

# Crystallinity in the Polypropylene/Cellulose System.

## II. Crystallization Kinetics

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### SYNOPSIS

Nonisothermal differential scanning calorimetry data for neat polypropylene and polypropylene with variously treated cellulose fillers has been used to solve for the Avrami exponent,  $n$ . Results show neat polypropylene to have an Avrami exponent value very close to the theoretically expected value of 4.0. The addition of untreated cellulose fiber to polypropylene, which has been shown to produce a transcrystalline region, results in an exponent value of 2.7–2.9 for the initiation stage, followed by a value of 3.9 for the bulk stage. Treatment of the cellulose with alkyl ketene dimer, alkenyl succinic anhydride, or stearic acid results in intermediate exponent values from 2.7 to 3.9. These results verify the effectiveness of surface treatments in reducing the natural nucleating ability of cellulose. Sample mixing and filler content were also shown to play a role in the crystallization process. © 1994 John Wiley & Sons, Inc.

### INTRODUCTION

The introduction of reinforcing fillers in crystalline polymers can have a pronounced effect on the kinetics of the crystallization process. This influences the resultant morphological structure, that is, nucleation density, spherulite size and shape, as well as bulk crystallization rate. For polypropylene, the effect of various fillers on crystallization kinetics has been investigated. A number of researchers<sup>1–3</sup> found that the addition of glass fibers increased the rate of polypropylene nucleation and reduced the crystallite size. Isobutyric acid-treated sepiolite was found by Acosta et al.<sup>4</sup> to act as a nucleating agent and hence affect the kinetics of crystallization as well as the crystal structure. Kowalewski and Galeski<sup>5</sup> also found chalk to act as a weak nucleating agent that increased the crystallization rate. Carbon and Kevlar fibers have also been shown<sup>6</sup> to influence the kinetics of polypropylene crystallization.

Crystallization kinetics can be examined using the Avrami equation<sup>7</sup> for isothermal transformations:

$$x(t) = 1 - \exp(-kt^n); \quad T = \text{const.} \quad (1)$$

where  $x(t)$  is the volume fraction of transformed material,  $k$  is a temperature dependent rate constant, and  $n$  is known as the Avrami exponent. The exponent  $n$  is assumed to indicate the type of nucleation and dimensionality of crystal growth. It should be noted that although various values of  $n$  have been given theoretical meaning (that is,  $n = 4$  for sporadically nucleating 3-dimensional spherulites;  $n = 1$  for rods or disks simultaneously nucleated), the situation is more complicated when a filler is introduced in the crystallizable polymer. Certain areas of the filler may initiate nucleation prior to bulk nucleation, or the filler may inhibit normal crystal growth due to its close proximity to the nucleation center. Hence, values of the Avrami exponent that are calculated for two-component systems are actually composite values of several simultaneous events.

In order to calculate the Avrami exponent using differential scanning calorimetry (DSC) data, the

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nonisothermal crystallization method developed by Harnisch and Muschik<sup>8</sup> can be used. When two constant cooling rates  $\beta_1$  are used,

$$n = 1 + \left( \ln \frac{\dot{x}_1}{1 - x_1} - \ln \frac{\dot{x}_2}{1 - x_2} \right) / \ln(\beta_2/\beta_1);$$

$$T = T_c \quad (2)$$

where  $x = x(t)$  is the volume fraction of transformed material, and  $\dot{x} = \dot{x}(t, T)$  is the rate of crystalline material formation. On a DSC crystallization curve,  $x$  is calculated by integrating the curve to a particular crystallization temperature,  $T_c$ , and  $\dot{x}$  is equivalent to the absolute height of the thermograph trace at a particular crystallization temperature,  $T_c$ . The limits to this application are from  $x = 0$  up to the temperature where  $x \approx 50\%$ . Above this point, application of the Avrami equation is known to be invalid because the transformation has proceeded beyond the primary crystallization process for which it applies.

As reported in a previous article,<sup>9</sup> cellulose fibers act as natural nucleating agents for polypropylene, and surface treatment of these fibers reduces this ability. The focus of this study was to use nonisothermal DSC crystallization studies to investigate the effects of treated and untreated cellulose fibers on the crystallization kinetics of polypropylene.

The surface treatments investigated were alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), and stearic acid. AKD and ASA are both chemical sizing agents widely used in the alkaline papermaking process to increase the hydrophobic

**Table I Results of Avrami Exponent Calculation**

Sample	$n_{1-2}$	$n_{2-3}$
PP	4.1 ± 0.2	4.0 ± 0.2
PP/cellulose		
Unmixed		
Initiation	2.7 ± 0.2	2.9 ± 0.2
Bulk	—	3.9 ± 0.9
Well-mixed		
Initiation	1.1 ± 0.6	— <sup>a</sup>
Bulk	4.2 ± 0.5	5.1 ± 1.3
PP/AKD-treated	3.8 ± 0.1	3.9 ± 0.5
PP/ASA-treated	3.5 ± 0.1	3.0 ± 0.5
PP/stearic acid-treated	2.7 ± 0.1	2.9 ± 0.1

1 = 10°/min; 2 = 5°/min; 3 = 2.5°/min;  $n_{1-2}$  and  $n_{2-3}$  are Avrami exponents calculated from experiment data for rates 1 and 2 and 2 and 3, respectively. PP, polypropylene.

<sup>a</sup> Curves do not overlap.

**Table II Crystallization Characteristics of DSC Thermograms**

Sample (PP/Cellulose)	$T_{on}^a$ (°C)	$T_f^b$ (°C)	Peak <sup>c</sup> (°C)	Crystallinity <sup>d</sup> (%)
10°/min cool				
Neat PP	123.3	101.4	110.9	46.3
PP/untreated	131.1	100.1	113.8	47.0
(Well-mixed) <sup>e</sup>	129.4	104.0	115.6	47.7
PP/AKD	124.7	100.6	111.8	46.9
PP/ASA	125.8	101.8	111.4	45.6
PP/stearic acid	128.1	101.9	112.8	46.7
5°/min cool				
Neat PP	125.7	105.9	115.3	45.8
PP/untreated	131.7	107.2	115.3	46.0
(Well-mixed)	133.0	112.4	120.3	48.5
PP/AKD	130.4	104.4	116.6	44.8
PP/ASA	128.9	106.6	116.5	46.8
PP/stearic acid	133.7	105.9	116.6	47.7
2.5°/min cool				
Neat PP	129.0	111.5	119.6	47.7
PP/untreated	136.5	110.6	119.1	49.4
(Well-mixed)	137.1	116.7	127.8	46.0
PP/AKD	132.3	108.7	119.0	49.3
PP/ASA	131.2	109.2	118.0	47.9
PP/stearic acid	135.9	111.3	119.3	47.9

PP, polypropylene.

