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RESEARCH AND DEVELOPMENT

PA 6, Co-polyamides of ε-Caprolactam with Nylon Salt of Diethylenetriamine + Adipic Acid and their Thermal Properties

Abstract
The synthesis of co-polyamides consisting of ε-caprolactam and 5.9-19.7 wt.% of nylon salt ADETA, prepared from adipic acid + diethylenetriamine and the physical & thermal properties of polyamide 6 and co-polyamides, are reported. The content of this low molecular compound is comparable with that reported for crude polyamide 6. The molecular weight of each co-polyamide is lower. The melting temperature is lower in comparison with PA6, and corresponds to that of the nylon salt ADETA. The crystallisation ability of co-polyamides is higher, and secondary crystallisation mainly contributes to the higher degree of crystallinity. The state of organisation in co-polyamides, on the basis of ΔS_m values, seems to be better, mainly for the samples with developed crystallisation (i.e. after a long period of crystallisation).

Key words: *ε-caprolactam, adipic acid, diethylenetriamine, co-polyamides, synthesis, thermal properties.*

■ Introduction

Thermal characteristics are very important for all polymers processed by moulding, injection or spinning. This applies not only to the melting temperature, but also the temperature of decomposition, the crystallisation temperature and other characteristics. In addition, the enthalpies of melting and crystallisation are important for semi-crystalline polymers as well. The DSC study of all components of blends (used for any product prepared via melting) therefore gives us basic information about the components' future behaviour in the blend and during processing.

When some derivatives, such as co-polymers, are prepared, we have to compare the properties of the synthesised copolymers with the original homopolymer. This is necessary mainly in the blends of the homopolymer and derived copolymer(s).

Some properties of homopolymers are not always satisfying for their application in certain fields. Copolymer based on a certain monomer with some amount of another, functional co-monomer may have specific characteristics which predestine this copolymer as raw material for products with better properties, or as an additive for homopolymer, and may thus improve the properties of the product. Copolymers are able to improve many properties, including thermal properties [1, 2].

Copolymer has one great advantage, good compatibility with relevant homopolymers, and from this point of view the deterioration of the blend properties is lower. Semi-crystalline (block) copolymers can co-crystallise with homopolymers, several type of crystals with various sizes and levels of perfection can be formed, and blocks of copolymer can create their own crystallites [3, 4].

Co-polyamides from ε-caprolactam (CL) with the functional co-monomer can be applied as compatible additives for modified polyamide (PA 6) fibres [5, 6].

The crystallisation ability of co-polyamides based on CL depends on the chemical nature and molecular length of the other functional co-monomer, which determines the longitudinal (dis)order of the co-polyamide macromolecules. In certain instances, however, the crystallinity is not essentially reduced because the monomer unit cell of the co-monomer is similar in size to that which is being replaced [7], and we can assume that the monomer units cells with different chemical natures but with similar lengths could co-crystallise, or at least have good compatibility each other.

The replacement of adipic acid by terephtalic acid exhibits such an effect [7], and the replacement of hexamethylenediamine by 1-(2-aminoethyl)piperazine, N2 does not fundamentally deteriorate the thermal properties of co-polyamides containing N2 [8].

Because the length of the diethylenetriamine (DETA) molecule is very similar to those of hexamethylenediamine or N2, we can assume that replacing hexamethylenediamine with DETA would not negatively influence the properties of the co-polyamides containing ADETA, mainly from the point of compatibility (crystallinity, processability et al.).

Naturally, the properties of co-polyamides based on ε-caprolactam, adipic acid and diethylenetriamine will change in comparison with those of other co-polyamides and homopolyamide PA 6 as well. Therefore co-polyamides with different amount of the nylon salt ADETA from adipic acid and diethylenetriamine were synthesised, and together with commercial PA 6 their properties were evaluated, mainly from the point of their thermal characteristics.

