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Influence of interchange reactions on the crystallization and melting behaviour of polyamide blends as affected by the processing conditions

K. L. L. Eersels and G. Groeninckx*
Catholic University of Leuven, Department of Chemistry, Laboratory for Macromolecular Structural Chemistry, Celestijnenlaan 200 F, 3001 Heverlee, Belgium
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Blends of aliphatic polyamide PA 46 and aromatic polyamide PA 6I were obtained by coprecipitation from a common solvent and by melt mixing using a mini-extruder. The polyamides were found to be fully miscible by both blending methods. However, there are large differences in crystallization and melting behaviour when the blends obtained by the two methods of blending are compared to each other. This can be ascribed to the occurrence of transamidation processes during the melt mixing of the homopolyamides resulting in the formation of block copolyamides composed of crystallizable and non-crystallizable segments. The extent of the transreaction processes is dominated by the extrusion temperature and the extrusion time. Increasing one of these processing parameters will enhance the transamidation reactions and shorten the crystallizable segment lengths. This will be reflected in a decreasing crystallization rate and lower melting points of the melt-mixed blends.

(Keywords: polyamides; blends; crystallization)

INTRODUCTION

The pronounced interest in polymer blends during the past decade is reflected by the large number of papers published in this research area. This interest is not only academic, as polymer blends are also particularly attractive for industrial applications. This is not surprising taking into account the wide range of features that can be achieved by blending existing polymers. Moreover, development of new polymeric materials by this route implies a reduction of production costs and time. One of the largest concerns in blending is the miscibility or 'compatibility' of the blend components, which often determines the possibility of combining the good properties of the components.

The miscibility of polyamides has been extensively studied by Ellis. A mean-field binary interaction model was used to predict the phase behaviour of blends containing two aliphatic[1] or two aromatic[2] polyamides. Of particular interest with respect to the present paper are two publications that describe the miscibility of binary blends composed of an aliphatic and an aromatic polyamide[3,4]. The blends studied, however, were prepared by coprecipitation from a common solvent in a non-solvent.

Melt-mixing of polyamides results in interchange reactions between the blend components[5–8]. Similar observations have been done in the case of melt mixing of other polycondensates such as polyesters and polycarbonates[9–13]. However, very little information is available in the open literature about interchange reactions in melt-mixed polyamide/polyamide blends. As it is very difficult to prevent these exchange reactions in the melt, there is interest in the understanding of the interchange reactions, as they occur for example during melt extrusion and injection moulding.

Possible transreaction processes that might occur in polyamide blends are represented in *Figure 1*. The types of interchange reactions in which the end-groups react are aminolysis and acidolysis. Reaction of the amide groups in the polymer chains is called amidolysis. It is possible to form block copolymers in this way if two different homopolyamides are used as blend components. If one succeeds in controlling the interchange reactions during melt blending, tailored block and random copolymers can be obtained with potentially useful properties. In a non-miscible binary system, exchange reactions between the two components can only occur at the interface of the separated phases; the *in situ* formation of block copolymers consisting of the two blend components will decrease the interfacial tension and a possible result is self-compatibilization[1,14].

In this paper, polyamide 46 (PA 46) and polyamide 6I (PA 6I) are used to study the transreaction processes during melt blending. PA 46 is a semicrystalline aliphatic polyamide while PA 6I is an aromatic polyamide that is completely amorphous when solidified from the melt. Aliphatic polyamides are known to have good

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*To whom correspondence should be addressed

