

Fibres Made of Co-polyamides Modified with Polyetheramines. Studies of the Supermolecular Structure

Abstract

The usability of commercial polymer materials is significantly limited by the unfavourable effect exerted on them by high or low temperatures. For example, it is known that the impact of polyamides considerably decreases at temperatures below 0°C. The aim of numerous studies have thus been to improve the impact properties of polyamides. In this paper, an attempt has been made to modify polyamides by incorporating elastic segments into their structure. The resulting block copolymer is characterised by better impact properties than the initial homopolymer. The copolymer investigated in this study was the product of anionic copolymerisation of a caprolactam/laurinolactam mixture (80:20 wt), modified with a macroactivator obtained from 1.6-hexamethylene di-isocyanate and polyoxypropylene-diamine in the amount of 15 wt % of the lactam mass. Next, the co-polyamide was cut into flakes and subjected to thermal treatment at temperatures ranging from 220°C to 260°C. To obtain fibres from the co-polyamide, a melt spinning method was applied. The modified copolymer and the fibres spun from it were analysed with regard to their chemical composition, thermal properties and supermolecular structure, using IR spectrophotometry, DSC and wide-angle X-ray scattering (WAXS). The preliminary tests confirm that the impact properties and elasticity of the fibres obtained are better than those of commercial polyamides.

Key words: co-polyamide, supermolecular structure, IR, DSC, WAXS.

Materials

The impact properties of polyamides can be modified by introducing elastic segments into their macromolecules. The

block copolymer obtained is characterised by better impact resistance than that of a corresponding homopolymer. In our studies, modification was carried out by the application of the urea pre-polymer as an

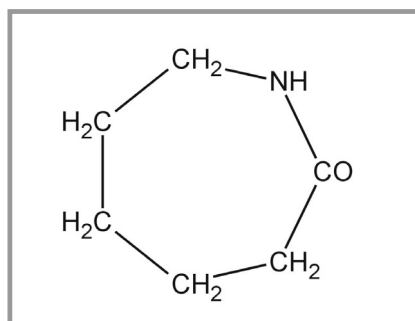


Figure 1. ϵ -caprolactam.

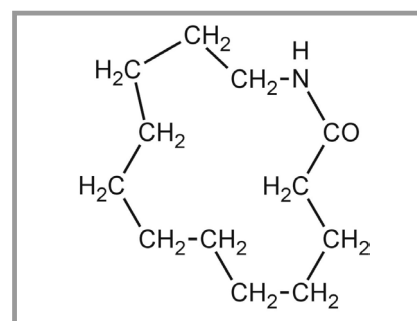


Figure 2. λ -laurinolactam.

Introduction

All polymers, fibre forming polyamides included, can be manufactured on a large scale or in much smaller amounts for special purposes, such as for use at high or low temperatures. Below 0°C, standard non-modified polyamides undergo unfavourable changes. Polyamides are especially sensitive with regard to their impact properties. For this reason many studies have been carried out to obtain modified products with the impact properties improved in comparison with standard commercial polyamides [3 - 5].

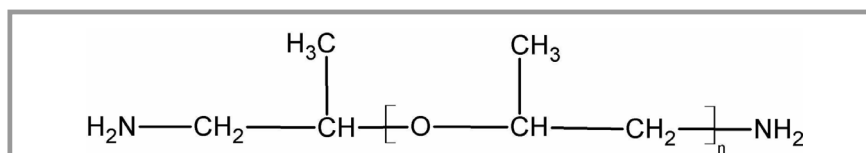


Figure 3. Polyoxyalkylenediamine.

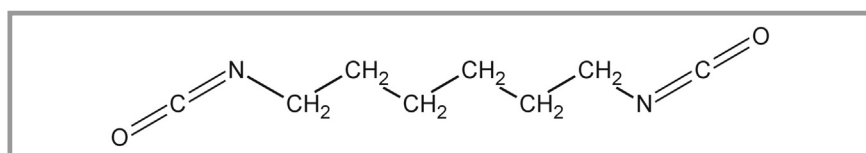


Figure 4. Di-isocyanate.

activator in anionic copolymerisation of λ -caprolactam with ϵ -laurinolactam. The urea pre-polymer was prepared from polyoxyalkylenediamine and suitable diisocyanates (Figures 1 – 4) [1, 2].

