Miscibility, crystallization and melting behaviour, and semicrystalline morphology of ternary blends of poly(ε-caprolactone), poly(hydroxy ether of bisphenol A) and poly(styrene-*co*-acrylonitrile): 1. Miscibility, crystallization and melting behaviour

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The phase behaviour of ternary polymer blends consisting of poly(ε-caprolactone) (PCL), poly(hydroxy ether of bisphenol A) (Phenoxy) and poly(styrene-*co*-acrylonitrile) with an acrylonitrile content of 15 wt% (SAN15) was examined by means of visual observations, light transmission measurements, differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.). The influence of the blend composition, the crystallization temperature, the crystallization time and the d.s.c. scanning rate on the crystallization and the melting behaviour of the blends was investigated.

(Keywords: blend miscibility; phase behaviour; ternary polymer blends)

INTRODUCTION

As a consequence of the expensive development costs that are involved when synthesizing new polymers, there is an increasing interest in the blending of polymers. Most of the fundamental studies have been performed on binary polymer systems while investigations on ternary blends most often deal with systems in which only two binary combinations are totally miscible[1–6]; in this case one component is able to 'miscibilize' the immiscible or partially miscible blend. It is only recently that ternary blends, in which all three binary combinations are miscible, have been considered[7–9]; a phase separation is then often observed due to the 'Δχ-effect'[10]. Following this concept, all binary combinations should then have a negative, and similar χ-parameter in order to form a totally miscible ternary polymer system. These conditions were fulfilled for the ternary system consisting of PCL, Phenoxy and poly(vinyl methyl ether) (PVME), which was found to be miscible over the whole composition range[8].

The study of the phase behaviour of the binary PCL/SAN blend has been the subject of various investigations[11–15]. Chiu and Smith have examined the influence of the copolymer composition of SAN on its miscibility with PCL[14]. A miscibility window was found which included the SAN copolymers containing 8–28 wt% acrylonitrile; the PCL/SAN combinations located at the borders of this window exhibit a lower critical solution temperature (*LCST*) phase behaviour. The crystallization and melting behaviour of binary PCL/SAN blends was studied by Rim and Runt[16–19]. Examination of the influence of the method of preparation led to the conclusion that solvent-cast blends only exhibit one melting endotherm while melt blended samples show a double-melting behaviour due to recrystallization. Adding SAN to PCL results in a melting point depression[15,19].

PCL/Phenoxy blends were found to be miscible over the entire composition and temperature range[20–22] as a result of specific interactions between the hydroxyl groups of Phenoxy and the carbonyl groups of PCL[23–26]. A previous study in our laboratory[20] revealed a depression of the spherulite growth rate of PCL, as well as in the observed melting point, with increasing Phenoxy concentration. A double-melting behaviour was observed for the semicrystalline blends which was attributed to a secondary crystallization phenomenon.

The binary Phenoxy/SAN combinations have been investigated in previous work from this laboratory[27]. The acrylonitrile content of the SAN copolymer was varied (5, 10.4, 15, 16.9, 29 and 34 wt% AN) in order to examine its influence on the miscibility of the blends. All binary blends were concluded to be partially miscible over the whole concentration and temperature range that was studied.

While PCL is totally miscible with Phenoxy and SAN15, there is a fair chance that it is able to 'miscibilize' these components, at least to some degree, in a ternary system. Moreover, PCL is a crystallizable polymer; as a consequence, the liquid–solid phase separation due to

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crystallization, and the melting behaviour of the ternary blends, were also investigated.

EXPERIMENTAL

Blends of poly(ε-caprolactone) (PCL), poly(hydroxy ether of bisphenol A) (Phenoxy) and poly(styrene-*co*-acrylonitrile) with an acrylonitrile content of 15 wt% (SAN15) have been prepared from a THF solution (3% wt/vol) followed by precipitation in a tenfold excess of hexane. Phenoxy was obtained from Aldrich, PCL was kindly supplied by Solvay (Capsa 630), and the SAN copolymer was provided by DOW Benelux, The Netherlands. The molecular characteristics of these polymers are presented in *Table 1*.

The criteria used to confirm miscibility are the transparency of the blends and the presence of a single glass transition temperature. The former property was determined both by means of visual observations and also light transmission measurements (as a function of temperature). Differential scanning calorimetry (Perkin–Elmer Delta Series DSC-7) and dynamic mechanical thermal analysis (Polymer Laboratories DMTA MKII) were used to measure the glass transition temperatures, using scanning rates of 20°C min^{-1}, and 3°C min^{-1} (at a frequency of 1 Hz), respectively. The T_g was taken as the half-height of the transition in the d.s.c. scans and the maximum of the tan δ *versus* temperature curve in the d.m.t.a. studies. Samples for the d.m.t.a. scans (1 × 10 × 55 mm) were prepared by means of compression moulding at 160°C over a period of 10 min. Glass transition measurements were only performed on the blends containing a small concentration of PCL, because these can be made amorphous by quenching. In this case, the samples were heated on a hot stage (Mettler FP82) at 100°C for 5 min and then quenched in liquid nitrogen.

The study of the crystallization and melting behaviour was performed by d.s.c., using a scanning rate of 5°C min^{-1}, except where reported otherwise.

