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Optimisation of Properties of Ternary Co-polyamides Based on ε-Caprolactam

Abstract
The synthesis and evaluation of properties displayed by ternary co-polyamides prepared from co-monomers such as ε-caprolactam, AH salt and nylon salt of 1,4-bis(3-aminopropyl)piperazine and adipic acid (ANB) are discussed. The properties are evaluated in accordance with the principles of the five-level three-factor experimental design, which allows the concentration of ε-caprolactam, the ratio of two other co-monomers and the polyreaction time to be selected. The procedure is aimed at predetermining the values of the content of low-molecular compounds, the melting temperature and the limiting viscosity number of the synthesised copolyamide to a certain extent.

Key words: *co-polyamides, ε-caprolactam, adipic acid, hexamethylenediamine, 1,4-bis(3-aminopropyl)piperazine, nylon salt.*

■ Introduction

Because well-known polyamides like PA6, PA66 and PA610 have favourable properties, they are used as fibre-forming polymers not only in the textile industry but also in different technical spheres. However, some textile properties (e.g. sorptive, electric, elastic, etc.) do not fulfil the requirements of today's customers. Therefore, the question of the preparation of suitable fibre-forming polyamides or co-polyamides is still relevant as far as improving these properties is concerned.

Polyamide properties are influenced by molecular characteristics such as the chemical composition, the methylene ratio, the amidic and other functional groups or atoms, the content of co-monomers, the regularity of the chain macromolecular structure [1] and, subsequently, by supermolecular characteristics such as the degree of crystallinity and orientation [2], evenness [3], the cross-sectional shape [4], etc.

The high crystallinity of polyamides and the great number of intermolecular bonds induce their high melting temperature T_m and insufficient sorption ability. Nor are the electric properties of polyamide fibres considered satisfactory.

The research works dealing with the preparation of (co)polymers and mainly (co)polyamides containing piperazine derivatives have indicated that it is possible to decrease their melting temperature T_m [5] and improve their sorptive, electric and other properties [2,6-8]. The decrease in T_m can be utilised in their application as adhesives or thermally bonded fibres, whereas the increase of sorption and the improvement of electric properties are employed for the better performance of fabrics produced from

them. The copolymers which are used as additives to polyamide and polypropylene fibres also improve the dyeability [9] and thermal stability [10] of the blended fibre-forming melt [5].

The simultaneous application of two co-monomer types (lactam and diaminoderivative of piperazine with dicarboxylic acid) leads to a shortening of the time necessary to prepare co-polyamides of a sufficiently high molecular mass [6]. The different mechanism of the chain construction and the different reactivity of co-monomers can lead to the block character of co-polyamides [11].

The content of low-molecular compounds (LMC) extractible with hot water in polyamides and co-polyamides is important with respect to their extraction before processing into textile products, especially when their concentration is higher. Some types (for example a co-polyamide prepared from 90% AH salt and 10% ε-caprolactam) do not require any extraction, and make monomers more efficient.

As for the properties, it is suitable for (co)polyamides to have a sufficiently high molecular mass and a low LMC content. The level of melting temperatures as well as that of other properties predetermine them either for the production of textile fibres or for the preparation of thermally bonded fibres, or adhesives.

In the case of co-monomers, the main factors influencing the melting temperature, LMC content and molecular mass are their ratio and the polyreaction time.

The prime objective of this work was to propose an experimental procedure which would enable the thorough evaluation of individual system components or condi-

tions for the synthesis of polyamides, and at the same time would afford the possibilities to optimise conditions for the preparation according to the requirements for final polymer characteristics. To achieve this objective, it is useful if the experimental method used in the form of the multilevel experiment design allows one to describe (by mathematical dependencies that can be subsequently used in the calculations with optimal solutions) not only the statistically evaluated importance and quality of the influence of factors examined, but also the dependence of output properties exerted on these factors (parameters). The description and optimisation of the synthesis have been accomplished using the five-level experiment. The mathematical conditions of the construction of these projects are described in the literature [12-14].

