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The conditions under which the LCP reinforced thermoplastc composites can be thermoformed have been investigated. Two liquid crystalline polymers(a copolyester of terephthalic acid,phenyl hydroquinone,and phenyl ethyl hydroquinone and a copolyester of p-hydroxy benzoic acid and 6-hydroxy-2naphthoic acid)were used. An amorphous(polyetherimide) and a semi-crystalline(polypropylene)have been used as the matrix materials for making the composites. The thermoformability has been studied as a function of the sheet preheating temperature, and the mold temperature for various compositions of composites. Morphology and molecular orientation of the thermoformed parts before and after thermoforming have also been studied.

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Thermoforming of Insitu Reinforced Thermoplastic Composites

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INTRODUCTION

The ways of using liquid crystalline polymers (LCP's) to in situ reinforce thermoplastics have engaged the attention of many researchers [1-5]. In our laboratory, we have studied the use of various LCP's to improve the mechanical properties of high performance thermoplastics such as PPS, PEEK, and PEI [6] as well as commodity resins such as PET and PP [7,8]. The conditions under which the LCP reinforced thermoplastic composites can be thermoformed have been investigated in the present paper. An amorphous and a semi-crystalline polymer have been used as the matrix material for making the thermoplastic composites. The thermoformability has been studied as a function of the sheet preheating temperature, and the mold temperature for various compositions of composites. Morphology and molecular orientation of the thermoformed parts before and after thermoforming have also been studied.

EXPERIMENTAL

Materials Two liquid crystalline polymers were used for this study. The first LCP, Vectra A900, is a copolyester of p-hydroxy benzoic acid and 6-hydroxy-2 naphthoic acid and was supplied by Hoechst Celanese. The second LCP, Granlar, is a copolyester of terephthalic acid, phenyl hydroquinone, and phenyl ethyl hydroquinone and was provided by Istituto Donegani (Montedison). The amorphous matrix polymer was the polyetherimide (General Electric Ultem 1000) while the semi-crystalline matrix polymer was polypropylene, (Himont PRO-FAX 6823).

Pellets of Ultem, Vectra, and Granlar were dried in a vacuum oven at 150 C for at least twenty-four hours before being processed. The matrix (Ultem and PP) and the liquid crystalline polymer were premixed in a specific weight ratio and tumbled together to make blended injection molded plaques . To study the effect of mixing history, double pass blend pellets were also used. For this purpose, the premixed mixtures of matrix and reinforcing LCP were tumbled and extruded in a 25.4 mm diameter single screw extruder (Killion KL-100) having a L/D ratio of 24. The extrudates were quenched in ice-water and continuously pelletized. The blended pellets were then used to make injection molded plaques. The matrix/LCP blends containing x wt % matrix and y wt % LCP will be denoted henceforth by matrix/LCP x/y.

Injection Molding Rectangular plaques measuring approximately 75 mm x 85 mm x 1.75 mm were molded using an Arburg 221-55-250 Allrounder injection molder. The processing conditions used for both Ultem/Vectra and Ultrm/Granlar were as follows: temperatures were set on 300 °C, 360 °C, and 370 °C, in zones 1, 2, 3 of the barrel, respectively and 370 °C in the nozzle. The mold was held at 90 °C. The barrel temperatures for injection molding the PP/Vectra plaques were 230 °C for the first zone and 295 °C for the last two zones. The nozzle temperature was was 250 °C and the mold was kept at room temperature.

Thermoforming A labform thermoforming unit (Hydro-Trim Corporation Model 1114) was used for thermoforming studies. Injection molded Ultem/LCP plaques were dried in the vacuum oven at 120 °C for four hours before thermoforming. The Ultem/LCP and PP/LCP plaques were preheated to a preset temperature in an infra-red radiation chamber for 100 seconds and thermoformed in a temperature controlled mold. The depth of the drape is 25.4 cm and the gap between the plug and the drape is 1.4 mm. To evaluate the thermoformablility, a given composite plaque was thermoformed at different preheating and mold temperatures. The increment of the preheating temperature and mold temperature was 5 C and 35 C, respectively for the Ultem/LCP blends. Four preheating temperatures between 155 and 200 °C were used for PP/Vectra blends while the mold was kept at 80 °C and room temperature.

Dynamic Mechanical Analysis Dynamic mechanical analyses for the neat matrix polymers, neat LCP, and their composites were carried out in the torsional mode in a Rheometrics Mechanical Spectrometer (RMS 800). For torsional modulus measurements, rectangular samples with dimensions of 45 x 12.5 mm were cut from the injection molded plaques. G, G" (elastic and viscous components, respectively of the torsional modulus) and tan delta of the samples were monitored and recorded as a function of temperature. The frequency of oscillation was 10 rad/sec and the strain was between 0.05 to 0.07%. In the temperature sweep experiments, the temperature was raised at a rate of 5 C per minute until the modulus of a given sample dropped appreciably.

Structure and Morphology Wide angle x-ray diffraction (WAXD) was carried out by using a Phillips 1720 table-top X-ray generator equipped with a fixed copper target X-ray tube and Warhus camera. The diameter of the pin-hole collimator was 0.5 mm and the sample-to-film distance was 76 mm. The beam conditions were at 40 kv and 20 mA and the patterns were recorded under vacuum.

The morphology of the composites was determined by scanning electron microscopy (SEM), using a Cambridge Stereoscan S200 with an accelerating voltage of 25 kV. All samples were fractured perpendicular or parallel to the draw direction after immersing them in liquid nitrogen. The fractured surfaces were sputter coated with gold to provide enhanced conductivity.

RESULTS AND DISCUSSION

The thermoformability of a given Ultem/Vectra composite was studied as a function of the preheating temperature (Tph) and the mold temperature (Tmd) and the dynamic torsion test results in Fig. 1 were used to determine these parameters. The glass transition temperature, Tg, of the individual components of the blend is clearly noticeable in Fig. 1 in the case of Ultem/Vectra systems. Ultem/Vectra composites of various compositions show a glass transition temperature at 228 °C for pure Ultem and 105 °C for pure Vectra. From G" vs Temperature plots (Fig. 1), it can be noted that the onset of softening of the neat Ultem and Ultem/Vectra composites is around 200 °C. Based on the Tg and the temperature for the onset of softening, the mold temperatures were initially kept above 200 °C. When the mold temperatures exceeded 200 °C, the thermoformed parts were severely deformed when they were removed from the mold after thermoforming. To overcome this problem, the upper limit of the temperature in this study was held below 180 °C as seen in Fig 2. On the other hand it is reasonable to expect that the preheating temperature should not exceed the melting point, Tm, of the Vectra (i.e. 284 °C, see Fig. 3) so that the oriented Vectra microfibrils in the Ultem/Vectra plaques can still be retained after the thermoforming process.

In Fig. 2, the preheating and the mold temperatures for which the Ultem/Vectra composites with various compositions can be thermoformed are presented. The thermoformability curve of the Ultem is also given as a reference. For any particular Ultem/Vectra composition, the area above the given curve gives all the possible combinations of preheating and mold temperature for which the corresponding composite was thermoformable. The area below the curve shows an unthermoformable zone due to the brittleness of the material for the given conditions. As seen from Fig. 2 the higher the mold temperature, the lower is the required preheating temperature. However, the curve is shifted upward to the higher temperature as the content of Vectra in the composites increases. The area between the Ultem/Vectra 7/3 curve and the horizontal line (Tm of Vectra) is definitely thermoformable zone for the Ultem/Vectra 7/3 composite in which the Vectra microfibrils will be retained in the thermoformed parts.