RESULTS AND DISCUSSION

Phase behaviour

Miscibility *versus* composition diagrams were established for the binary and ternary blends of PCL, Phenoxy and SAN15 based on the results of visual observations and light transmission measurements. These diagrams are presented at different temperatures (120, 175 and 210°C) in *Figure 1*. As can be seen, PCL is not a good 'miscibilizer' for the binary Phenoxy/SAN15 blends; only some ternary combinations with 80 and 90 wt% PCL are found to be miscible. In general, induction of miscibility in a partially miscible system by the addition of a third component is only possible when that system is located near the miscibility–immiscibility border. The demixing in the Phenoxy/SAN15 blends is apparently too strong for PCL to be able to 'miscibilize' them. In addition, an LCST phase behaviour is noticed for the PCL-rich ternary blends (80 and 90 wt% PCL).

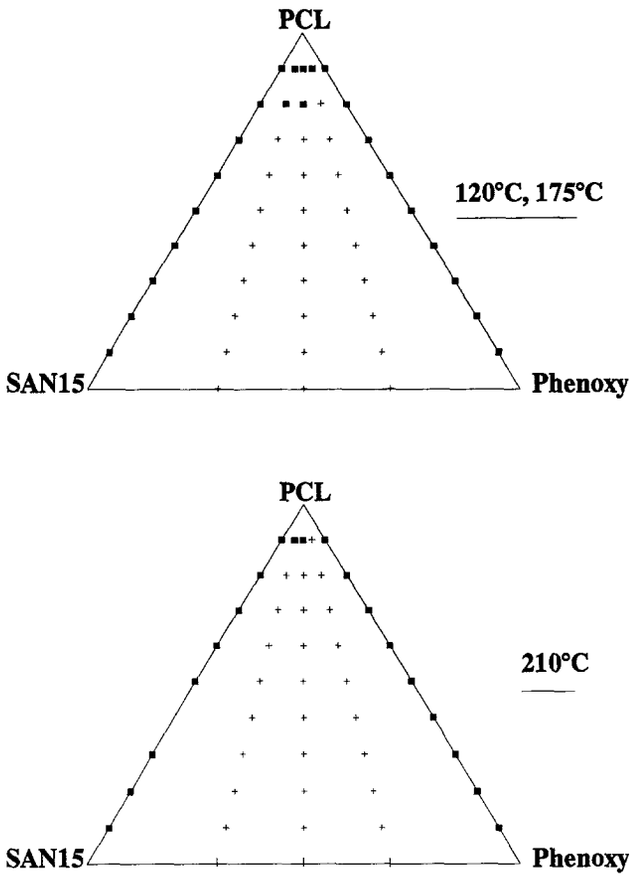


Figure 1 Miscibility *versus* composition diagrams of the binary and ternary PCL/Phenoxy/SAN15 blends at 120, 175 and 210°C: (+) partially miscible and; (■) miscible combinations

D.s.c. and d.m.t.a. experiments reveal that the binary PCL/Phenoxy and PCL/SAN15 blends containing 10 wt% PCL are totally miscible, whereas all ternary combinations with 10 wt% PCL show two glass transition temperatures corresponding to partial miscibility (*Figures 2* and *3*). These blends are completely amorphous. Variation of the Phenoxy/SAN15 ratio in the ternary blends containing 10 wt% PCL results in a temperature shift of only the lower glass transition temperature; the higher T_g seems to be independent of the blend composition. A similar behaviour was noticed for some Phenoxy/SANx (x = 5, 10.4, 15, 16.9, 29 and 34 wt% AN) blends examined in a previous study[27]. Phenoxy/SANx combinations with a high acrylonitrile content of the SAN copolymer showed two glass transitions of which one stays nearly constant with varying blend composition and corresponds roughly to that of the pure SAN; the T_g of the Phenoxy-rich phase increased with an increasing SAN concentration.

Ternary blends with a PCL content higher than 10 wt% show two T_gs, both of which vary with composition (*Figure 4*). However, the temperature shift of the highest glass transition temperature is smaller than that of the lower one.

Table 1 Molecular characteristics of PCL, Phenoxy and SAN15

Polymer	$\bar{M}_w$[a]	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]	T_g[b] (°C)	T_m[c] (°C)
PCL	57000	38000	1.49	−55	60
Phenoxy	45000	18000	2.60	91	–
SAN15	124000	65000	1.91	113	–

[a] Molecular weights and polydispersity determined by g.p.c. in THF at room temperature using polystyrene standards
[b] Measured by d.s.c., using a scan rate of 20°C min^{-1}
[c] Measured by d.s.c. using a scan rate of 5°C min^{-1}