Experimental end results

The polymerisation was carried out with a different contribution of each co-monomer and various amounts of diamine, which resulted in products with different compositions. Some of the modified copolyamides obtained were characterised by excellent impact properties at very low temperatures (up to -60°C), and these products were selected for further investigation.

The polyamides modified in this way constitute completely new kinds of material. Some of them also possess fibre-forming properties. The aims of the studies presented were to obtain fibres from the modified polyamides and characterise their structure.

Fibres can be formed from a melt or from a solution, so attempts were made to dissolve or melt the modified co-polyamides obtained. However, the samples examined did not dissolve in most known solvents. Moreover, it appeared that a deep polymer degradation took place in some solutions. Therefore the investigation was aimed at determining the conditions of the thermal processing that allowed fibres to be obtained from the melt.

The co-polyamide was examined while it was heated and melted. The microscopic observations proved very helpful in determining the melting point values and the behaviour of the samples after melting (particularly the evaluation of their melting ability), as well as the behaviour of the samples during cooling (Figure 5).

The melting point values were determined by observing the sample in polarised light. The following samples were eliminated from further examination:

- those with a viscosity that did not ensure the thermal processing of the polymer,
- those that underwent decomposition when heated,
- those in which no polymer crystallisation took place after cooling.

Table 1. Impact properties [7, 8].

Sample	Tensile strength, MPa	Elongation, %	Impact notched strength -40°C , kJ/m^2
PA-6	78,8	32	6,8
PA-12	37,5	17	24,6
80KL 20LL	41,8	18,8	8,5
80KL 20LL D4000-15	26,6	166	34,7

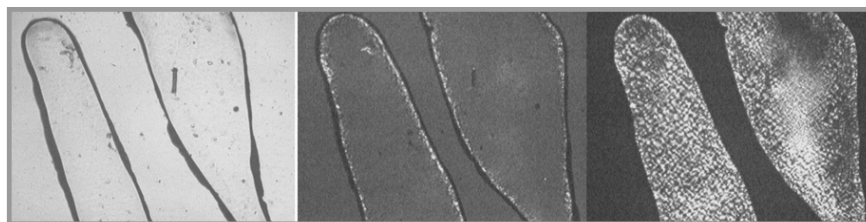


Figure 5. Microphotographs of crystallisation process.

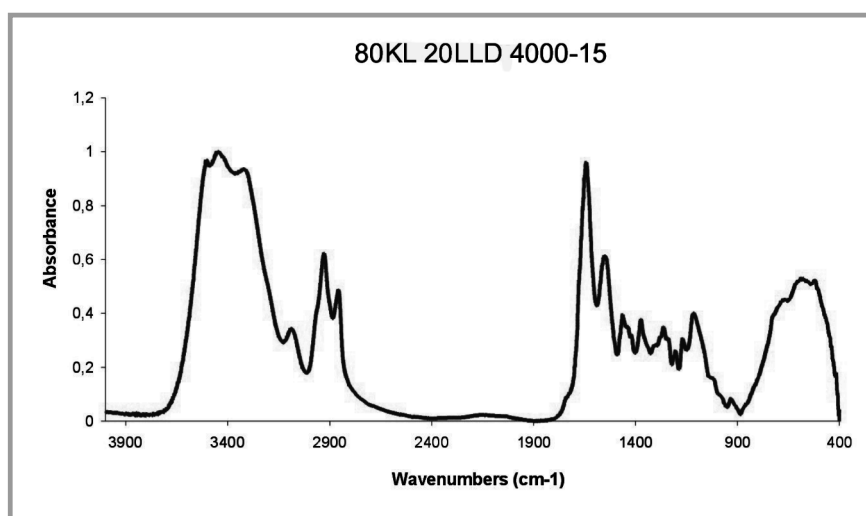


Figure 6. FTIR Spectrum of sample 20LL80KL D4000-15.

