Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 357–369

THE DSC STUDY OF PA 6, POLYAMIDES AND COPOLYAMIDES

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(Received October 30, 1999)

Abstract

The DSC method was used to obtain more information on changes of thermal properties connected with different comonomers bound in the (co)polymer chains. The copolyamides propered were block ones which were less crystalline and compatible with poly-ε-caprolactam. The results have confirmed the crystalline nature of polyamides and copolyamides.

Keywords: blends of polyamides, copolyamides, crystallization, DSC, melting point, structure

Introduction

Thermal properties of linear homopolymers have been investigated to a great extent. The character of various copolymers depends on the chemical nature as well as on the ratio of the comonomer involved. The complete different situation arises in the case of blends of both polymers and copolymers. In this case it should be remembered that besides the ratio and the character of the comonomers the mutual interactions of each component have a pronounced influence on their properties. From the workability point of view, the DSC method is suitable to study the influence of physicochemical parameters of polymers, copolymers and their blends on fibres and films.

Copolymers compatible with relevant homopolymers do not deteriorate blend properties. Several melting peaks indicate that under non-isothermal conditions of crystallization the crystals of various sizes and different levels of perfection were formed [1]. The study of two poly(ether-block-amide) polymers has shown that both polymers are separated. Multiphase systems include a well-defined polyamide crystalline phase, a polyamide amorphous phase and a predominantly amorphous polyether phase. DSC data suggest the existence of polyether-based crystallites with poorly defined characteristics [2].

Among the copolymers that improve the properties of different polymers can be found: copolyamides [3, 4], copolyamideureas [5], polyetherureas [6] or their combinations [7].

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The mixed melts with similar rheological properties [6], better thermal and UV stability [8, 9], better dyeability, electric and sorption properties [10–12] compared with basic polymers were obtained at lower contents of the above-mentionned additives (<10 wt%).

The main features governing the preparation, morphological structure and properties of blended products are thermal characteristics of copolymers and their blends with polymers as well as the crystallization and content of the crystalline phase.

In this paper, an evaluation of the structure of polyamides, binary and tertiary copolyamides and their blends will be discussed.

Experimental

Material used

Poly-ε-caprolactam (PA 6), Chemlon- Rhône Poulenc.

Polyamides of the adipic acid (A) and 1,4-bis(3-aminopropyl)piperazine(NB) - formula 2, code ANB, or adipic acid and 1-(2-aminoethyl)piperazine (N2)-formulas 3, 3A, 3B, code AN2.

Copolyamides of ε-caprolactam (CL) and ‘nylon salts’ AH, AN2, ANB, SNB – formulas C–H, S – sebacic acid.

It is well known that properties of polymers and copolymers depend especially on their composition structure, molecular mass, the presence of low molecular compounds and on the molecular mass distribution. In order to compare the behaviour of poly-ε-caprolactam, polyamides and copolyamides we synthesized two types of polyamides from the adipic acid (A) and 1,4-bis(3-aminopropyl) piperazine (NB) and from the adipic acid (A) and 1-(2-aminoethyl)piperazine (N2), and also four types of binary copolyamides from CL and the nylon salt of adipic acid with 1,4-bis(3-aminopropyl)piperazine and 1-(2-aminoethyl)piperazine and from the nylon salt of sebacic acid with 1,4-bis(3-aminopropyl)piperazine and 1-(2-aminoethyl)piperazine both, having the same proportion of CL/nylon salt equal to 8/1 mol and some tertiary copolyamides. From all samples, we removed low molecur compounds by the extraction in hot water during 2 h.

The polyrecaction conditions, polymers composition and some characteristics of PA 6, polyamides and copolyamides are given in Table 1.

Preparation of polymer blends and fibres

The mixtures of 50 wt% of PA 6 and 50 wt% of copolyamides (in the casc of CI-CIII) were melted in a laboratory single-ribbon extruder TE∅ 30 at temperatures of T=518–533 K.

PA 6 and blended granulates (PA 6+copolyamides) were spun at T=523 K in the laboratory equipment. Fibres were drawn to the ratio of 1:3 at the temperature of T=393 K.