The results presented in *Figures 2* and *3* can be explained by the presence (in minor quantities) of PCL; only 10 wt% of PCL is present and this has to be divided over two phases because PCL is miscible with Phenoxy as well as with SAN15. It appears that the miscibility of PCL with Phenoxy is better than with SAN15 since the T_g of the Phenoxy-rich phase is lower than the glass transition of the binary PCL/Phenoxy blend, in contrast to the SAN15-rich phase which has a higher T_g than the binary PCL/SAN15 blend. This better miscibility could be explained in terms of stronger specific interactions (e.g. hydrogen bonding). A surprising tendency with respect to the shift of the glass transitions when varying the blend composition in the ternary blends is observed in *Figures 2, 3* and *4*. Increasing the concentration of SAN15 (possessing the highest T_g) for a constant amount of PCL leads to a decrease of the glass transitions, instead of the expected increase. A possible explanation is the existence of an almost pure SAN15 phase with only a small concentration of PCL when compared to the amount of PCL present in the Phenoxy-rich phase. The amount of PCL in the SAN15-rich phase slightly increases, however, with increasing PCL concentration because the T_g corresponding to the SAN-rich phase decreases with increasing PCL concentration (compare *Figures 2* and *4*). As a result of the existence of an almost pure SAN15 phase, the ratio of PCL to Phenoxy in the Phenoxy-rich phase (lowest T_g) increases with increasing SAN15 concentration (since the amount of PCL stays constant and the Phenoxy concentration decreases) and leads to a decrease in the T_g. It is, however, possible that some SAN15 is present in the Phenoxy-rich phase since Phenoxy and SAN15 are partially miscible. This concentration must, however, be very small since no obvious effect on the glass transition temperature (such as an increase of T_g) of the Phenoxy-rich phase is noticed when increasing the amount of SAN15.

The partial miscibility of the crystallizable ternary blends is also seen in their melting behaviour, where a 'splitting' of the melting endotherms is noticed (see later).

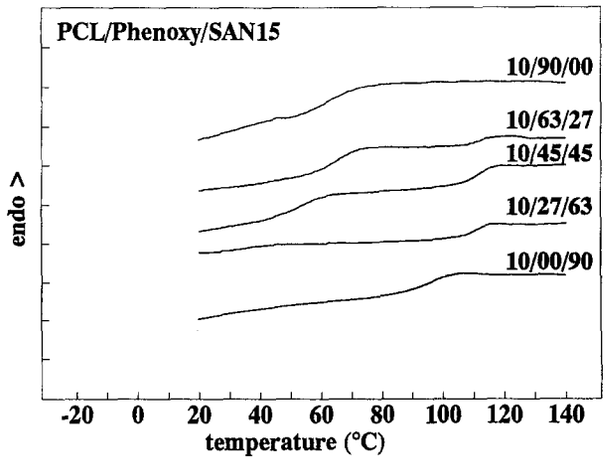


Figure 2 D.s.c. thermograms of the binary and ternary PCL/Phenoxy/SAN15 blends which contain 10 wt% PCL

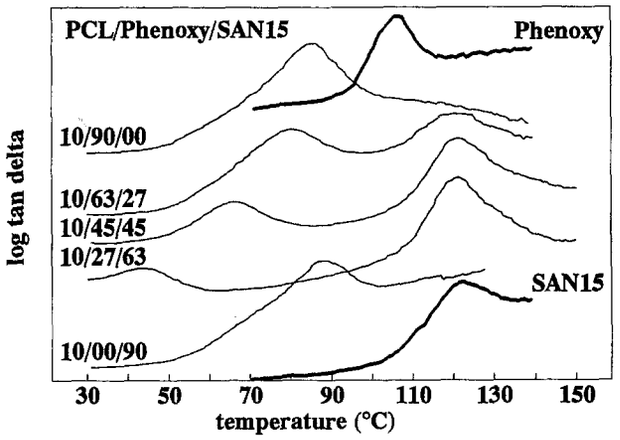


Figure 3 D.m.t.a. scans of the binary and ternary PCL/Phenoxy/SAN15 blends which contain 10 wt% PCL

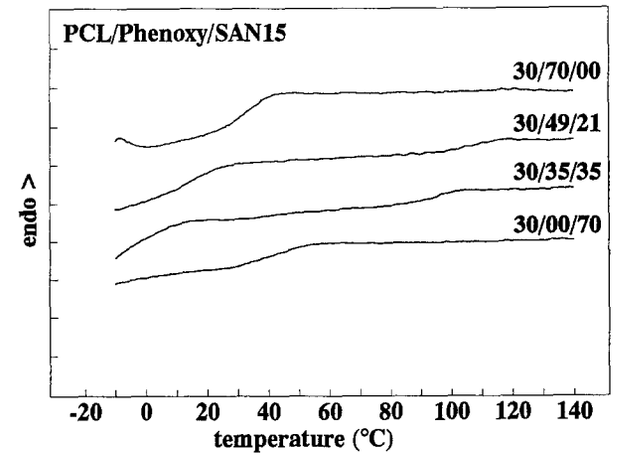


Figure 4 D.s.c. thermograms of the binary and ternary PCL/Phenoxy/SAN15 blends containing 30 wt% PCL

Crystallization and melting behaviour

Polymer blends with PCL as the semicrystalline component often show a double-melting behaviour. Runt and Rim[16] studied melt blended PCL/SAN samples and found a double-melting behaviour due to recrystallization. The d.s.c. thermograms of PCL/chlorinated polyethylene (CPE)[28], PCL/Phenoxy[20] and PCL/poly(styrene-*co*-maleic anhydride) (SMA)[29] blends prepared by the dissolution/coprecipitation method, followed by crystallization from the melt, also show two melting endotherms, in contrast to pure PCL; a mechanism of secondary crystallization was proposed, leading to the formation of thin crystalline lamellae which are located between thicker ones forming the spherulites.

Since a different melting behaviour for the PCL/Phenoxy/SAN15 blends is observed when varying the crystallization time, a distinction will be made between long- and short-term phenomena. In addition, the miscible and partially miscible blends will be discussed separately.

