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Ternary blends of PCL, SAN15 and SMA14: miscibility, crystallization and melting behaviour, and semicrystalline morphology

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The miscibility and phase behaviour of the ternary blend consisting of poly(ε-caprolactone) (PCL), poly(styrene-*co*-acrylonitrile) with 15 wt% acrylonitrile (SAN15) and poly(styrene-*co*-maleic anhydride) with 14 wt% maleic anhydride (SMA14) have been investigated by means of visual observations, light transmission measurements, differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis. The influence of the molecular weight of the components and of the blend composition is discussed. All crystallizable blends show two melting endotherms in the d.s.c. thermograms. The crystallization conditions were varied to examine this complex melting behaviour. The lamellar morphology of the semicrystalline blends was studied to obtain information about the most important morphological parameters (e.g. long spacing, thickness of the crystalline and amorphous layers, and width of the transition layer). On the basis of these morphological parameters, it was possible to get an idea about the type of segregation of the amorphous components (SAN15 and SMA14) in the blends during crystallization.

(Keywords: blend miscibility; *LCST* behaviour, crystallization and melting behaviour; secondary crystallization; lamellar morphology)

INTRODUCTION

The blending of polymers to obtain new polymeric materials is a strategy that has been used for some years now. As a consequence of the unfavourable enthalpy of mixing and the negligible entropy of mixing, thermodynamics predicted that only a small number of miscible blends could be obtained[1]. A proper choice of the blend components with respect to specific interactions can, however, lead to miscibility[2]. When dealing with copolymers another concept should be taken into account: the repulsion effect[3–6].

An immiscible blend can be made attractive by addition of a compatibilizer[7], but also by adding a third polymer, resulting in a ternary polymer system. Klotz and Cantow[8] calculated some possible phase behaviours for ternary blends based on the blend interaction parameters of the three binaries involved in the ternary blend. An interesting phenomenon was the existence of a kind of a closed-loop phase-separated area for a ternary system of which all three binaries were miscible. The demixing of these ternary combinations is explained by the $\Delta\chi$ effect[9]. Such a phase behaviour was experimentally observed in our laboratory for the ternary blend consisting of poly(ε-caprolactone) (PCL), poly(styrene-*co*-acrylonitrile) (SAN) and poly(styrene-*co*-maleic anhydride) (SMA), namely SAN24 and SMA25 where the number refers to the acrylonitrile (AN) or maleic anhydride (MA) content in wt%[10]. To investigate the influence of the copolymer composition of SAN and SMA, a ternary blend of PCL with SAN15 and SMA14 was investigated. The phase behaviour of the three binaries involved in the ternary system is already mentioned in the literature. PCL/SAN[11–18] shows a miscibility window within the range SAN6 to SAN28. PCL/SMA has been studied in the past using SMA copolymers with 14 and 28 wt% of maleic anhydride[19], while recently the PCL/SMA blend systems using an SMA copolymer with a MA content of 2, 8, 14, 17 and 20 wt% were examined[20]. PCL/SMA2 is an immiscible blend; the blends of PCL with SMA8 and SMA14 exhibit lower critical solution temperature (*LCST*) behaviour while the mixtures of PCL with SMA17, SMA20 and SMA28 are totally miscible. The binary blend consisting of SAN and SMA is only miscible when the amount of styrene (by weight) in both copolymers is nearly the same[21–25]. Based on this information, the components of the ternary system were chosen to be PCL, SAN15 and SMA14. In agreement with the literature data the three binaries should be miscible. Other factors such as molecular weight and polydispersity must, however, also be taken into account.

The crystallization and melting behaviour of PCL[26–33] and its blends[16–42] have been the subject of many investigations because of the often complex melting behaviour ascribed to recrystallization[34–39], demixing[39] or secondary crystallization[10,19,20,39]. Not only binary[16,19,20,32–35] but recently also ternary blends[10,36–40,42] were examined.

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Table 1 Some molecular characteristics of the polymers used in this study

Material[a]	M_w[b]	M_n[b]	M_w/M_n	T_g (°C)[c]	T_m (°C)[c]
PCLH	101 000	53 000	1.90	−56	61
PCLL	57 000	38 000	1.49	−55	60
PCLa	30 000	15 000	2.00	−61	
PCLb	22 500	14 000	1.60	−63	
SAN15	124 000	65 000	1.91	113	–
SMA14H	489 000	119 000	4.10	131	–
SMA14Lb	134 000	58 900	2.26	130	–

[a] H and L denote high and low molecular weight components; a = poly(ϵ-caprolactone) used in ref. 15; b = poly(ϵ-caprolactone) and poly(styrene-*co*-maleic anhydride) used in ref. 19

[b] Molecular weights were determined in THF by means of gel permeation chromatography, at room temperature using polystyrene standards

[c] Glass transitions and the d.s.c. melting peak temperatures were measured with d.s.c. (scanning rate: 20 and 5°C min^{-1}, respectively)

The crystallizable binary blends used in this study have already been mentioned in the literature. For the PCL/SAN system, different preparation methods have been used and the complexity of the melting behaviour seems to depend upon the sample preparation. A single melting endotherm is observed by dynamic scanning calorimetry (d.s.c.) when the blends are prepared by melt blending[34,35], while solvent casting[34,35] and solution-coprecipitation[10,39] reveal multiple melting endotherms due to recrystallization and/or secondary crystallization, respectively. To our knowledge, the binary polymer system of PCL and SMA has only been examined in our laboratory[19,20]. All crystallizable blends prepared by the solution-coprecipitation technique showed a double melting behaviour due to secondary crystallization.

Small angle X-ray scattering (SAXS) has proved to be a powerful tool in the investigation of the semicrystalline morphology of polymers. The morphology of PCL and some of its binary blends[15,19,41–46] has been considered in the past. To our knowledge, no fundamental morphology studies were performed on ternary PCL blends using SAXS.

In this paper the influence of the molecular weight and the blend composition of the ternary polymer blend PCL/SAN15/SMA14 is discussed with respect to miscibility, crystallization and melting behaviour, and semicrystalline morphology. The crystallization conditions (temperature, time, scanning rate) are varied to examine the double melting behaviour. Some morphological parameters are determined and related to the complex crystallization and melting behaviour.