Table 1 Conditions of polyreaction and some characteristics of PA 6, polyamides and copolyamides

N°	Code of polymer	Components	Proportions/%		[η]/ ml g^{-1}	$t_{\mathrm{prep.}}$/min	Conc. of N/	$\Delta_{m_{300}}$/
			mol	wt			wt%	
1	PA 6	ε-CL	–	–	120	900	12.3	0
2	ANB	ANB	–	–	57	150	17.45	3
3	AN2	AN2	–	–	67	295	16.81	3
E	CLANB	CL+ANB	8/1	72.3/27.7	110	190	13.33	3
F	CLAN2	CL+AN2	8/1	76.8/23.2	109	240	13.2	2.5
G	CLSNB	CL+SNB	8/1	69.3/30.7	112	155	12.9	2
H	CLSN2	CL+SN2	8/1	73.3/26.7	91	155	12.75	1.7
CI	CLAH15ANB	CL+AH+ANB	10/3/1	50/30/15	113	130	13.05	4.0
CII	CLAH20ANB	CL+AH+ANB	7/2/1	50/30/20	120	100	13.14	5.6
CIII	CLAH30ANB	CL+AH+ANB	5/1/1	50/20/30	109	130	13.77	4.8
DI	CLAH15AN2	CL+AH+AN2	16/5/2	50/35/15	92	130	12.81	4
DII	CLAH30AN2	CL+AH+AN2	35/6/9	50/20/30	95	130	13.71	4.8

[η] – measured in 95% H_2SO_4 at T=293 K
$\Delta_{m_{300}}$ – the mass loss at 573 K from TG curve of measurement on Derivatograph Q-1500D
Conc. of N – concentration of nitrogen from elementary analyzer CHNS-O type EA 110 S

DSC study of polyamides and copolyamides

Thermal properties were studied by using the DSC 7 Perkin Elmer Co. equipment. The different heating and cooling rates of 5, 10, 15 and 20 K min^{-1} were used to examine the influence on thermal properties (Table 2). On the basis of the results obtained we selected the rate of 10 K min^{-1} for our next experiments.

Table 2 Thermal properties of PA 6 *vs*. heating and cooling rate

V_0/ K min^{-1}	1st heating			1st cooling	
	T_m/K	ΔH_m/J g^{-1}	β	T_c/K	$-\Delta H_c$/J g^{-1}
5	494.4	54.2	0.28	464.7	57.9
10	494.2	66.1	0.35	460.1	61.0
15	493.9	66.2	0.35	457.3	59.4
20	494.2	68.1	0.36	454.2	60.6

Five cycles were applied to a sample in order to get more information about the thermal properties influenced by a number of cycles.

The following accuracy of the DSC measurements (5 samples of PA 6 polymer) was found as follows:

– temperature of melting: $\overline{T}_m=493.8\pm0.34$ K
– enthalpy of melting: $\overline{\Delta H}_m=66.2\pm1.28$ kJ kg^{-1}
– degree of crystallinity: $\overline{\beta}=0.346\pm0.009$
– temperature of crystallization: $\overline{T}_c=460.0\pm0.35$ K
– enthalpy of crystallization: $\overline{\Delta H}_c=61.1\pm0.54$ kJ kg^{-1} (all for PA 6)

All values of the cystallinity degree β (for PA 6 and copolyamides) were calculated by means of the theoretical value of $\Delta H_m^o=190.6$ kJ min^{-1} [14] except for some blends, the β_{calc} value of which was calculated using the mass amount of the involved components and their β value. The other source [15] indicates the value of $\Delta H_m^o=190.0$ kJ g^{-1}, which is practically the same.