Processes due to long crystallization times. The ternary PCL/Phenoxy/SAN15 blends show a double-melting behaviour similar to that of the binary PCL/Phenoxy blends[20] mentioned above. In *Figure 5*, the d.s.c. data of the miscible binary and ternary blends containing 90 wt% PCL, isothermally crystallized at 22°C for 13 days, are presented and compared with the melting behaviour of pure PCL. The temperature of the highest melting endotherm is decreased with respect to the melting peak of pure PCL and an additional lower endotherm is observed. For pure PCL no clear lower-temperature melting peak is noticed, but instead a deviation from the base line can be seen.

Variation of the crystallization temperature results in a clear distinction of a lower-temperature melting endotherm for PCL (*Figure 6*); the higher the crystallization temperature the better the double-melting behaviour is detected. Increasing the crystallization temperature for the binary and ternary blends results in a shift of both endotherms to higher temperatures (*Figures 7* and *8*), which is, however, more pronounced for the lower-temperature melting peak.

From these observations it is clear that a slower crystallization, which takes place at higher crystallization temperatures, results in a double-melting behaviour in

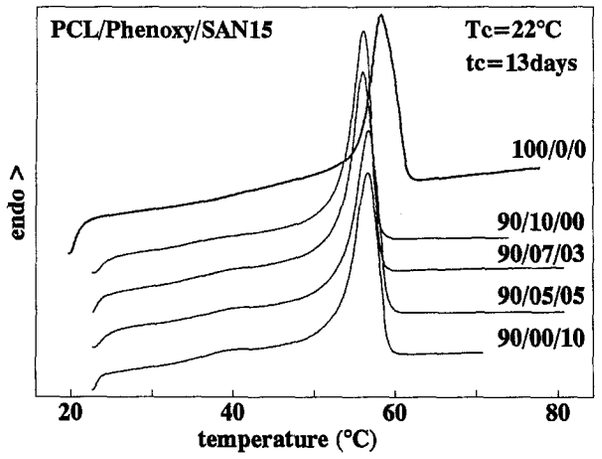


Figure 5 D.s.c. thermograms showing the double-melting behaviour of pure PCL and of the PCL/Phenoxy/SAN15 blends containing 90 wt% PCL; $T_c = 22°C$, $t_c = 13$ days

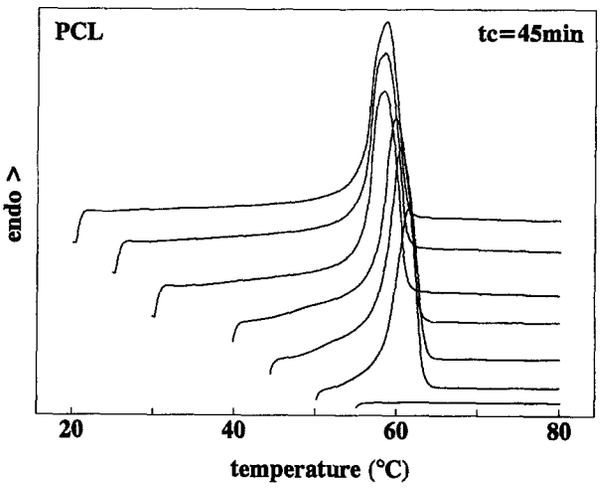


Figure 6 D.s.c. thermograms showing the influence of the crystallization temperature on the melting behaviour of pure PCL; $t_c = 45$ min

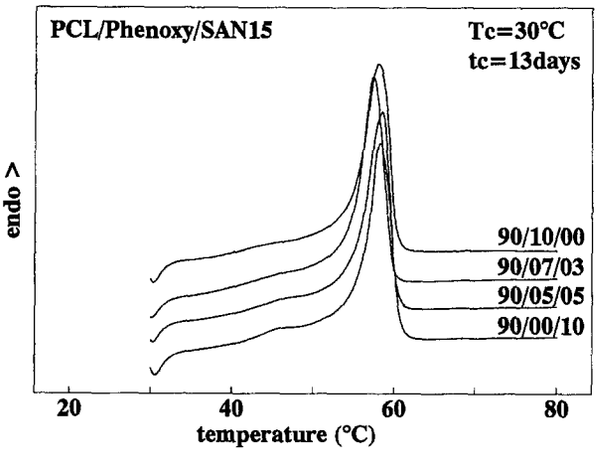


Figure 7 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 blends containing 90 wt% PCL; $T_c = 30°C$, $t_c = 13$ days