EXPERIMENTAL

Blends of poly(ϵ-caprolactone) (PCL), poly(styrene-*co*-acrylonitrile) with 15 wt% acrylonitrile (SAN15) and poly(styrene-*co*-maleic anhydride) with 14 wt% maleic anhydride (SMA14) were prepared using the solution-coprecipitation method. After dissolution of the polymers in tetrahydrofuran (THF) (3% w/v), the solution was added to an excess of hexane. The resulting coprecipitate was filtered and dried in a vacuum oven at 45°C for 3 days. Some molecular characteristics of the polymers involved in this study are presented in *Table 1*. PCLH was obtained from Union Carbide (P-700) and PCLL from Solvay (CAPSA 630). The SAN15 copolymer was kindly provided by Dow Benelux, The Netherlands and the SMA14 copolymers (SMA14H and SMA14L; H and L denote high and low molecular weight) by DSM Research, The Netherlands.

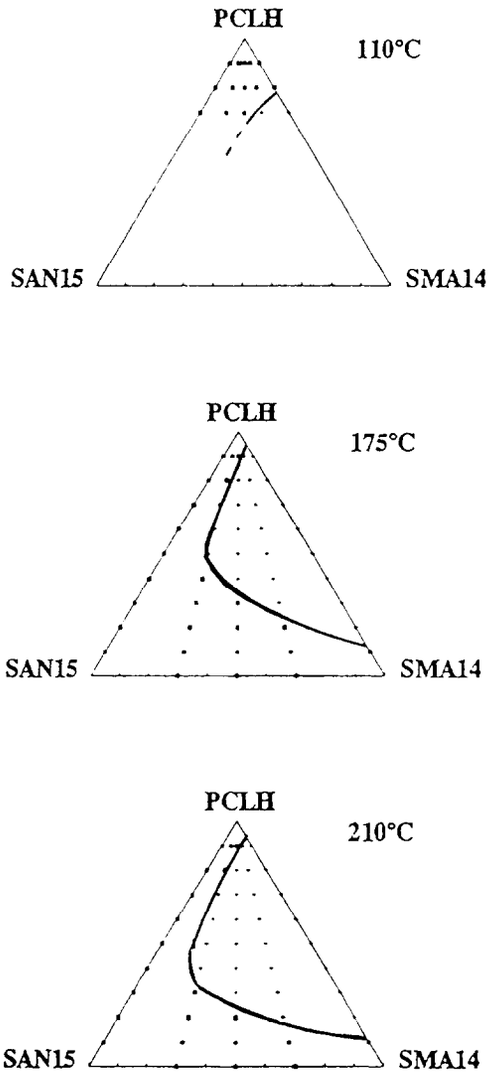

Figure 1 Miscibility *versus* composition diagrams of the ternary PCLH/SAN15/SMA14 polymer system determined at different temperatures (110, 175 and 210°C): +, partially miscible (i.e. phase-separated in different phases consisting of a mixture of the components, but with different compositions); ■, miscible; —, suggested phase boundary

Visual observations were used to monitor the transparency of the blends above their melting temperature. The blends were considered to be miscible when transparent and phase-separated when opaque. Light

Table 2 Influence of molecular weight of PCL and SMA14 on the phase behaviour of the binary PCL/SMA14 blend as examined by visual observations and light transmission measurements. Molecular characteristics of the different polymers are given in *Table 1*

	PCLH/SMA14H			PCLb/SMA14H			PCLa/SMA14L		
	100°C	200°C	300°C	100°C	200°C	300°C	100°C	200°C	300°C
0/100	t	t	t	t	t	t	t	t	t
10/90	t	o	o	t	t	t	t	t	t
20/80	t	o	o	t	t	t	t	t	t
30/70	o	o	o	t	t	t	t	t	t
50/50	[a]	o	o	[a]	t	t	[a]	t	t
70/30	[a]	o	o	[a]	t	t	[a]	t	t
80/20	[a]	o	o	[a]	t	t	[a]	t	t
90/10	[a]	o	o	[a]	t	t	[a]	t	t
100/0	[a]	t	t	[a]	t	t	[a]	t	t

t, transparent (= miscible); o, opaque (= partially miscible)
[a] It was impossible to study these blends at this temperature because the temperature was too low to bring them to the molten state

transmission measurements were performed in the temperature range 80 to 300°C.

Glass transition temperatures of the amorphous blends were recorded using d.s.c. (20°C min^{-1}) and dynamic mechanical thermal analysis (d.m.t.a.; 3°C min^{-1} and 1 Hz). The d.m.t.a. specimens (60 × 10 × 1 mm) were prepared by compression moulding at 160°C and were scanned in the dual cantilever mode.

D.s.c. experiments were performed on 5 mg of polymer (blend) to investigate the crystallization and melting behaviour. A scanning rate of 5°C min^{-1} was used, except when stated otherwise. All blends were given a thermal pre-treatment (10 min at 100°C to remove all crystalline residues) before crystallization of PCL at a specific temperature was performed. Relative crystallinity values were determined with d.s.c. by dividing the integrated area under the melting endotherm by the melt enthalpy of the 100% pure PCL ($\Delta H^{\circ}_{PCL} = 135.6\,J\,g^{-1}$).

SAXS measurements were performed on pure PCL and on the binary and ternary blends which were found to be totally miscible. The same sample preparation was used as mentioned above for the d.m.t.a. specimens. A Rigaku rotating anode, operating at 7.5 kW, was provided with a Kratky camera in the infinite slit geometry. Ni-filtered Cu$K\alpha$ radiation was used throughout. The SAXS data were acquired by means of the photographic method or using a one-dimensional position sensitive proportional counter. Data treatment was performed using the FFSAXS-5 program of Vonk[47]. A more detailed description of the experimental route and the data treatment used, has been given elsewhere[48].

