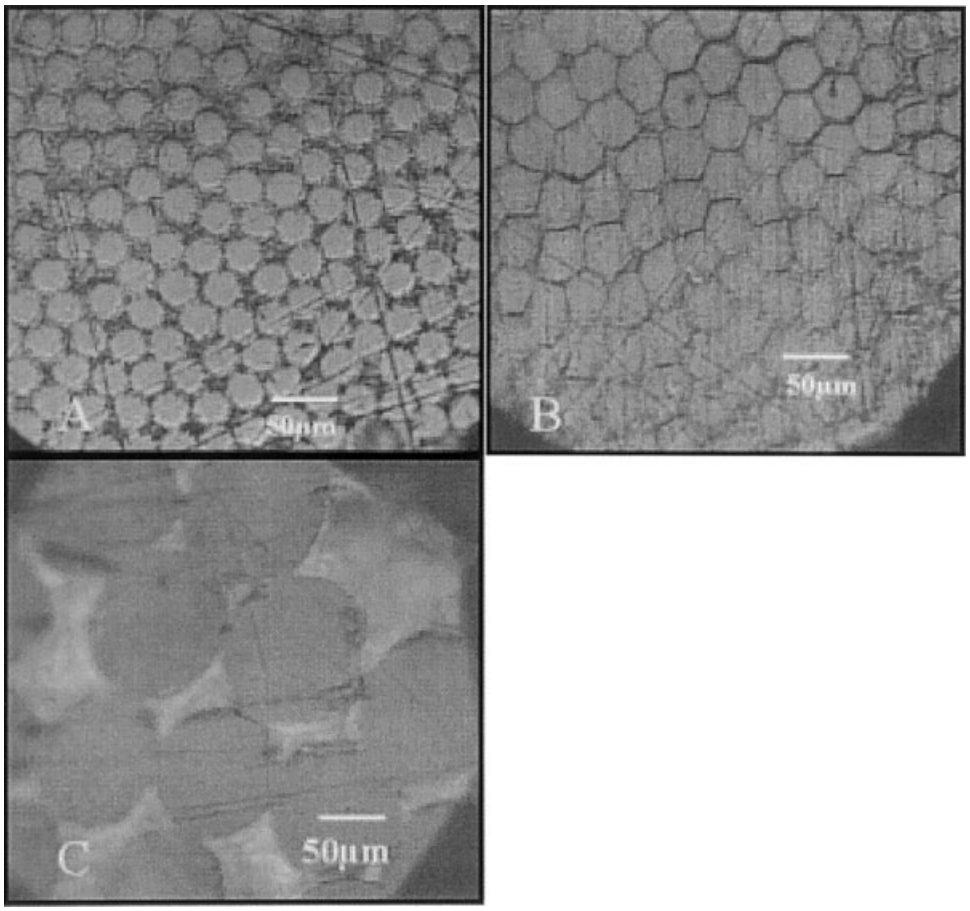

Figure 3 Optical image of composite cross-sections at 20× magnification. Fibers exhibit an increase in diameter as a function of applied normal force in SC CO_2. Control Composite CC (A), Composite C1 (B), and Composite C2 (D).

some semicrystalline polymers have been seen to anneal during SC CO_2 processing at elevated temperatures,[15] it is important to verify that increases in long spacing are not due to annealing of crystals. To verify this, a control experiment was run with Nylon fabric soaked in SC CO_2 under identical thermal conditions as the composite fabrication discussed previously. The results of DSC analysis showed that there was no change in percent crystallinity or melting temperature of the Nylon compared to the untreated Nylon fabric. These results indicate that Nylon crystallinity does not change simply by processing it at elevated temperatures in SC CO_2.

Using the Nylon reference information from the experimental section of this article, a sample of Nylon/PMMA composite was placed in the DSC and submitted to the same thermal cycling experiment discussed. The constrained composite, C1, was chosen for this experiment because it possesses the most promise for a practical composite system with minimal fiber modification. It is important to note that although the PMMA adds mass to the sample, it does not produce any endotherm or exotherm of energy

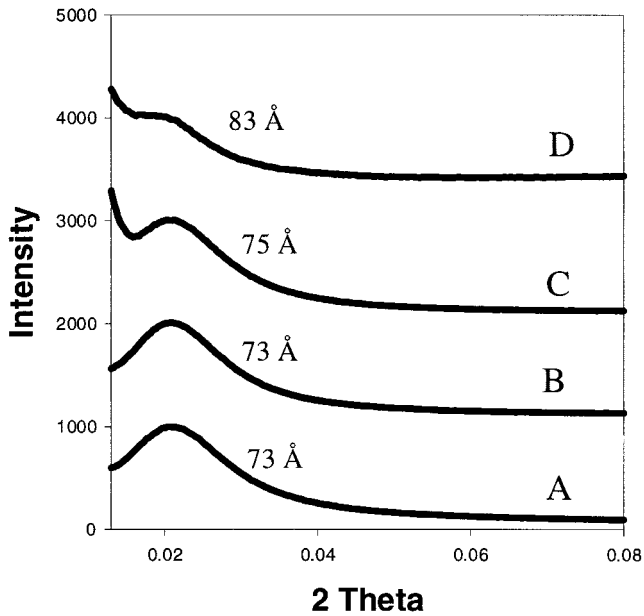

Figure 4 SAXS for Nylon 6,6 (A), Control Composite CC (B), Composite C1 (C), and Composite C2 (D). Increases in d-spacing are evident with increasing PMMA incorporation in the Nylon 6,6.

