"Orientation Induced Memory Effect" in Polyamides and the Relationship to Hydrogen Bonding

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ABSTRACT: The influence of molecular orientation on the "memory effect" of polyamides was investigated by differential scanning calorimetry. Melt crystallization of undrawn and drawn polyamide 6 (N6) and polyamide 66 (N66) fibers showed no difference either in the rate of crystallization or crystallization temperature. We demonstrated that hydrogen bonding does not play a major role in melt crystallization kinetics of polyamides (N6 and N66), and the "memory effect" is only retained for polymers, including N6 and N66, because of insufficient time spent above the melting temperature. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 772–775, 2003

Key words: polyamides; memory effect; melting; FTIR spectroscopy; crystallization

INTRODUCTION

In the case of semicrystalline polymers, the final structure property relationship of a product is in general dependent on a number of fabrication operations, where crystallization and orientation take place simultaneously.[1,2] Typical examples of these processes are melt spinning, drawing, and heat setting of fibers or extrusion of films. It has been shown previously that the rate of polymer crystallization is considerably influenced by impurities, additives, and nucleating agents and prior thermal history.[3] It is well documented that crystallization of semicrystalline polymers either from solution or melt is enhanced by the presence of oriented polymer chains with an extended conformation.[4]

A number of articles have been published on crystallization of polymers in oriented and deformed states.[5,6] Crystallization of poly(ether ether ketone) (PEEK) has been investigated by Porter et al.,[7] who demonstrated that the crystallization of drawn PEEK was slower than that of the undrawn PEEK films. Crystallization of polyamide films drawn at room temperature has been studied by Khanna et al.,[8] who have shown that the crystallization of drawn polyamides is different from that of other semicrystalline oriented polymers, such as polyethylene terephthalate (PET), polytetrafluroethylene (PTFE), and polyethylene (PE). The differences in crystallization behavior have been attributed to the "orientation memory effect". It has been argued that polymers containing hydrogen bonds retain the prior history much longer than other polymers that cannot form hydrogen bonds.

The purpose of this article is to revisit the effect of hydrogen bonding on the so-called "memory effect" in polyamides. The effects of molecular orientation on the crystallization, melting, and crystallization kinetics of polyamide 6 (N6) and polyamide 66 (N66) fibers were investigated. For comparison, crystallization kinetics and melting of non-hydrogen-bond-forming polymers, such as PET and PEN, were also compared.

EXPERIMENTAL

Samples

Polyamide 66 and 6 fibers, drawn to different draw ratios, were obtained from Solutia and BASF, respectively. These fibers were prepared without any additives. The birefringence, crystallinity, and orientation measurements were carried out in our laboratory and are reported in Table I.

Thermal analysis

Isothermal crystallization and melting behavior of various fiber samples were measured with a Perkin Elmer differential scanning calorimeter (DSC 7). The instrument was calibrated with indium and zinc at several times during these measurements. Onset values were used as melting and crystallization temperatures. The samples were heated to 20°C above the melting temperature and cooled down rapidly to a predetermined crystallization temperature for isothermal crystallization and cooled at the rate of 10°C/min for nonisothermal crystallization.

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TABLE I
Crystallinity, Birefringence, and Amorphous and Crystalline Orientation In Drawn N6 and N66 Fibers

Sample	Draw ratio	Crystallinity	Birefringence	f_c[a]	f_a[b]
N66	1	0.27	0.0044	0.15	0.03
	1.5	0.27	0.0133	0.25	0.15
	2	0.27	0.0192	0.38	0.21
	2.4	0.27	0.0252	0.5	0.28
	2.9	0.27	0.0331	0.64	0.38
	3.5	0.27	0.0424	0.78	0.48
N6	1	0.31	0.0120	0.35	0.04
	2	0.34	0.0430	0.65	0.45
	3	0.39	0.0520	0.81	0.50
	4	0.50	0.0580	0.86	0.50

[a] f_c is crystalline orientation.
[b] f_a is amorphous orientation.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were taken with a Nicolet 560 FTIR spectrometer attached to an Advantage microscope. A resolution of 4 cm^{-1} and 256 scans were used to collect the spectra. Polarized IR spectra were measured with the polarizer placed parallel and perpendicular to the draw direction.

RESULTS AND DISCUSSION

The objective of this study was to investigate the effects of hydrogen bonding on melt crystallization and the melting behavior of polyamides. The melting endotherms obtained for N6 and N66 fibers drawn at different draw ratios at a heating rate of 10°C/min are shown in Figure 1. It is apparent from these results

Figure 1 DSC scans of drawn polyamide fibers (a) N66 and (b) N6 on heating.