<sup>a</sup> Temperature of crystallization onset.

<sup>b</sup> Temperature of crystallization finish.

<sup>c</sup> Average peak temperature of crystallization thermogram.

<sup>d</sup> Calculated using a value of 50.0 cal/g for 100% crystalline material.

<sup>e</sup> See text for discussion.

character of the naturally hydrophilic cellulose surface through covalent bonds to the surface.<sup>10,11</sup> Stearic acid will also create a hydrophobic surface, but without covalent bonding.<sup>12</sup>

## EXPERIMENTAL

### Materials

The polypropylene used for all DSC measurements was Danaklon SOFT 71 fiber, without any surface finishes, obtained from Danaklon A/S (Denmark). This polypropylene typically has a number-average molecular weight of 51,700 and a weight-average molecular weight of 186,000.

Avicel PH101 microcrystalline cellulose (FMC Corp.) was used for all DSC samples instead of fibers due to its greater surface area. Avicel has an average particle size of 50  $\mu\text{m}$ , a specific surface area of approximately 1.84  $\text{m}^2/\text{g}$ , and a crystallinity index of 84.5.<sup>13</sup>

The alkyl ketene dimer used was Aquapel 364 (Hercules) AKD wax, produced from a mixture of 55% stearic acid and 45% palmitic acid.<sup>14</sup> Commercial grade ACCOSIZE 18 synthetic ASA size (American Cyanamid) was also used. Impurity content for the ASA is low and consists mainly of residual olefin or maleic anhydride.<sup>15</sup> The stearic acid (99+%) used was obtained from Aldrich. All chemicals were used in reagent-grade toluene solutions to treat the cellulose.

### Treatment Method

Avicel microcrystalline cellulose was treated with AKD, ASA, and stearic acid solutions in toluene at approximately a 1 : 1 weight ratio (Avicel : treatment). Treatment time was for 10 min at room temperature. After decanting the excess solution, the fiber was allowed to air dry in a laboratory hood for 10 min. This was followed by an additional 20 min in a 105°C circulating oven for drying and/or curing. This resulted in a weight gain of approximately 0.1%. If an orientation perpendicular to the surface is assumed for all of the molecules, surface

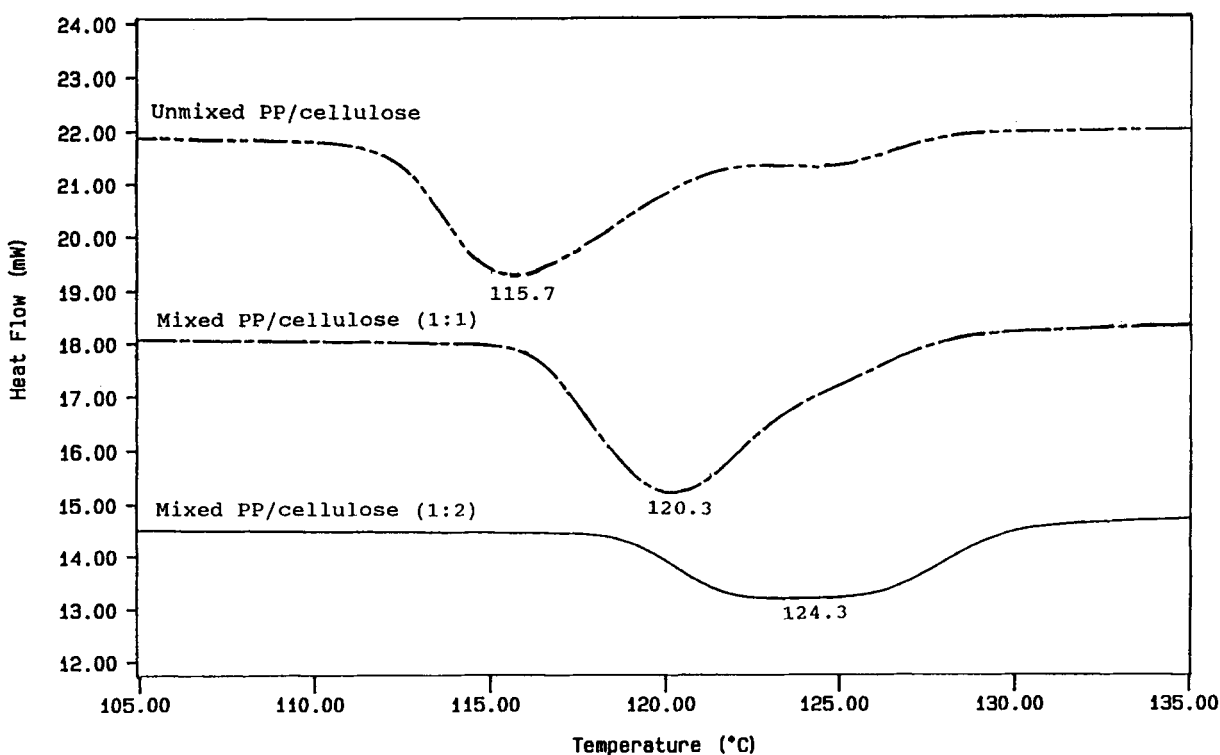
coverage is approximately 23–29% of a planar oriented monolayer (POML).

