

Interactions at the PA-6/PA-66 Interface

FRANTIŠEK RYBNIKÁŘ and P. H. GEIL*

Polymer Group, Department of Materials Science and Engineering,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

SYNOPSIS

Refrigerant tubing used in some mobile air conditioning systems has a nylon core, often consisting of nylon 6, nylon 66, or a copolymer thereof. A blend of the homopolymers would be more economical than the copolymer. This article deals with the structural stability of such blends during processing. The crystallization and melting behavior of laminates and solution cast blends of nylon 6 and 66 were examined. Although they do not cocrystallize readily, their at least partial miscibility in the melt and possible incorporation as crystal defects cause reductions of the melting points and heats of crystallization and fusion of both polymers. The crystallization temperature of the nylon 6, however, increases with increasing nylon 66 content, up to ca. 60% nylon 66, a feature attributed to nucleation of the 6 by the 66. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

With growing interest in polymer blends, knowledge of interactions at the phase boundaries is essential because the types and extent of interactions influence not only mechanical, physical, and optical properties but also the process of nucleation and crystallization and the resulting morphology.¹ Refrigerant tubing used in some mobile air conditioning systems has a nylon core, often consisting of nylon 6, nylon 66, or a copolymer thereof. A blend of the homopolymers would be more economical than the copolymer. This article deals with the structural stability of such blends during processing and shows our results concerning the interface of poly-6-caproamide (PA-6) and poly(hexamethylene-adipamide) (PA-66). Morphological studies of these blends will be discussed in a subsequent article. Even though PA-6 and PA-66 are widely used in practice, information on their behavior in blends is scarce.²⁻⁴

EXPERIMENTAL

Materials

All measurements were performed with commercial samples of PA-6 Amilan (Toray Company) and PA-66 Nylon 66 (DuPont Company). Samples were in the form of pressed sheets of each polymer (type 1). Some measurements were also done with PA-6/PA-66 blends prepared by evaporating HCOOH from 0.5% blend solutions at 25°C (type 2).

Crystallization and Melting

The course of crystallization and melting was investigated using a Perkin-Elmer differential scanning calorimeter (DSC)-4. Two discs (ϕ 6 mm), one of each polyamide, were placed in the DSC sample pan forming one contact area. The respective sample thickness was adjusted to get various PA-6 to PA-66 ratios, the total sample weight being 6–12 mg. The thermal history was always identical: heating (100°C/min) to 270°C, melting 3 min, cooling (20°C/min) to 100°C while recording the crystal-

* To whom correspondence should be addressed.