It is believed that the reinforcing microfibrils as well as their molecular orientations are possibly retained even when the Ultem/Vectra blends are thermoformed above the melting point of the Vectra. This is owing to the long relaxation time of the liquid crystalline polymers coupled with the much higher viscosity of the matrix polymer Ultem (compared to that of the Vectra) and the drawing effect during thermoforming. For this purpose the Ultem/Vectra 7/3 blend plaques have been preheated to 285 °C, 315 °C, and 345 °C (i.e. Tph > Tm of Vectra) and then thermoformed. The neat Vectra plaque was also heated above its melting point for checking if the fibrillar morphology and the molecular orientation in the original plaque were retained after long period heating. The morphology and the molecular orientation of the composites and the neat Vectra, with different thermal and processing histories are presented in Figs. 4 to 7. As seen form Figs. 4 and 5, the neat Vectra plaque shows distinct fibril morphology and retains most of LCP molecular orientations even after being heated at 285 °C for 240 min. This is most likely due to the long relaxation time of the rod-like macromolecular chains. Also Vectra microfibrils (Fig. 6) and molecular orientation (Fig. 7) can be retained in the Ultem/Vectra 7/3 blend composites after preheating them at 315 °C and even at 345 °C for a short time interval of 100 sec by using an infra-red radiation heat source. This preheating time of 100 seconds is long enough for further thermoforming. Compared to the Ultem/Vectra 7/3 plaque annealed at the same temperature but not thermoformed, the thermoformed part shows a higher degree of molecular orientation of Vectra in the side wall (Fig. 6, 7). This higher degree of molecular orientation can be attributed to the drawing effect in the thermoforming process.

It has been found previously that in contrast to the immiscible Ultem/Vectra blend system, Ultem and Granlar showed partial miscibility in their blends [9]. The partial miscibility has also been confirmed by the dynamic torsional analysis reported in Fig. 8. For the neat Granlar, a Tg can be observed at 150 °C; for the Ultem/Granlar 9/1 blend only one Tg can be detected and its value matches well with that predicted by the Fox equations (9). This indicates that at a *Granlar loading* of 10 wt % in Ultem/Granlar composite, the components are miscible. As the Granlar content in the blend increases, two separate Tgs can be observed and the higher one (corresponding to the Tg of the Ultem phase) begins to deviate from the Fox equation and becomes relatively insensitive to the Granlar content. These results suggest that these two components are partially miscible and the limit of their misciblility for a single pass Ultem/Granlar composite system is between 15 to 20 % of the Granlar loading. One also notes that G′ of the blends drops remarkably in a temperature range form 210 to 230 °C. Therefore, the actual plaque temperature during thermoforming should be beyond 240 °C.

Thermoformability of the Ultem/Granlar composite as a function of preheating temperature, mold temperature, and blend composition is shown in Fig. 9. For the Ultem/Granlar 9/1 (single pass) composite due to the miscibility of component polymers, its thermoformability resembles that of the meat Ultem. For the Ultem/Granlar 8/2 (1p) (1p means single pass) composite higher preheating temperature and mold temperature are needed to make the plaques thermoformable. It is most likely caused by the coexistence of free Granlar reinforcing phase in the Ultem/Granlar 8/2 (1p) composite. It is expected that the extent of miscibility can be improved by increasing the number of passes. As seen in Fig. 10 for the Ultem/Granlar 8/2 (2p) (2p means double pass), the Tg of free Granlar phase observed in the case of the Ultem/Granlar 8/2 (1p) vanishes and the Tg of the Ultem phase shifts to a lower temperature and matches the Fox equation well. Correspondingly, the thermoformability curve of the Ultem/Granlar 8/2 (2p) (see Fig.9) coincides with that of Ultem/Granlar 9/1, which has been proved to be a totally miscible system (9). The Ultem/Granlar composites are too brittle to be thermoformed when the content of Granlar in the blends exceeds 30 %. This is possibly due to the coexistence of free Granlar domains which can be easily crystallized during the preheating period.

The thermoformability of the PP/Vectra blends as a function of several preheating temperatures and two mold temperatures is presented in Table 1. From Fig. 11 it can be seen that in order to thermoform, the PP/Vectra composites need to be preheated above the softening point of the torsional modulus as determined from the steep drop in G′ with temperature. However the minimum temperatures to which the PP/Vectra blends have to be preheated before they can be thermoformed are higher for the blends with higher LCP content than for the blends with lower LCP content. For a mold at room temperature, a higher preheating temperature is required for successful thermoforming.

The morphology and the WAXD results of the PP/Vectra blends follow the same pattern as the Ultem/LCP blends. Although both show the reinforcing LCP fibrils, there is no noticeable difference in the the morphologies of the PP/Vectra plaques before and after thermoforming and are thus not compared here. As seen in Figs. 12 and 13, the molecular orientation of the Vectra phase in the PP/Vectra plaques is retained in the side wall of the thermoformed parts. The latter possibly show a higher degree of orientation of owing to the drawing effect during the thermoforming process.

CONCLUSIONS

The thermoformability of in-situ reinforced thermoplastic composites is affected by miscibility between the matrix polymer and the LCP reinforcing polymer. Most of the immiscible Ultem/Vectra composites are thermoformable. The higher the mold temperature, the lower is the required preheating temperature. The thermoformability curve shifts to the higher temperature side as the content of Vectra in the composites increases. The insitu generated reinforcing Vectra microfibrils and molecular orientation in them can be retained in the thermoformed Ultem/Vectra composites even after preheating at a temperature above the Tm of Vectra. For the partially miscible Ultem/Granlar system, the thermoformability of the composite resembles that of the neat Ultem as far as the component polymers are miscible to each other. When the content of Granlar in the composite exceeds 30 %, the corresponding composites are too brittle to be thermoformed due to the existence of free Granlar domains, which are fast crystallized during the preheating process.

The PP/Vectra blends show trends similar to the Ultem/LCP system. Lower preheating temperatures are required for higher mold temperatures. Also the preheating temperature is higher for PP/Vectra blends containing higher wt % of LCP. The morphology and the molecular orientation of the insitu generated reinforcing Vectra phase in the blends can be retained after thermoforming. The molecular orientation of the LCP phase can possibly be further enhanced during thermoforming. In general successful thermoforming of the PP/Vectra blends are possible when they are heated above the softening point in the G′ vs temperature curve.