RESULTS AND DISCUSSION

Miscibility and phase behaviour

Miscibility *versus* composition diagrams (*Figure 1*) were established at different temperatures (110, 175 and 210°C) for the ternary PCLH/SAN15/SMA14 polymer system based on the results obtained by visual observations, light transmission experiments and glass transition measurements (it should be noted that throughout the text 'SMA14' is used for the high molecular weight SMA14, SMA14H, except when a comparison is made between two different grades of SMA). The diagram at a temperature of 110°C represents only the blends with a high concentration of PCLH (10 to 30 wt% amorphous material), since adding more SAN and/or SMA leads to blends which can not be molten at that temperature. An *LCST* phase behaviour was observed for some binary PCLH/SMA14 compositions in contrast with the results of Defieuw *et al*[19]. The occurrence of the *LCST* behaviour, however, can be explained by the higher molecular weight of both components used in this study.

The influence of molecular weight on the phase behaviour of the binary PCL/SMA14 system was investigated using different PCL and SMA14 polymers with respect to their molecular weight. The data used in *Table 2* are those obtained from visual observations and light transmission measurements. The use of low molecular weight poly(ϵ-caprolactone) resins (PCLa or PCLb) results in a totally miscible blend system. It is clear that increasing the molecular weight of PCL gives rise to an *LCST* behaviour which is located at a lower temperature for PCLH than for PCLb.

In *Figure 1* an area of partially miscible ternary blends is observed on the right-hand side of the diagrams. This region represents the ternary blends with a high amount of SMA14. Decreasing the molecular weight of PCL (from PCLH to PCLL: M_w = 101 000 to 57 000) results in a smaller demixing area (compare *Figure 1* with *Figure 2*).

Glass transition measurements were only performed on the blends with a low concentration of PCL (i.e. <50 wt% PCL, PCLH and PCLL). PCL is known to crystallize very rapidly and, as a consequence, quenching to the amorphous state of samples containing more than 50 wt% PCL is impossible. D.s.c. and d.m.t.a. scans of PCL-rich blends (>50 wt% PCL) are difficult to interpret because the glass transition can be broadened due to the demixing of the blend as well as to the crystallization of PCL. In addition, when PCL crystallizes, the composition of the amorphous phase, responsible for the value of the glass transition, changes. As a consequence, blends with a high concentration of PCL were not examined with d.s.c. and d.m.t.a.; only the binary and ternary blends with 30 and 40 wt% PCLH were measured. For these blends only one glass transition temperature was detected, consistent with the results from visual observations and light transmission measurements.

The partial miscibility of the binary and ternary blends is not expressed in the melting behaviour as was observed

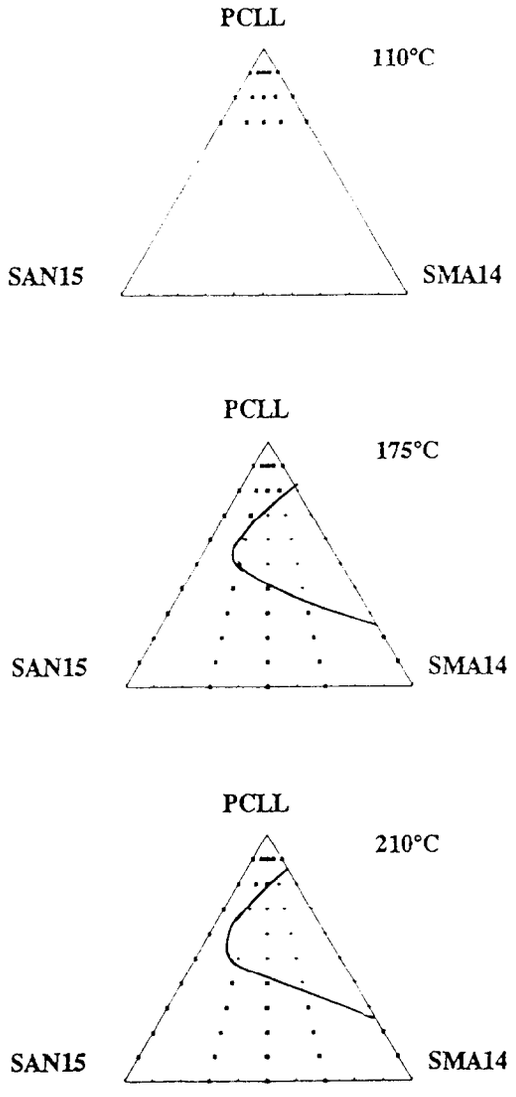

Figure 2 Miscibility *versus* composition diagrams of the ternary PCLL/SAN15/SMA14 polymer system determined at different temperatures (110, 175 and 210°C): +, partially miscible; ■, miscible; —, suggested phase boundary

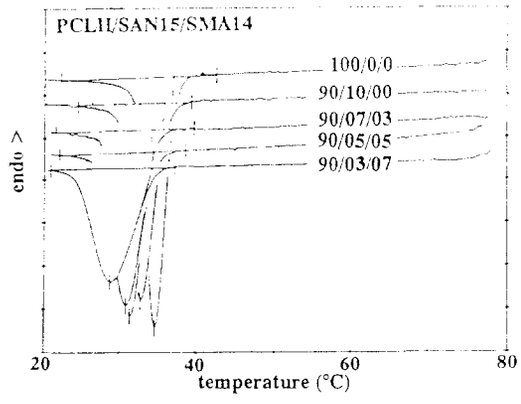

Figure 3 Crystallization exotherms of pure PCLH compared with some of the blends with 90 wt% PCLH

in the PCLL/phenoxy/SAN15 polymer system[39], where a splitting of the melting endotherms was noticed. This means that in the case of PCL/SAN15/SMA14 (PCLH and PCLL), only one phase contains sufficient PCL to be