### Differential Scanning Calorimetry

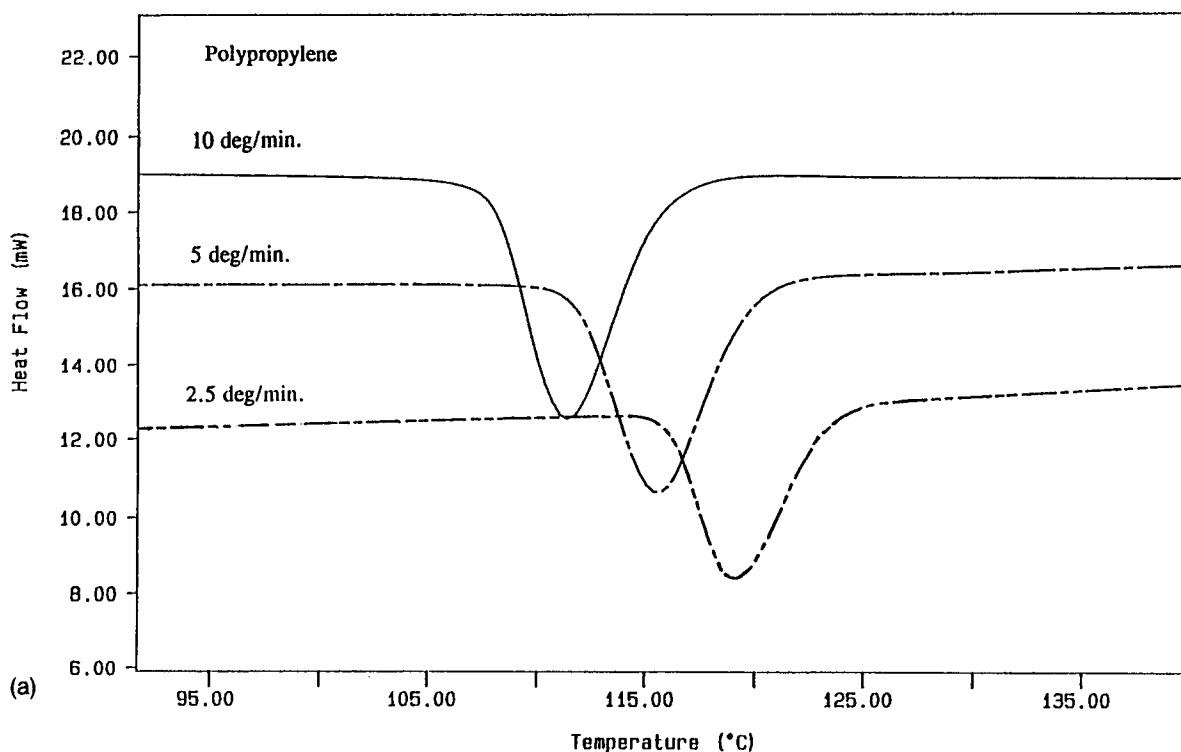
DSC samples used for the Avrami data were made by placing treated or untreated Avicel in the bottom of an aluminum sample pan and then placing polypropylene fiber on top. No premixing of the materials was done in order to avoid loss of any unreacted cellulose surface treatment before measurement.

In addition to these samples, a second set of samples were made using polypropylene fiber that had been cut into small pieces using a razor blade. This fiber was then weighed and mixed with untreated microcrystalline cellulose to produce a well-mixed sample.

DSC measurements were carried out under nitrogen using a Perkin-Elmer DSC 7 system. Three different heating and cooling rates were used: 2.5°C/min, 5°C/min, and 10°C/min. All samples were cycled from 30 to 200°C, held at that temperature for 2 min, and then cooled to 50°C. This cycle was repeated three times for samples run at 5 and 10°C/



**Figure 1** DSC thermograms of unmixed polypropylene/cellulose (top), well-mixed polypropylene/cellulose [1 : 1] (middle), and well-mixed polypropylene/cellulose [1 : 2] (bottom).



**Figure 2** Neat polypropylene (a) DSC thermogram and (b) plot of  $\ln(\dot{x}/1-x)$  versus temperature.

min, and repeated two times for samples run at 2.5°C/min. Repeated cycling was done to facilitate mixing and spreading of the polypropylene through the sample to increase interfacial contact. Data from the first cycle was not used because it was not representative of a mixed sample. Two or three samples were run (except for the well-mixed samples, where only one sample was used at each rate) to check reproducibility.

Reported data is for the final cycle of each run.

### Data Analysis

Crystallization onset and finishing temperatures were obtained from the DSC crystallization thermograms by examination of the first-derivative curve for each sample. Onset and finishing temperatures were taken as the points where the derivative curve becomes zero, indicating the start and finish of crystallization. Sample crystallinity was obtained by comparing the total heat of crystallization to a literature value<sup>16</sup> of 50.0 cal/g for a 100% crystalline material.

For calculation of the Avrami exponent, it should be noted that all quantities of  $x$  and  $\dot{x}$  were calculated on the basis of 100% crystalline polymer

weight. In addition, special treatment was given to data for polypropylene/untreated cellulose samples. As will be shown, this sample produced a shoulder peak on the DSC thermogram. In order to properly carry out the calculation for the Avrami exponent, this peak was deconvoluted into separate peaks. The shoulder peak ( $s$ ) was derived by subtracting out the curve for polypropylene/AKD-cellulose from the polypropylene/untreated cellulose curve. The polypropylene/AKD-cellulose peak was chosen for subtraction over that for neat polypropylene because the presence of a filler affects the thermal response of the sample and, due to thermal conductivity and heat transfer differences, results in a slightly broader curve. The exponent,  $n$ , was then calculated as described above, examining each of the deconvoluted curves separately. Because the Avrami calculation is valid to only  $\approx 50\%$  crystallinity, the calculation was only carried out to the midpoint of each peak.

Errors in the calculation of the exponent  $n$  may arise from uncertainty in the exact values of  $x$  and  $\dot{x}$ . When these values are very small, as is the case for the initial portion of each crystallization curve, small uncertainties result in large relative errors in the values of  $x$  and  $\dot{x}$ . As a result, the slope of the curve plotted for  $\ln(\dot{x}/1-x)$  may be lower or higher