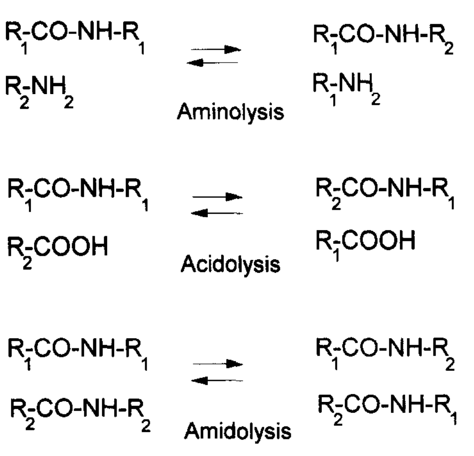


Figure 1 Possible transreaction processes in polyamides

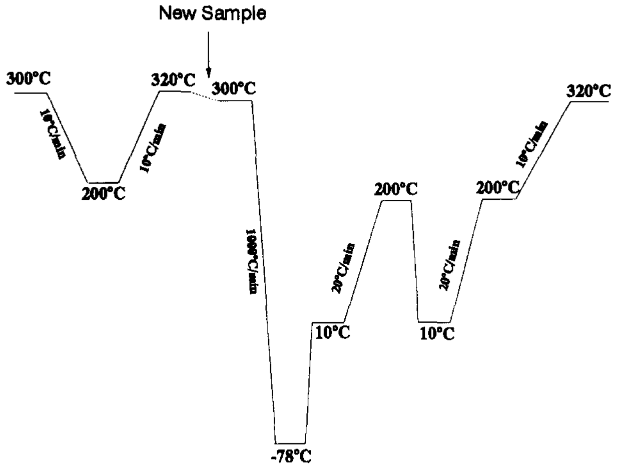


Figure 2 Thermal procedure applied during the calorimetric measurements

processability, high melting points and good mechanical properties. Aromatic polyamides on the other hand have a high glass transition temperature T_g and reduced moisture uptake but low stiffness above T_g.

The influence of transreaction processes occurring within this blend system on the crystallization and melting behaviour of PA 46 will be described. Several blending parameters such as the extrusion temperature, extrusion time and screw rotational speed have been varied. The obtained blend materials were subjected to thermal analysis to investigate the effect of the melt-blending conditions on their thermal behaviour.

EXPERIMENTAL

Materials

Polyamide 46 was obtained from DSM-Research (granulated compacted powder, without stabilizer). It is synthesized from the salt of 1,4-diaminobutane and adipic acid[15]. Polyamide 6I is a condensation product of isophthalic acid with 1,6-hexanediamine and was obtained from Bayer. The chemical structures of PA 46 and PA 6I are given in *Table 1*.

Blend preparation

Blends of PA 46 and PA 6I were prepared by coprecipitation from a common solvent and by melt mixing using a mini-extruder. The PA 46/PA 6I ratio was fixed at 50/50 by weight throughout this work.

Solution-prepared blends. After drying the polyamides at 100°C for 24 h under vacuum, the pre-weighed blends were dissolved into formic acid to obtain an approximate 2–3% solution by weight. Precipitation was carried out by adding the solution dropwise to an excess of deionized water, which was vigorously stirred. The filtered precipitates were then washed intensively with hot water and dried for more than 48 h at 100°C under vacuum.

Melt-mixed blends. The melt-blending experiments were performed on a mini-extruder, developed by DSM Geleen (Holland). The mini-extruder is a conical co-rotating, fully intermeshing twin-screw extruder. It is especially suitable for compounding small batches, typically 4 to 5 g, of polymeric materials. The extruder consists of a lengthwise-split shell that contains a conical mixing chamber. The material can be repeatedly processed by using a recirculation channel. Several processing conditions such as blending temperature, blending time and screw rotational speed can be varied in this way. All the blends were prepared under nitrogen atmosphere to prevent oxidative degradation of the polyamides. At the end of the mixing operation, the material flow is directed towards the die through a valve. A relative indication of the viscosity change during the

Table 1 Chemical structure and physical characteristics of PA 46 and PA 6I

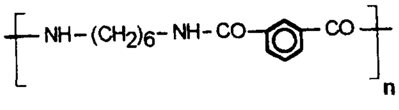
Polymer	Source	Structure	T_g (°C) (midpoint)	T_m (°C) (peak max)	M_n (g mol^{-1})
PA 46	DSM	$\left[\text{NH-(CH}_2)_4\text{-NH-CO-(CH}_2)_4\text{-CO}\right]_n$	75	290	20 700
PA 6I	Bayer		130	–	8 800

Table 2 Crystallization and melting behaviour of PA 46/PA 6I blends. Scanning rate: 10°C min^{-1}

	T_c (°C)	T_m (°C)
PA 46	262	293
PA 46/PA 6I (50/50 w/w)		
Solution-prepared	260	290
Melt-mixed	243	276

mixing operation is given by the force measuring device, which is located under the housing.