The entropy ΔS_m was calculated from the well-known equation:

$$T_m=\frac{\Delta H_m}{\Delta S_m}$$

Discussion

The reaction time for the preparation of polyamides and copolyamides is shorter in comparison with that for the preparation of PA 6 (due to the influence of the 'nylon' salt). The limiting viscosity number [η] of polyamides and copolyamides was determined for extracted and dried polymers. For the same or similar type of linear polymers the [η] value is proportional to the molecular mass M. In the case of PA 6, the relationship betwen [η] and the molecular mass M can be expressed by several equations. Although these equations cannot be used for our polyamides and copolyamides, the values of [η] enable one to compare the level of M. The [η] values for polyamides and copolyamides listed in Table 1 show that they are comparable with those for PA 6. Polyamides and copolyamides can be consider as polymers with probably the similar molecular mass and molecular mass distribution (due to the same mechanism of the macromolecular formation valid for all copolyamides). A comparison between the value $[\eta]=120$ ml g^{-1} for PA 6 (corresponding to the approximate value of $M\cong30\,000$) and the values of [η] for polyamides and copolyamides supports our affirmation. The normal molecular mass distribution do not influence the crystallinity of semicrystalline polymers at all if the molecular mass of the samples is on the appropriate level.

All polymers prepared can be considered to have a good thermal stability (measured up to 593 K), the maximum mass loss being 5.6 wt% in the case of the sample CII (Table 1). Differences in the basic thermal characteristics such as melting temperature, temperature of crystallization and the degree of crystallinity result from different monomer unit lengths, their ordering and structural regularity.

The PA 6 is a crystalline polymer with regularly repeated monomer units of caprolactam and with the degree of crystallinity $\beta=0.3–0.4$ ($\beta=0.35$; $\Delta H=66.2$ kJ kg^{-1}).

Changes of the basic parameters such as melting temperature T_m, enthalpy of melting ΔH_m, the degree of crystallinity β, temperature of crystallization T_c and enthalpy of crystallization ΔH_c, which have influence on the rate of heating and cooling, are given in Table 2. The melting temperature varies with the heating rate insignificantly. At the low heating rate conclusions given in [13] have confirmed that:

1. Imperfectly developed crystallites recrystallise (in the first step of heating) to more ordered structures with a higher T_m at the lower heating rate.

2. The samples were overheated as a consequence of the high heating rate.T_m increases due to the higher heat content in the sample as it is necessary for the fusion of crystallites already existed.

The effect of a number of both heating and cooling cycles was studied. All investigated parameters decreased. Thus, as shown in Table 3, the changes of ΔH_m in the first cycle result from the transition to less ordered structures.

Table 3 Thermal properties of PA 6 fibres *vs*. number of heatings and coolings

Number of heatings/coolings	1st heating			1st cooling	
	T_m/K	ΔH_m/J g^{-1}	β	T_c/K	$-\Delta H_c$/J g^{-1}
1	494.2	66.1	0.35	460.1	61
2	493.8	51.9	0.27	459.9	60.9
3	493.6	51	0.27	459.7	58.6
4	493.4	49.9	0.26	459.6	57.7
5	493.2	48.7	0.26	459.3	56.6

An inccrease of the cooling rate leads to a decrease of T_c (and thus to an increase of ΔH_m) due to the gradually proceeding crystallization.The crystallization is determined by the formation of the buds of crystallites and their growth [13]. The lower temperature promotes the rate of the formation of buds while the rate of growth of crystallites is shifted to the area of higher temperatures. An area A of the maximum rate of growth of crystallites lies at higher temperatures in the case when the PA 6 sample originates from the molten state (temperature is falling). The consequent gradual cooling favours suitable conditions for the maximum rate of the formation of buds (B). Within the A period, only a few buds can be formed and thus the number of bigger crystallites is limited. The range of crystallization of the sample is restricted to a rise of the cooling rate. This can be seen in Table 2. All crystallization enthalpy values ΔH_c are generally lower than the value of ΔH_m.

In [15], some other polyamides from piperazine are described. As a consequence of the regular structure, high concentration of piperazine rings and of the absence of aliphatic segments the value T_g is rather high.