ACKNOWELDGEMENT

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Table I Thermoformability of PP/Vectra A Blends
A) PP/Vectra A 80/20

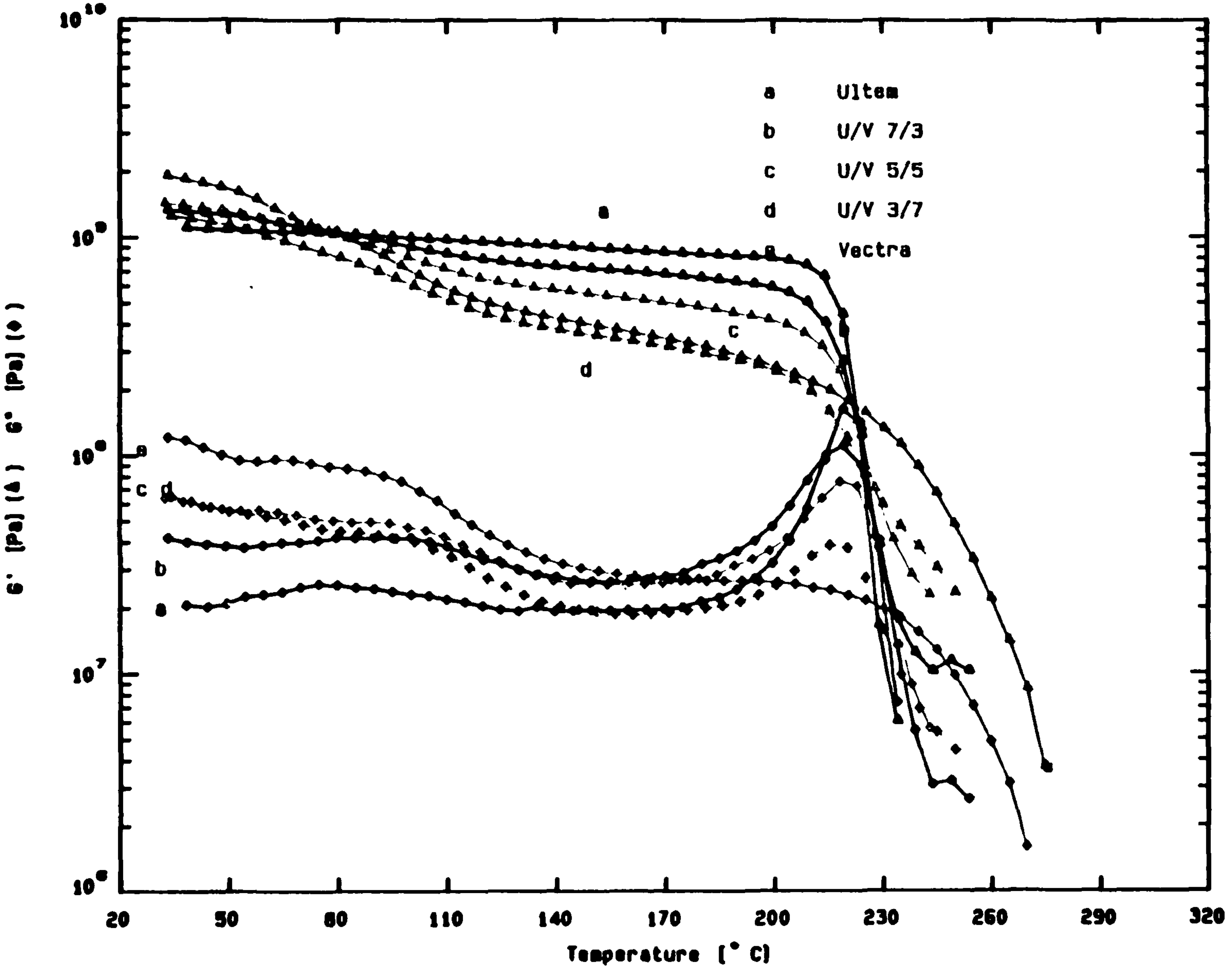
	Preheating Temperature °C			
Mold Temperature	155	170	185	200
80°C	NTh	Th	Th	Th
Room temperature	NTh	NTh	Th	Th

Table I Thermoformability of PP/Vectra A Blends
B) PP/Vectra A 70/30

	Preheating Temperature °C		
Mold Temperature	170	185	200
80°C	NTh	Th	Th
Room Temperature	NTh	NTh	Th