■ Experiment

Materials used:

■ ε-caprolactam (CL);
■ poly-ε-caprolactam, PA 6, both from Nylstar Slovakia, Humenné;
■ adipic acid analytically pure (A);

- diethylenetriamine (DETA) both from Aldrich, DETA vacuum distilled once;
- nylon salt (ADETA) synthesised from adipic acid + diethylenetriamine;
- co-polyamides (KOPA) synthesised from CL and ADETA using 5.9, 9.9, 13.7 and 19.7 wt.% of ADETA and the appropriate amount of CL respectively;
- sulphuric acid, 93% analytically pure;
- water.

Reaction scheme

The preparation of the linear alkaline co-polyamide from ε-caprolactam, adipic acid and diethylenetriamine is presented in Scheme 1.

The co-polyamides were synthesised in a melt in a nitrogen atmosphere. Powdered and dry CL and ADETA salt were mechanically mixed and put into a glass apparatus immersed in a thermostatted oil bath. The temperature of the reaction mixture was raised from room temperature, and the polyreaction started by evaporation and condensation of the reaction water after melting and homogenisation of the mixture, and upon the temperature reaching about 180 °C. After that, the temperature was gradually increased to 270 °C. The poly(addition-condensation) reaction was completed in 60 and 150 minutes respectively, according to Table 1. At the end of the polyreaction, the co-polyamides were poured onto a metallic plate and cut into chips. After

synthesis, all co-polyamides were treated in the same way.

To determine the amount of low molecular compounds (LMC) each co-polyamide sample (used as an additive for PA 6 blend fibres) was extracted in boiling water:
a) for 1 hour, 1 g of polymer to 100 ml water (values LMC 1)
b) for 2 × 1 hour, 1 g of polymer to 8 ml water (values LMC 2), and
dried at T = 105 °C for 2 hours.

Co-polyamides used for DSC measurements were extracted over 2 h in water at 40 °C and dried at room temperature, and then at 40 °C.

The amount of low molecular compounds (values LMC1 and LMC2) was determined from the difference in weights before and after extractions & drying.

The intrinsic viscosity, [η], was determined viscosimetrically in a solution of 93% H_2SO_4, at 25 °C.

The thermal properties were studied using the DSC 7 Perkin Elmer Co. equipment at 10 $Kmin^{-1}$ heating and cooling rates. Three cycles (heating-cooling-heating, within the range of 40 °C to 250 °C) were applied in order to obtain information about the thermal properties. Under these conditions, the glass temperature, T_g, could not be estimated.

Results and discussion

Some properties of polymer products (such as mechanical properties) depend on the molecular weight of the polymer and additives used. A lower molecular weight negatively influences the mechanical properties mainly in oriented products such as fibres, films etc.
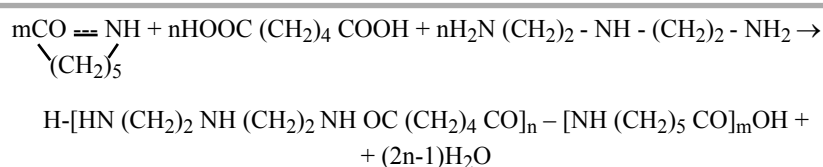
For this reason, evaluation of the molecular weight (or other dependent characteristic) of the component of the blend is important. The amount of low molecular (hot water-soluble) compounds (LMC) is also important from the point of view of the efficiency of the polymer blend's production (and the recycling of the reaction components).

The results in Table 1 show that the intrinsic viscosity of co-polyamides is (much) lower in comparison with homopolyamide PA 6. The amount of low molecular compounds (LMC) is practically the same for all co-polyamides, and is higher in comparison with value (already known and cited in literature)for crude PA 6, i.e. 8-12 wt.%. (according to the polyreaction temperature). An exact comparison cannot be given because it is not possible to obtain PA 6 with high molecular weight within the polyreaction times of 60 and 150 min respectively which we applied for the synthesis of the co-polyamides.