The macromolecules of polyamides AN2 and ANB are composed of the constituent containing the piperazine ring. The latter polyamide contains the symmetrically oriented piperazine ring, the hydrogen bonds being probably formed. This fact was confirmed by

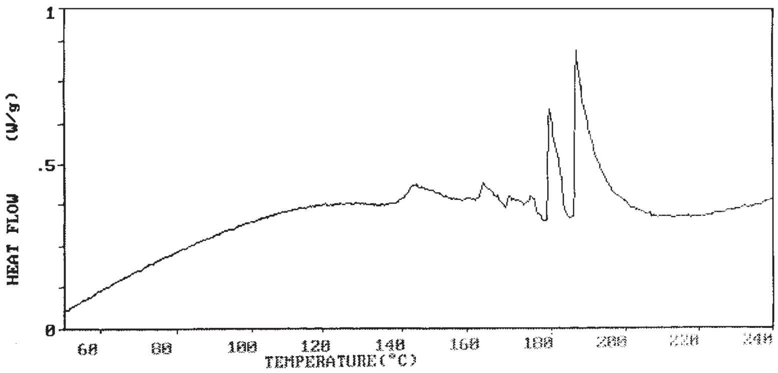

Fig. 1 DSC diagram of polyamide AN2

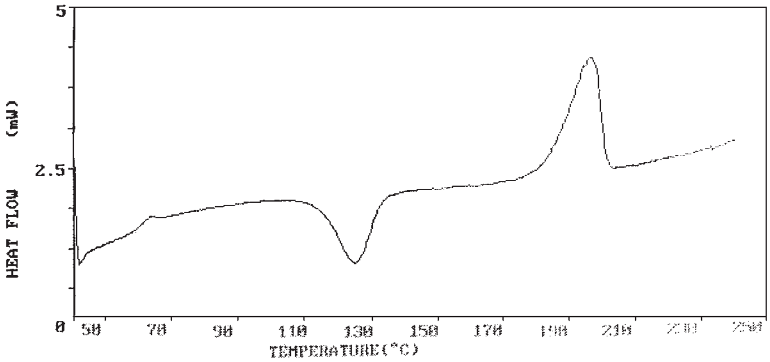

Fig. 2 DSC curve of polyamide ANB ('cold' crystallization)

Table 4 Thermal properties of PA6, polyamides and copolyamides

Code		1st heating				1st cooling		2nd heating			
Chemical	Sample	T_m/K	ΔH_m/J g^{-1}	ΔS_m/J g^{-1}K^{-1}	β	T_c/K	$-\Delta H_c$/J g^{-1}	T_{cc}/K	$-\Delta H_{cc}$/J g^{-1}	T_m/K	ΔH_m/J g^{-1}
PA 6	1	493.8	66.2	0.138	0.35	452.9	58	–	–	488.9 495.9	50
ANB	2	469.6	32.8	0.07	–	398.4	5	398	26	468.8	36.1
AN2	3	*	25.3	0.055	–	–	–	–	–	–	–
CLAN2	F	461	46.1	0.1	0.24	397.7	32	–	–	459.3	27.8
CLSN2	H	454.1	38.2	0.084	0.2	399.6	31.8	–	–	459.2	8.7
CLANB	E	450.5	42.5	0.094	0.22	384.2	26	–	–	452	27.5
CLSNB	G	450.2	35.9	0.08	0.19	386.2	22.2	–	–	441.4	15.8
CLAH 15ANB	CI	430.5	30.1	0.07	0.16	367.2	7.4	360	10.6	435.8	26.2
CLAH 20ANB	CII	422.7	24.1	0.057	0.13	366	16.1	–	–	–	–
CLAH 30ANB	CIII	413.1	22.6	0.055	0.12	–	–	–	–	–	–
CLAH 15AN2	DI	432.7	35.6	0.082	0.19	367.9	8.9	359	10.6	434.2	26
CLAH 30AN2	DII	421.5	22.1	0.052	0.12	–	–	–	–	419.3	1.9