The starting materials were first dried under vacuum at 100°C for at least 24 h. Filling the extrusion chamber took between 1 and 1.5 min, and downloading about 1 min (this is an unavoidable experimental error).

Calorimetric measurements

Thermal analysis was performed on a Perkin-Elmer Delta Series DSC 7. The sample size was about 10 mg. Liquid nitrogen was used for cooling and the sample was surrounded by a nitrogen atmosphere.

The thermal treatment given to the obtained blends during the calorimetric measurements is schematically represented in *Figure 2*. The samples were first heated at 300°C for 1 min. From 300°C, they were cooled down to 200°C at a rate of 10°C min^{-1} to determine the crystallization temperature of the blends. The subsequent heating up to 320°C was also performed at 10°C min^{-1}. During this process, the melting temperature of the crystallized blends was registered. Other samples were first heated at 300°C for 1 min and then quenched in cooled isopropanol (−78°C). The obtained samples were brought to 10°C, from where they were heated up to 200°C at a scanning rate of 20°C min^{-1} to measure the glass transition temperature T_g. The second heating scan was mentioned to measure any possible changes in thermal behaviour such as an increase of the T_g due to possible crystallization processes during the first heat treatment. This was done by cooling the annealed samples to 10°C and then heating them up again at 20°C min^{-1}. Above 200°C, the scanning rate was set at 10°C min^{-1} to measure the melting temperature of the quenched blends.

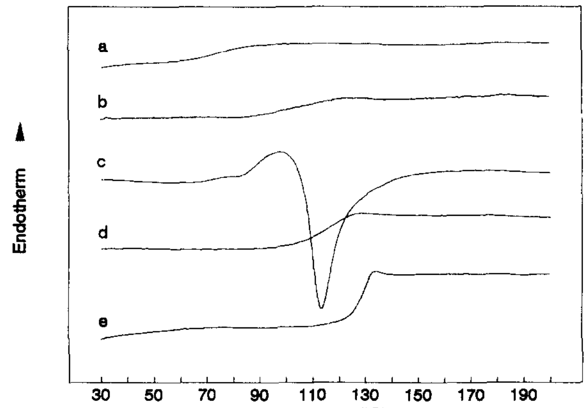


Figure 3 Representative thermograms of the homopolyamides and the blends after quench cooling from the melt: (a) PA 46; (b) solution-prepared blend of PA 46/PA 6I (50/50 w/w); (c) melt-mixed blend of PA 46/PA 6I (50/50 w/w)—first heating scan; (d) melt-mixed blend of PA 46/PA 6I (50/50 w/w)—second heating scan; (e) PA 6I

RESULTS AND DISCUSSION

Coprecipitation versus *melt mixing*

Melt extrusion of polymers always has to be carried out with the necessary caution, especially if reactive polymers are melt processed. A wide range of possible reactions during the extrusion time can completely alter the final properties of the polymer material. This will be illustrated in this paper where the thermal properties of polyamide blends obtained by coprecipitation and melt mixing are compared to each other.

Table 2 represents the crystallization behaviour of pure PA 46 and blends with PA 6I prepared by both coprecipitation and melt extrusion. Pure PA 46 crystallizes at 262°C when cooling from the melt at 10°C min^{-1}. The blend composed of 50% PA 46 and 50% PA 6I that was prepared by coprecipitation crystallizes a few degrees lower than the pure PA 46 at 260°C. However, the polyamide blend that was melt processed crystallizes at 243°C; this is almost 20°C below the crystallization temperature of pure PA 46. Obviously, the crystallization rate of PA 46 is affected to a large extent by melt mixing PA 46 with PA 6I.