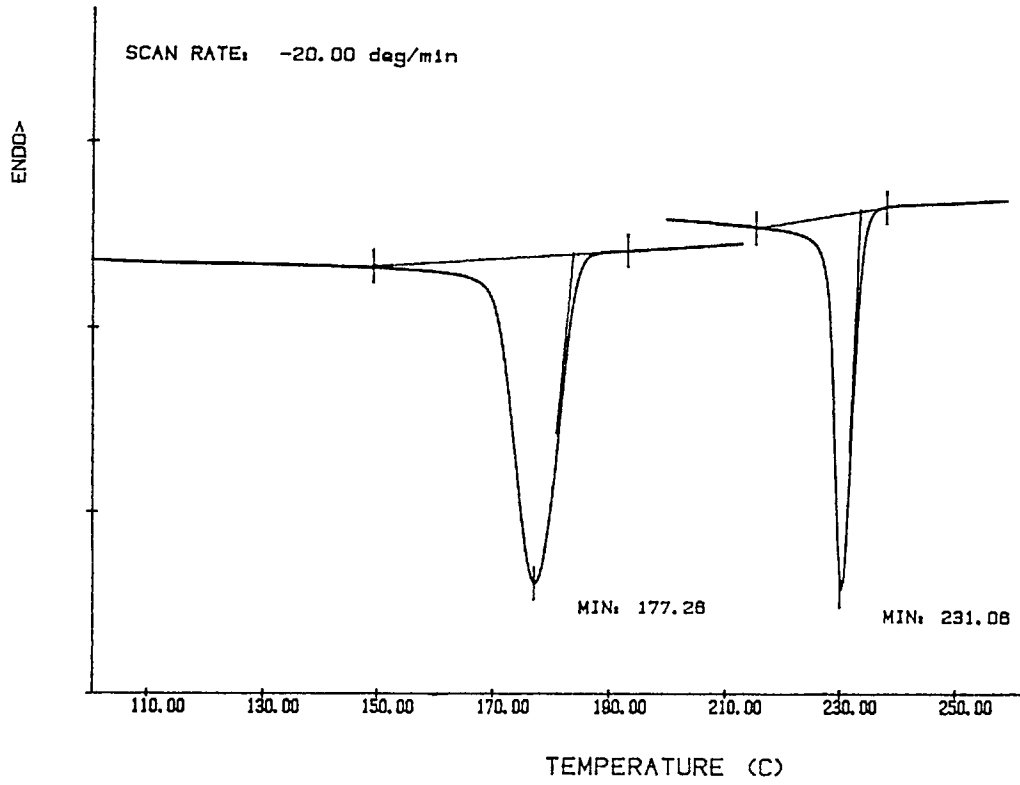


Figure 1 DSC crystallization scans of PA-6 and PA-66 during cooling from 270 to 100°C. The cooling rate is 20°C/min.

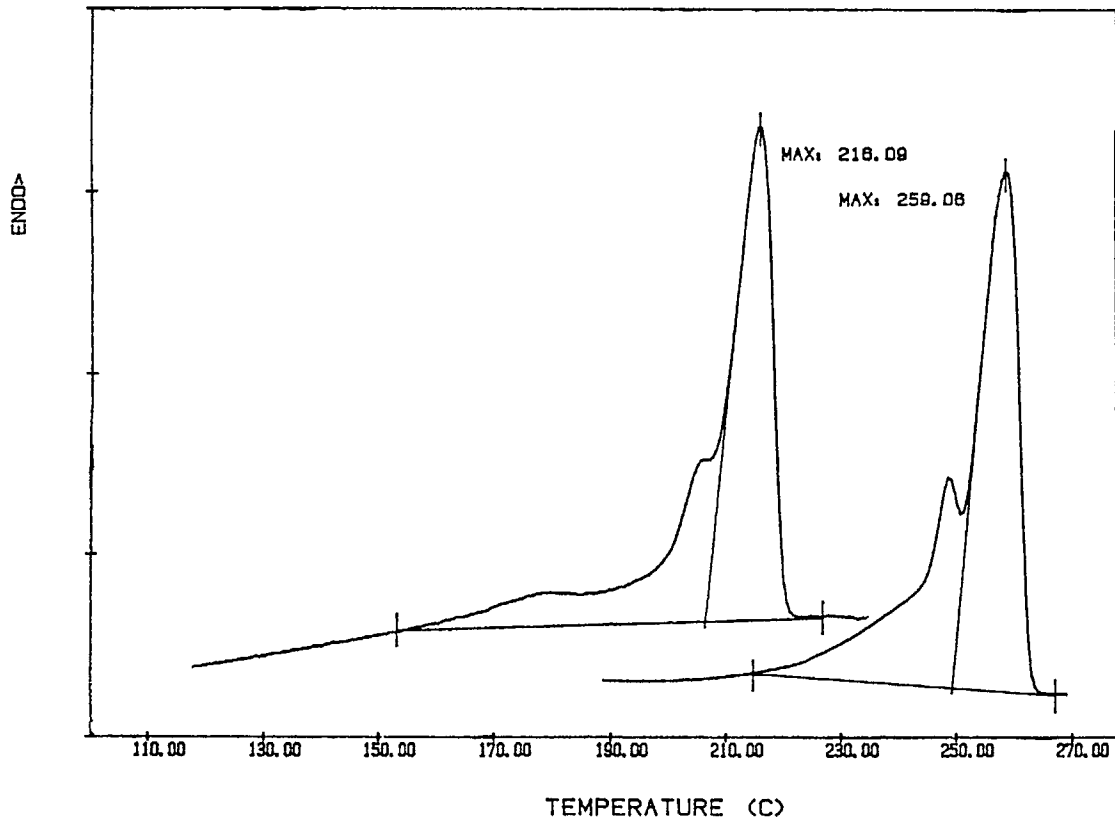


Figure 2 DSC melting scans of PA-6 and PA-66 crystallized by a standard procedure shown in Figure 1. Heating rate was 20°C/min.