that the melting temperatures of N6 and N66 fibers depend on draw ratios. N6 shows two endothermic peaks at a draw ratio >3, suggesting that both α and γ crystal forms are present, which is consistent with our FTIR observations. On the other hand, only one endotherm is observed for N66 at a draw ratio of 1, confirming that N66 crystallizes only one crystal form. Increases in melting temperature may be attributed to differences in crystallite size. Similar observations have been made for PEEK films, where melting temperature shifts to higher values with increasing draw ratios.[7] These shifts have been attributed to crystallite size increases with increasing draw ratio. In fact, we have investigated the crystallite size of N6 fibers.[9] Crystallite size for the γ crystals in the undrawn fiber is ~33 Å and increases to ~53Å at a draw ratio of 4. Total birefringence, crystallinity, crystalline orientation, and amorphous orientation of drawn N6 and N66 fibers are presented in Table I. It is evident that crystallinity increases during drawing of N6 fibers, whereas there is no observable change in crystallinity for N66 fibers with increasing draw ratio at room temperature. On the other hand, both decreases and increases in density have been observed for several semicrystalline polymers (e.g., PET, PEEK, and PEN).

Overall crystallization rate is usually related to crystallization temperature (T_{cc}), which may be one of the critical parameters for examining the influence of the "memory effect" on melt crystallization. The crystallization curves for drawn N6 and N66 fibers on cooling from the melt are shown in Figure 2. It is clear from Figure 2 that there is no change in T_{cc} with increasing draw ratio. This result is different from a prior observation made by Khanna et al.,[8] who had demonstrated that T_{cc} of 300% stretched N6 film increased by 3–5°C from unstretched film. It was argued that polymers with strong intermolecular forces retain their orientation memory at higher temperatures. The experiment had been carried out by heating the sample to 280°C and keeping it at 280°C for 5 min, followed by cooling
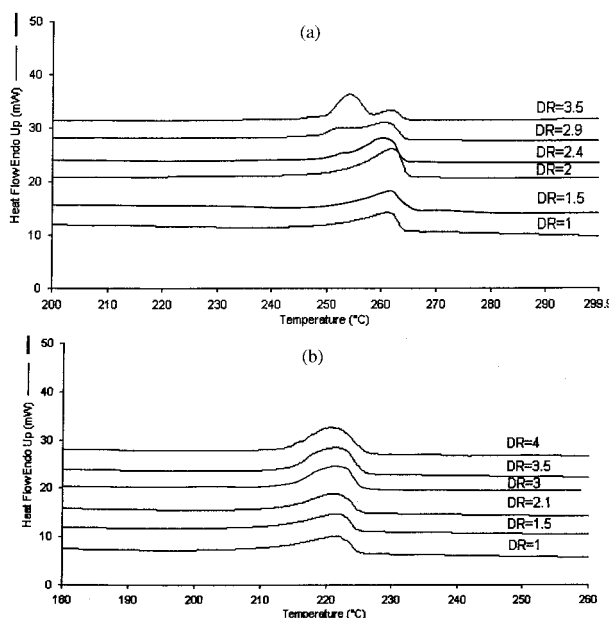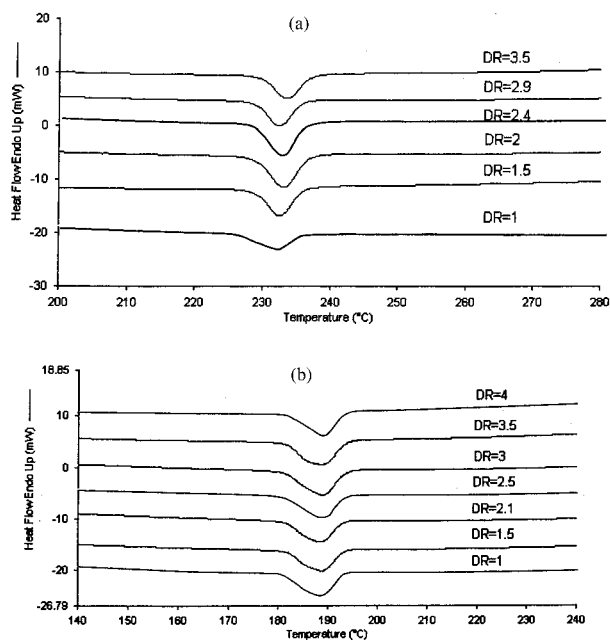
Figure 2 DSC scans of drawn polyamide fibers (a) N66 and (b) N6 on cooling from the melt.

to T_{cc} at $10°C/min$. If this postulated retention of orientation memory were true, we would expect to see a difference in T_{cc} for N6 and N66 fibers drawn to different draw ratios. These fibers have different crystalline and amorphous orientation values. Furthermore, we have carried out similar experiments for non-hydrogen-bond-forming polymers, such as PET and PEN, and we have not found noticeable differences in their T_{cc}s. From these observations we conclude that hydrogen bonding does not have a significant effect on the crystallization of polyamides.