The decrease of the crystallization rate of PA 46 in the melt-mixed blends can also be illustrated by quench-cooling experiments from the melt. The solution-prepared blend shows a broad T_g region located between the T_g values of the homopolymers, from which miscibility can be concluded (*Figure 3*). It can also be noticed that the crystallization rate of PA 46 in the pure state and in the precipitated blend is even high enough to allow complete crystallization during the melt-quenching process. Measurements of T_g of the quenched blend, obtained by melt mixing, also reveal a T_g intermediate between the two homopolyamides, indicating miscibility of both polyamides. This is in agreement with the mean-field interaction model of Ellis; the expression for χ_{blend} for a mixture of PA 46 (A_xB_{1-x}) and PA 6I (A_yC_{1-y}) is given by[4]:

$$\chi_{\text{blend}} = (y-x)(1-x)\chi_{AB} + (1-y)(1-x)\chi_{BC} + (x-y)(1-y)\chi_{AC} \quad (1)$$

The subscripts x and y refer to the respective mer contribution to the molar volume of the polymer ($x = 0.7255$, $y = 0.4702$). With $\chi_{AB} = 7.984$, $\chi_{AC} = 1.584$ and $\chi_{BC} = -2.288$, χ_{blend} is found to be equal to -0.0126.

Above the T_g of the quenched melt-mixed polyamide blend, a cold-crystallization process takes place. It appears that the crystallization rate of PA 46 in the melt-mixed blend has decreased to such an extent that complete crystallization during melt quenching is no longer possible. Further crystallization of PA 46 in this blend can only occur when the crystallizable PA 46 chains gain enough mobility at elevated temperatures, i.e. above the glass transition temperature of the blend.

The same trend in thermal behaviour can be observed in *Table 2* where the crystallized blends are being melted after slow cooling from the melt (10°C min^{-1}). Pure PA 46 melts at 293°C, the blend obtained from coprecipitation at 290°C, and the melt-mixed blend at 276°C. The pronounced decrease in melting temperature for the latter blend is much larger than one would expect for a purely physical blend; this can be accounted for

Table 3 Influence of the extrusion time on the crystallization and melting behaviour of PA 46/PA 6I blends (50/50 w/w). Scanning rate: $10°C\,min^{-1}$

Extrusion time (min)	T_c (°C)	T_m (°C)
0.5	251	285
1	250	283
3	247	280
5	243	276

by the formation of block copolyamides during the reactive blending process[16].

Influence of processing conditions

The extent of the transamidation reactions are dominated by the processing conditions. This will be reflected by a change in thermal behaviour (crystallization and melting) of the polyamide blends as a function of the varying mixing parameter(s). The processing parameters concern the screw rotational speed, the extrusion temperature and the extrusion time. Their influence on the thermal behaviour of the blends will be examined separately by changing only one parameter while the other two parameters are being kept constant.

Influence of the screw rotational speed. The influence of this processing parameter was determined by varying the rotational speed of the twin-screw mini-extruder from 50 to 200 rev min^{-1}. The extrusion temperature was set at 300°C and the extrusion time at 2 min. When the blends processed at different screw rotational speeds were compared to each other, no significant differences could be observed in the thermal behaviour. The crystallization temperature stays at about 253–254°C and the melting temperature is located around 287°C. It is assumed that, once the polyamides have been mixed on a molecular level, the progress of the transamidation processes is not affected by more intensive mixing. This can be understood on the basis of the miscibility of the blend system studied; more intensive mixing will not change the reaction volume in the blend where the transamidation processes are occurring and thus the rate of the transreaction processes will remain unaffected. For this reason, the rotational speed in further experiments is set at 100 rev min^{-1} and remained unchanged. With respect to immiscible polyamide blend systems, it is expected that the extent of the transreaction processes will be affected by the intensity of mixing as the interfacial surface between the phases, where the transreaction processes occur in immiscible blend systems, can be changed by this mixing parameter.