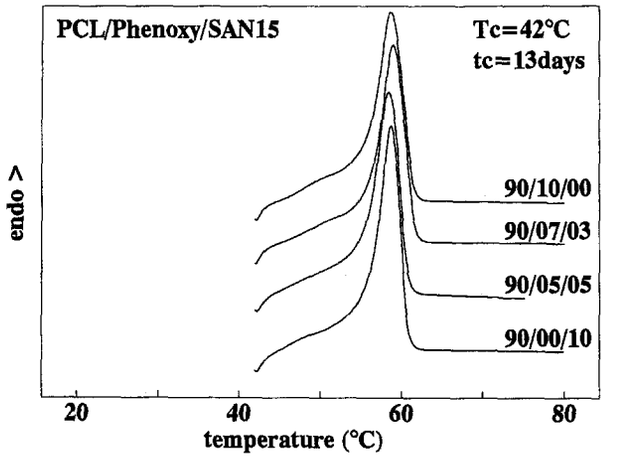
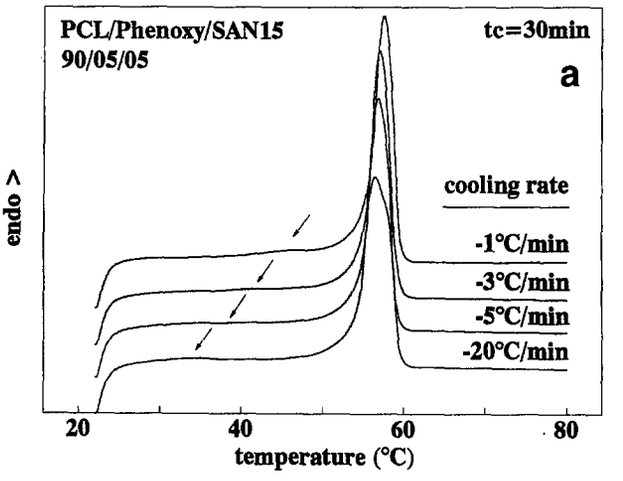


Figure 8 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 blends containing 90 wt% PCL; $T_c = 42°C$, $t_c = 13$ days



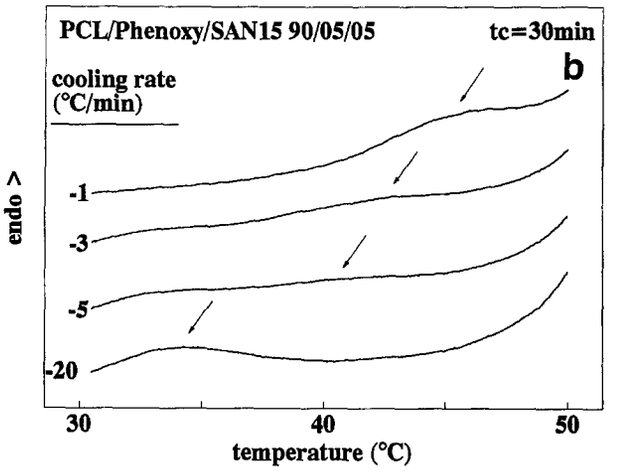


Figure 9 (a) D.s.c. thermograms showing the influence of the cooling rate before crystallization on the melting behaviour of the PCL/Phenoxy/SAN15 (90/05/05) blend; $T_c = 22°C$, $t_c = 30$ min. (b) Enlargement of the temperature range from 30 to 50°C to highlight the position of the first-melting endotherm

which both endotherms are separated only by a few degrees. For very slow crystallization rates a single-melting behaviour would perhaps be observed. Therefore, the rate at which the samples were cooled from the melt to the crystallization temperature was varied from 20 to 1°C min^{-1} (see *Figure 9*). A shift of the lower-temperature endotherm to higher values with a decreasing cooling rate is observed, as was also noticed when increasing the crystallization temperature. A single-melting behaviour may be possible when extremely low cooling rates are used.

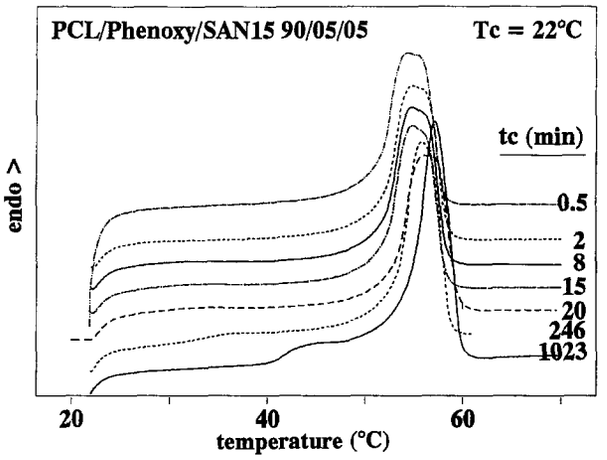


Figure 10 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 (90/05/05) blend crystallized for different times at $T_c = 22°C$

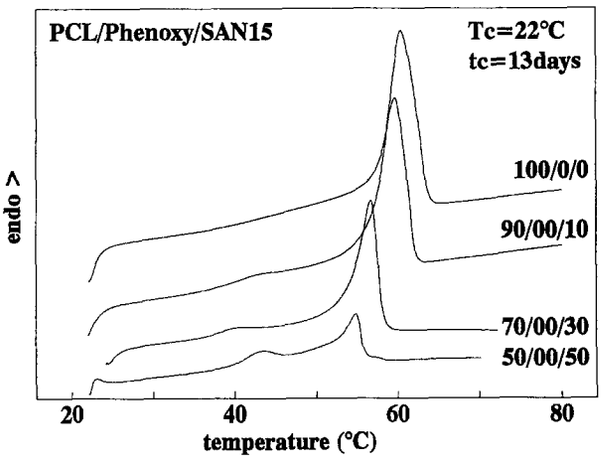


Figure 11 D.s.c. thermograms showing the influence of the blend composition on the double-melting behaviour of the binary PCL/SAN15 blends; $T_c = 22°C$, $t_c = 13$ days

Crystallization as a function of time reveals that the lower-melting peak only arises after prolonged crystallization times (*Figure 10*). Recrystallization cannot be responsible for this behaviour, since in this case two melting endotherms should be present from the start and the lower-melting peak should disappear with increasing crystallization time.