Table I Heat of Melting and Crystallization of PA-6/PA-66 Polyamide Contact Laminates

% PA-6	PA-6		PA-66	
	ΔH_c (cal/g) ^a	ΔH_m (cal/g)	ΔH_c (cal/g)	ΔH_m (cal/g)
100	15.7	16.7	—	—
90.8	14.6	15.8	12.2	15.3
89	15.4	16.7	11	15.6
83.2	15.3	15.9	12.2	15.6
81	15.2	16.5	12.5	15.4
72.5	15.1	16.4	12.8	15.5
67.5	—	14.5	—	16.4
62.6	15.5	16.4	13.4	14.9
53	15.1	15.1	12.7	15.2
48	13.4	—	13.1	—
45.3	15.8	15.6	12.9	16
42	14.1	14	12.6	15.5
37.4	15.3	14.5	12.9	16
27.3	13.4	10.1	13.5	16.2
20	8.9	—	15.1	—
17	9.9	—	14.7	—
16.8	9.1	9.2	14.1	17.2
15.5	8.8	8.6	14.3	17.1
0	—	—	15.5	17.6

^a Per g PA-6 or PA-66 in the laminate.

lization curve, heating from 100°C (20°C/min) to 270°C, and recording the melting curve. Occasionally, melting runs were done with as-prepared samples. The recorded data for the crystallization (T_c) or melting temperatures (T_m) correspond to peak values and represent averages of at least two independent measurements. For wide-angle X-ray diffraction (WAXD) a Scintag X-ray goniometer (Santa Clara, CA) equipped with heating stage was used with Cu K_α radiation (Ni filtered) and a Ge solid-state detector.

RESULTS

Crystallization and Melting

Typical DSC crystallization and melting scans of individual PA-6 and PA-66 polymers are shown in Figures 1 and 2. PA-66 crystallizes faster than PA-6 as follows from its narrower T_c range. As the samples were crystallized under nonisothermal conditions, the melting scans have, besides the main melting peak, one or two smaller peaks at lower T_m .

Table II Crystallization and Melting Temperatures of PA-6/PA-66 Polyamide Contact Laminates

% PA-6	PA-6		PA-66	
	T_c (°C)	T_m (°C)	T_c (°C)	T_m (°C)
100	177.5	217.5		
90.8	176.7	217	228.5	260.5
89	178.8	217.1	228.2	255.6
83.2	179.3	192	216.6	256.8
81	177	217.6	228.2	257.3
72.5	177.2	193	217.2	229.2
65.7		215		258
62.6	180.2	192	215.6	229.2
53	180.4	192	215.8	229.9
48	181	190		256.7
45.3	182.5	193	215.6	230.6
42	181.4	192	215	229.8
37.4	182.8		215.7	230.2
27.3	181.1	192	214.9	230.2
20	180.5	189		256.8
17	179.8	189		230.9
16.8	182	193	215	228.8
15.5	180.7	192	214.9	229.3
0				257.7
				259.3
				259.8
				259.8
				259

The crystallinity of both polyamides is practically equal as follows from heats of fusion (see Table I). DSC scans of laminated samples (type 1), at first glance, were such as expected for immiscible polymer blends. But, a closer examination revealed that the crystallization and melting of both individual polymers is influenced by the presence of the other polymer. This is apparent from the data in Tables I and II and Figure 3. Especially at lower PA-6 content the crystallization range of the PA-6 component was broadened and shifted to higher T_c . Besides the main PA-6 T_c peak, there was also present a shoulder on