To evaluate the properties of co-polyamides based on ε-caprolactam, a series of co-polyamides with a different ratio of ε-caprolactam, AH salt (nylon salt of hexamethylenediamine and adipic acid) and nylon salt of the adipic acid and 1,4-bis(3-aminopropyl)piperazine, ANB, was prepared in the first part of the work in accordance with the principles of the experimental design. In the second part, the T_m parameters, LMC content and molecular mass expressed by the limiting viscosity number [η], were evaluated by both the method analysis of variance and the complete regression analysis.

■ Experimental

Applied monomers and chemicals
- ε-caprolactam, Chemlon-Rhône Poulenc firm, T_m=70°C,
- AH salt, Chemlon-Rhône Poulenc firm, T_m=196°C,
- adipic acid, p.a., Aldrich firm, T_m=153°C,
- 1,4-bis(3-aminopropyl)piperazine, Aldrich firm,
- nylon salt from the adipic acid, p.a. and from 1,4-bis(3-aminopropyl)piperazine,
- ANB, T_m=193°C,
- 93% sulphuric acid, p.a.

Preparation of nylon salt, ANB, and ternary co-polyamides

The synthesis of polyamides from diamines and dicarboxylic acids can be performed from separate components. On a laboratory scale, however, the more advantageous option is to prepare the so-called nylon salt as a crystalline

compound of both components in the accurate molar ratio 1:1, which ensures the maximum molar mass of the polymer.

The nylon salt ANB was prepared by mixing hot equimolar solutions of the adipic acid and distilled 1,4-bis(3-aminopropyl)piperazine in 96% ethanol, and by the gradual evaporation of ethanol and thickening the solution up to a honey-like consistency. After pouring out into Petri dishes, ethanol evaporated in a fume chamber up to the point at which the nylon salt ANB crystallised. Then the nylon salt was pulverised, and the ethanol residues were quantitatively removed by vacuum drying.

The following co-monomers were weighed into polymerisation soft-glass test tubes: ε-caprolactam (CL), AH salt and ANB salt to the total amount of 6 g and in the ratio according to conditions of experimental design (Table 1). The polymerisation test-tube neck was pulled into the 60-70 long capillary which was functioning as an air cooler, and at the same time as a plug preventing the entry of air oxygen into the melt. The test-tubes were inserted into the polymerisation block heated to the temperature of T_1=254-259°C. The temperature variation was caused by the inertia of the heating system, and one cycle (254-259-254°C) lasted 12 min. At time intervals t_p, determined within the experimental design, the test-tubes were withdrawn from the polymerisation

block, and the copolyamide melt was isolated by pouring it onto the glass base. After stiffening, the copolyamide was cut into granules and three characteristics were defined: LMC content, melting temperature T_m, and limiting viscosity number [η], as a value corresponding to the molecular mass.

The conversion of co-monomers or the content of water-soluble LMC were established by extraction of the co-polyamides of the mass a proceeding in water with the temperature T_2=80°C for 2 h. Before extraction, the co-polyamides were dried for 2 h at 105°C; then, the co-polyamide mass b without LMC and the LMC content expressed in the percentage by mass were calculated according to the equation:

$$\% \text{ LMC} = 100(a-b)/a$$

The calculated values are in Table 1. The melting temperatures of co-polyamides T_m were determined in extracted samples as an average of five values obtained by measuring on the Kofler block. The data is given in Table 1.

The extracted and desiccated copolyamide samples were dissolved in sulphuric acid. Next, the viscosimetric method was used to define the rates of flow t_x for four solutions with different polymer concentrations, as well as the rate of flow t_0 for the solvent at T_3= 20°C. On the basis of the defined values t_x and t_0, the specific viscosity values were expressed as

Table 1. Composition of polymerisation mixtures and properties of co-polyamides.