TABLE I
Effects of Compressive Load During Fabrication

Sample	Compressive load (MPa)	Avg. fiber diam. (m)	Fiber content by vol. (%)
CC	0.3	28	75
C1	2.8	37	85
C2	0.3	103	81

over the melting range of the Nylon. In this case the energy absorption measured on the initial heating cycle, although completely related to the Nylon, could not be used directly to calculate the percent crystallinity because the exact mass of the Nylon in the sample is unknown. However, after erasure of the thermal history and the imposing of a known thermal history as discussed, it is assumed that the Nylon in the composite sample should produce the same percent crystallinity as that seen in the second heating of the control experiment, 35%. This is based on the knowledge that at 280°C, the Nylon and PMMA, both in a liquid state, will phase separate, and that, during cooling, the PMMA will then have no effect on the crystallization kinetics of the Nylon. With the knowledge then, that the second heating endotherm of the composite corresponds to Nylon with a percent crystallinity of 35%, one can then backcalculate the mass of Nylon in the composite based on the heat of fusion of Nylon, 190 J/g. Once the mass of the Nylon in the composite is known, the initial heating endotherm of the composite can then be analyzed and a percent crystallinity of the modified fibers determined (Table II). Based on these results the wt % of Nylon in the composite is calculated to be 43%. This is different from the more conventional fiber volume parameter reported earlier, as that was based on the swollen fiber size, and did not take into consideration the PMMA inside the fibers. This wt % was corroborated by a rough gravimetric analysis that put the wt % at 40%. The percent crystallinity of the modified fibers was calculated to be 44%, compared to the unmodified fiber crystallinity of 45%. This technique was additionally corroborated by placing a known mass of PMMA and a known mass of Nylon 6,6 into the DSC pan and repeating the experiment. These results accurately

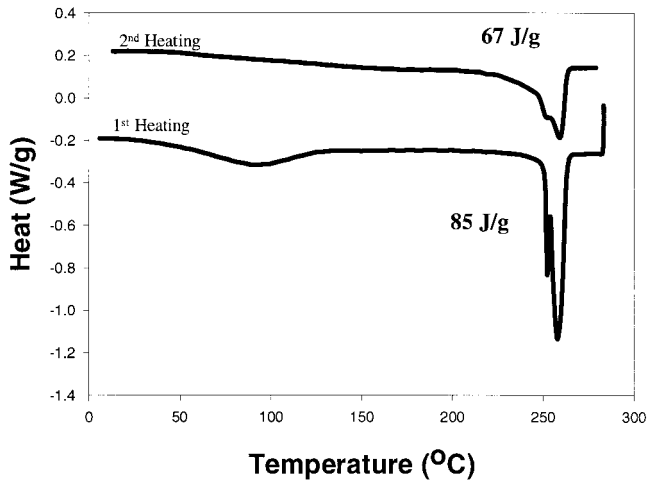

Figure 5 DSC thermal cycling of Nylon 6,6. Shown is only the first and second heating cycles.

identified the percent crystallinity of the Nylon within 4%. Given the accuracy of the experiment, it is reasonable to conclude that the modification of the fibers does not significantly reduce crystallinity.

There is an interesting artifact in the thermal analysis data that needs to be addressed. It is known that Nylon 6,6 often exhibits a double melt peak (Fig. 5). Haberkorn et al.[16] first identified this behavior in 1979, and it was later discussed by Starkweather et al.[17] This double melt peak is ascribed to the existence of two triclinic crystal structures, only differing in their degree of order. The more ordered α_1 phase is created during crystallization above 220°C, while the less ordered α_2 phase is due to crystallization that occurs below 100°C. Our control Nylon exhibits this double peak in both melting endotherms. The modified composite, C1, only exhibits the double peak on the second endotherm, and then not nearly as pronounced (Fig. 6). Initially, this was taken to be a sign of changing crystal structure in the modified fibers, however, the control composite CC, exhibits exactly the same behavior. Because the control composite, CC, is known to be unmodified, this led to the conclusion that the absence of the second peak is likely an artifact of the experiment and is not a significant indication of changing crystal structure.