Influence of the extrusion time. Blends were extruded at a constant extrusion temperature (325°C) but with varying extrusion times (0.5–5 min). Longer extrusion times were avoided to prevent excessive thermal degradation. In contrast to the rotational speed, the extrusion time is of importance with respect to the thermal behaviour of the blends obtained. As shown in *Table 3*, longer extrusion times result in lower crystallization temperatures of the crystallizable component. The crystallized blends also exhibit lower melting temperatures with increasing extrusion time. The melting enthalpy decreases to a small extent with increasing extrusion time, but it is, however, incorrect to draw conclusions from these data with respect to the degree of volume crystallinity[17].

An explanation for the decrease in crystallization and melting temperature can be found in the transamidation reactions. In *Figure 4* it is schematically shown how block copolymers are being formed in the beginning of the transamidation reactions with rather long sequences of the crystallizable PA 46 component. However, with increasing transamidation reactions as a function of the extrusion time, the crystallizable sequences are becoming shorter and as a consequence crystallization is becoming more difficult. This results in a decreasing crystallization temperature.

The correlation of the melting temperature with the semicrystalline morphology of the copolymers formed during melt mixing is presently under full investigation using wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). It will be the subject of a further publication.

When the blends of PA 46 and PA 6I are melt quenched in cooled isopropanol, cold crystallization of PA 46 is observed. *Figure 5* shows the first heating scan of the blends after the quenching process. Between 85

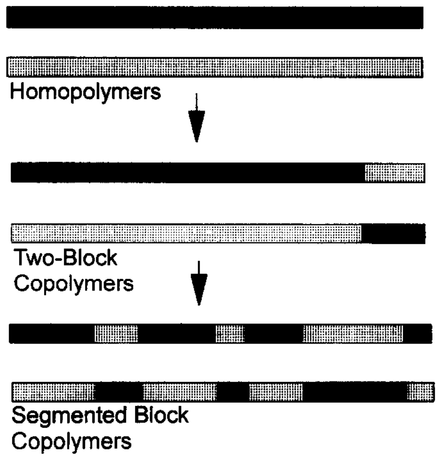


Figure 4 Schematic representation of the molecular changes resulting from transamidation processes in polyamide blends

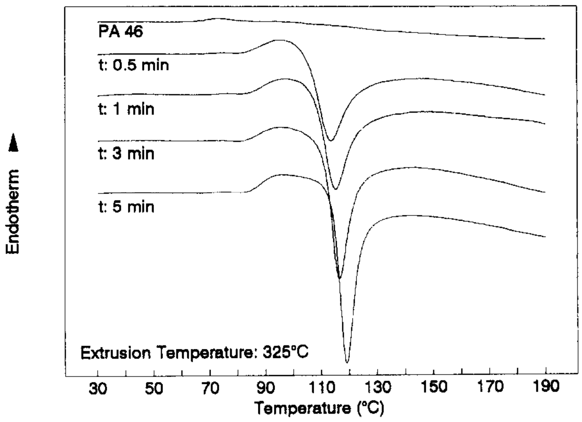


Figure 5 Influence of the extrusion time on the cold-crystallization process of PA 46/PA 6I blends (50/50 w/w), after quench cooling from the melt

and 90°C, a clear T_g is obtained for the blends. Above T_g, a cold-crystallization process takes place. As can be seen, the peak crystallization temperature increases with increasing extrusion time. The peaks are also becoming more narrow with increasing extrusion time. It can be concluded from these observations that the formation of copolymers with shorter crystallizable segment lengths of PA 46 resulting from longer extrusion times definitely hinders the crystallization process of PA 46. At 200°C, before melting, the sample is cooled down again to 10°C and a second heating scan is carried out. The former T_g, which was located between 85 and 90°C, is now shifted to 115–120°C (*Figure 3*). This is still between the T_g of PA 46 (70°C) and PA 6I (130°C). This shift of the T_g results from the additional cold-crystallization process of PA 46 during the first heat treatment of the blend. During the additional crystallization process of PA 46, crystallizable PA 46 is extracted from the miscible amorphous phase, which changes the composition of this phase to a higher content of PA 6I. Moreover, the additional crystallization of PA 46 will also restrict its chain mobility in the remaining amorphous phase to a larger extent. These two phenomena will both result in a higher T_g of the blend.