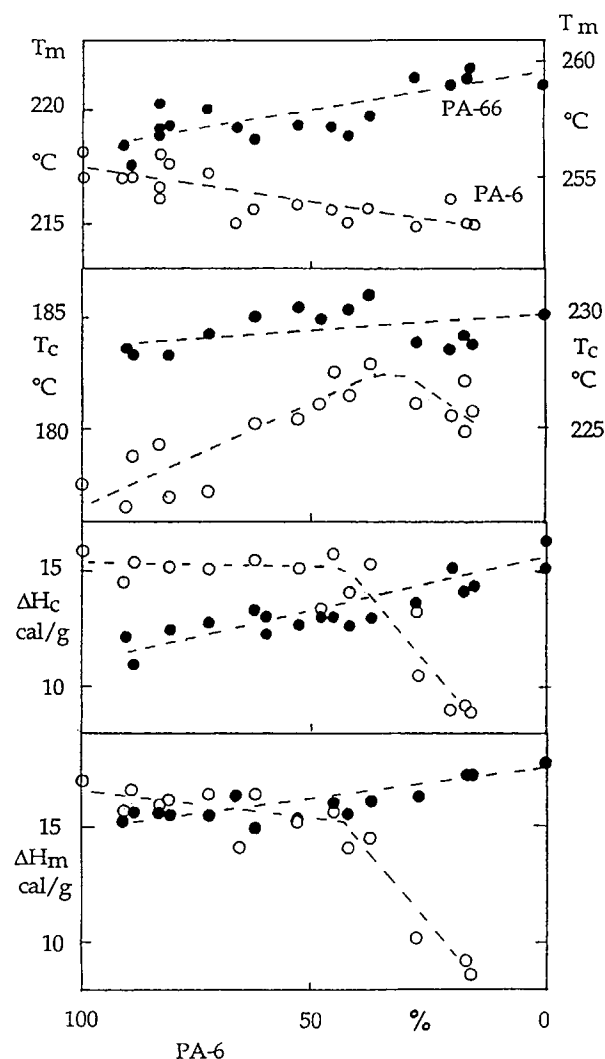


Figure 3 DSC-measured melting (second scan) and crystallization temperatures, heats of crystallization, and fusion of PA-6/PA-66 contact laminates as a function of blend composition.

the higher T_c side, marked by an arrow in Figure 4. This crystallization shoulder has no counterpart in the melting run. We suggest that the faster crystallizing material represents either PA-6 crystals nucleated by the already present PA-66 crystals or co-crystals of PA-6 and PA-66; in either case, they do not show up separately during melting.

First, we consider the melting and crystallization behavior of the PA-66 component. With increasing PA-6 content in the laminate the T_m , T_c , ΔH_m and ΔH_c values of PA-66 slightly decrease. This is consistent with the assumption that during first melting a certain amount of PA-6 dissolves in PA-66 and acts as a diluent during crystallization and second melting. The situation concerning crystallization and melting of the PA-6 component is more complex. The decrease of T_m values with increasing PA-66 content indicates that also in PA-6 some amount of PA-66 is dissolved and/or that the PA-6 crystals are smaller or more imperfect with increasing PA-66 content. On the other hand, the T_c values of PA-6 component increase with increasing PA-66 in the laminate up to about 60% and then slightly decrease. To understand this trend, one has to realize that the crystallization of PA-6 and PA-66 takes place under different circumstances. When PA-66 crystallizes, the PA-6 component is in the liquid state, whereas PA-6 crystallizes in the presence of solid PA-66. Because of similar chemical and crystal structure, it seems probable that PA-6 can easily nucleate on solid PA-66 surface. So, increasing PA-66 content may increase the overall crystallization rate of PA-6. However, it is noted the initial surface area of the laminates in contact was the same for all ratios; thus, the amount of PA-66 surface area in contact with the PA-6 could increase only if there was diffusion of the PA-66 into the PA-6 and subsequent PA-66 domain formation. It is also possible that an increased concentration of PA-66 stays dissolved in the PA-6, explaining the decreasing crystallinity of PA-6, as is seen from the drop of ΔH_m or ΔH_c values for large PA-66 content. We would expect higher T_m values for the PA-6 component in the case of higher T_c , but apparently the lower T_m values are due to dissolved PA-66 and possibly to some degree of cocrystallization. In the composition range $< 40\%$ PA-6, the ratio volume/surface area of PA-6 in the laminate diminishes and the effect of dissolved PA-66 on decreasing crystallization rate and crystallinity of PA-6 dominates. The results show that there is an important interaction of the solid PA-66 and liquid PA-6 interface. Although the