Th: thermoformable NTh. non-thermoformable

Fig. 1 Dynamic torsional analysis of Ultem/Vectra blends



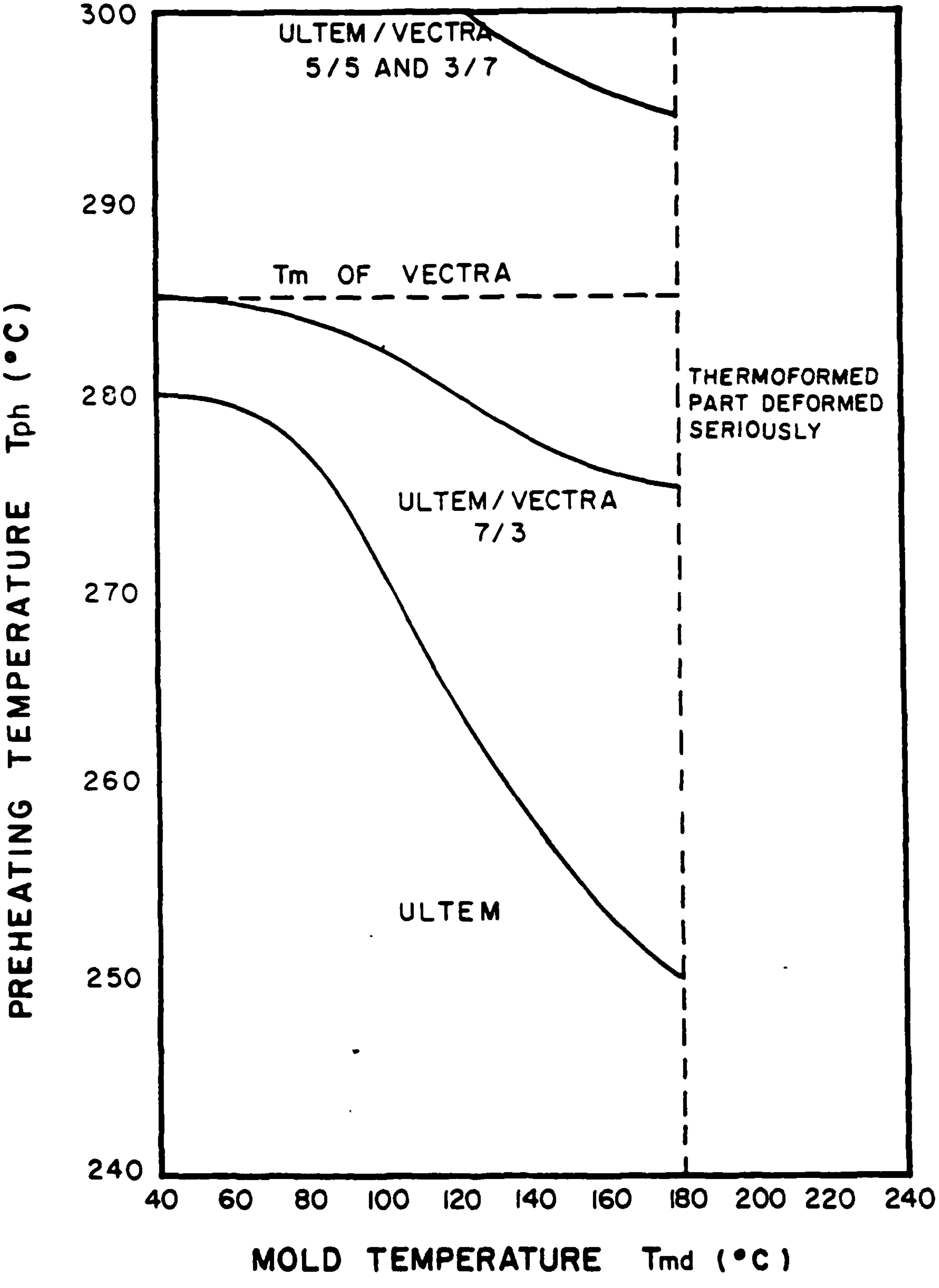
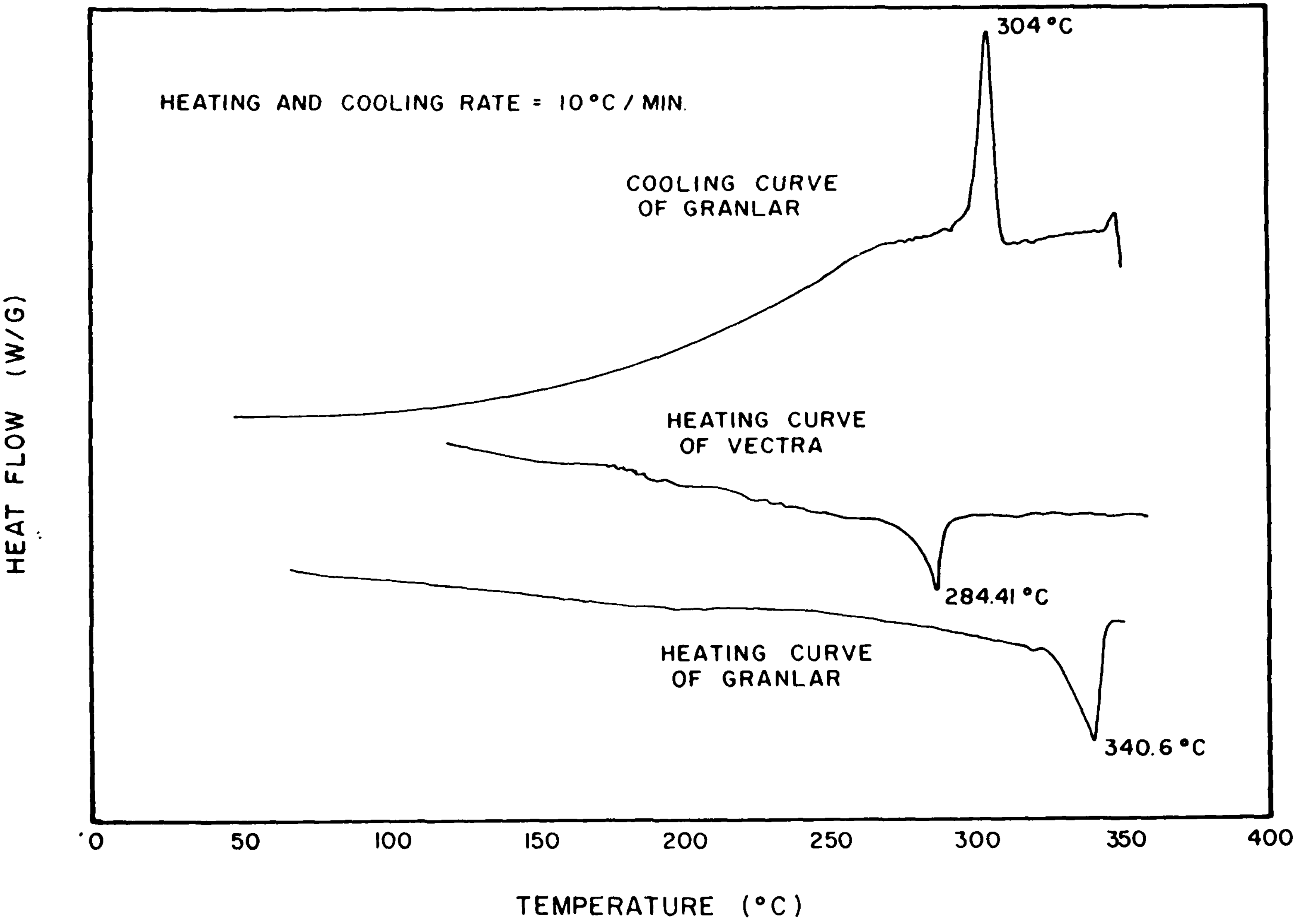


Fig. 2 THERMOFORMABILITY OF ULTEM / VECTRA BLEND PLAQUES AS A FUNCTION OF PREHEATING TEMPERATURE, MOLD TEMPERATURE AND BLEND COMPOSITION.

Fig. 3 DSC THERMOGRAMS OF VECTRA AND GRANLAR



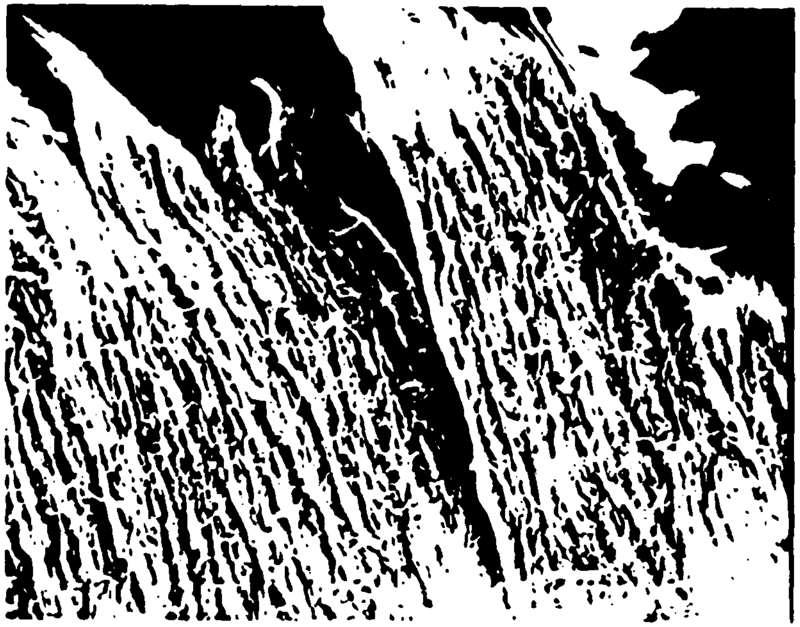
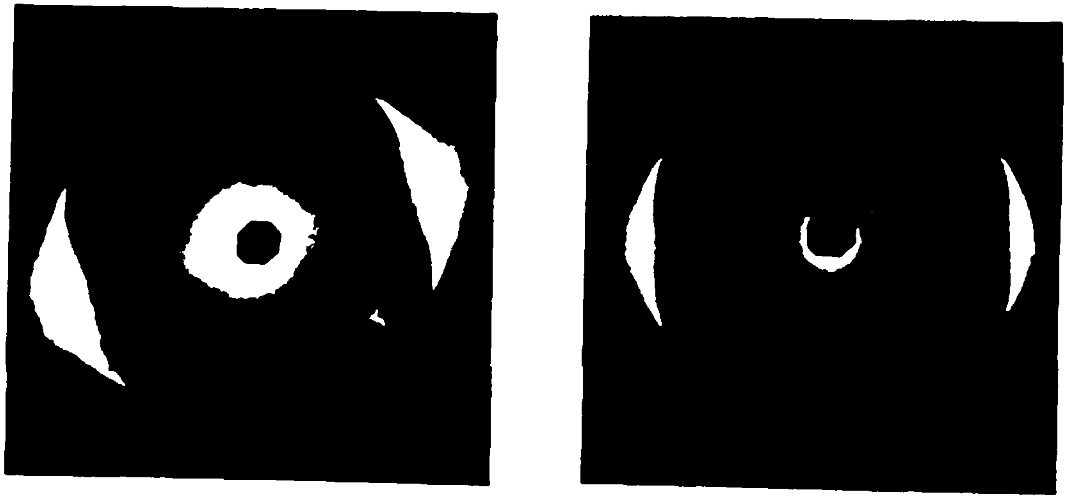