Therefore, a secondary crystallization process is responsible for this behaviour, probably due to the fast crystallization of PCL. The more amorphous material is added, the more significant the low-temperature endotherm becomes (*Figure 11*). This means that the presence of the amorphous components is clearly hindering the crystallization process of PCL. The presence of a totally or partially miscible amorphous phase is responsible for the fact that the diffusion of the semicrystalline and amorphous components, *in opposite directions*, which is necessary for the crystallization process, cannot take place in the proper way. When the concentration of amorphous material is increased, it seems that more and more PCL molecules become trapped in the remaining amorphous phase and therefore cannot reach the crystal nuclues in sufficient time. These 'isolated' PCL chains are able to crystallize only after prolonged times, i.e. when the primary crystals forming the spherulites are already completely formed (*Figure 12*). Moreover, the increase of the T_g of the remaining amorphous phase during crystallization also reduces the crystallization window (between T_g and T_m), and as a consequence of this the diffusion rate is also reduced.

The miscibility of the PCL/Phenoxy/SAN15 blends is also exhibited in the melting behaviour. Totally miscible blends show a double-melting behaviour due to secondary crystallization. For partially miscible blends two lower-melting endotherms can be distinguished (indicated by the arrows in *Figure 13*), while only one higher-melting peak is observed, probably due to an overlap of two different peaks. This means that two phases with sufficient PCL, and which are able to crystallize, are present. Ternary blends with 50 wt% PCL show a rather

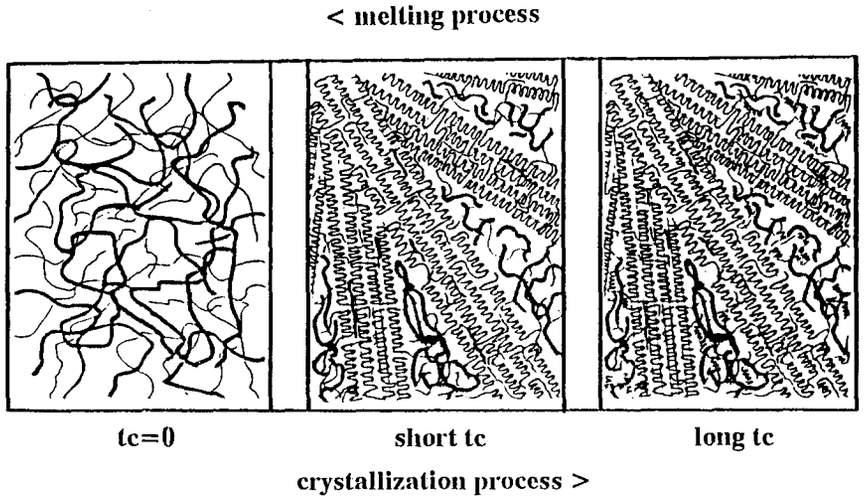


Figure 12 Schematic representation of the secondary crystallization process: thin lines, crystallizable component; thick lines, amorphous material

complex melting behaviour which makes it difficult to allow an exact determination of the various peaks (*Figure 14*). A broad, low-temperature melting endotherm is observed, in addition to a double, higher-temperature peak for some combinations of the components.

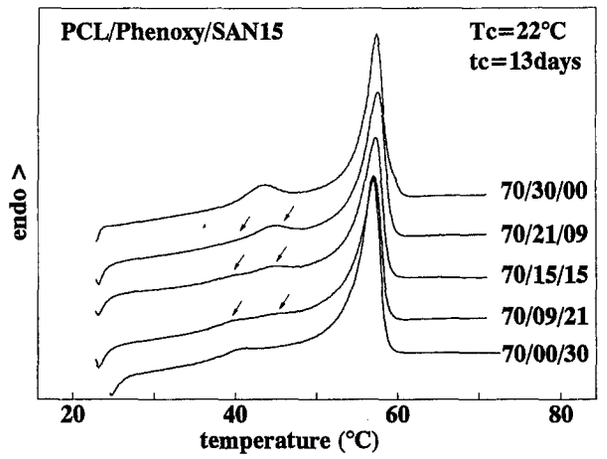


Figure 13 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 blends containing 70 wt% PCL, indicating the state of blend miscibility; $T_c = 22°C$, $t_c = 13$ days

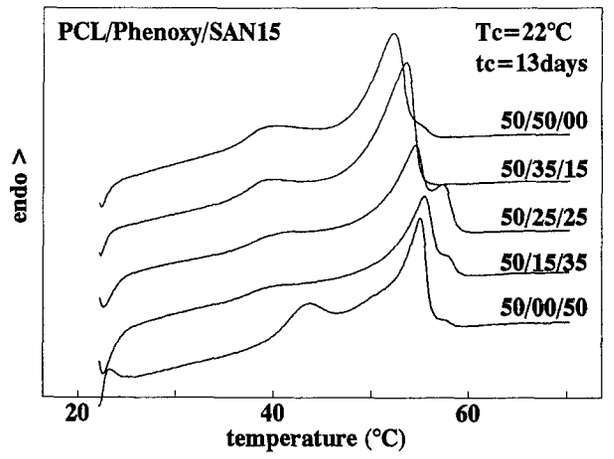


Figure 14 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 blends containing 50 wt% PCL, indicating the state of blend miscibility; $T_c = 22°C$, $t_c = 13$ days. Note that the scale of the vertical axis is reduced by a factor of 2, when compared to the previous thermograms