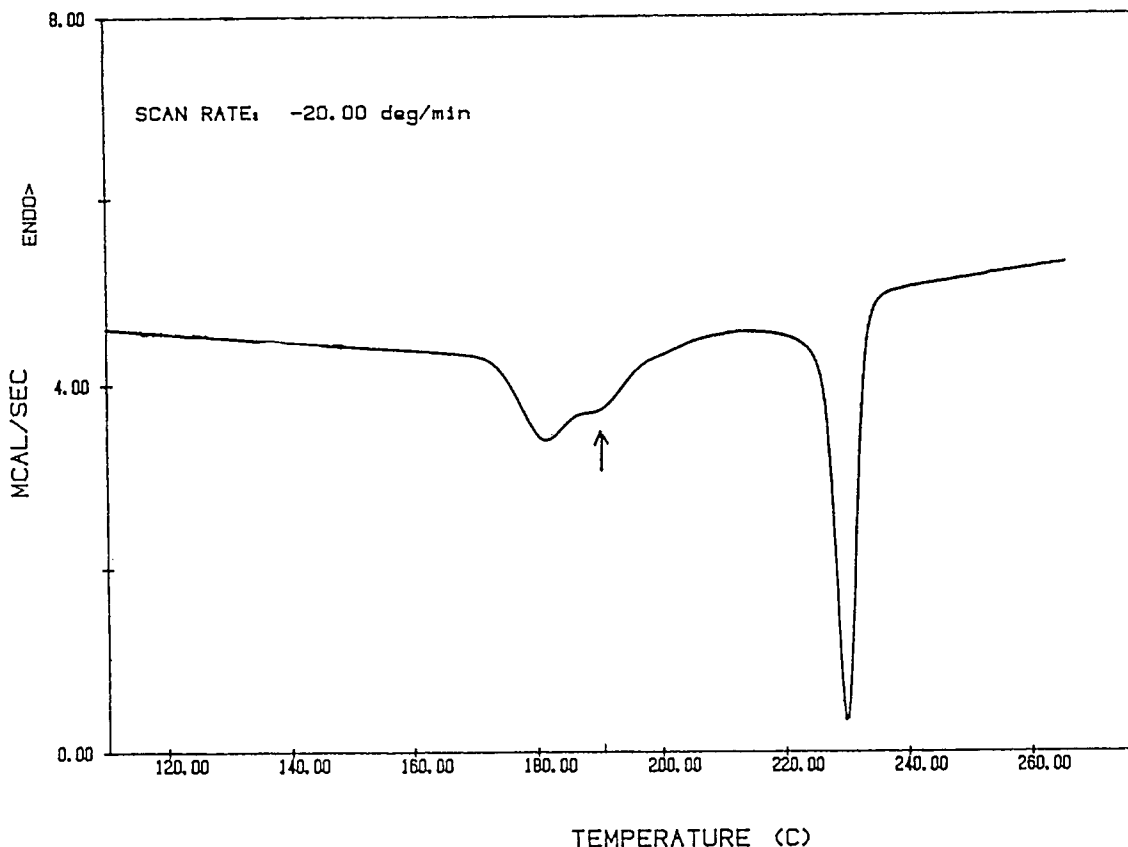


Figure 4 DSC crystallization scan of the PA-6/PA-66 (1 : 1) contact laminate. Arrow shows the additional shoulder of PA-6 crystallization peak at higher T_c .

original contact area is relatively small, the surface nucleation influences the crystallization of a substantial portion of the PA-6 phase. As indicated, this suggests substantial and large-scale interdiffusion of both polyamides in the melt.