Factor	x_1	$x_2 = w(ANB)/w(AH)$		x_3	Property		
No	w(CL), %	w(ANB), %	w(AH), %	t_p, min	w(LMC), wt.%	T_m, °C	[η], cm³g⁻¹
1	40	30	30	105	10.5	150	74
3	60	20	20	105	8.7	171	109
4	40	40	20	105	17.8	138	92
5	60	26.67	13.33	105	9.9	175	87
6	40	30	30	195	9.9	138	110
7	60	20	20	195	7.3	162	90
8	40	40	20	195	9.5	137	98
9	60	26.67	13.33	195	8.1	163	114
10	33.18	40.09	26.73	150	5.0	147	121
11	66.82	19.91	13.27	150	7.7	167	76
12	50	19.86	30.14	150	5.5	160	63
13	50	35.07	14.93	150	5.7	157	80
14	50	30	20	75	8.8	153	70
15	50	30	20	225	12.2	149	109
16	50	30	20	150	6.2	151	101
17	50	30	20	150	5.6	151	97
18	50	30	20	150	8.7	151	100
19	50	30	20	150	7.2	150	96
20	50	30	20	150	6.5	150	97
	50	30	20	150	7.5	150	96

$$\eta_{mer} = t_x/t_0 - 1,$$

and on the basis of the graphic dependence

$$\eta_{mer}/c = f(c)$$

the limiting viscosity number value $[\eta]$ was determined by extrapolation to the value of c=0. The results achieved are shown in Table 1.

■ Results and Discussion

The selected five-level three-factor experimental design, the factors and parameters of which are shown in Tables 2 and 3, was used to study the influence of the content of Cl, AH salt and ANB salt and of the poly(addition-condensation) reaction time t_p on the LMC content in the copolyamide, on the melting temperature T_m and on the limiting viscosity number of co-polyamides $[\eta]$.

All three of the output qualities which were investigated were evaluated in accordance with the theory of experimental design by means of the analysis of variance and the complete regression analysis. The regression coefficients of the complete quadratic model of the following type were defined as follows:

$$Y = b0 + bl \cdot xl + b2 \cdot x2 + b3 \cdot x3 + \\ + b12 \cdot xl \cdot x2 + b13 \cdot xl \cdot x3 + \\ + b23 \cdot x2 \cdot x3 + b11 \cdot xl^2 + \\ + b22 \cdot x2^2 + b33 \cdot x3^2.$$

The results of the measured values which were processed by the PC program are summarised in Table 4. The table indicates only statistically significant coefficients and values of the mean square error of the mathematical estimation (s_{LF}), as well as the values of the mean square error representing an experimental inaccuracy (s_E). In calculating the respective property on the basis of the regression equation obtained, one can approximately estimate the total average error as a sum of $s_{LF}+s_E$. It follows from Table 4 that the factors under investigation have a great influence on all three of the measured properties.

By increasing the content of CL (factor xl) and the poly-reaction time (x3) the LMC content decreases linearly, and by increasing the ratio of ANB/AH (x2) it increases linearly. In this dependence, the quadratic effects manifest themselves only slightly, while the individual interactions of factors show themselves more

Table 2. *Experimental design conditions - recalculation of factors from coded levels to real values ($x_{iR}=x_{i,R0}+x_{i,C}I_i$, where: $x_{i,R}$ - the real value for factor x_i at calculated coded value; $x_{i,R0}$ - the real value for factor x_i at coded value = 0; $x_{i,C}$ - the coded value for factor x_i; I_i - the real value of step for factor x_i).*

Factor/Coded level	-1.682	-1	0	1	1.682	I_i
x_1 = w (CL)	33.18	40	50	60	66.82	10
x_2 = w(ANB)/w(AH)	0.659	1	1,5	2	2.341	0,5
x_3= reaction time	74.31	105	150	195	225.69	45