## Polypropylene

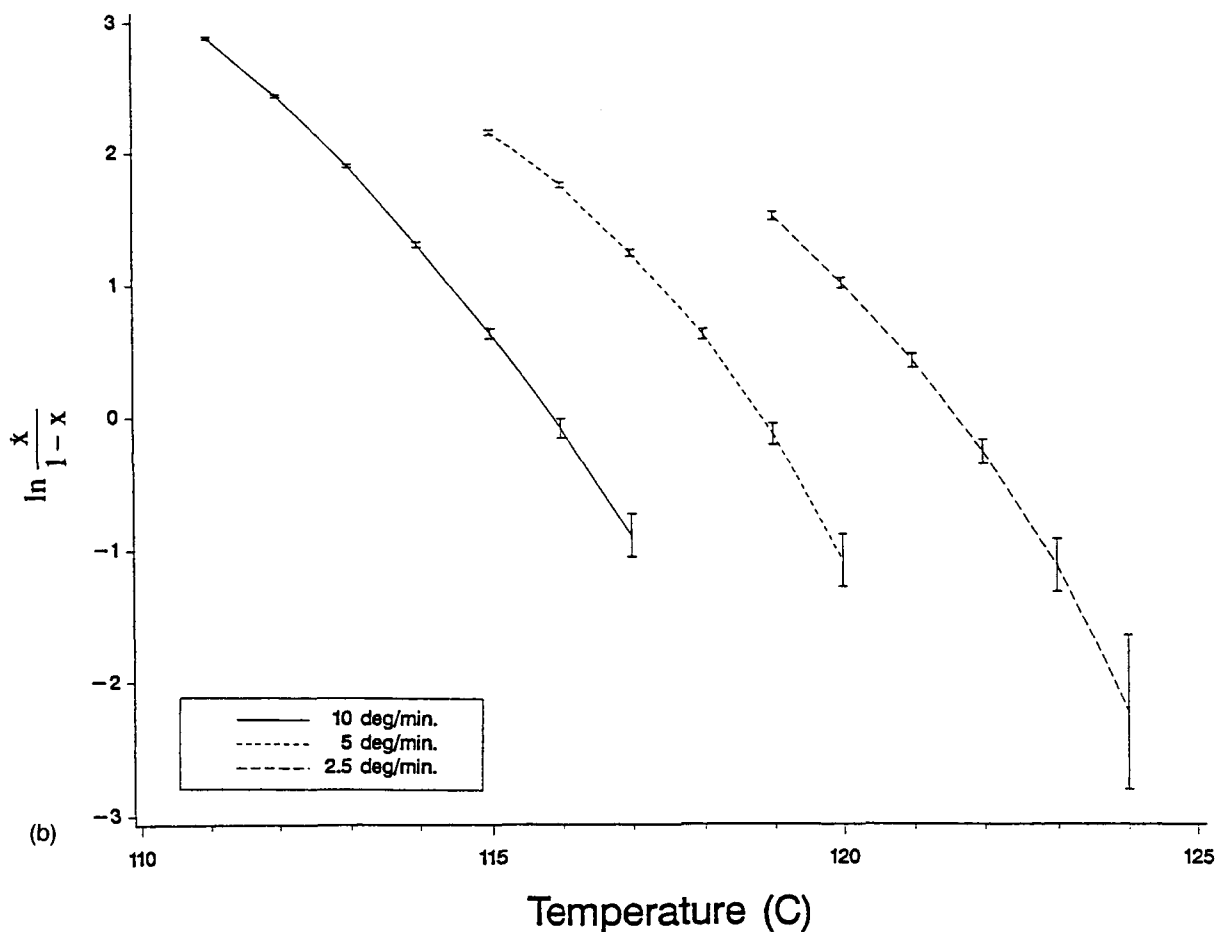


Figure 2 (Continued from the previous page)

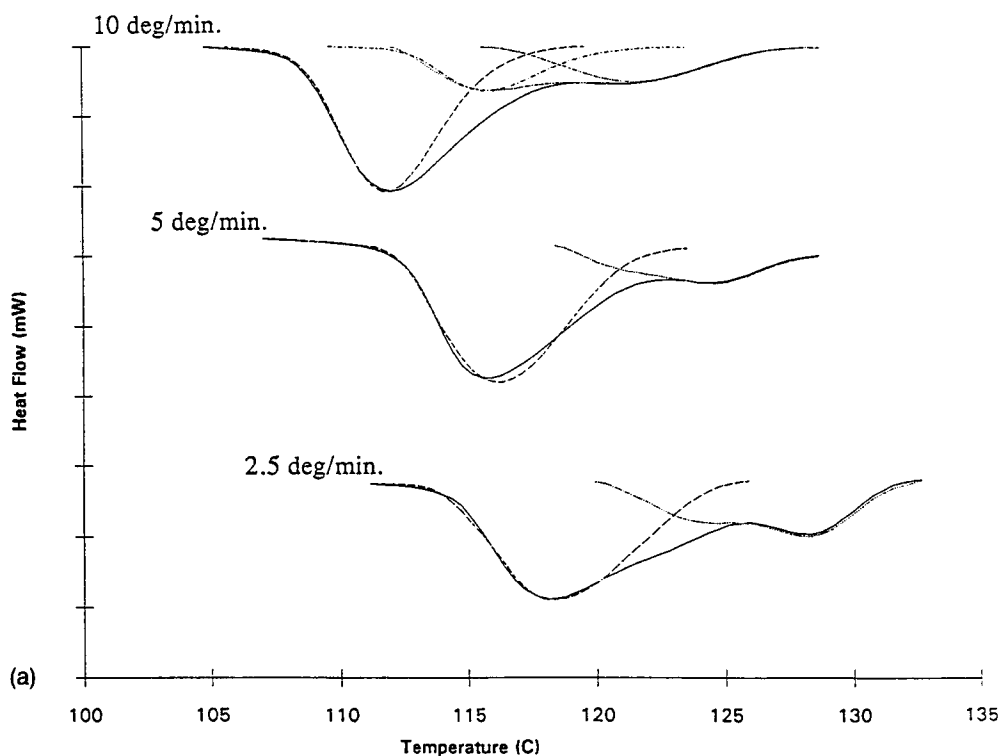
than the true value. Because  $n$  is calculated as the difference between these curves [see eq. (2)], errors in their slopes could result in incorrect values of  $n$ . Deviations in  $n$  given in Table I were calculated using an estimated error in normalized peak height ( $\dot{x}$ ) of 0.03 mW. Errors in  $x$  should be significantly smaller than in  $\dot{x}$  and were hence neglected.

## RESULTS AND DISCUSSION

Table II shows crystallization characteristics obtained from the DSC thermograms. In general, the presence of a cellulose filler (unmixed) results in a shift up in onset crystallization temperature of 1.4–8.0°. The crystallization finishing temperatures do not appear to vary in any systematic way. Little variation (0–2.9°C) in peak crystallization temper-

ature is observed for unmixed samples at all cooling rates. Sample crystallinity as measured in this experiment appears to generally increase slightly (0.5–1.0%) when a cellulose filler is present.

Also included in Table II is data for well-mixed polypropylene/untreated cellulose samples. As can be seen, onset and finishing temperatures for these samples are dramatically different than for unmixed samples. For well-mixed samples, the onset of crystallization occurs within 1–2° of unmixed samples, but finishes several degrees higher. This implies that in well-mixed samples, a greater portion of the molten polypropylene is in contact with the cellulose nucleating agent and the entire sample finishes crystallizing much sooner than for the unmixed samples, where heat transfer through the cellulose filler on the bottom of the sample pan and intimacy of contact plays a crucial role in the observed crys-



**Figure 3** Polypropylene/untreated cellulose (a) deconvoluted DSC thermograms, (b) plot of  $\ln(\dot{x}/1-x)$  versus temperature for the initial stage, and (c) plot of  $\ln(\dot{x}/1-x)$  versus temperature for the bulk stage.

tallization onset and finishing temperatures of the bulk polypropylene, even after three meltings and recrystallizations.