To investigate the mutual solubility of PA-6 and PA-66 more closely, we prepared films from PA-6/PA-66 blends (4 : 1, 1 : 1, and 1 : 4) by evaporating HCOOH from solutions at room temperature (type 2 samples). The films were white opaque and X-ray diffraction confirmed that they were crystalline in the α -modifications. It is noted X-ray diffraction cannot be used to distinguish a mixture of homopolymer crystals and cocrystallization. All reflections have similar spacings except for the PA-66 002 reflection ($13.8^\circ 2\theta$), which is absent from the PA-6 pattern. This reflection was present in all samples with an intensity proportional to the PA-66 content. Also, DSC scans showed that they were crystalline; the degree of crystallinity was about the

same as that of films from the individual blend constituents, prepared from solution in the same way. The DSC melting scans of melt-crystallized samples

Table III Crystallization and Melting Temperatures of PA-6/PA-66 Blends Prepared by Evaporation of 0.5% HCOOH Solution at 25°C

% PA-6	PA-6		PA-66	
	T_c (°C)	T_m (°C)	T_c (°C)	T_m (°C)
100	177.5	216	—	—
80	187.6	200s 211.2	212	247
50	188	207	216	249.3
20	175b	200.1	220	250
0	—	—	230	259

s, shoulder; b, very broad peak.

(second scans) showed again two separate melting peaks. If the concentration of one component was lower than 20%, only single crystallization and melting peaks are seen, approaching that of the prevailing component. As expected, by increasing the contact area between the two polyamides the mutual interactions became more pronounced than in the type 1 samples. As follows from Table III and Figure 5, the T_m values decrease markedly with increasing content of the second blend component, which is consistent with mutual, at least partial solubility in the amorphous regions. From the shape of the T_m composition curves, it follows that the solubility of PA-66 in PA-6 is greater than vice versa.

In their crystallization behavior, the two polyamides in the type 2 samples differ in the same way as was seen with type 1 samples. PA-66 T_c values decrease monotonically with increasing PA-6 content to some limiting value, similarly as T_m values.

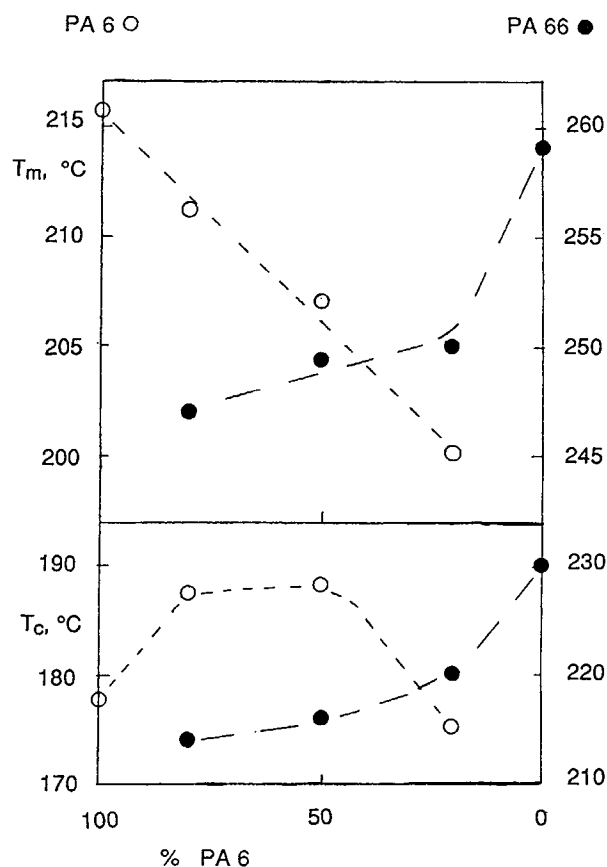


Figure 5 DSC-measured melting and crystallization temperatures of PA-6/PA-66 solution prepared blends as a function of blend composition.

The T_c values of PA-6, on the other hand, show again a maximum at the midcomposition. With increasing time or temperature in the melt, the T_c and T_m values of both polyamides shifted closer together and eventually merged into one broad peak for both laminates [Fig. 6(a)] and solution cast blends [the solution blends crystallized separately on initial crystallization, as shown by separate melting points and their morphology (to be published)]. This suggests that the two polyamides form a miscible solution in the melt after sufficient time that can be retained in the amorphous regions when cooled below T_m . Unfortunately, the T_g s of the homopolymers are sufficiently close that the effect of miscibility on them cannot be determined. The broad melting range with "peaks" at temperatures below those of the corresponding pure components suggests cocrystallization, to some degree, and/or small imperfect crystals. However, annealing a sample such as 2' (Fig. 6) at a temperature such as 205°C, well below either T_m , the individual melting peaks reappeared similar to those in curve 1'. Although the thermal treatment in the melt could lead to transamidation and the formation of copolymers, their reappearance suggests the effects are due to small, imperfect crystals that are improved by the annealing.