This procedure made it possible to select a sample which could be subjected to further detailed investigation, and next to form the fibres from the sample at various processing temperatures, suitably higher than the melting temperature but lower than the temperature of fibre destruction. In this way, a modified copolyamide was selected for the research, which was denoted as 80 KL 20LL D-4000-15. This product resulted from the copolymerisation of 80 wt.% of caprolactam and 20 wt.% of laurinolactam, in the presence of a macroactivator (which was a urea prepolymer formed from 1,6-Diisocyanohexane and 15 wt.% addition of polyoxypropylenediamine in relation to the total mass of lactams.

The chemical structure of the selected product was examined using FTIR spectrometry in order to determine the range and the character of the possible trans-

formations occurring during further processing (Figure 6).

The initial attempts to form fibres from co-polyamides modified with polyetheramines were carried out on a very small scale. For these experiments, a product denoted as 80 KL 20LL D-4000-15 was selected, which was characterised by the lowest viscosity in comparison with other products. However, its viscosity was high enough to make the formation of the fibres from this co-polyamide difficult. Despite the difficulties, the processing conditions for the selected co-polyamide at 220°C , 240°C and 260°C were determined. This temperature range appeared to be the most favourable for the processing because it ensured the polymer melt of the desired viscosity could be obtained, and also at the same time it was possible to draw fibres from a polymer stream coming out of the spinneret. The fibres

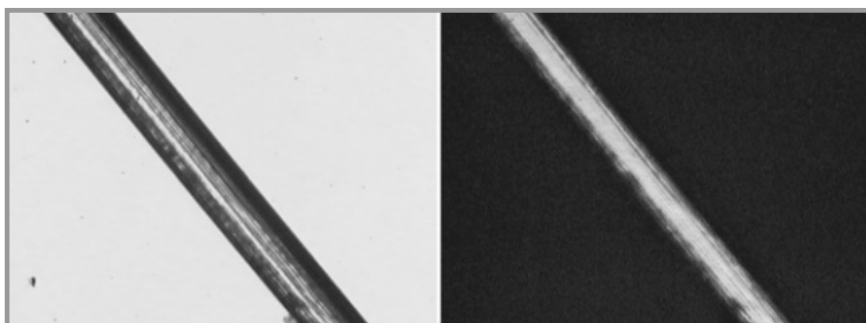


Figure 7. Microphotographs of fibre in the white and polarized light.

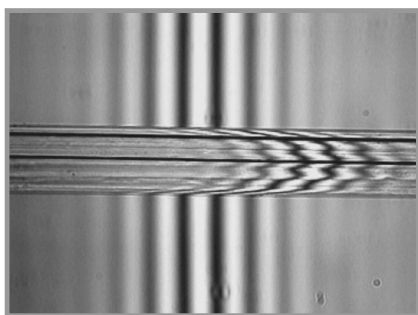


Figure 8. Fibre in the spectral line field.



Figure 9. Fibre breakages.

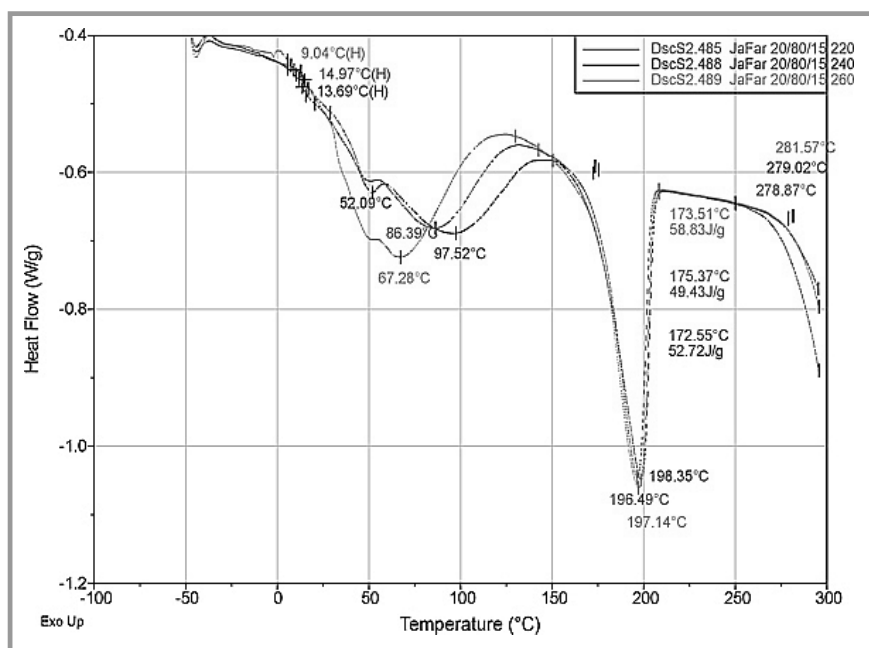


Figure 10. Thermogram of the co-polyamide samples.