To further investigate the effects of nucleation on the crystallization process, a well-mixed sample was prepared that contained approximately 67 wt % cellulose fiber and 33 wt % polypropylene fiber (all other samples were closer to a 1 : 1 ratio). This sample was cycled at 5°C/min. Figure 1 shows the thermograms for an unmixed polypropylene/untreated sample (top), a well-mixed sample with approximately a 1 : 1 ratio of cellulose to polypropylene (middle), and the well-mixed sample with a 2 : 1 cellulose:polypropylene ratio (bottom). All samples were run at 5°C/min. It can be seen that the presence of a cellulose filler has a dramatic effect on the crystallization of polypropylene. For the high-cellulose content sample, it appears that a large portion of the polypropylene is in contact with cellulose and virtually the entire sample nucleates at the same time. This is much different than the unmixed sample or even the well-mixed sample with a lower filler content where interfacial crystallization and bulk crystallization appear as two distinct events. As a result, the degree of supercooling needed to crystal-

lize the samples is significantly different, as seen in the difference of 4–8.6° in peak crystallization temperatures between the samples (see Fig. 1).

Figure 2 shows examples of (a) DSC thermograms and (b) the resulting plot of  $\ln(\dot{x}/1-x)$  versus  $T$  for neat polypropylene. Figure 3 shows (a) similar deconvoluted DSC thermograms for polypropylene/untreated cellulose, as well as the results of (b) the Avrami calculation for the initial (shoulder) peak, and (c) the bulk peak. Figure 4 shows these same data for polypropylene/ASA-treated cellulose. Results similar to Figure 4 were also obtained for polypropylene/AKD-treated cellulose and polypropylene/stearic acid-treated cellulose. No shoulder peaks were observed for any treated samples. Using these data, the Avrami exponent,  $n$ , can be calculated for each sample using eq. (2).

Results of this calculation are listed in Table I. Consistent results are found when calculations are done using two different pairs of cooling rates. Neat polypropylene shows an exponent  $n$  of 4.0–4.1. Although this is significantly different from the 2.2 value reported by Harnisch and Muschik,<sup>8</sup> it is in reasonable agreement of the 4.3 value reported by Acosta et al.,<sup>4</sup> and the theoretical value of 4 that

## Cellulose/Polypropylene (Deconvoluted – small peak)

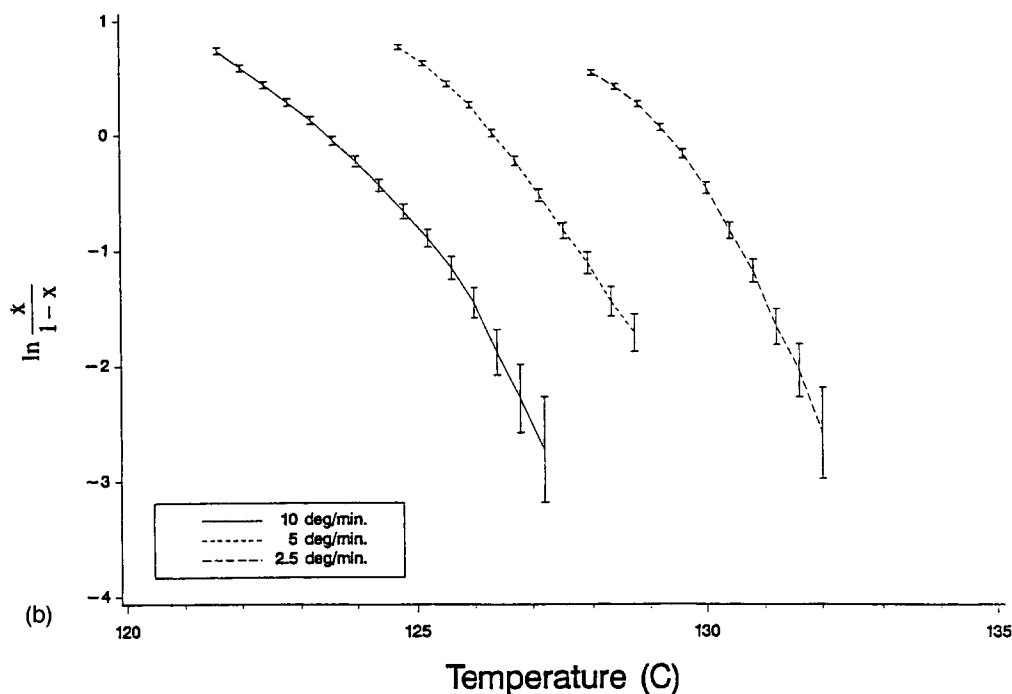


Figure 3 (Continued from the previous page)

would be expected for sporadically nucleated spherical growth.<sup>17</sup>

For the case of polypropylene with untreated cellulose, the exponent for the initial stage (i.e., the shoulder peak region) is calculated to be 2.7–2.9. These values are in between the theoretical values of 2 expected for sporadically nucleated rod-like structures and 3 expected for sporadically nucleated disk-like structures.<sup>17</sup> These results agree well with optical results<sup>9</sup> showing the formation of a sheath-like, transcrystalline region around the fiber. Growth in this region begins with disk-like structures that eventually impinge on one another to yield more rod-like structures. Hence an exponent between the theoretical values of 2 and 3 would be expected.

For the larger, deconvoluted bulk peak also shown in Figure 3(a), calculations yield an exponent (3.9) very close to the theoretical value of 4 expected for spherulitic structures sporadically nucleated. Due to the appearance of a third, intermediate small peak (discussed below) in the 10°C/min sample [Fig. 3(a)], data from the bulk peak for this sample proved to be unsuitable for use in the Avrami exponent calculation.

The effect of cooling rate on the position of the shoulder peak in relation to the bulk peak should also be noted. As the rate of cooling is decreased, the shoulder peak moves closer to the bulk peak. This suggests that the transcrystalline growth that occurs at slower rates is closer to an equilibrium structure (i.e., more perfect) than occurs at faster cooling rates. Hence, for 10°C/min cooling, the deconvoluted intermediate crystallization peak between the initiation (shoulder) peak and bulk peak could be the result of a recrystallization process that occurs in the less-perfect transcrystallized region.