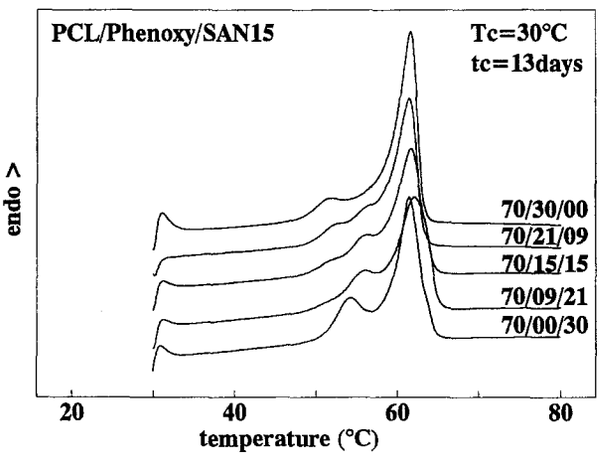


Figure 15 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 blends containing 70 wt% PCL; $T_c = 30°C$, $t_c = 13$ days

When the crystallization temperature is increased, the same tendency is observed as seen for the fully miscible blends (*Figures 15* and *16*). However, the higher the PCL content in the blend, then the smaller is the temperature shift. Variation of the crystallization time (*Figure 17*) shows again that the lower-temperature endotherm only appears after a few minutes. The time at which

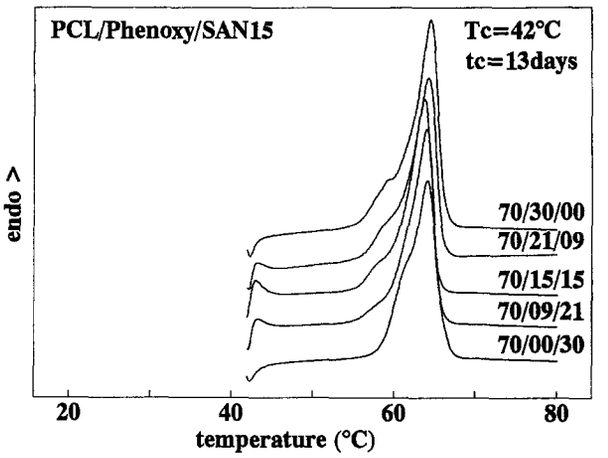


Figure 16 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 blends containing 70 wt% PCL; $T_c = 42°C$, $t_c = 13$ days

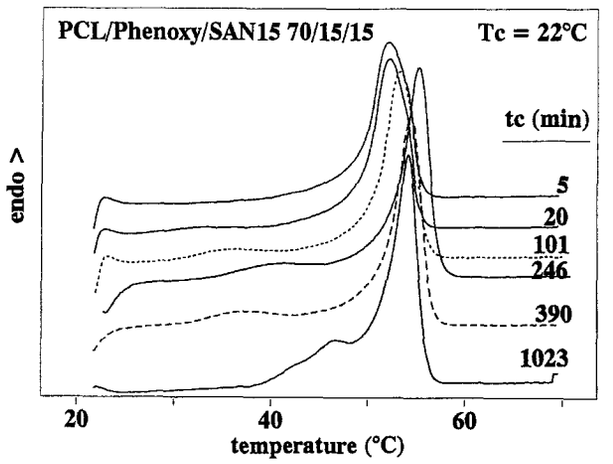


Figure 17 D.s.c. thermograms showing the melting behaviour of the PCL/Phenoxy/SAN15 (70/15/15) blend crystallized for different times at $T_c = 22°C$

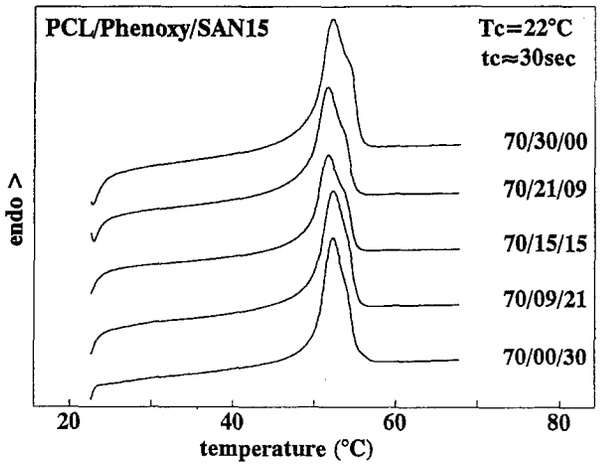


Figure 18 Secondary d.s.c. thermograms of the PCL/Phenoxy/SAN15 blends containing 70 wt% PCL; $T_c = 22°C$

this lower-melting peak arises depends on the blend composition (compare *Figures 10* and *17*).