Table 3. *Conditions for individual trials in experimental design.*

| Trial No	x_1	x_2	x_3	w(CL), wt.%	w(ANB), wt.%	w(AH), wt.%	T, °C
		real value					
1	40	1	105	40	30	30	105
2	60	1	105	60	20	20	105
3	40	2	105	40	40	20	105
4	60	2	105	60	26,67	13,33	105
5	40	1	195	40	30	30	195
6	60	1	195	60	20	20	195
7	40	2	195	40	40	20	195
8	60	2	195	60	26.67	13.33	195
9	33.18	1.5	150	33.18	40.09	26.73	150
10	66.82	1.5	150	66.82	19.1	13.27	150
11	50	0.659	150	50	19.86	30.14	150
12	50	2.341	150	50	35.07	14.93	150
13	50	1.5	74.31	50	30	20	75
14	50	1.5	225.69	50	30	20	225
15	50	1.5	150	50	30	20	150
16	50	1.5	150	50	30	20	150
17	50	1.5	150	50	30	20	150
18	50	1.5	150	50	30	20	150
19	50	1.5	150	50	30	20	150
20	50	1.5	150	50	30	20	150

Table 4. *Statistically significant coefficients of the complete regression model.*

| Parameter	w(LMC), wt.%	T_m, °C	$[\eta]$, cm^{3}g^{-1}
b_0	6.862	150.550	97.43
b_1	-	10.370	-4.37
b_2	-	-0.955	1.95
b_3	-	-2.980	9.20
b_{11}	-	1.970	2.81
b_{12}	-	2.250	-
b_{13}	-	-1.000	-5.50
b_{22}	-	2.500	-6.74
b_{23}	-1.013	1.000	-
b_{33}	1.826	-	-
s_E	1.097	0.547	2.13
s_{LF}	3.888	7.100	21.6

Table 5. *Results of the optimisation for the synthesis of co-polyamides.*

| Parameter	Calculated values			Mean square error of estimation
	opt 1	opt 2	opt 3	
x_1	-0.776	-1.682	-1.682	
x_2	-1.682	-0.0205	0.611	
x_3	-0.094	1.327	1.682	
w(LMC)/, wt.%	5.9	10.0	11.4	± 5.0
$[\eta]$, cm^{3}g^{-1}	80	136.6	141.4	± 24
$|T_m|$, , °C	155.7	136.7	135.1	± 7.6
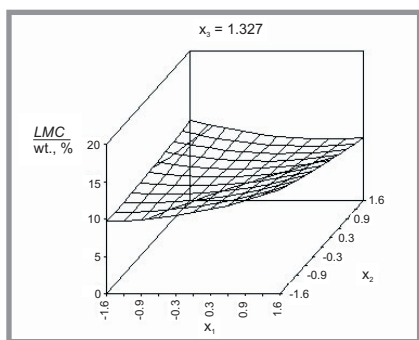
Figure 1. *The response surface of the dependence of the w(LMC) content on the w(CL) (x1) and the ratio w(ANB)/w(AH) (x2) at the time of the poly(addition-condensation) reaction $t_p=209.7$ min (x3=1.327).*
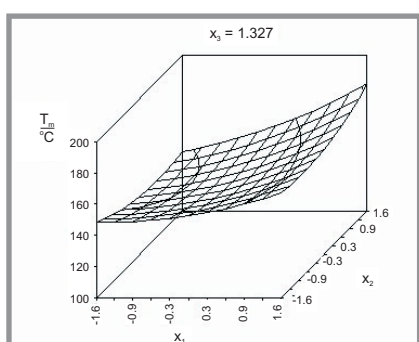
Figure 2. *The response surface of the dependence of T_m on the w(CL) (x1) and the ratio w(ANB)/w(AH) (x2) at the time of the poly(addition-condensation) reaction $t_p=209.7$ min (x3=1.327).*
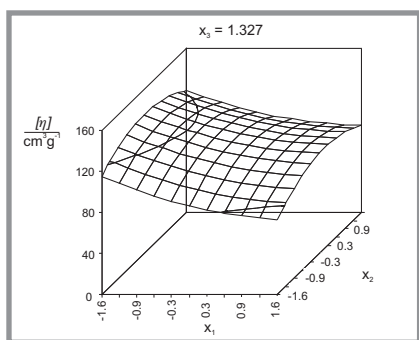
Figure 3. *The response surface of the dependence of [η] on the w(CL) (x1) and the ratio w(ANB)/w(AH) (x2) at the time of the poly(addition-condensation) reaction $t_p=209.7$ min (x3=1.327).*

intensively. The most remarkable effect is exerted by the interaction of factors x2-x3, i.e. the interaction between the ratio of ANB/AH and the polyreaction time (Figure 1).