For polypropylene with ASA-, AKD-, or stearic acid-treated cellulose, the exponent values are representative of the effectiveness of the treatment in suppressing the surface characteristics of cellulose that are responsible for nucleating polypropylene. Stearic acid, which is not covalently linked to the cellulose surface and is freer to migrate, yields the smallest exponent of the treated samples,  $n = 2.7$ – $2.9$ . Although optical microscopy<sup>9</sup> shows that only a few nuclei appear on stearic acid-treated cellulose, these exponent values are identical to those for the initial stage nucleation seen with untreated cellulose

## Polypropylene/Cellulose (Deconvoluted – large peak)

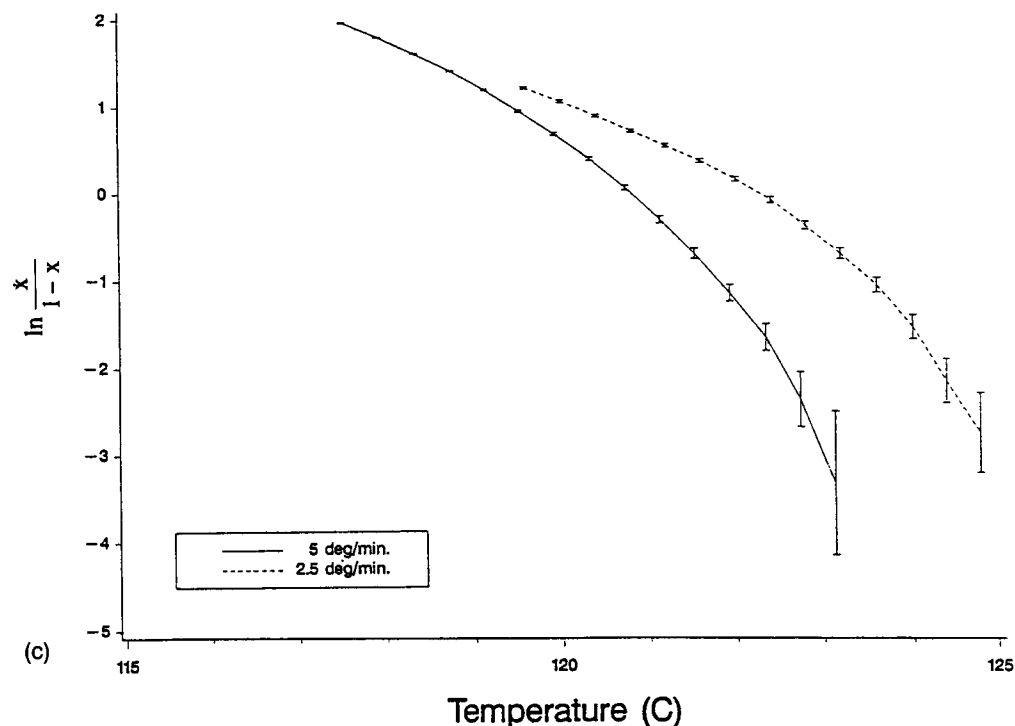


Figure 3 (Continued from the previous page)

fiber. Hence, these values indicate that stearic acid not only inhibits the formation of transcrystalline structures on the cellulose, but due to its mobility, must also play a role in the nucleation and/or growth of the bulk-nucleated spherulites. The result is an exponent value less than the expected value of 4.

ASA, with a single  $C_{16}$ — $C_{20}$  carbon chain per covalently bonded molecule, is slightly more efficient at covering the cellulose surface, with  $n = 3.0$ – $3.5$ ; AKD with two  $C_{14}$ — $C_{18}$  carbon chains per covalently bonded molecule, is the most effective, yielding a  $n = 3.8$ – $3.9$  value that is very close to the value for neat polypropylene. This suggests AKD is the most effective of the three treatments at covering the nucleating features of the cellulose with non-nucleating hydrocarbon chains. These results yield additional details about the crystallization process that are not readily available through direct optical observation.

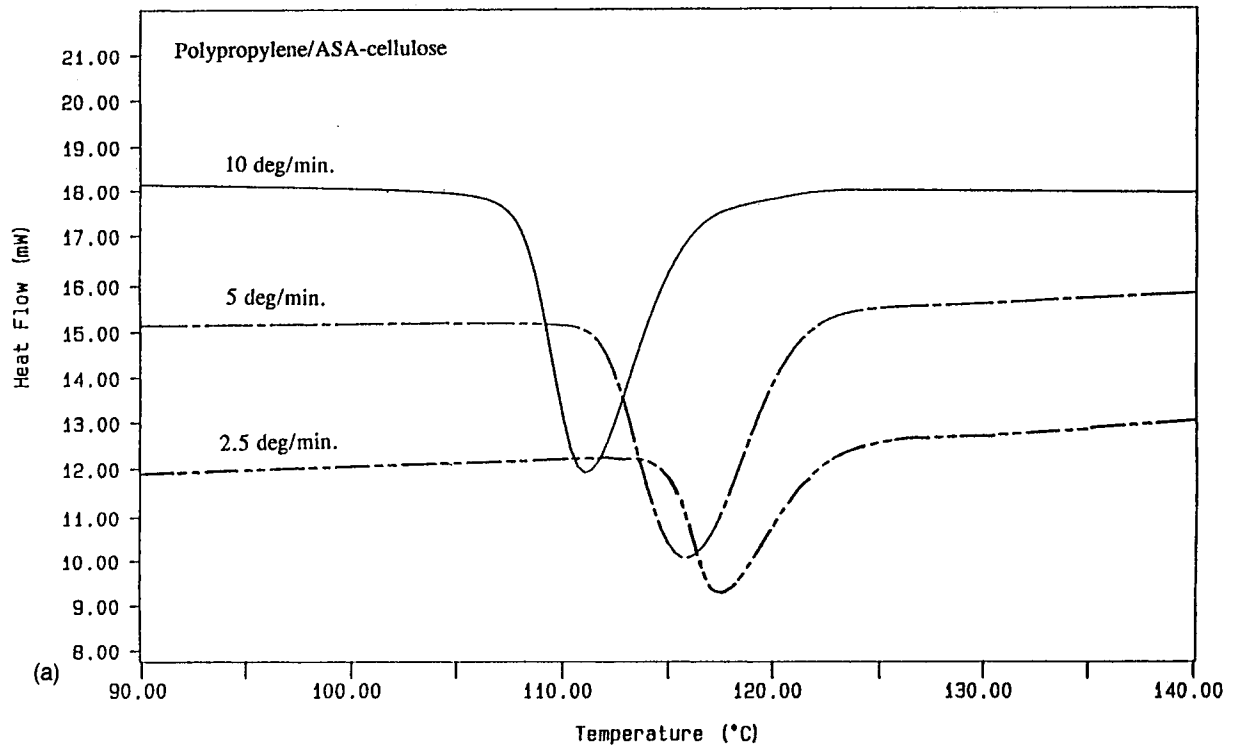
It is also of interest that polypropylene/stearic acid-treated cellulose samples show certain dynamic mechanical responses more akin to polypropylene/

untreated cellulose samples than polypropylene/ASA- and polypropylene/AKD-treated cellulose samples. This will be addressed in a future article.