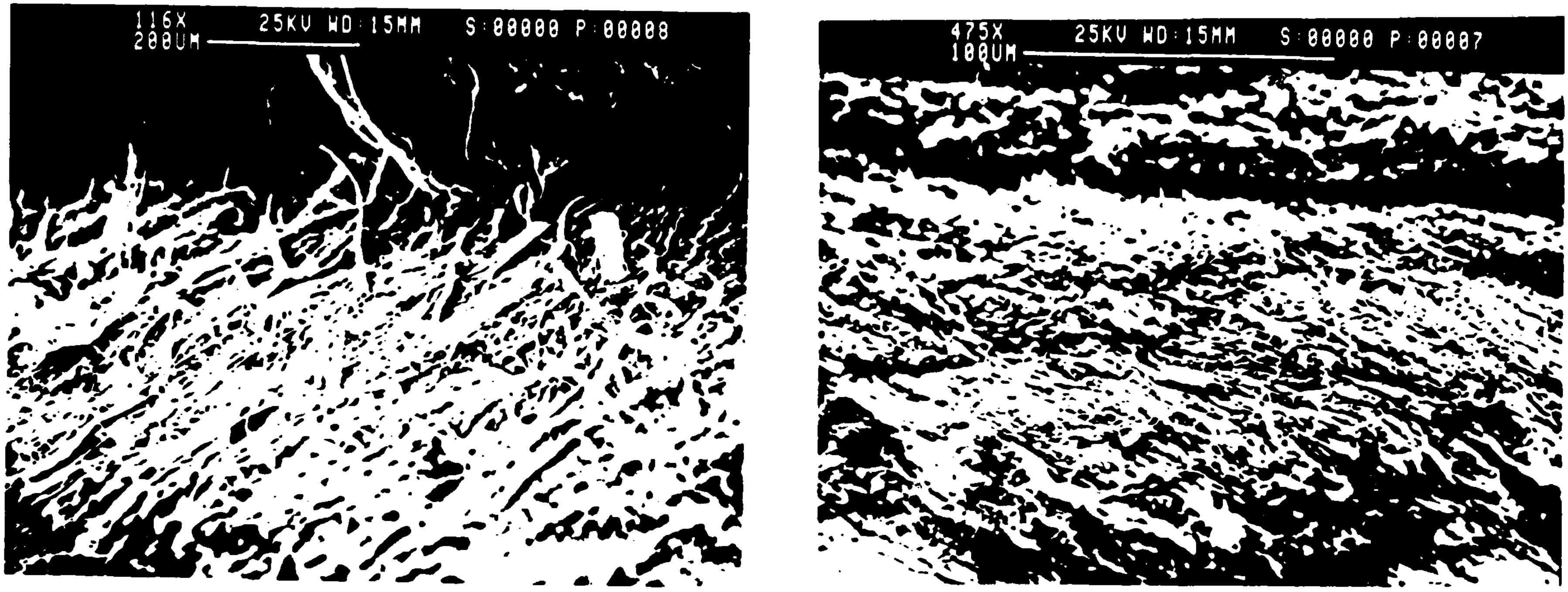
Fig.4 SEM micrograph of fractured surface of extruded Vectra sheet annealed at 285°C for 240 min.

Fig 4



(a) (b)

Fig.5 WAXD patterns of injection molded Vectra plaques
(a) As injection molded
(b) After heating at 285°C for 240 min.



(a)

(b)

Fig.6 SEM micrographs of fractured surfaces of thermoformed part (side wall) based on injection molded Ultem/Vectra 70/30 blend composite
(a) Preheated at 315C for 100 sec., thermoformed at 25C for 20 sec.
(b) Preheated at 345C for 100 sec., thermoformed at 25C for 20 sec.