In the poly(addition-condensation) reaction, important roles are played by both of these factors:
- the addition reaction of ε-caprolactam,
- the condensation reaction of ε-amino-caproic acid (formed during the reaction), and mainly nylon salt ADETA as well (added before the beginning of the reaction).

Both the ε-aminocaproic acid and the nylon salt ADETA function as activators, and accelerate the polyreaction and formation of macromolecules with high degrees of polymerisation. The higher concentration of nylon salt (and ε-aminocaproic acid as well) causes the formation of larger amounts of reaction water, which could promote the hydrolysis of macromolecules mainly in connection with the longer polyreaction time. The combined influence of the above-mentioned aspects created the situation wherein the higher amount (19.7 wt.%) of ADETA and the lower polyreaction time (60 min) determine the higher intrinsic viscosity of KOPA, i.e. 19.7. For each polyreaction

$$mCO \textendash NH + nHOOC\,(CH_2)_4\,COOH + nH_2N\,(CH_2)_2 - NH - (CH_2)_2 - NH_2 \rightarrow$$
$$(CH_2)_5$$

$$H\texttext{-}[HN\,(CH_2)_2\,NH\,(CH_2)_2\,NH\,OC\,(CH_2)_4\,CO]_n - [NH\,(CH_2)_5\,CO]_m\,OH + $$
$$+\,(2n\text{-}1)H_2O$$

Scheme 1. Preparation of the linear alkaline co-polyamide from ε-caprolactam, adipic acid and diethylenetriamine.

Table 1. Properties of PA 6 and co-polyamides.

Polyamide and co-polyamides	Time of preparation, min	[η], ml/g	LMC 1, wt.%	LMC 2, wt.%
PA6	CP	92	-	-
KOPA 5.9	150	52	10.3	13.5
KOPA 9.9	150	31	10.5	13.3
KOPA 13.7	150	21	12.7	15.0
KOPA 19.7	60	46	10.5	13.5

CP   – *commercial product, low molecular compounds (LMC) are extracted by the producer*
LMC1 – *amount of low molecular compounds after the extraction in boiling water, 1 h, ratio polymer/ water = 1 g/100 ml*
LMC2 – *amount of low molecular compounds after the extraction in boiling water, 2×1 h, ratio polymer/water =1 g/8 ml*

Table 2. Thermal properties of PA 6 and co-polyamides.

(Co)poly-amide	1st heating				1st cooling		2nd heating				
	T_{m1}, °C	ΔH_{m1i}, J/g	ΔH_{m1c}, J/g	ΔS_{m1c}, J/g K	T_c, °C	ΔH_c, J/g	T_{m2}, °C	ΔH_{m2i}, J/g	ΔH_{m2c}, J/g	ΔS_{m2c}, J/g K	ΔH_{mc2} - ΔH_{mc1}, J/g
PA 6	226.0		72.8	0.146	178.9	62.5	179.1 224.3	0.8 53.9	54.7	0.110	18.1
KOPA 5.9	205.3 215.0	46.3 29.8	76.1	0.157	168.9	56.0	172.9 213.8	0.95 49.4	50.35	0.103	25.7
KOPA 9.9	201.8 208.5	49.0 31.0	80.0	0.160	158.9	52.8	160.4 206.3	0.8 45.7	46.5	0.097	33.5
KOPA 13.7	194.6	-	76.9	0.164	148.4	46.5	149.9 199.0	0.6 42.7	43.3	0.092	33.6
KOPA 19.7	190.8	-	69.8	0.150	134.9	39.5	184.9	34.9	34.9	0.076	34.9

ΔH_{m1i} – partial values, ΔH_{m1c}, ΔH_{m2c}, ΔS_{mc} – total values

composition, the relevant optimal polyreaction time from the point of maximal intrinsic viscosity exists [9].