obtained were at once subjected to hot and cold drawing. Fibre drawing brings about changes in the internal structure of the material, causing the orientation of the crystalline structure to be formed. The fibres obtained in this way were then further investigated.

A series of microphotographs were taken in white and polarised light (Figure 7). The diameter of the fibres obtained, ranging from 70 to 80 μm , was also deter-

mined. The photographs in polarised light reveal the depolarising ability of the fibres which is characteristic of materials containing a crystalline phase. Moreover, the crystalline structures in the examined samples of fibres are highly oriented.

The high orientation of the crystalline structures is confirmed by birefringence results which are illustrated by the microphotographs of the fibres in the spectral line field (Figure 8) of an interference-

polarisation microscope with a Wollaston prism.

Another interesting feature of the fibres observed in these microphotographs is the fact that they may undergo fibrillation in the course of their drawing. It is worth mentioning that they split into separate fibrils in the areas of fibre and fibril breakages.

In order to confirm the occurrence of the crystalline phase in the fibres obtained, DSC and WAXS examinations were carried out. The DSC investigation within the temperature range of 50°C to 300°C was performed for the co-polyamide sample that was not thermally processed, as well as for the samples drawn at 220°C, 240°C and 260°C (Figure 10).

On the thermogram of the modified co-polyamide that was not previously melted, an endothermic peak appears which illustrates the melting of the crystalline phase. Its minimum occurs at 190.83°C and the transformation starts at 176.86°C. The melting process finishes at about 210°C. The melting energy value is 238 J/g.

The thermogram of the polymer samples thermally processed by melting and then by extruding and drawing fibres reveals a certain differentiation. For these samples, the T_g signal appears at different temperatures. Its value decreases as the extruding temperature grows. For the sample processed at 260°C, the T_g is lowest and is equal to 9.04°C, while for the sample processed at 220°C, the T_g value is highest and equals 14.97°C. The fibre thermograms in the range from 60°C to 150°C show a peak broadening of the thermal transformations. It should be noted that a clear minimum appears at 52.09°C for the samples processed at 140°C.

On the thermograms it is possible to find asymmetrical endothermic peaks originating from the melting of the crystalline phase. Their minima oscillate around 197°C, which proves that the sizes of crystallites in all the examined samples do not vary significantly. Melting transformation finishes similarly to the case of a thermally untreated product, i.e., at about 210°C. The determined energy of transformation for the 220°C sample equals 49.43 J/g, for the 240°C sample 52.72 J/g, and for the 260°C sample 58.83 J/g. The energy grows as the extrusion temperature rises, which may prove that

the amount of the crystalline phase in the sample increases. The DSC examination of the extruded samples gives the important information that the destruction of the material begins at about 260°C which limits the processing range of polymer from 210 to 250°C. The optimum processing temperature that affects the viscosity of the polymer should be within this range. The wide-angle X-ray measurements of the test samples and the initial material were carried out in the manner illustrated in Figures. 11 and 12.

On the diffractogram of the initial sample, there are two peaks with the maxima occurring at 20.3° and 23.8° respectively, which suggests the existence of an α -phase in the polymer. The crystallinity degree of the thermally processed polymer equals 40.8%. Such a considerable ordering of the structure resulted from the self-ordering processes during cooling of the melt after copolymerisation. The diffractograms of the fibres formed at 220°C, 240°C, and 260°C are different from the diffractogram of the initial sample. Beside the two peaks which prove the existence of an α -phase, a single peak appears when the 2Θ angle equals 21.3°. This probably arises from the crystalline γ -phase, which is asymmetric and clearly higher than the accompanying peaks from the α -phase.