– index cc is related to cold crystallization

*460.0 K 16.0 J g^{-1};
452.8 K 5.5 J g^{-1};
417–447.7 K 3.8 J g^{-1}

the values of ΔH_m and T_m (32.8 kJ kg^{-1} and 469.6 K, respectively). In the former polyamide the piperazine ring units are oriented in several ways (formulae 3, 3A, 3B), which can lead, in some cases, to more rigid stuctures. This statement was confirmed by DSC measurements. On the DSC curve, two or three main peaks and some secondary ones could be found, which was interpreted in terms of different structures (Fig. 1). The certain positions of piperazine units in the polymer chains reduce the macromolecular symmetry and thereby also the crystallization. Parallel macromolecules containing the long segments with symmetrically oriented piperazine rings can form the regions with the higher amount of intermolecular bonds and crystallinity and therefore they have the higher values of T_m and ΔH_m. The more symmetrical is the structure of macromolecules the higher are the values of T_m and ΔH_m. The value for AN2 (ΔH_m=25.3 kJ kg^{-1}) compared with that for ANB (ΔH_m=32.8 kJ kg^{-1}) confirms our assumption.

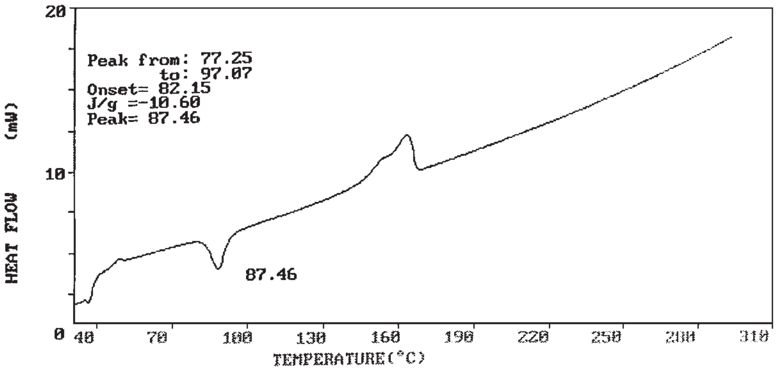

Fig. 3 DSC curve of tertiary copolyamide CL15AHANB

The polyamide ANB (with symmetrically placed piperazine rings) resembles the polyethyleneterephthalate (with symmetrically placed benzene rings). The so-called ‘cold crystallizaion’ i.e. the transformation into the pseudocrystalline state, occurs (with the maximum at 393 K) near the T_c=373 K with the value of ΔH_{cc}= –26 kJ kg^{-1} (Fig. 2). The similar general description is also valid for the investigated tertiary copolyamides containing 15 wt% ‘nylon’ salt of ANB and AN2 (Table 4, CI, DI) with ΔH_{cc}= –10.6 kJ kg^{-1} for both copolyamides and T_{cc}=359 K for ANB and 360 K for AN2 (Fig. 3). Because the conditions of DSC measurements were the same for all samples, the formation of non-equilibrium crystals during the cooling cycle (i.e. cold crystallization) had to be a symptom of a certain macromolecular structure.

Binary copolyamides (samples E–H) were prepared from CL and from the ‘nylon’ salt of other two components. These copolyamides could theoretically be (at the molar ratio of CL/salt=8/1) either random or block ones. The temperature of fusion of binary copolyamides, T_m, is lower than that of polyamides AN2 and ANB, the ΔS_m values of which are, however, higher. From the values obtained it turns out that samples undergo the crystallization process easier in the form of block copolymers or at least when poly-ε-caprolactam segments are of the sufficient length. In the case of polymers with random copolyamide segments (with various monomer units such as CL and derivatives of piperazine) the non-crystalline form prevails. In addition to the foregoing discussion, CL reacts by a polyaddition mechanism and the 'nylon' salt does by a polycondensation mechanism. The crystallization of the poly-ε-caprolactam segments is reduced due to the present piperazine comonomer (in the case of ANB the calculated value of ΔH_{mtheor}=58.6 kJ kg^{-1} and the measured value of ΔH_{mreal}=42.5 kJ kg^{-1}; for AN2 the value of ΔH_{mtheor}=58.5 kJ kg^{-1} and that of ΔH_{mreal}= 46.1 kJ kg^{-1}).