TABLE II
Experimental and Calculated Results from DSC Thermal Analysis

	Endotherm 1			Endotherm 2		
Sample	Heat (J/g)	T_m(°C)	%Cryst	Heat (J/g)	T_m(°C)	%Cryst
Nylon 6,6	84.7	258	45	66.9	259	35
Composite	40.3	257	44[a]	35.6	259	35[b]

[a] Note that all calculations consider PMMA mass loss during experiment.
[b] Calculated from results.
[c] Assumed to be equal to Nylon 6,6 endotherm 2.

Fiber morphology

As mentioned earlier, the resin that impregnates the fibers is preferentially partitioned into the amorphous regions of the fiber. This preference opens up the possibility that very ordered crystalline systems could template the polymerization of resin. Figure 7 shows a TEM micrograph of a longitudinal section of a fiber in a Polystyrene (PS)/Nylon fiber composite. The styrene phase is preferentially stained dark with ruthenium tetroxide. The PS appears in bands, sometimes bead like, which have a preference to align from top left to bottom right. This image supports the earlier assertion that the crystalline structure is not destroyed in this process, as can be see from the white crystalline regions in the TEM micrograph. It is apparent from this image that even though the Nylon is only 45% crystalline, it templates the polymerization of the PS to a large extent. This templated polymerization leads to a fairly ordered morphology wherein Nylon crystals are reinforced with PS. This creates a structure with amorphous Nylon and PS sandwiched between crystalline Nylon lamellae. This morphology leads to a situation wherein the composite exhibits an ordered structure not only on the macroscale of fiber reinforcement, but also on a nanoscale of crystal structure reinforcement. This ultralong-range order, from the nano- to the macroscale is very interesting, and will no doubt have significant ramifications on mechanical behavior in these systems.

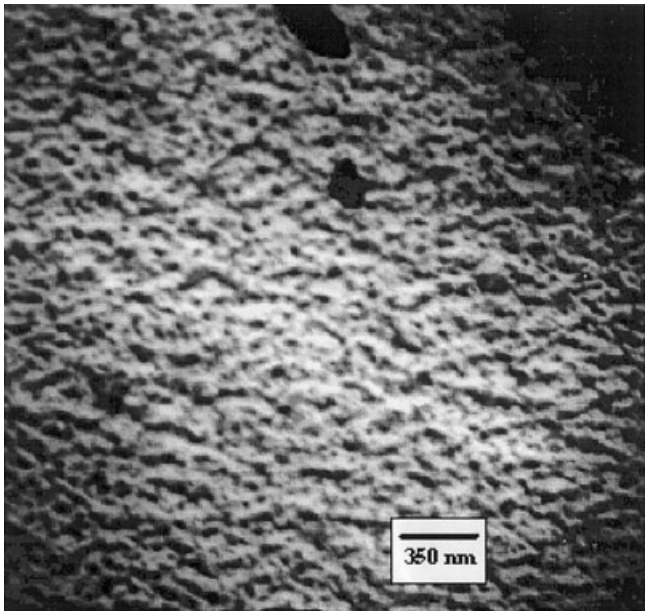

Figure 7 TEM micrograph of polystyrene modified Nylon 6,6 fiber. PS is stained black with RuO_4. The PS appears in bead-like structures that have a tendency to align from top left to bottom right.

CONCLUSIONS

In this article we have introduced a unique fiber reinforced composite fabrication technique that employs SC CO_2 as a reaction/processing medium. The processing apparatus is similar to currently used commercial processes, with the added capacity for high pressure. It is also important to note that this process is not chemistry specific, and could therefore be applied to a wide range of organic fiber/resin systems as long as the fibers exhibit some nonzero CO_2 uptake. It was shown that these composites could be made with excellent integrity, and that the fiber reinforcements themselves could be modified with resin in a controlled way. This fiber modification is shown to be templated by the ordered Nylon crystal structure. This templating effect leads to a composite with ultralong-range order from nanoscale reinforcement of crystals to macroscale fiber orientation in the composite layup. All of this is accomplished using a commercial polymer in a new environmentally friendly process.

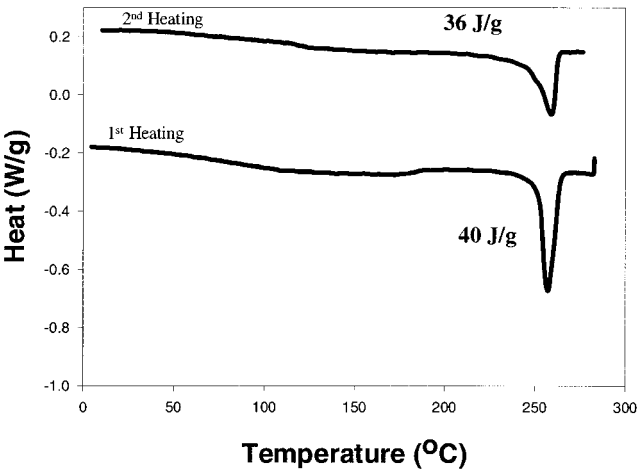

Figure 6 DSC thermal cycling for Nylon 6,6/PMMA composite. Shown is only the first and second heating cycles.

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