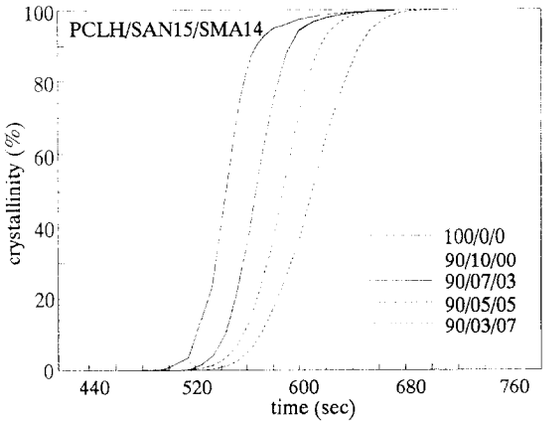

Figure 4 Crystallinity as a function of time of pure PCLH and the blends with 90 wt% PCLH (derived from *Figure 3*)

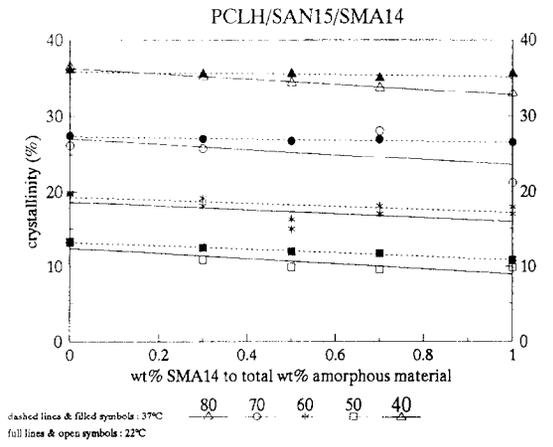

Figure 5 Influence of blend composition and crystallization temperature on the PCL crystallinity in binary and ternary blends with SAN15 and SMA14 (Symbols: wt% PCLH)

able to crystallize, whereas in the PCLL/phenoxy/SAN15 blends, two phases with a sufficiently high PCLL concentration are present. The reason therefore can be found in the different phase behaviour of both ternary blends. Both ternary polymer systems have two totally miscible binary blends and one binary combination that is partially miscible. In the case of PCLL/phenoxy/SAN15, the partially miscible one is an amorphous blend (i.e. phenoxy/SAN15). When a ternary PCLL/phenoxy/SAN15 blend phase separates, it is obvious that a phenoxy-rich phase and a SAN15-rich phase will be formed. Since PCLL is miscible with both components, both phases will contain sufficient PCLL to be able to crystallize. The partially miscible binary blend in the PCL/SAN15/SMA14 system is a crystallizable one (i.e. PCL/SMA14). Here, phase separation will result in a PCL-rich phase and a SMA14-rich phase (in which the concentration of PCL is low) and only the former will crystallize (see below).

Crystallization behaviour

In *Figure 3* the d.s.c. crystallization exotherms of pure PCLH and of the binary and ternary PCLH/SAN15/SMA14 blends with 90 wt% PCLH during cooling from the melt ($-5°C\,min^{-1}$) are presented. The peak position is shifted to lower temperatures when amorphous

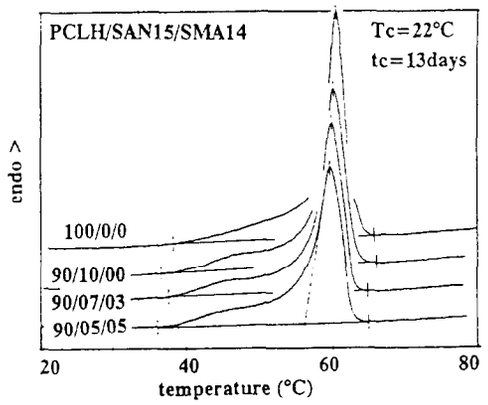

Figure 6 Melting behaviour of pure PCLH compared with that of some binary and ternary blends with 90 wt% PCLH ($T_c = 22°C$, $t_c = 13$ days)

material is added to PCLH. This decrease is more pronounced the higher the SMA14 content in the blends. The evolution of the crystallinity as a function of time (*Figure 4*) can be deduced from the former data. The onset of the sigmoidal curves represents the induction time while the slope is a measure of the crystallization rate. A longer induction time and a slower crystallization rate are observed when the amount of SMA14 increases. The same observations were noticed when performing isothermal crystallization experiments at 45°C.

The influence of blend composition on the crystallinity of PCLH in the blends (*Figure 5*) was determined by calculating the area under the melting peak of the d.s.c. thermograms of the blends crystallized at 22, 37 and 44.5°C during a period of 13 days ($\Delta H°_{PCL} = 135.6\,J\,g^{-1}$). Adding amorphous material results in a decrease of the crystallinity compared with that of pure PCLH. SMA14 seems to depress the crystallinity of PCLH more than SAN15. An explanation for these observations can be found in the segregation behaviour of the amorphous components during the crystallization of PCLH (see the section on 'Lamellar morphology'). Since both components are incorporated inside the spherulites of PCLH (intraspherulitic) they hinder the crystallization, which results in a lower crystallinity. The influence of the crystallization temperature on the crystallinity is also shown in *Figure 5*: raising the crystallization temperature increases the crystallinity of PCLH in the blends.

Melting behaviour

The d.s.c. thermogram of pure PCLH crystallized at room temperature (22°C) shows a melting endotherm with a peak temperature at 60°C. However, the melting trace starts at 40°C (*Figure 6*). When adding SAN15 and/or SMA14 an additional melting peak located at a lower temperature is observed. The higher the total amount of amorphous material (SAN15 and SMA14), the more significant the lower melting endotherm becomes; for blends with a PCLH concentration of 50 wt% or lower, the melting enthalpy of the low temperature peak is higher than that of the high temperature melting endotherm (*Figure 7*).