Copolymerisation influences the regularity of the polymer chain, and usually contributes to its mobility. One consequence of this influence may be the higher tendency to secondary (re)crystallisation, mainly in cases when primary crystallisation cannot be developed during cooling of the melt, due to set conditions.

The first DSC heating of co-polyamides was realised several weeks after their synthesis (time X) and extraction in 40 °C hot water. The value of ΔH_{m1c} (Table 2) expresses the melting enthalpy of the crystalline portion formed during the solidification of the co-polyamide melt at the end of the synthesis plus the melting enthalpy of the crystalline portion arising during the long period from the synthesis to the first heating of the DSC measurement, when the co-polyamides have enough time to (re)crystallise to their maximum possible level. Therefore ΔH_{m1} values are much higher than ΔH_{m2} values, and this difference expresses the contribution of the secondary crystallisation (under the T_g), and confirms the higher mobility of the co-polyamide macromolecular segments of the co-polyamides (Table 2).

A study of both T_{m1} and T_{m2} values (Table 2) suggests that the number of intermolecular (hydrogen) bonds in co-polyamides is reduced as a dependence of the co-monomer ADETA amount. This is a logical influence of the increasing amount of ADETA, which causes the structure of the co-polyamide′s macromolecules to become ever more disordered, and also reduces the amount of hydrogen bonds.

For KOPA 5.9 and KOPA 9.9 at the first heating, two values of T_m (with ΔH_m high enough) are registered, which indicates the creation of two crystalline modifications. After the cooling, practically only one crystalline modification is observed for all samples, in both PA 6 and the co-polyamides. Another confirmation of the presence of only one crystalline modification (T_{m2}) is the unique crystallisation temperature for all co-polyamides and PA 6 as well.

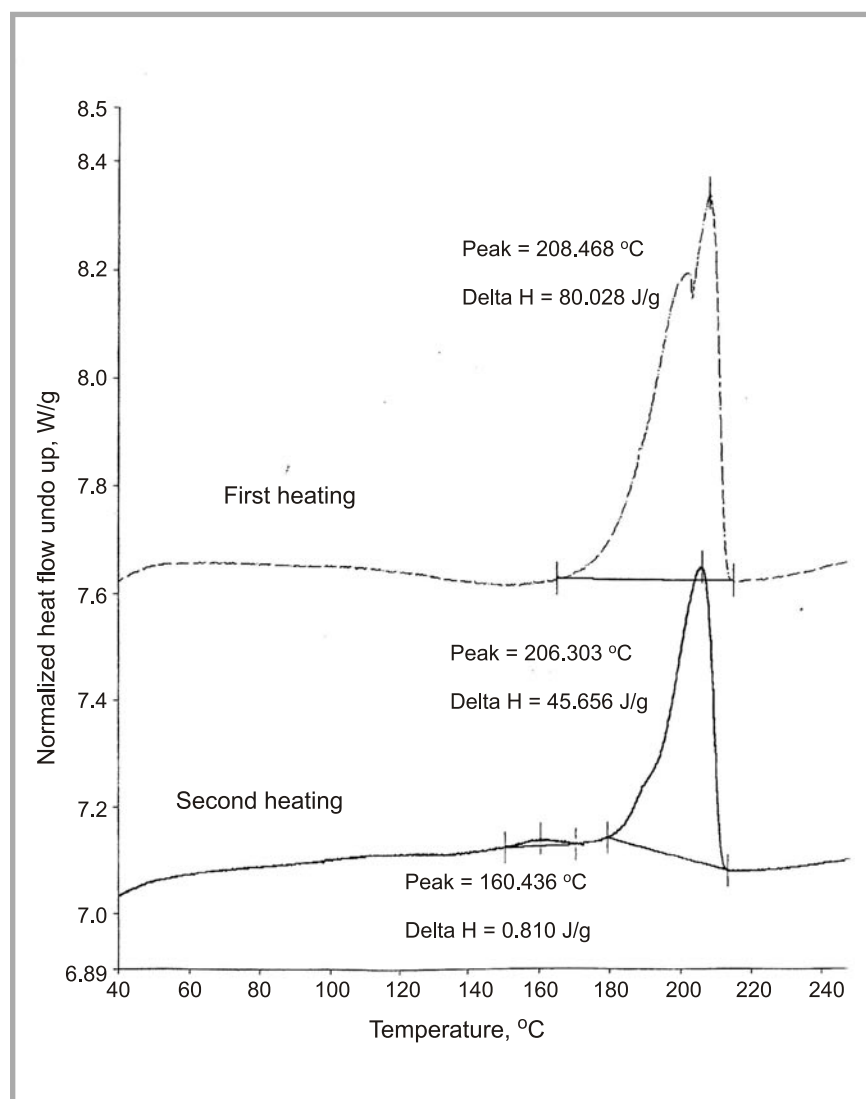A study of the thermal properties reveals that the amount of co-polyamide crystal-