Influence of the extrusion temperature. Blends were extruded during a constant extrusion time (5 min) but at varying extrusion temperatures (295–325°C). The influence of the extrusion temperature on the thermal behaviour is very similar to that of the extrusion time. *Table 4* for example clearly indicates that higher extrusion temperatures lead to lower crystallization temperatures. Also the melting temperature of the blend decreases with increasing extrusion temperature. *Figure 6* summarizes the effect of the melt blending time on the peak crystallization temperature of PA 46/PA 6I blends (50/50) at different extrusion temperatures. It thus clearly appears that the transamidation processes are not only proceeding as a function of the extrusion time, but they are also favoured by higher extrusion temperatures.

Varying these two extrusion conditions alters the extent of the transamidation processes in the same way. It is possible to reach a certain degree of transamidation by either extruding the blend at high temperatures for short extrusion times or by extruding at lower temperatures for longer extrusion times. It can be concluded that there exists a time–temperature equivalence effect with respect to the occurrence of the transamidation processes.

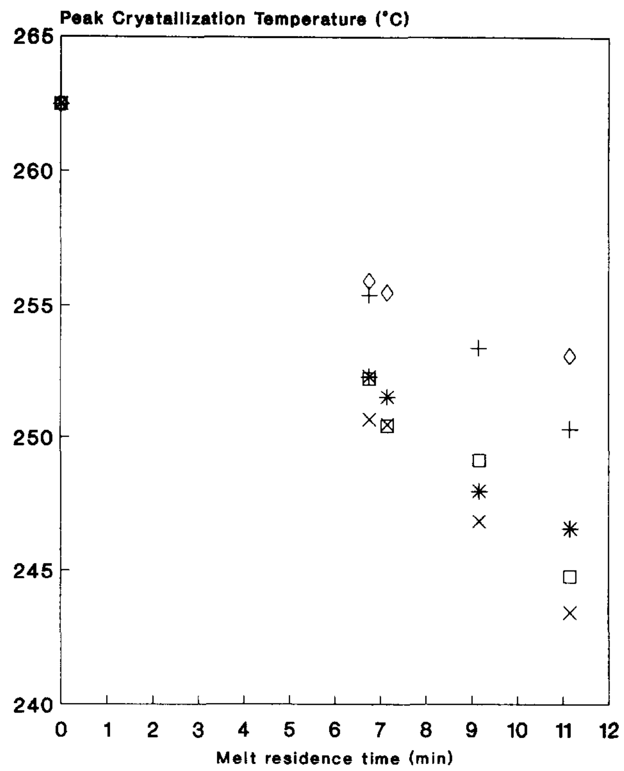


Figure 6 Influence of the extrusion conditions on the peak crystallization temperature of PA 46/PA 6I blends (50/50 w/w) during slow cooling from the melt (10°C min^{-1}). Extrusion temperature: (◇) 295°C; (+) 300°C; (★) 305°C; (□) 315°C; (×) 325°C

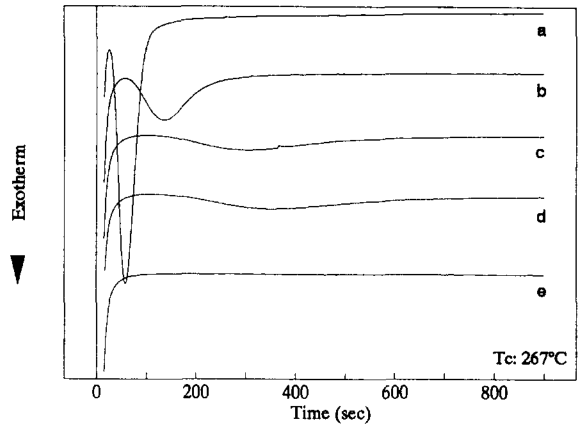


Figure 7 Influence of the extrusion conditions on the isothermal crystallization behaviour at 267°C of PA 46 (a) and of the PA 46/PA 6I (50/50) blends (b,c,d,e): (a) PA 46; (b) 300°C, 1 min; (c) 300°C, 5 min; (d) 325°C, 1 min; (e) 325°C, 5 min