The appearance of a clear peak from the γ -phase can be observed for all the samples of the formed fibres with the simultaneous decrease of the α -phase content. This confirms the effect of the thermal processing and mechanical action, i.e. drawing the fibre during cooling, on the crystalline structure of the obtained fibres.

As results from the calculations, the degree of crystallinity grew in relation to the initial sample, but the size of the α -phase crystallites shrank by more than half, whereas the interplanar distances slightly increased.

Conclusions

The results presented here constitute only an initial part of investigations into copolyamides modified with polyetheramines. The fibres from the modified copolyamides may prove useful for the production of textiles with high tenacity and elasticity at low temperatures.

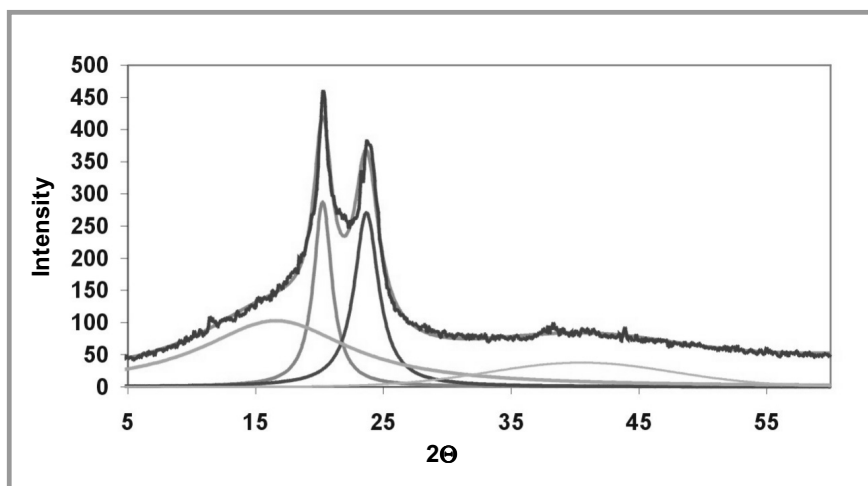


Figure 11. Peak deconvolution of the WAXS profile in the initial sample.

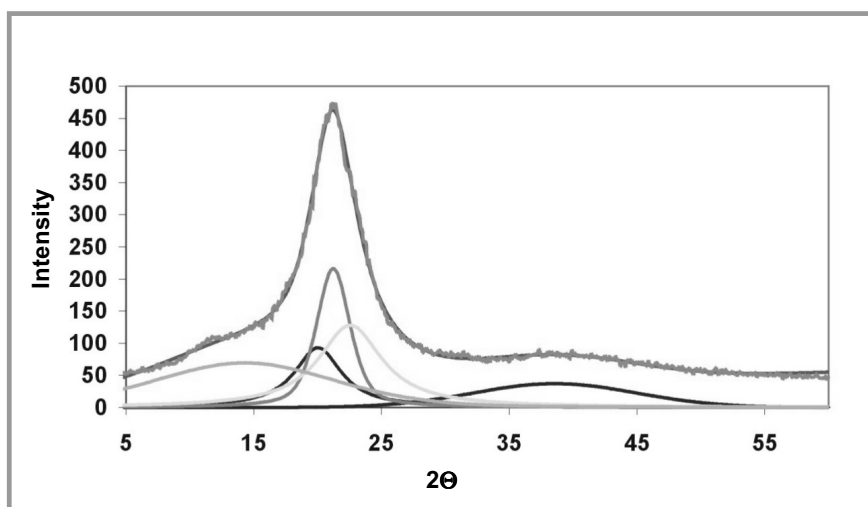


Figure 12. Peak deconvolution of the WAXS profile in the sample p-260.

Table 2. Size of crystallites.

sample	Degree of crystallinity	Dimensions of crystallites			Distance of surface		
		D α (200)	D γ (200)	D α (020+220)	D α (200)	D γ (200)	D α (020+220)
	%	nm	nm	nm	nm	nm	nm
initial sample	40,8	5,20	-	3,92	0,438	-	0,375
220	52,6	2,29	3,20	1,66	0,463	0,416	0,382
240	52,0	2,29	3,20	1,55	0,462	0,416	0,386
260	59,0	2,02	2,87	1,50	0,443	0,422	0,394

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Received 08.12.2004 Reviewed 10.02.2005