Figure 1. DSC thermogram of KOPA 9.9, first and second heating.

line portion is higher by up to 13.7 wt.% of the co-monomer ADETA, compared to PA 6, and it is not much less at 19.7 wt.% of the co-monomer. The maximum ΔH_{m1} value of 80.0 J/g is reached at the amount of 9.9 wt.% of ADETA. In comparison with PA 6, these co-polyamides have a high crystallisation ability and a high mobility of macromolecular chains as well, even at such a high content of co-monomer units as c. 20 wt.%. This is proved by the fact that $\Delta H_{m1c} >> \Delta H_{m2c}$ also.

The total value ΔH_{m1c} expresses the amount and quality of crystallites created during the long interval X from synthesis to the first heating of the DSC measurement. During the first cooling at the high cooling rate (i.e. 10 K.min^{-1}), the macromolecules have not had enough time to arrange themselves into crystallites with the maximum degree of organisation. The difference $\Delta H_{mc2} - \Delta H_{mc1}$ shows that the mobility of co-polyamide′s macromolecules, (mainly these with higher amounts of ADETA, i.e. 9.9-19.7 wt.%) is higher than the mobility of PA 6 macromolecules. Specifically, for KOPA 19.7 $\Delta H_{m1c} = 2 \Delta H_{m2c}$ and especially under T_g during X, the better mobility is proved by this difference.

The typical DSC thermogram is given in Figure 1 (see page 23), where two peaks for two crystalline modifications, as well as the impossibility of determining the T_g temperature are clearly shown.

The temperature of crystallisation, T_c, drops proportionally to the amount of co-monomer units. The enthalpy of crystallisation ΔH_c, drops proportionally as well, mainly because the co-polyamide with lower T_c has less time to crystallise during cooling.

Co-polyamides containing up to 30 wt.% of nylon salt ADETA are suitable additives for modifying fibre-forming PA 6. Polyamide fibres are able to absorb from 10 to 50 wt.% of such co-polyamides without any negative influence on the processability of the blend melt, i.e. during the spinning and drawing processes. It is principally the electrical and sorptive properties of such modified PA 6 fibres that are substantially improved [6].

PP fibres can be successfully modified by the co-polyamides reported in our contribution as well [10].

◼ Conclusions

1. Co-polyamides have a lower molecular weight and a comparable amount of low molecular compounds compared with PA 6.

2. The co-monomer decreases the co-polyamide's melting temperature T_m. The drop is proportional to the amount of the co-monomer.

3. The enthalpy of fusion, ΔH_m, is positively influenced by co-monomer up to 13.7 wt.% with a maximum at 9.9. wt.% of the co-monomer.

4. Secondary crystallisation at room temperature for co-polyamides is more important.

5. The higher the amount of the co-monomer, the lower are both the crystallisation temperature and the enthalpy of crystallisation.

6. The reported co-polyamides are suitable additives for improving the electric and sorptive properties of PA 6 and PP fibres.

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