(Re)crystallization and melting behaviour as a function of the extrusion conditions

Besides the former dynamic crystallization experiments, the decrease of the crystallization rate as a function of the blending conditions can also be measured by performing isothermal crystallization experiments. In *Figure 7*, it is shown how the crystallization rate at 267°C decreases with increasing extrusion temperature and extrusion time. Pure PA 46 crystallizes fast at 267°C; the blend obtained after melt extrusion at 325°C for 5 min seems to fail to crystallize at this temperature. The crystallization rate of the blends obtained under the other extrusion conditions is intermediate between that of the former ones. The crystallization rates of the blends that have been extruded for 5 min at 300°C and for 1 min at 325°C are nearly the same. This

Table 4 Influence of the extrusion temperature on the crystallization and melting behaviour of PA 46/PA 6I blends (50/50 w/w). Scanning rate: 10°C min^{-1}

Extrusion temperature (°C)	T_c (°C)	T_m (°C)
295	253	286
300	250	283
305	247	280
315	244	278
325	243	276

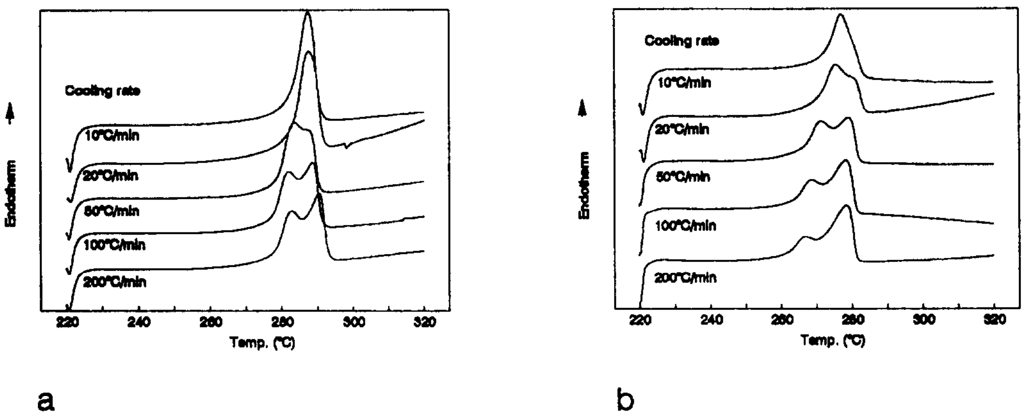


Figure 8 Melting thermograms of the PA 46/PA 6I blends (50/50 w/w) obtained at different extrusion conditions and after varying cooling rates from the melt: (a) 300°C, 1 min; (b) 325°C, 5 min