Differences in the T_m and ΔH_m values arise, to a certain extent, from the different length of the structure unit. The length of the monomer unit for the adipic acid and that for 1-(2-aminoethyl) piperazine is approximately of the same order like the length of the monomer unit for CL. On the other hand, the sebacic acid and 1,4-bis(3-aminopropyl) piperazine are bulkier and hence they form more irregular structures. Changes of the measured parameters were also found in the case of the sample N2, which revealed the most randomising effect (as can be seen from the values of ΔH_m and ΔS_m in Table 4).

The highest values of ΔH_m and ΔS_m were established for the CLAN2 copolyamide (sample F) containing two 'good' comonomers, i.e. adipic acid and N2. The lower values were ascertained in the case of the copolyamide CLANB (sample E) composed of the symmetric but longer NB and of a 'good' adipic acid, whereas the CLSNB (sample G) exhibits the lowest values of the measured characteristics.

Tertiary copolyamides (C, D) show the more pronounced decrease of T_m, ΔH_m and β. The temperature differences in T_m are proportional to the content of the 'nylon' salt AN2 or ANB; in the case of AN2 (CI–CIII samples) the value of ΔT_m=20–37 K and in the case of ANB (DI, DII samples) ΔT_m=30–40 K. Tertiary copolyamides with 15 wt% of ANB or AN2 have a special position among all samples. The values of all measured parameters are relatively high, which indicates the better crystallization compared with homopolyamides AN2 and ANB.

The data of the measured characteristics of tertiary copolyamides containing 20 and 30 wt% of the 'nylon' salt ANB and/or AN2 indicate only the small influence on thermal properties.

When comparing the properties of the tertiary copolyamides CI and CII (Table 4) and their blends with 50 wt% of PA 6 (Table 5) one can see that for copolyamides CI and CII the value of T_m is equal to 430 for the former and 423 K for the latter copolyamide; for the blend of PA 6+CI the value of T_m=444 K and for that of PA 6+CII the value of T_m=447 K. The melting temperature of PA 6 (T_m=497.8 K) falls in the blend to 492 K. The fall of T_m can be explained in terms of the mutual interactions between the macromolecules of PA 6 and those of copolyamides resulting in the transition of the copolyamides portion into the molten state at higher temperatures. The PA 6 macromolecules melt at lower temperature due to the action of the copolyamide.

In this assessment it should be remembered that the value of ΔH_m which was theoretically calculated on the basis of the additivity principle decreases with the increasing content of the 'nylon' salt of ANB (the content of the AH salt decreases in

Table 5 Thermal properties of PA 6 and blends of PA 6+copolyamide C

System	T_{m_1}/K	T_{m_2}/K	ΔH_{m1}/	ΔH_{m2}/	$\Sigma\Delta H_m$/	ΔH_{mcalc}/J g^{-1}			ΔS_m/J g^{-1} K^{-1}			β	Σβ
				J g^{-1}		PA 6	CI–III	Σ	PA 6	CI–III	Σ		
PA 6	–	497.8	–	66.2	66.2	66.2	–	66.2	0.138	–	0.138	0.35	0.35
PA 6+CI	444.3	492.1	4.6	29.1	33.7	34.3	15	49.3	0.01	0.059	0.069	0.15	0.18
PA 6+CII	447.3	491.8	0.9	36.1	37	34.3	12	46.3	0.002	0.073	0.075	0.19	0.19
PA 6+CIII	–	493.5	–	42.5	42.5	34.3	11.3	45.6	–	0.086	0.086	0.22	0.22

Table 6 Thermal properties of PA 6 and blended fibres 50 wt% of PA 6+50 wt% of copolyamide C, v_0=10 K min^{-1}