Tonelli et al.[10] studied the formation of the α-cyclodextrin (α-CD) and N6 inclusion compound (IC), and the N6 subsequently coalesced from its α-CD, using FTIR, DSC, and solid state NMR spectroscopy. They demonstrated that the coalesced N6 melts at a higher temperature than the as-received/control N6 (219.3 versus 215.6°C). The crystallinity of coalesced N6 was almost double that of the control N6. FTIR spectroscopic analysis showed that coalesced N6 retained its orientation after decomplexation of N6–α-CD–IC. The T_{cc} observed on cooling was ~$180.0°C$ for both samples. This result confirms again that an orientation-induced memory effect is not retained for a long time in the melt, as suggested by Khanna et al.[8]

Lee and Porter[7] studied nonisothermal crystallization of PEEK film. They demonstrated that crystallization of drawn PEEK film is slower than that of the undrawn sample. This difference has been attributed to the time required for complete relaxation of the polymer chains before they can be folded and crystallized. Observations made for polyamides are different from those made for PEEK film. To see the effect of
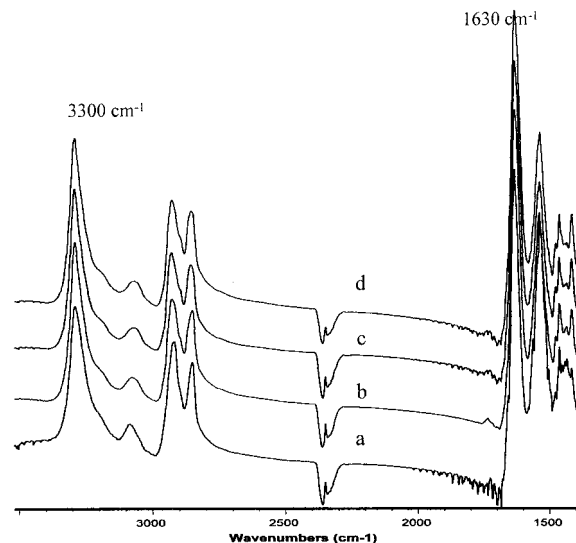
Figure 3 FTIR spectra of drawn N6 fibers drawn into different draw ratios: (a) DR = 1; (b) DR = 2; (c) DR = 3; and (d) DR = 4.

hydrogen bonding, we obtained IR spectra of N6 and N66 fibers as a function of draw ratio. These spectra are shown in Figure 3. It is well known that N—H stretching and C=O stretching (amide 1) vibrations are very sensitive to hydrogen bonding. The C=O stretching vibration occurs at 1630 cm^{-1} and N—H stretching vibration occurs at 3300 cm^{-1}. We have not seen any effect on the half widths and peak positions of these vibrations for fibers drawn at different draw ratios, confirming that there is no noticeable change in hydrogen bonding with draw ratios.

The draw ratio versus half-time of crystallization of N66 is plotted in Figure 4. It is noted from the data in Table I that overall orientation increases with increasing draw ratio. We did not observe any effect of increasing draw ratio on the half-time of crystallization. However, it is well known that crystallization kinetics
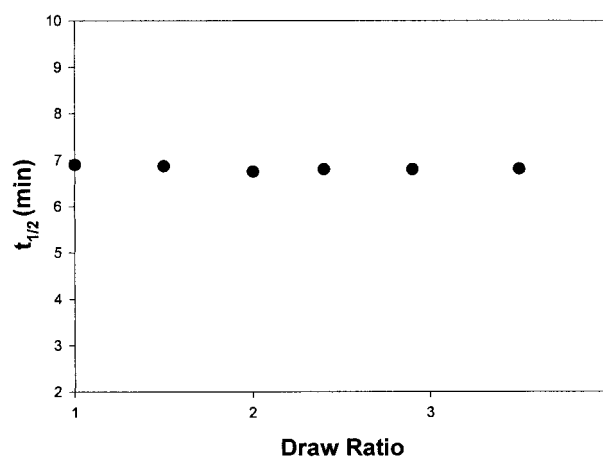
Figure 4 Half-time of crystallization, $t_{1/2}$, versus draw ratio for N66 fibers.

of semicrystalline polymers from the glassy state strongly depends on orientation of the amorphous phase. It has been demonstrated that the rate of melt crystallization does not depend on orientation for several semicrystalline polymers. We have also observed similar behavior for N6 and N66 fibers drawn at different draw ratios. Khanna et al.[8] have shown that melt crystallization kinetics depend on orientation history of polyamides and attributed it to strong intermolecular interactions, such as hydrogen bonding. In our investigation, we did not see any support for their conclusion. Crystalline memory can be deleted by melting the polymer at a temperature well above the equilibrium melting temperature and keeping it there for a sufficient time. If the crystalline memory is retained due to insufficient temperature or time kept above T_m, it can act as a seed for crystal nucleation.

In conclusion, drawing of N6 and N66 fibers enable us to obtain samples with different orientation history. The crystalline and amorphous orientation of polyamide fibers drawn at different draw ratios were measured using a combination of birefringence measurements and IR spectroscopy. It has been demonstrated that melt crystallization of N6 and N66 fibers is similar to that of PE, PET, and PEN. Hydrogen bonding apparently does not have a significant effect on the melt crystallization of N6 and N66 fibers.

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