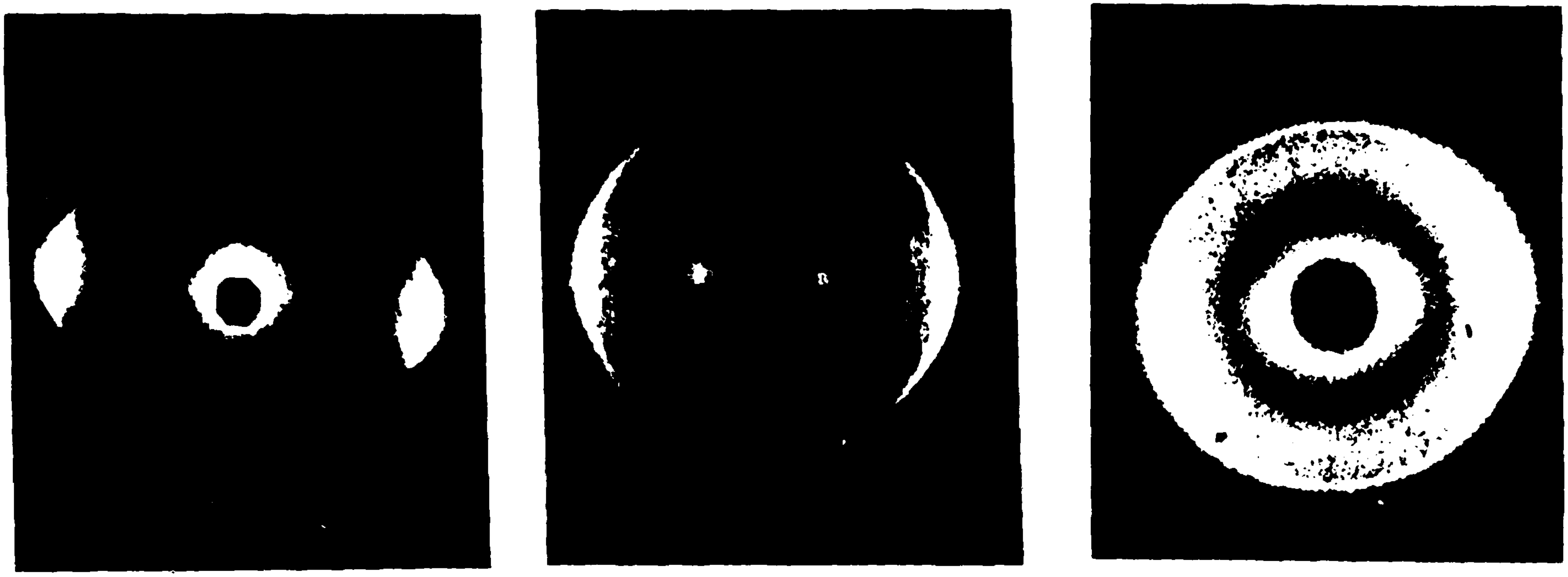
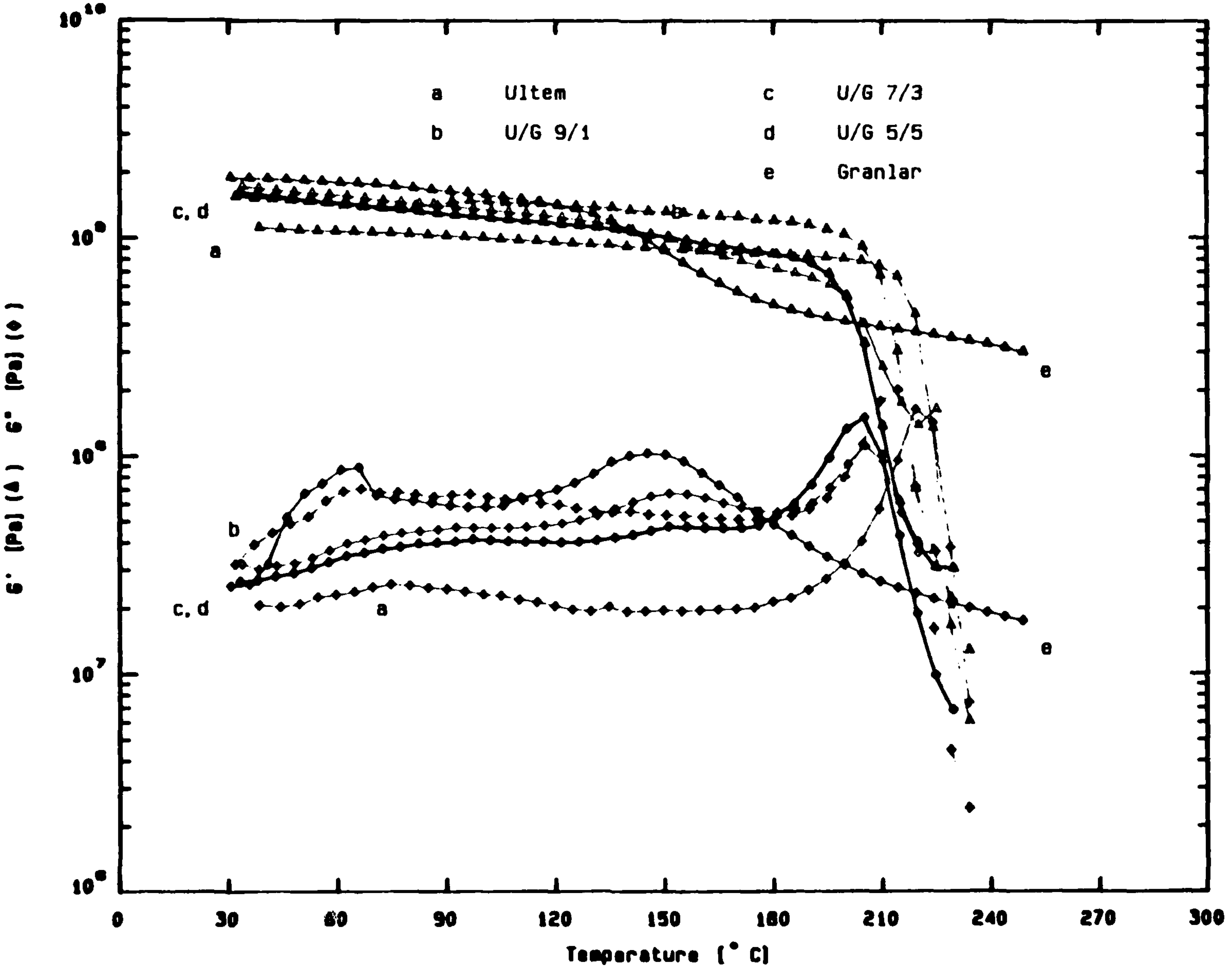

(a) (b) (c)

Fig.7 WAXD patterns of Ultem/Vectra 70/30 blends.
(a) Injection molded plaque,
(b) Injection molded plaque after annealing at 345C for 100sec, and then thermoformed at 25C. Side wall of thermoformed part.
(c) Injection molded plaque after annealing at 345C for 100sec.