When the crystallization temperature is increased, the presence of a lower melting endotherm is more obvious

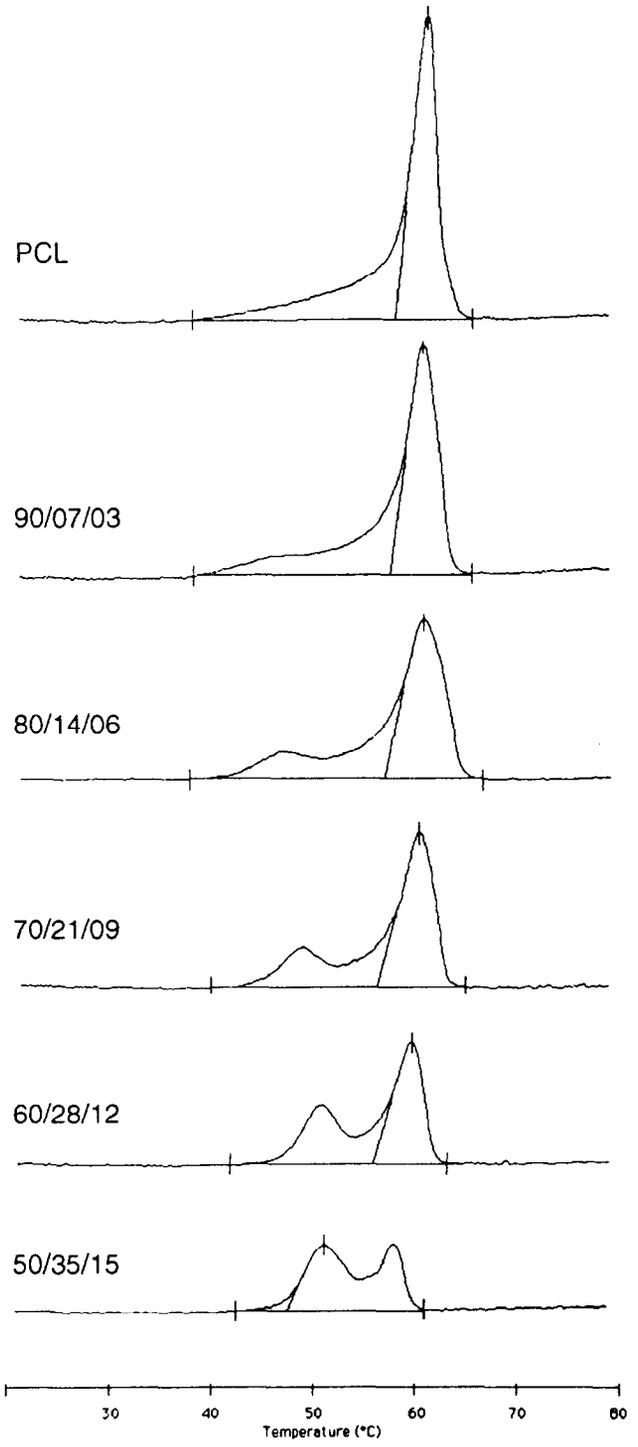

Figure 7 Influence of concentration of the amorphous components (SAN15 and SMA14) on the double melting behaviour of PCLH/SAN15/SMA14 blends ($T_c = 22°C$, $t_c = 13$ days)

for pure PCLH (*Figure 8*). For the blends both melting peaks shift to higher temperatures; this is however more pronounced for the lower melting endotherm (*Figure 9*). At the highest crystallization temperatures studied (>45°C), the double melting behaviour is less pronounced; both melting endotherms seem to overlap. This is probably due to the slow crystallization rate at a temperature very close to the melting point of PCLH. The crystallization of a polymer in a miscible blend involves the diffusion of the crystallizable component

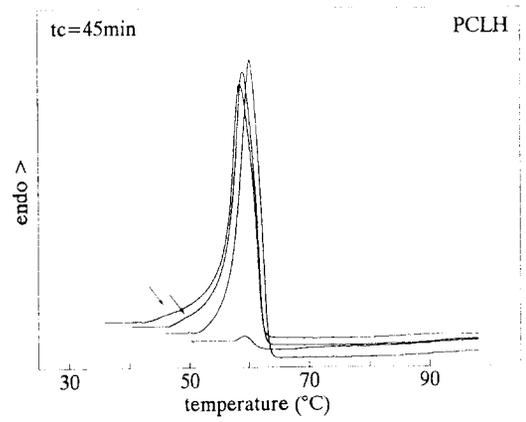

Figure 8 Influence of crystallization temperature on the melting behaviour of pure PCLH to illustrate the presence of a second melting endotherm

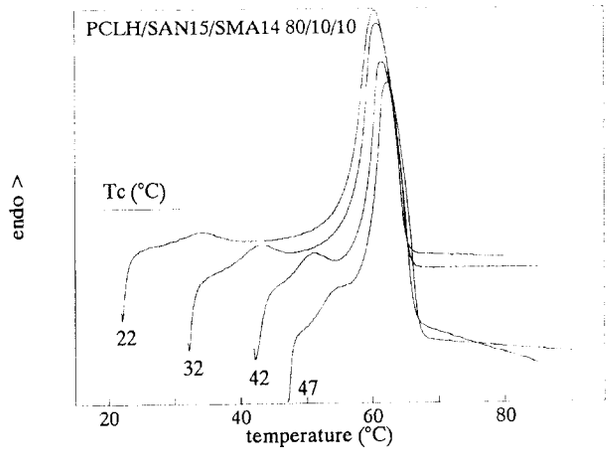

Figure 9 Influence of crystallization temperature on the melting behaviour of the ternary blend PCLH/SAN15/SMA14 80/10/10 (t_c = 30 min)