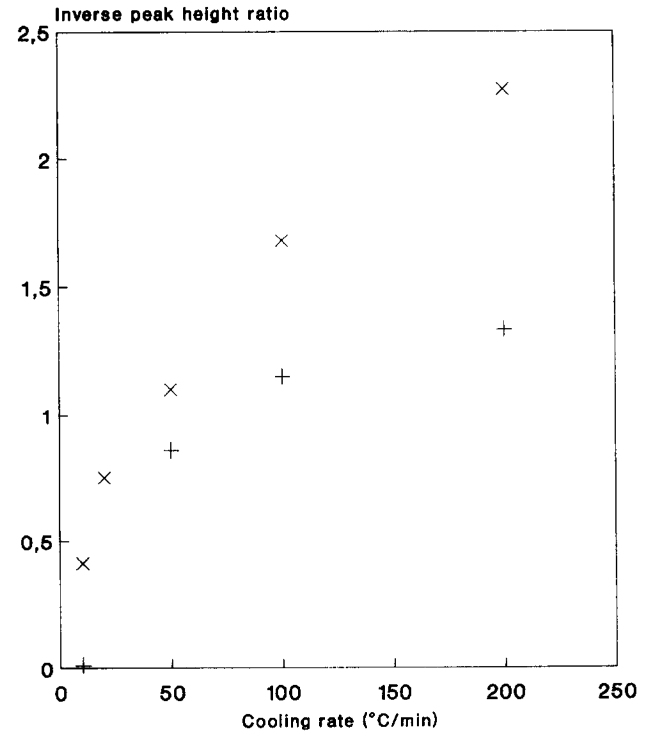


Figure 9 Inverse ratio of the height of the first melting endotherm over the second melting endotherm as a function of the extrusion conditions: (+) 300°C, 1 min; (×) 325°C, 5 min

illustrates once more the equivalence of the effect of time and temperature.

The variation of the crystallization rate as a function of the blending conditions can also be revealed by recrystallization experiments. The melting thermograms of crystallized PA 46 reveal a single melting peak when the crystallization occurs during slow cooling (10°C min^{-1}) from the melt. However, when the crystallization process occurs at high cooling rates from the melt, a double melting endotherm appears resulting from recrystallization during the melting of imperfect crystals, formed at high melt-cooling rates. This has also been observed for other aliphatic polyamides[18]. The amount of recrystallization reflects the amount of imperfect crystal structures formed during cooling from the melt and can be derived from the inverse ratio of the height of the first melting endotherm over the second one.

The degree of crystal imperfection is dominated by the crystallization rate and/or crystallization temperature with respect to the cooling rate. *Figure 8* represents the melting endotherms of the blends, obtained at different extrusion conditions, as a function of the cooling rate. It can be seen that a single melting endotherm is obtained for all the blends at a cooling rate of 10°C min^{-1}, irrespective of the extrusion conditions. The blend that has been extruded for 1 min at 300°C starts to show a double melting behaviour at a cooling rate of 50°C min^{-1}. However, the blend that has been extruded at 325°C for 5 min already reveals a double melting endotherm at a cooling rate of 20°C min^{-1}. Moreover, it can be seen from *Figure 9* that for this blend the inverse ratio of the height of the first melting endotherm over the second one at a cooling rate of 200°C min^{-1} is higher than the inverse ratio of the melting endotherms of the former blend, indicating more recrystallization. This can be ascribed to the lower crystallization rate of the blends that have been melt mixed under more severe extrusion conditions. The lower crystallization rate will result in the formation of more imperfect crystals at high cooling rates and thus more recrystallization during the melting process. As already mentioned before, it is assumed that this decreasing crystallization rate as a function of the extrusion conditions is due to the decreasing crystallizable sequence lengths in the copolymers with increasing extrusion temperature and time.

CONCLUSIONS

Different mixing conditions of amorphous/crystalline polyamide blends result in different thermal properties of the obtained blends. Transreaction processes between the blend components during melt extrusion are responsible for the large changes in crystallization and melting behaviour of the crystallizable component. The transreaction (transamidation) processes, which are unavoidable during melt processing, result in the formation of block copolyamides if two chemically different homopolyamides are being used as starting polymers. As a consequence, if one of the homopolyamides is amorphous and the other one is semicrystalline, noncrystallizable sequences will be built-in between the crystallizable sequences of the semicrystalline polyamide. This leads to a decrease of the crystallization rate of the crystallizable component and also affects the melting temperature of the crystals formed. The melt-processed blends with a reduced crystallization rate fail to create high-melting and thus rather perfect crystals at high cooling rates from the melt.

It is also observed that transamidation reactions are enhanced by higher extrusion temperatures, and proceed as a function of the melt-processing time. This affects the segment lengths of the copolymers, which become shorter with increasing transreaction processes. Shorter crystallizable segment lengths give rise to lower crystallization and melting temperatures of the melt-mixed blends. Finally, it can be derived from recrystallization experiments during the melting process that the blends obtained at high extrusion temperatures and long extrusion times contain a large amount of low-melting, imperfect crystals.

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