Fig. 8 Dynamic torsional analysis of Ultem/Granlar blends



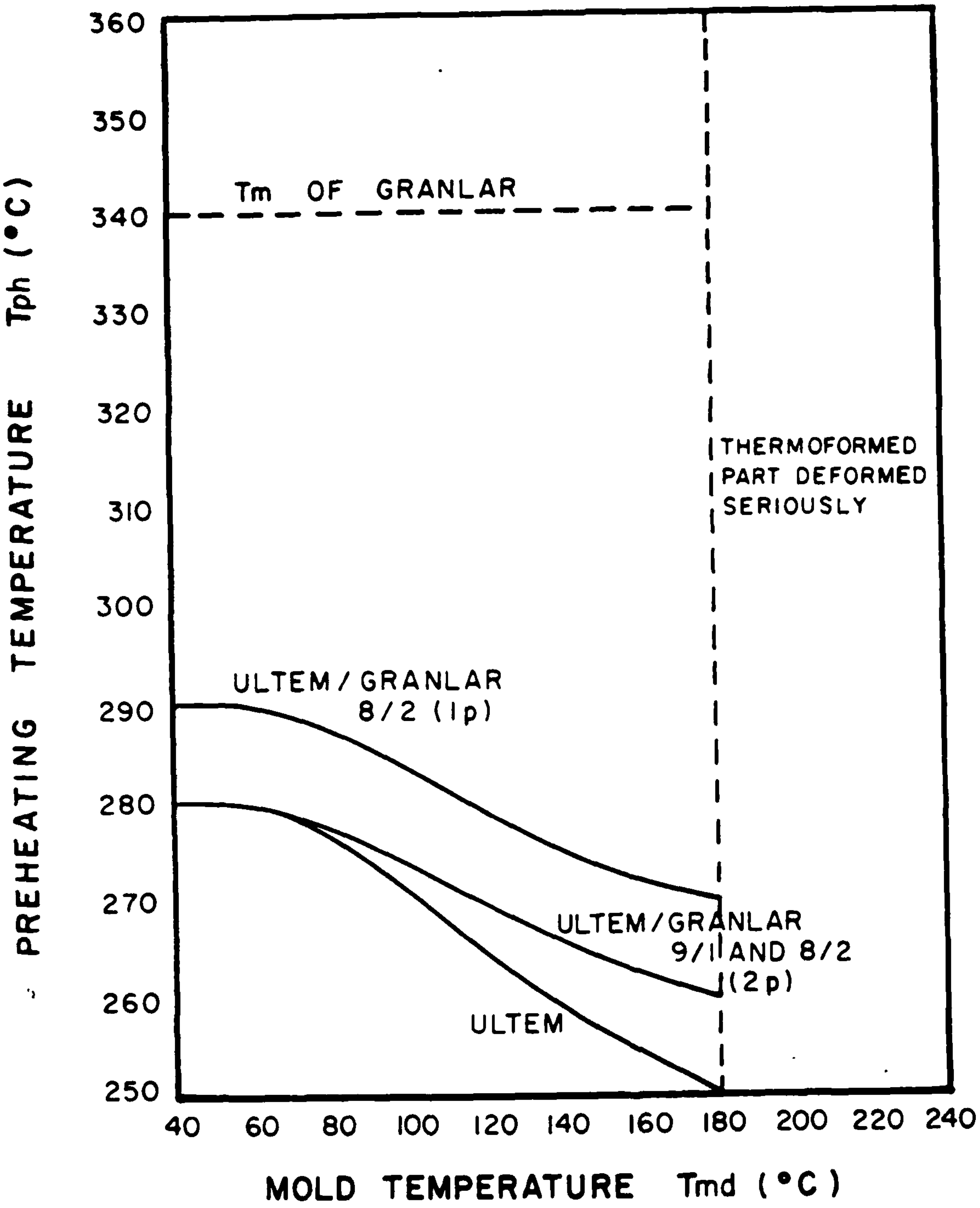


Fig. 9 THERMOFORMABILITY OF ULTEM / GRANLAR BLEND PLAQUES AS A FUNCTION OF PREHEATING TEMPERATURE, MOLD TEMPERATURE AND BLEND COMPOSITION.

* ULTEM / GRANLAR 7/3, 5/5, 3/7, AND 0/10 CAN NOT BE THERMOFORMED.

Fig. 10 Dynamic torsional analysis of Ultem/Granlar 80/20 blends

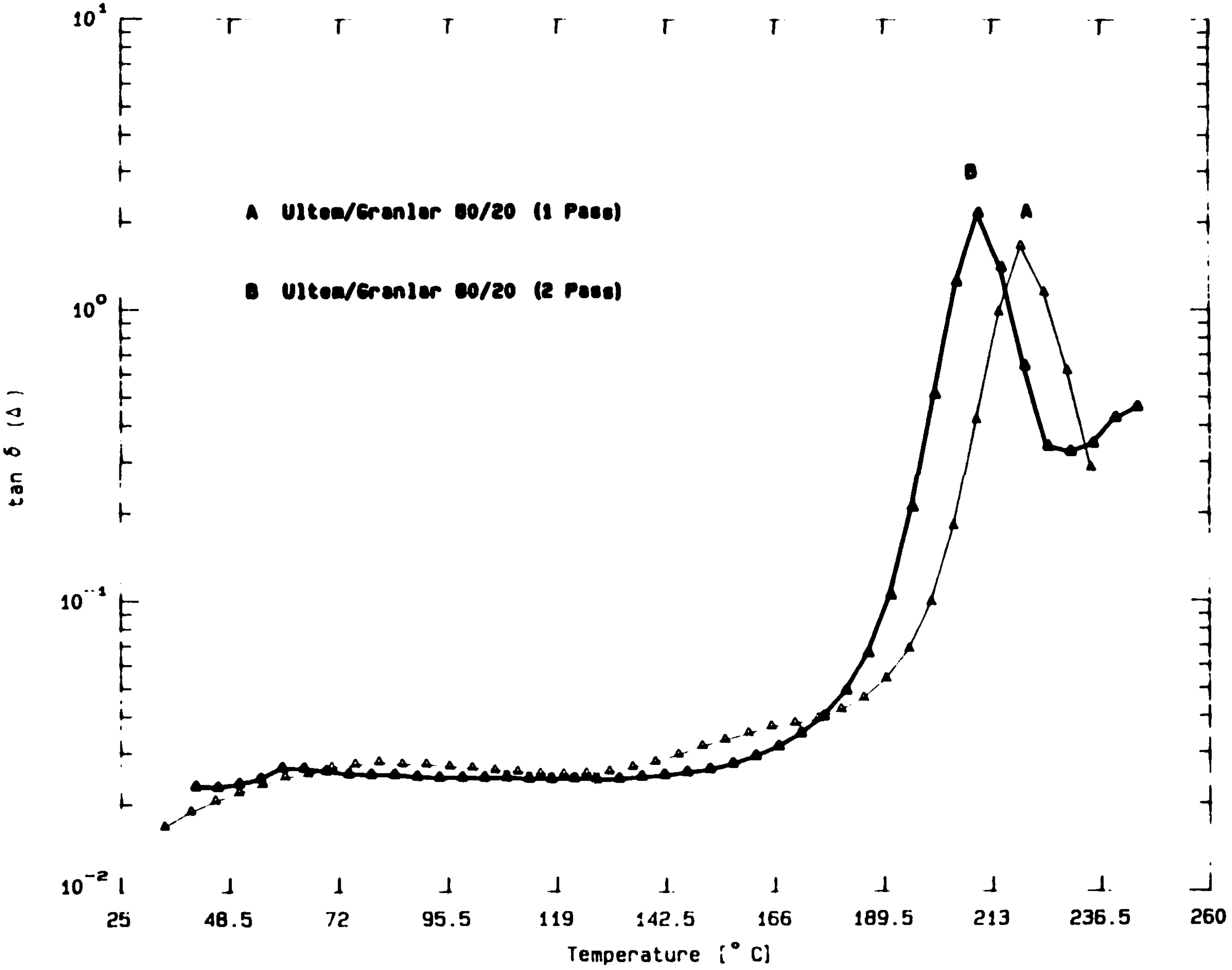


Fig 10

Fig.11 Dynamic Torsional Modululus vs Temperature of PP/Vectra A Blends.