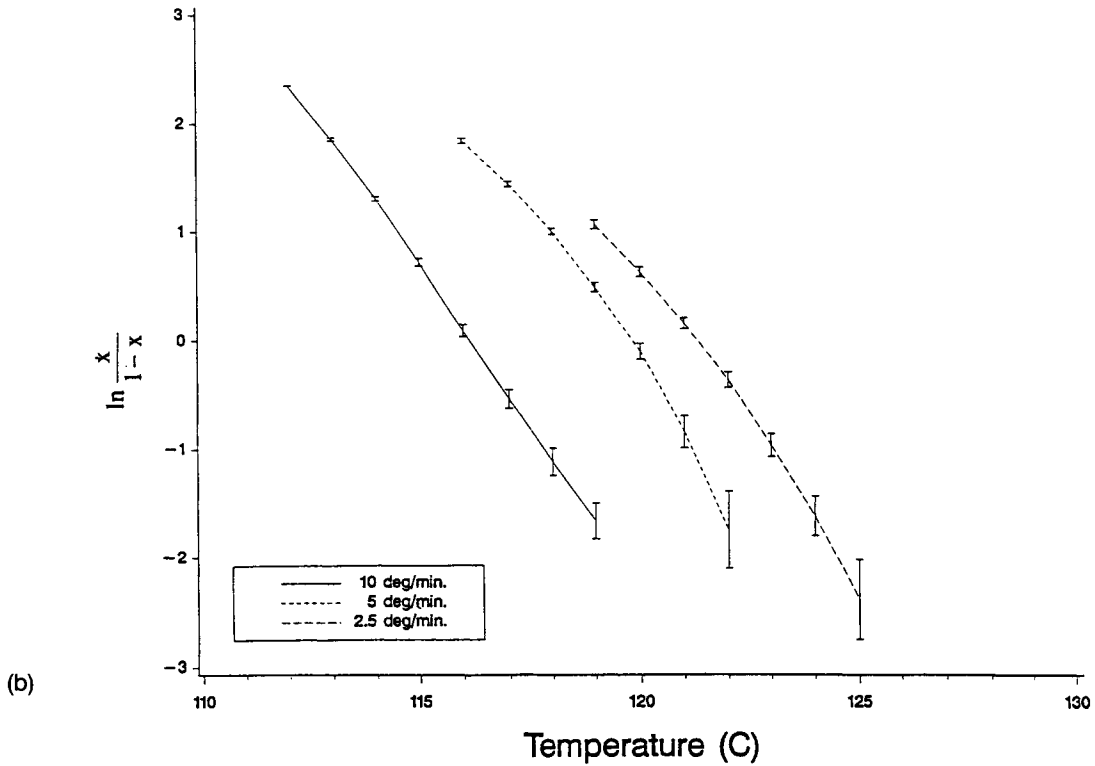
### Results From Well-Mixed Samples

DSC thermograms for well-mixed samples of polypropylene and untreated cellulose are shown in Figure 5(a). As can be seen, these samples show no separate shoulder region, but a single unsymmetric peak. This indicates that there is no distinct two-stage nucleation for these samples, as is the case for the unmixed samples (Fig. 3). But Figure 5(b) shows that this single peak can also be deconvoluted to yield distinct peaks. These peaks differ from those seen in the unmixed samples in that the onset for each bulk peak occurs much closer to the onset of the initial shoulder peak, regardless of cooling rate. For example, in samples run at  $10^{\circ}\text{C}/\text{min}$ , the onset of the bulk peak for the well-mixed sample occurs approximately  $4^{\circ}$  from the onset of the shoulder peak; for unmixed samples, this difference is approximately  $9^{\circ}$ . Differences in thermal response between the samples may account for a portion of this