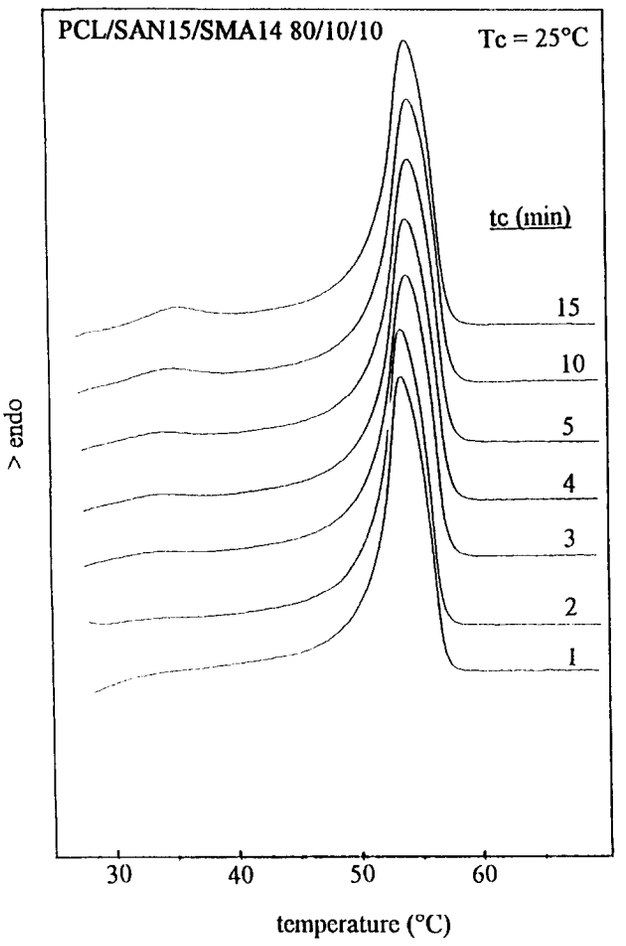

Figure 10 Influence of crystallization time on the melting behaviour of the ternary PCLH/SAN15/SMA14 80/10/10 blend (T_c = 25°C)

towards the crystal growth front and the segregation of the amorphous component(s) away from the nucleus. At low crystallization temperatures (e.g. 22 and 37°C), the primary crystallization is fast, and as a consequence there is not enough time for all the PCLH chains to participate in the spherulite growth process. When the spherulites are formed, there is still enough PCLH present inside them which is able to crystallize after some time; smaller lamellae are then formed within the existing spherulites giving rise to a second melting peak at a lower temperature. The higher the concentration of the amorphous components, the more difficult the diffusion of PCL taking place, especially because of the interlamellar segregation of the amorphous components (see section on 'Lamellar morphology'). Crystallization at temperatures near the melting point is much slower and causes less diffusion problems, and as a result less secondary crystallization is observed.

In *Figure 10* the influence of crystallization time (at T_c = 25°C) on the melting behaviour of the ternary blend PCLH/SAN15/SMA14 80/10/10 is presented. After small crystallization times, a single melting behaviour is seen; the lower temperature endotherm arises only after prolonged crystallization times. This behaviour is common for all crystallizable binary and ternary blends studied. The crystallization time necessary to give rise to this second melting peak, however, depends on the blend composition.

From the former results it is clear that diffusion seems to play an important role in the occurrence of the secondary crystallization process. The faster the primary crystallization, the more pronounced the secondary crystallization behaviour becomes. Therefore, the scanning rate at which the blends are cooled from the melt to the crystallization temperature was varied (*Figure 11*). A decrease of the scanning rate (e.g. cooling rate) before crystallization results in a shift of both melting endotherms to higher temperatures. In agreement with the experiments in which the crystallization temperature was varied, a more obvious shift is observed for the low temperature endotherm.

Lamellar morphology

Crystallization in a polymer blend involves two types of polymer transport: diffusion of the crystallizable component towards the crystal growth front and a simultaneous rejection of the amorphous component(s). The latter phenomenon is called segregation. Segregation can take place on three different levels: interspherulitic, interfibrillar and interlamellar (*Figure 12*). Interspherulitic segregation, in which the spherulites are embedded in an amorphous matrix, can be distinguished from the other two types by optical microscopy. In the case of intraspherulitic segregation, a volume-filling texture is observed.

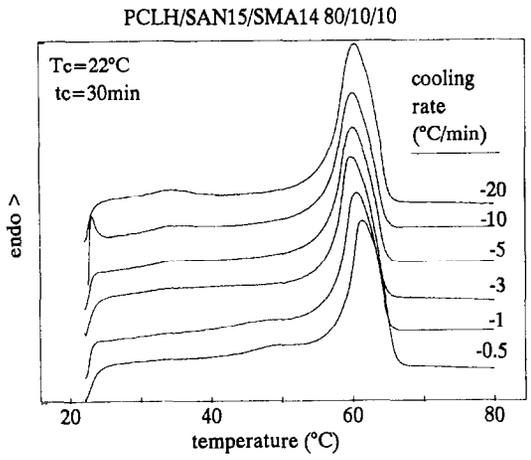

Figure 11 Influence of d.s.c. cooling rate on the melting behaviour of the ternary PCLH/SAN15/SMA14 80/10/10 blend ($T_c = 22°C$, $t_c = 30$ min)

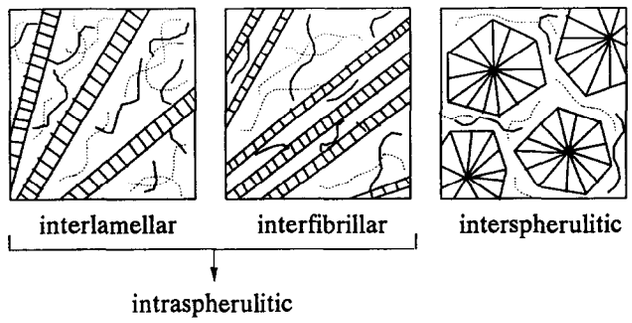

Figure 12 Schematic presentation of the different types of segregation of the amorphous component(s) in crystallizable polymer blends: —, crystallizable component; ---, amorphous component)

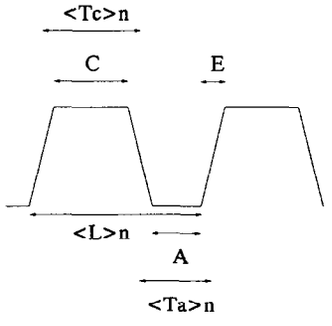

Figure 13 Pseudo two-phase model of alternating crystalline and amorphous layers ($C = \langle T_c \rangle n - E$, crystalline core; $A = \langle T_a \rangle n - E$, amorphous layer thickness; E, transition layer)