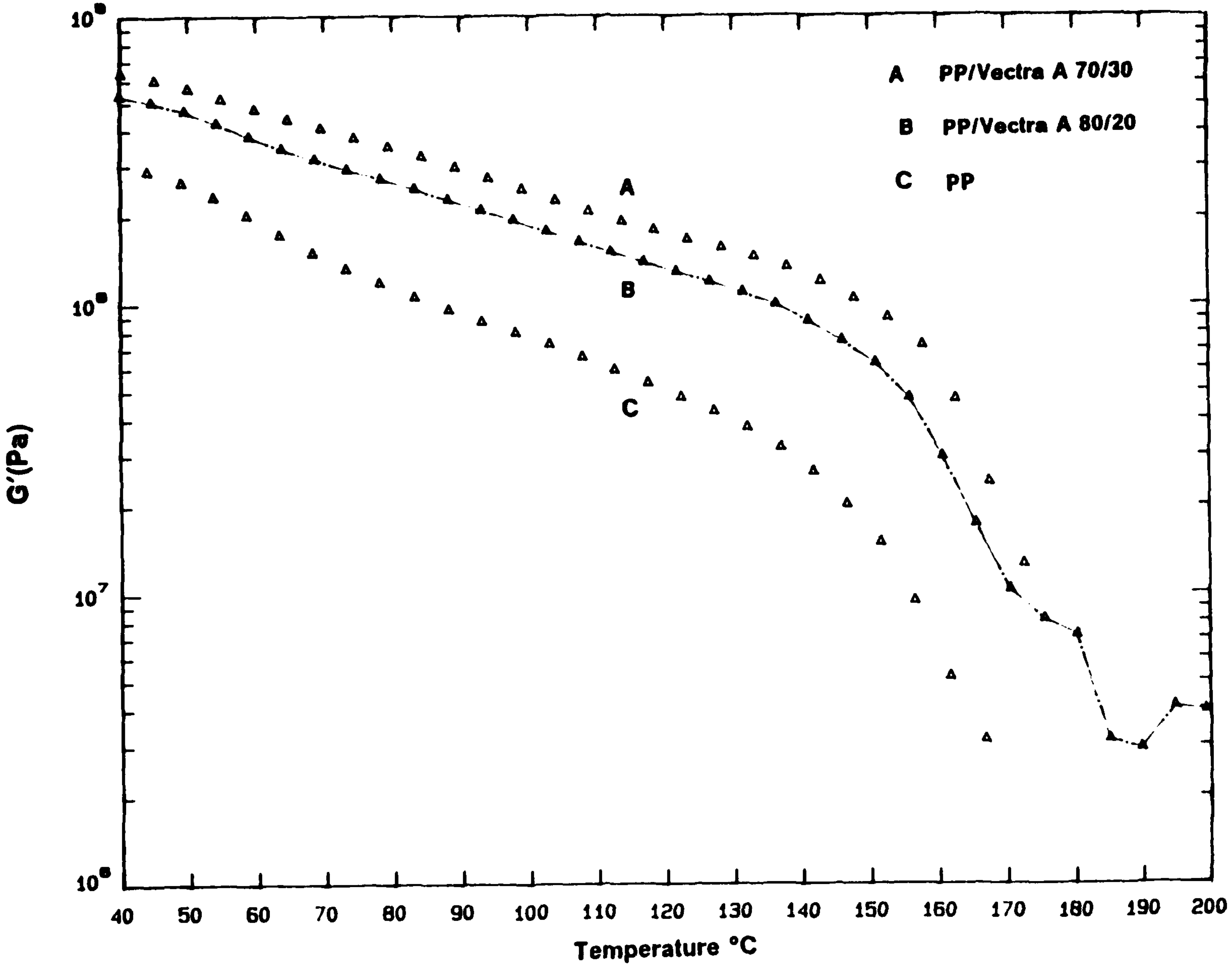
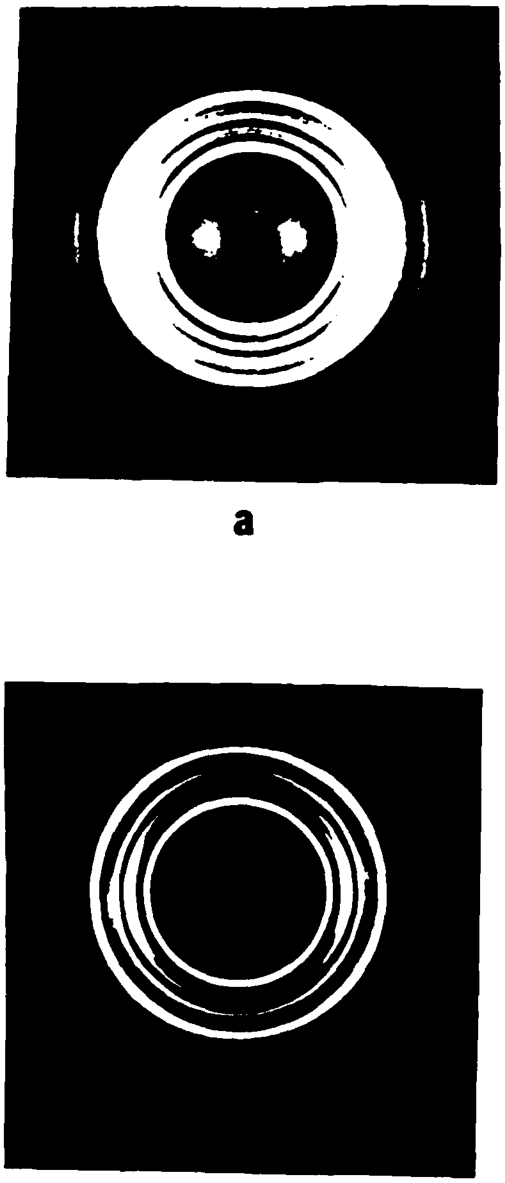


Fig 11



a

b

Fig. 12 WAXD patterns of PP/Vectra 70/30 blends (a) Injection molded plaque (b) Side wall of thermoformed part preheated to 200 °C

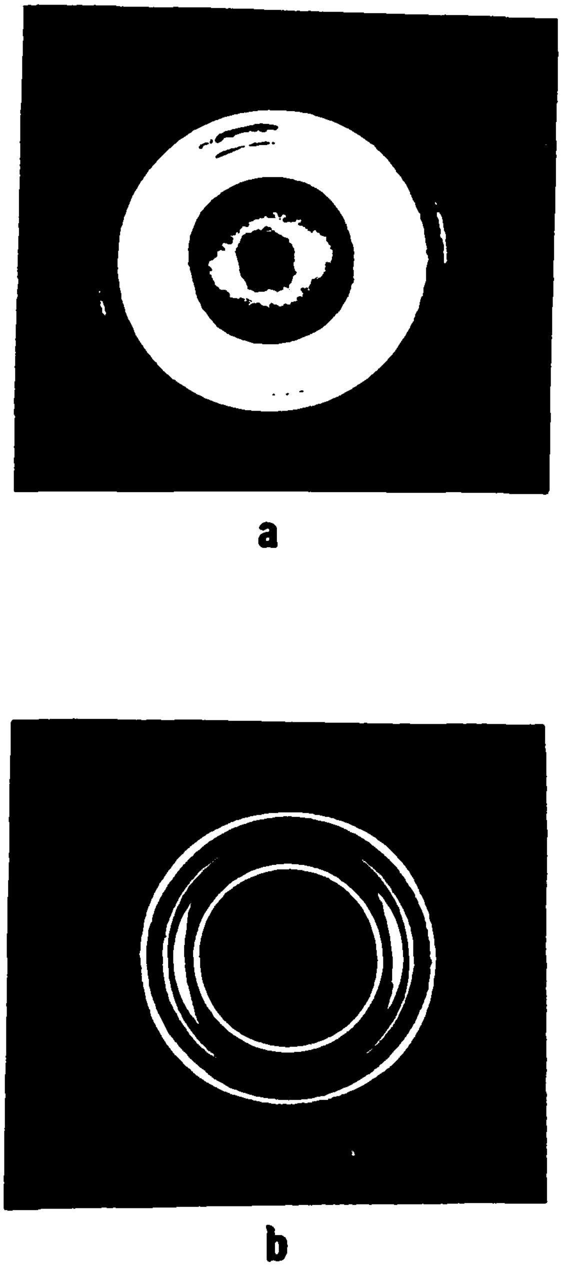


Fig. 13 WAXD patterns of PP/Vectra 80/20 blends (a) Injection molded plaque (b) Side wall of thermoformed part preheated to 200 °C