The melting temperature T_m increases linearly in dependence on the content of CL (x1) and, at the same time, a moderate fall in values occurs in dependence on the ratio of ANB/AH (x2) and the poly-

reaction time (x3). Of the quadratic effects, only the content of CL (x1) and the ratio of ANB/AH (x2), which cause the curvature of the response surface along the respective axis to the minimum, have any statistically significant influence. All interactions of the factors examined, i.e. the interactions x1-x2, x1-x3 and x2-x3, respectively, are statistically significant (Figure 2).

The values of [η] increase linearly with the ratio of ANB/AH (x2) and the poly-reaction time (x3) (the most remarkable influence being exerted by the factor x3), and fall with a growing CL content (x1). This is in agreement with the slower polyaddition reaction of CL, in comparison with the more rapid polycondensation reaction of nylon salts. However, in the case of [η] the quadratic influences of individual factors are more distinct, in contrast to the previous two properties, and the curvature of the response surface along the axis x1 reaches the minimum, and the maximum along the axis x2. In addition to this, the shaping of the response surface is largely shared by interactions x1-x3 and x2-x3. Both the quadratic contribution of the factor x3 and the interaction x1-x2 are statistically insignificant.

For all three qualities examined, the error of the mathematical estimation based on the regression model (s_{LF}) is relatively high with regard to the experimental error (s_E), and therefore the equations calculated are unable to describe individual dependencies accurately within the experimental space. Of course, for this reason the error of the estimation has a tendency to rise during the calculations based on regression equations. In this case, the total average error of estimation according to the regression equation is: for T_m ±7.6°C, for LMC ±7.5 wt.% and for [η] ±0.23 dl·g^{-1}.

On the basis of the results given above, three optimisation variants of the synthesis of the copolyamide were given as follows:
1. to minimise the LMC content so that the [η] should not decrease below the value of 80 cm^3·g^{-1} (Figure 1),
2. to maximise the [η] so that the LMC content should not exceed 10 wt.% (Figure 3)
3. to minimise the T_m so that the [η] should not drop below the value of 80 cm^3·g^{-1} (Figure 2).

According to the requirements stated above, the tasks of optimisation were solved using the subprogram of the optimiser program MS EXCEL 97. The data referring to individual marginal conditions have included the average errors of estimation for the individual evaluated properties. The results of optimisation are listed in Table 5. The response surface diagrams (Figures 1-3) demonstrating the studied properties for one variant of the optimum have a defined constant factor x3 for each diagram, or else they have a polyreaction time equal to the value calculated for the respective optimum (x3=1.327).

■ Conclusions

■ Ternary co-polyamides prepared from CL and ANB and AH nylon salts of the high molar mass can be synthesised in a relatively short time.

■ The content of low-molecular compounds in synthesised co-polyamides is comparable to that in the poly-ε-caprolactam. The ratio of ANB/AH becomes more noticeable only in the first stages of the polyreaction (short spaces of time), during which the content of LMC rapidly increases with the growing ratio of ANB/AH. Over a longer period of time of the polyreaction, this factor loses its significance and the LMC content is not practically influenced. Similarly, the content of LMC is influenced by the concentration of CL, which means that its concentration loses significance over a longer period of time.

■ The [η] value is especially influenced during the whole course of the polyreaction by the ratio of ANB/AH, and its growth (with a growing ratio of ANB/AH) can be observed practically within the whole range of the ratio indicated above. However, this growth is already insignificant at the highest values of the ratio of ANB/AH. The higher concentration of CL and the small ratio of ANB/AH, mainly at higher polyreaction times, unambiguously decrease the [η] of the copolyamide.

■ Within the whole range of the polyreaction time, the T_m increases at the growing concentration of CL and the rising ratio of ANB/AH. The growth of T_m is the greatest if the concentration of CL and the ratio of ANB/AH grow simultaneously.

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