Small angle X-ray scattering is a useful tool to find out whether or not interlamellar segregation occurs. An increase of the long spacing with increasing concentration of the amorphous component has been considered in the past to be a decisive proof for interlamellar segregation. The long spacing, L, is defined as the sum of the average thicknesses of crystalline and amorphous layers: $L = \langle T_a \rangle + \langle T_c \rangle$. The long spacing can be determined using the Lorentz corrected intensity function (weight-average long spacing, $\langle L \rangle_w$) and also by means of the one-dimensional correlation function (number-average long spacing, $\langle L \rangle_n$). A more detailed study of the X-ray scattering data using the correlation

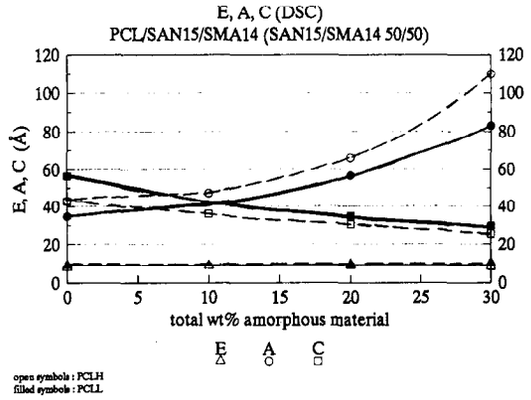

Figure 14 Influence of molecular weight of PCL on the morphological parameters of pure PCL and some ternary blends (SAN15/SMA14 = 1): filled symbols, PCLL; open symbols, PCLH

Table 3 Number and weight-average long spacing ($\langle L \rangle_n$ and $\langle L \rangle_w$, respectively) and amorphous layer thickness (A) of pure PCLH and some of its miscible blends (use of photographic detection system)

Morphological parameter (Å)	PCLH/SAN15/SMA14				
	PCLH	90/10/00	90/07/03	80/20/00	80/14/06
$\langle L \rangle_n$	144	144	148	144	164
$\langle L \rangle_w$	146	143	147	144	164
A	44	61	56	65	74

function approach[49,50], which takes into account the presence of a transition layer (E) between the amorphous and crystalline layers, results also in the determination of the thickness of the crystalline core ($C = \langle T_c \rangle_n - E$) and the amorphous layer thickness ($A = \langle T_a \rangle_n - E$) (see *Figure 13* for the schematic representation of the various parameters).

From *Table 3* the type of segregation of SAN15 and SMA14 in some miscible binary and ternary blends can be derived. Due to the sample preparation (compression moulding at 160°C) no miscible blends of PCLH and SMA14 could be obtained. Nevertheless, relying on the results of pure PCLH and on those of the miscible binary and ternary blends, it was still possible to derive the segregation behaviour of SMA14. The results suggest that SAN15 and SMA14 are segregated in the interlamellar region since there is a tendency to an increase of the long spacing (L) and of the amorphous layer thickness (A) with increasing concentration of the amorphous components. These results are confirmed in *Table 4* where the morphology of the ternary blends with an SAN15 to SMA14 ratio = 1 is studied. Due to the difference in detection system (photographic method in *Table 3* and one-dimensional position sensitive detector in *Table 4*), different values are obtained from the various morphological parameters of the blends. However, the tendencies observed are the same.

The influence of the molecular weight of the crystallizable component (PCLL and PCLH) on the lamellar morphology of pure PCL and some ternary blends with the same ratio of SAN15 to SMA14 (e.g. 1:1) is presented in *Figure 14* and *Table 4*. The width of the transition layer (E) seems to be independent of the molecular weight of PCL. The number-average long spacing ($\langle L \rangle_n$) and the amorphous layer thickness (A) increase the more amorphous material is added to PCL

Table 4 Influence of the molecular weight of PCL[a] and of the total amount of amorphous material on the morphological parameters of pure PCL and some ternary blends (SAN15/SMA14 = 1) (use of a one-dimensional position sensitive proportional counter)

Morphological parameter (Å)	Pure PCLH	90% PCLH	80% PCLH	70% PCLH	Pure PCLL	80% PCLL	70% PCLL
$\langle L\rangle_n$	127	134	150	158	120	133	149
E	8	9	9	8	9	9	10
$\langle T_c\rangle_n$	56	46	39	34	66	44	40
$\langle T_a\rangle_n$	51	56	75	118	44	66	93
C^b	48	37	30	26	57	35	30
A^b	43	47	66	110	35	57	83
Φ (%)[c]	52	44	34	22	60	41	29

[a] Concentration of PCL in the blends is expressed in wt%; L = low and H = high molecular weight
[b] $C = \langle T_c\rangle_n - E$; $A = \langle T_a\rangle_n - E$
[c] Relative crystallinity as measured with d.s.c.

due to the interlamellar segregation of the amorphous components. Increasing the molecular weight of PCL results in a higher value for $\langle L\rangle_n$. An opposite influence of the molecular weight of PCL on both the crystalline (C) and amorphous layer thickness (A) is noticed. Decreasing the molecular weight of PCL leads to a lower value of A and concomitantly to a higher C value. The latter observation points to the presence of more perfect spherulites in pure PCLL (and its blends) compared with pure PCLH (and its blends) when the same crystallization conditions are used for both polymer(blend)s.

CONCLUSIONS

The miscibility of the ternary polymer system consisting of PCL, SAN15 and SMA14 was studied using several techniques. An *LCST* phase behaviour was observed for the binary PCL/SMA14 blends and for the ternary blends with a high SMA14 to SAN15 ratio. A decrease of the molecular weight of the blend components results in a smaller phase-separated region in the miscibility *versus* composition diagram. Since no effect of the phase separation can be detected in the melting behaviour of the crystallizable blends, it is clear that only one phase contains sufficient PCL to be able to crystallize whereas the other phase remains amorphous.

The crystallization and melting behaviour of the ternary PCLH/SAN15/SMA14 blends was studied using d.s.c. Addition of SAN15 and/or SMA14 results in a decrease of the crystallinity and the crystallization rate; the more SMA14 is present in the blends, the more pronounced this tendency is. The d.s.c. thermograms of PCLH and all crystallizable blends show a multiple melting behaviour due to secondary crystallization which is probably caused by a hindered diffusion of the crystallizable chains during the fast crystallization process of PCLH.