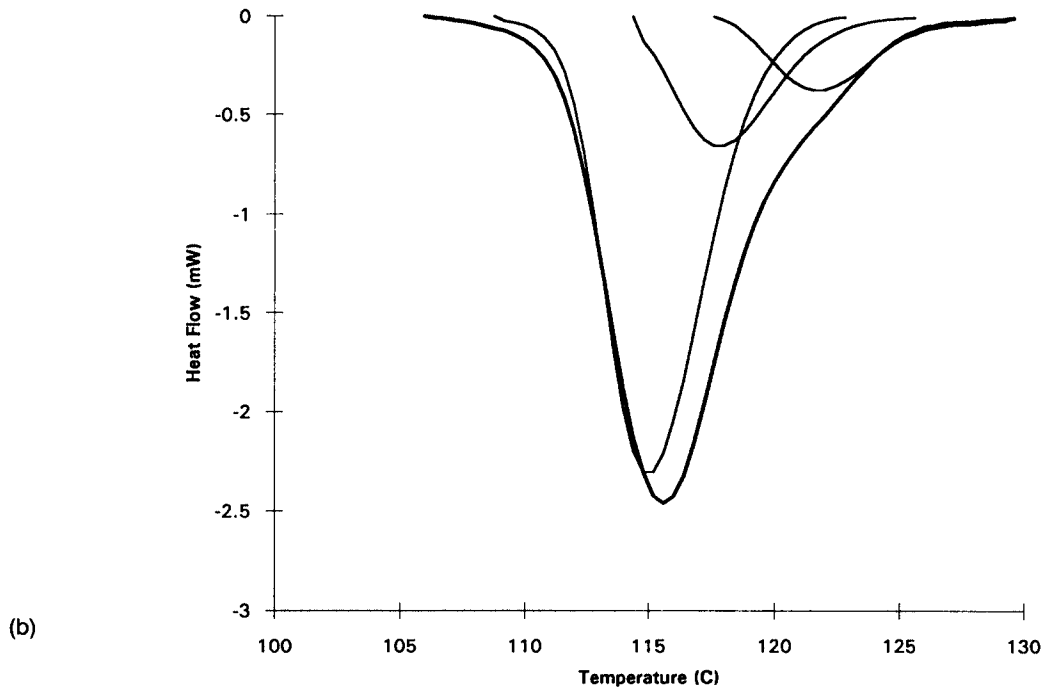
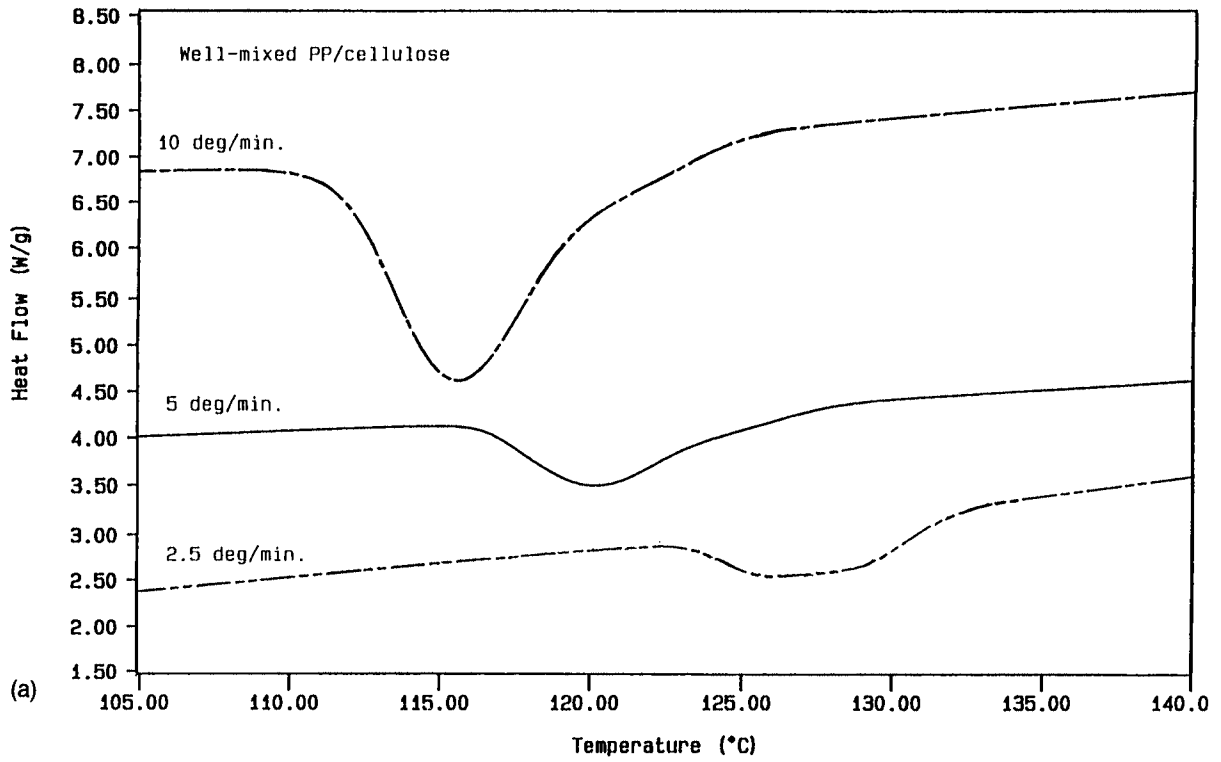




**Polypropylene/ASA – cellulose**



**Figure 4** Polypropylene/ASA-treated cellulose (a) DSC thermogram and (b) plot of  $\ln(x/1 - x)$  versus temperature.



**Figure 5** Well-mixed samples of polypropylene and untreated cellulose (a) DSC thermograms and (b) deconvoluted peak (10°C/min).

difference; however, it seems apparent that the close proximity of a larger number of growing crystallites to the bulk melt in well-mixed samples results in a smaller necessary degree of supercooling to initiate bulk crystallization.

As can be seen in both Figures 3(a) and 5(b), deconvolution of the 10°C/min peak results in three separate peaks, whether the sample is unmixed or well mixed. Because this is not apparent at slower cooling rates, this third (intermediate) peak may be a result of a recrystallization process to correct imperfections that occur in the initially nucleated crystallites. Crystallites formed at a slower cooling rate do not have these imperfections and no recrystallization occurs.

Included in Table I are results of the Avrami exponent calculation for the untreated, well-mixed samples. As can be seen, the exponent value for the initiation stage is 1.1. This value is very close to the theoretical value of 1.0 that would be expected for simultaneously nucleated rods or disks.<sup>17</sup> This suggests that for well-mixed samples, a large portion of the molten polypropylene is nucleated at the same time on the cellulose surfaces and a large amount of transcrystalline growth occurs. For the bulk peak calculation, an exponent value of 4.1–5.2 is obtained, again in good agreement with the theoretical value of 4.0 expected for sporadically nucleated spherulites.

## CONCLUSIONS

The presence of treated and untreated cellulose fibers in polypropylene has a dramatic effect on the kinetics crystallization, as determined by nonisothermal DSC analysis. The crystallization mode of neat polypropylene is characterized by random melt nucleation of spherulites; an untreated cellulose surface induces a rod- or disk-like transcrystalline nucleated structure. Surface treatments of the cellulose can markedly reduce this transcrystallization effect. In this study, AKD proved to be the most effective at preventing the cellulose surface from nucleating polypropylene, followed by ASA, and then stearic acid. This order corresponds well with the structure of the surface-modifying molecule. In addition, well-mixed samples give rise to a smaller degree of supercooling necessary to nucleate bulk crystallinity compared to unmixed samples, with increased filler content intensifying the effect. Both mixed and unmixed samples cooled at 10°C/min show an intermediate recrystallization event that is not present at slower cooling rates, which could be

due to recrystallization of the initially formed crystals.

As this study shows, factors such as surface treatment, cooling rate, intimacy of mixing, and filler content can play a significant role in the crystallization process of any filled thermoplastic. As a result, changes in the kinetics of crystallization will effect the structure and morphology of the crystalline phase and could result in measurable differences in the mechanical performance of the composite material.

The authors wish to acknowledge financial support for the project provided by USDA Competitive Grant No. 90-37291-5773 and through a generous S. C. Johnson Fellowship (D.T.Q.).

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Received February 3, 1993

Accepted October 1, 1993