Processes due to short crystallization times. Secondary d.s.c. melting behaviour scans (recorded immediately after the first ones and corresponding to a crystallization time of ~30 s) show, in addition to the melting endotherm at ~52°C, a shoulder at a higher temperature (*Figure 18*). Since the same observation is noticed for the miscible binary and the partially miscible ternary blends, the presence of the shoulder cannot be assigned to phase separation. A process of recrystallization could be responsible for these short-term observations. Therefore the melting behaviour was examined as a function of the heating rate. Increasing the d.s.c. scanning rate leads to an overlap of both peaks (*Figures 19*, *20* and *21*). A disadvantage of such experiments, however, is the broadening of the peaks with increasing heating rate, which makes the interpretation very difficult. Since the melting behaviour is recorded after short crystallization times ($t_c \approx 30$ s), the lower-melting peak is absent.

This recrystallization effect was also noticed when crystallization experiments were performed as a function of time (see *Figure 17*). The recrystallization shoulder is also present after a crystallization time of 30 s for the miscible PCL/Phenoxy/SAN15 (90/05/05) blend (*Figure 10*). For longer crystallization times (246 and 1023 min) no recrystallization is occurring and the melting peak is located at an even higher temperature than that at which the recrystallization shoulder occurs.

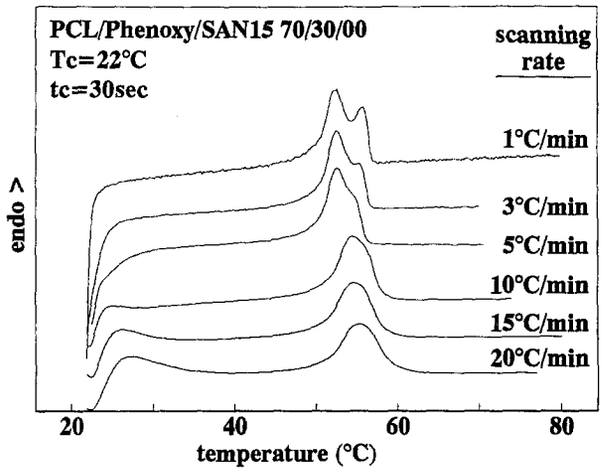


Figure 19 D.s.c. thermograms showing the influence of the scanning rate on the melting behaviour of the PCL/Phenoxy/SAN15 (70/30/00) blend; $T_c = 22°C$, $t_c = 30$ s

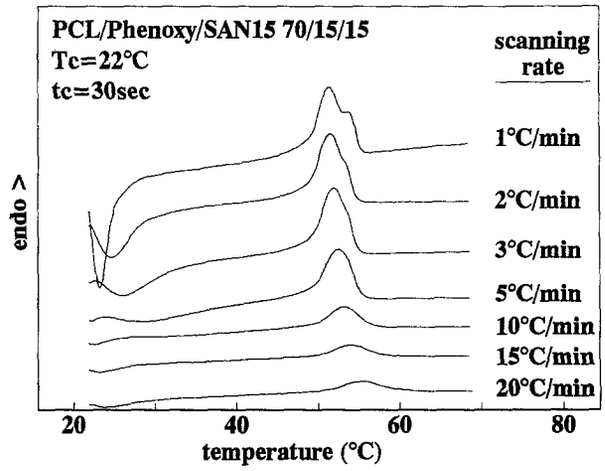


Figure 20 D.s.c. thermograms showing the influence of the scanning rate on the melting behaviour of the PCL/Phenoxy/SAN15 (70/15/15) blend; $T_c = 22°C$, $t_c = 30$ s

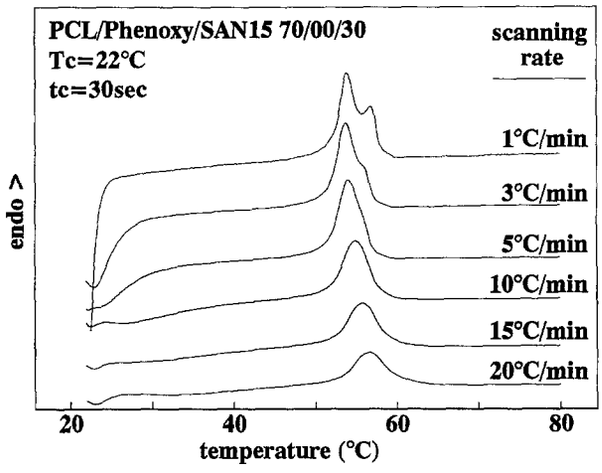


Figure 21 D.s.c. thermograms showing the influence of the scanning rate on the melting behaviour of the PCL/Phenoxy/SAN15 (70/00/30) blend; $T_c = 22°C$, $t_c = 30$ s

CONCLUSIONS

The phase behaviour of the ternary PCL/Phenoxy/SAN15 polymer blend system was studied using several characterization techniques. Only a few ternary blends with a high content of PCL (e.g. 90 and 80 wt%) were found to be miscible over the whole temperature range that was studied, while most of the blends were already phase-separated at room temperature. A rather complex melting behaviour, which depends both on the state of miscibility and also on the crystallization conditions, is observed for all of the blends. Miscible blends that have been crystallized for several days show a double-melting behaviour as a result of secondary crystallization. For the partially miscible blends an even more complex behaviour is seen, since a splitting of the melting endotherms takes place on account of phase separation. For small crystallization times the secondary crystallization is absent, but a recrystallization effect can then be observed for the miscible as well as for the partially miscible blends.

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