The evaluation of the morphological parameters of pure PCL and of some crystallizable, miscible binary and ternary blends using the one-dimensional correlation function approach leads to the conclusion that both amorphous components (SAN15 and SMA14) are rejected into the interlamellar zones of the spherulites. Decreasing the molecular weight of PCL results in the formation of more perfect spherulites with a thicker crystalline core and smaller amorphous zones. The width of the transition layer seems to be independent of the molecular weight of PCL and of the total amount of amorphous material (SAN15 and SMA14).

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REFERENCES

1 Flory, P. J., 'Principles of Polymer Chemistry,' Cornell University Press, Ithaca, NY, 1953, Ch. 12
2 Olabishi, O., Robeson, L. M. and Shaw, T. M. 'Polymer Miscibility', Academic Press, New York, 1979, Ch. 2, 19
3 ten Brinke, G., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1983, **16**, 1827
4 Shiomi, T., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1986, **19**, 2274
5 Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* 1987, **27**, 1482
6 Aoki, Y. *Macromolecules* 1988, **21**, 1277
7 Teyssié, Ph., Fayt, R. and Jérôme, R. *Makromol. Chem.* 1986, **187**, 837
8 Klotz, S. and Cantow, H. J. *Polymer* 1990, **31**, 315
9 Su, A. C. and Fried, J. R. *Polym. Eng. Sci.* 1987, **27**, 1657
10 Defieuw, G., Groeninckx, G. and Reynaers, H. 'Contemporary Topics in Polymer Science: Multiphase Macromolecular Systems', Plenum, New York, 1989, Vol. 6, p. 423
11 McMaster, L. P. and Olabishi, O. *ASC Div. Coat. Plast. Chem. Prepr.* 1975, **35**, 322
12 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909
13 Chiu, S.-C. and Smith, T. C. *J. Appl. Polym. Sci.* 1984, **29**, 1781
14 Chiu, S.-C. and Smith, T. C. *J. Appl. Polym. Sci.* 1984, **29**, 1797
15 Vandermarliere, M. *Ph.D. dissertation*, KU Leuven, 1986
16 Kressler, J. and Kammer, H. W. *Polym. Bull.* 1988, **19**, 283
17 Li, W. G. and Prud'homme, R. E. *J. Polym. Sci.: Part B: Polym. Phys.* 1993, **31**, 719
18 Li, W. and Prud'homme, R. E. *Polymer* 1994, **15**, 3260
19 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1989, **30**, 2158
20 Vanneste, M. and Groeninckx, G. unpublished results
21 Paul, D. R. and Barlow, W. *Polymer* 1984, **25**, 487
22 Kressler, J., Kammer, H. W., Schmidt-Naake, G. and Herzog, K. *Polymer* 1988, **29**, 686
23 Maruta, J., Ougizawa, T. and Inoue, T. *Polymer* 1988, **29**, 2056
24 Hall, W. J., Kruse, R. L., Mendelson, T. A. and Trementozzi, Q. A. *ACS Div. Org. Coat. Plast. Chem. Prepr.* 1982, **47**, 298
25 Hall, W. J., Kruse, R. L., Mendelson, T. A. and Trementozzi, Q. A. *ACS Chem. Soc. Symp. Series* 1983, **229**, 49
26 Chatani, Y., Okita, Y., Tadokoro, H. and Yamashita, Y. *Polym. J.* 1970, **1**, 555

27 Bittiger, H. and Marchessault, R. H. *Acta Cryst.* 1970, **B26**, 1923
28 Perret, R. and Skoulios, A. *Makromol. Chem.* 1972, **156**, 157
29 Tanaka, H. and Nishi, T. *J. Chem. Phys.* 1986, **85**, 6197
30 Phillips, P. J., Rensch, G. J. and Taylor, K. D. *J. Polym. Sci.: Part B: Polym. Phys.* 1987, **25**, 1725
31 Phillips, P. J. and Rensch, G. J. *J. Polym. Sci.: Part B: Polym. Phys.* 1989, **27**, 155
32 Rim, P. B. and Runt, J. P. *Macromolecules* 1984, **17**, 1520
33 Rim, P. B. and Runt, J. P. *J. Appl. Polym. Sci.* 1985, **30**, 1545
34 Runt, J. and Rim, P. B. *Macromolecules* 1982, **15**, 1018
35 Rim, P. B. and Runt, J. P. *Macromolecules* 1983, **16**, 762
36 Tanaka, H. and Nishi, T. *J. Appl. Phys.* 1986, **59**, 1488
37 Tanaka, H. and Nishi, T. *Appl. Phys. Lett.* 1986, **48**, 393
38 Christiansen, W. H., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1987, **34**, 537
39 Vanneste, M. and Groeninckx, G. *Polymer* 1994, **35**, 1051
40 Shah, V. S., Keitz, J. D., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1986, **32**, 3863
41 Defieuw, G., Groeninckx, G. and Reynaers, H. *Polymer* 1988, **30**, 2164
42 Defieuw, G. *Ph.D. dissertation*, KU Leuven, 1988
43 Warner, F. P., MacKnight, W. J. and Stein, R. S. *J. Polym. Sci. Polym. Phys. Edn* 1977, **15**, 2113
44 Rusell, T. P. and Stein, R. S. *J. Macromol. Sci* 1980, **B17**, 617
45 Nojima, S., Tsutsui, H., Urushihara, M., Kosaka, W., Kato, N. and Ashida, T. *Polym. J.* 1986, **18**, 451
46 Li, Y. and Jungnickel, B.-J. *Polymer* 1993, **34**, 9
47 Vonk, C. G. *J. Appl. Cryst.* 1975, **8**, 340
48 Vanneste, M. *PhD dissertation*, KU Leuven, 1993
49 Strobl, G. and Schneider, M. J. *J. Polym. Sci., Polym. Phys.* 1980, **18**, 1343
50 Strobl, G., Schneider, M. J. and Voight-Martin, I. G. *J. Polym. Sci., Polym. Phys.* 1980, **18**, 1361