System				1st heating								1st cooling		
	T_{m_1}/	T_{m_2}/	ΔH_{m_1}/	ΔH_{m_2}/	$\Sigma\Delta H_m$/	β	Σβ	ΔS_{m_1}/	ΔS_{m_2}	$\Sigma\Delta S_m$/	T_{c_1}/	T_{c_2}/	$-\Delta H_{c_1}$/	$-\Delta H_{c_2}$ /
	K		J g^{-1}					J g^{-1} K^{-1}			K		J g^{-1}	
PA 6	–	494.2	–	66.1	66.1	0.35	0.35	–	–	0.1337	–	460.1	–	61
PA 6+CI	447.8	491.1	4.1	21.3	25.4	0.11	0.13	0.009	0.0434	0.052	408.5	450.8	2.9	37.1
PA 6+CII	452.9	490.8	0.4	31.6	32	0.17	0.17	0.0009	0.0652	0.066	403.5	448.5	0.7	38.6
PA 6+CIII	–	492.2	–	35.9	35.9	0.19	0.19	–	0.0729	0.073	–	452.9	–	38.3
				2nd heating								2nd cooling		
PA 6	–	486.6 493.4	–	52.9	52.9	0.28	0.28	–	–	0.108	–	459.9	–	59.1
PA 6+CI	432.3	477.8 489.6	10.8	34.5	45.4	0.18	0.24	0.0252	0.0716	0.097	408.9	450	2.4	36.7
PA 6+CII	427.6	475 487.6	7.8	34.4	42.2	0.18	0.22	0.0182	0.0714	0.090	–	447.4	–	37.7
PA 6+CIII	–	485.6 490.5	–	36.2	36.2	0.19	0.19	–	0.074	0.074	–	450.7	–	37.2
				3rd heating								3rd cooling		
PA 6		486.6 493.2	–	52.9	52.9	0.28	0.28	–	–	0.108	–	452.3	–	57.6
PA 6+CI	432.8	477.1 489.0	9	34.4	43.4	0.18	0.23	0.0208	0.0727	0.1035	408.9	449	1.4	37.4
PA 6+CII	432.7	474.2 486.9	6.3	34.4	40.7	0.18	0.21	0.002	0.0848	0.0868	400.9	448.6	0.3	37.9
PA 6+CIII		479.7 489.3	–	36.1	36.6	0.19	0.19	–	0.0744	0.0744	–	450.3	–	37.4

the same proportion of CL) in the copolyamide. This indicates that the higher amount of the 'nylon' salt has a lower deteriorating effect and contributes positively to the formation of its longer polymer segments which are able to crystallize. The theoretical additive value of $\Delta H_{\mathrm{mcalc}}$ for the blend of PA 6+CIII equals 45.6 kJ kg^{-1} on the assumption of the complete crystallization of both components. The experimentally obtained value of $\sum \Delta H_{\mathrm{m}}$= 42.5 kJ kg^{-1} fits well with the above-mentioned theoretical additive one.

The crystallization temperature of blends, T_c, lies in the range of 425–443 K, which is significantly higher than in the case of copolyamides themselves (T_c=366–367 K). Both the higher T_c of the blend and the unique peak of crystallization can be ascribed to the formation of a compatible system of PA 6 and the copolyamide, the balance of the system being reached within a short period of time in the extruder. DSC characteristics indicate the good miscibility of components.

The results given in Table 6 (several cycles of heating and cooling) have shown that the thermal properties do not change during the successive operations. Nevertheless, two peaks ascribed to the crystallization process indicate the partial separation of components after several moldings of the blended system.

The results obtained suggest that copolyamides can be used as additives to change the specific properties of the fibre-forming PA 6.

Summary

1. The polyamides and copolyamides studied have a good thermal stability.
2. The crystalline polyamides prepared exhibit the regular two-phase structure.
3. Binary copolyamides and tertiary copolyamides with 15 wt% of AN2 have the higher values of ΔH_{m} and ΔS_{m} in comparison with the piperazine polyamides of ANB and AN2. The other tertiary copolyamides have these values on the level of piperazine polyamides.
4. Comonomers decrease the enthalpy of fusion ΔH_{m} of the copolyamide, compared with PA 6. This results from a lower regularity of macromolecules and steric arrangement of the piperazine ring. Comonomers do not influence significantly the thermal properties of polymers but they do the kinetics of crystallization.
5. The thermal properties of copolyamides indicate their block character with long segments of CL and another comonomer, the CL being the most controlling component.
6. Mutual interactions between the macromolecules of PA 6 and the copolyamide were ascertained.
7. The blends of PA 6+copolyamide(s) reach during their processing the balanee within a short period of time and preserve their properties even after spinning.

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