CONCLUSIONS

PA-6 and PA-66, despite a great similarity in chemical and crystal structure, show no clear evidence of cocrystallizing. This similarity, on the other hand, favors at least partial mutual solubility in the melt that influences the crystallization and melting behavior of their laminates and blends. The crystallization rate of the PA-6 in the laminate and the blend is higher than in crystallizing PA-6 alone due to the PA-6 nucleation on the solid PA-66 surface. The surface nucleation of the PA-6 component and mutual or at least partial solubility in the melt results in some degree of cocrystallization but as defective crystals. This is the reason the crystallization and melting behavior differs from that of pure blend constituents of other polymers. It is noted the results suggest a rapid mutual interdiffusion in the laminates, as well as in the blends, in the melt state. They also suggest considerable care would be needed in processing to produce reproducible properties, particularly if mixing is poor or melt residence times short.

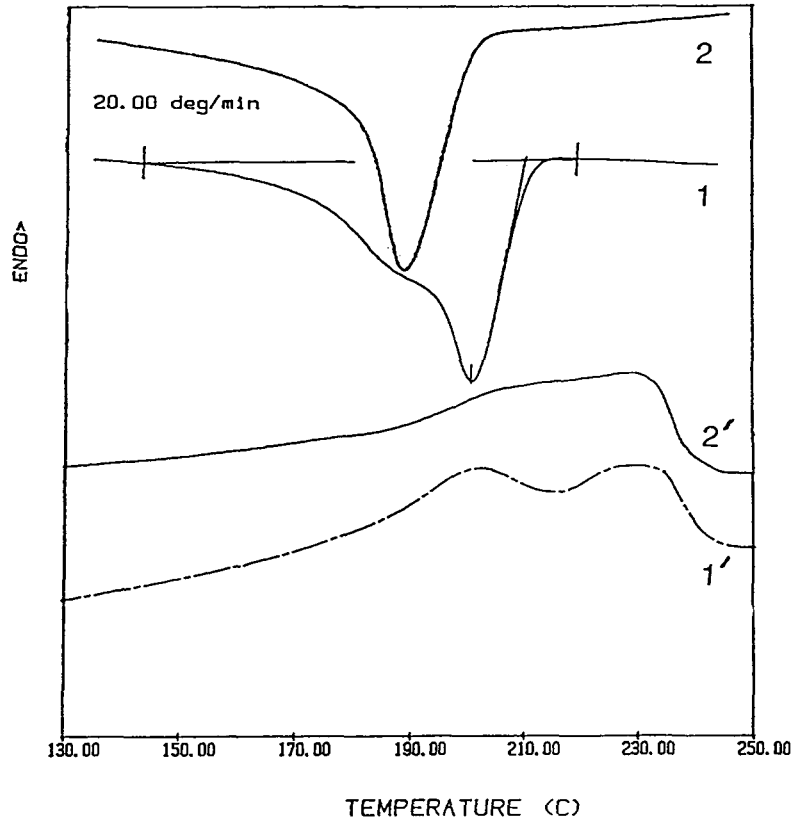


Figure 6 DSC crystallization and melting of PA-6/PA-66 (1 : 1) type 2 blend. Curves 2 and 2' belong to a sample melted 40 min at 270°C, whereas 1 and 1' were melted at 270°C for 3 min.

This research was supported by the University of Illinois Air Conditioning and Refrigeration Center, a National Science Foundation-Industry-University Cooperative Research Center.

REFERENCES

1. F. Rybníkář, *J. Macromol. Sci. Phys.*, **B27**, 125 (1988).
2. H. Mitomo and H. Tonami, *Chem. High Polym.*, **27**, 134 (1970).
3. E. S. Ong, Y. Kim, and H. L. Williamson, *J. Appl. Polym. Sci.*, **31**, 376 (1986).
4. D. R. Paul and S. Newman, *Polymer Blends*, Vol. 1, Academic, New York, 1978, p. 29.

Received August 26, 1991
Accepted December 9, 1991