

# Research on the Degradation of PA6 Waste and Utilisation of the Degradation Products for the Synthesis of Copolyamide Resins

## Abstract

We present herein the results of our investigations concerning the utilisation of polymer waste in the manufacture of polyamide fibres. The hydrolysis of the waste material into oligomeric products was investigated, varying the type and amount of the used catalyst, degradation time, reaction temperature, and proportion of the process components. After the studies, the degradation processes were aimed at applying the originated low-molecular products in the direct synthesis of copolyamide resins. As a result of the syntheses conducted, two types of copolyamides were obtained; their properties differed depending upon the kind of degradation products used and the way the process was run.

**Key words:** PA6 waste, recycling, waste utilisation, copolyamides.

ter, acids and alkali. A broad overview concerning the regeneration of caprolactam from industrial polyamide fibre wastes can be found in the publication of Dmitriewa et al. [4].

Several ways of depolymerisation may be distinguished by the following methods:

- Catalytic depolymerisation of dry PA6,
- Depolymerisation without catalyst in a stream of superheated steam,
- Catalytic depolymerisation in a stream of superheated steam,
- Catalytic depolymerisation of prehydrolysed PA6,
- Depolymerisation in the presence of caprolactam-dissolving fluids followed by steam distillation from the solution.

A complete depolymerisation of PA6 wastes with monomer separation may appear cost-inefficient or even unfeasible. The chemical recycling can be conducted in such a way that low molecular degradation products are obtained, instead of the monomer. The products obtained may be used as either a separate raw material or as an additive to other materials. This work presents the results of the investigation concerning the hydrolysis of PA6 wastes. The target was to find degradation process conditions under which low molecular oligomeric degradation products could be obtained and used as the basic raw material for the synthesis of copolyamide resins.

## Materials and Methods

The materials subjected to degradation were PA6 wastes without TiO<sub>2</sub> content characterised by a relative viscosity

of 2.55 in concentrated sulphuric acid, content of low polymeric compounds of 0.33%, and a melting temperature of 220-223°C. The agents to promote the degradation of PA6 were water (W), together with the following acids: phosphoric (PA), adipic (AA), terephthalic (TA), and sebacic (SA). Caprolactam (CL) was also used in some of the hydrolyses. The low molecular products which were obtained in the degradation of PA6 under selected conditions constituted a basic material for the synthesis of copolyamides. Other reaction components were monomers: hexa-methylenediamine and 6T salt (salt of hexamethylenediamine and terephthalic acid) and distilled water as the reaction activator. The properties of the copolyamides obtained from the degradation products were compared with those made of standard starting materials. Caprolactam, 6T salt and AH salt (salt of hexamethylenediamine and adipic acid) were used in the syntheses of the latter copolyamides.

## Degradation of PA6 waste

PA6 was hydrolysed according to a method applied in an earlier study [5]. The degradation processes were run on a laboratory scale in a 0.4 dcm<sup>3</sup> autoclave made of stainless steel, equipped with a temperature and pressure control recorder, reducing valve, cooler and a release orifice assembly in the lower part. The degradation processes were run at 220-250°C and under a pressure of 0.6 MPa over 0.5 to 4.0 hours.

## Synthesis of copolyamides

The synthesis of the copolyamides was accomplished on a laboratory scale in a 0.4 dcm<sup>3</sup> autoclave, the same as used for degradation. The maximum temperature

## Introduction

The manufacture of chemical fibres is, to a large extent, unfriendly to the environment. It contributes to the exhaustion of non-renewable resources, consumes much electrical energy, and produces considerable amounts of industrial effluents, toxic gaseous emissions and polymer wastes. For many years, the economy of manufacture and environmental problems have fostered the reuse of polyamide wastes by employing material recycling and chemical processing [1-3]. The waste products, which appear in the manufacturing process in the form of intermingled fibres, powder, granulate and lumps, may either be regranulated and reused or subjected to chemical degradation of the macromolecules to monomers and oligomers. Depolymerisation is usually applied when using waste in the manufacture of polyamide fibres to obtain regenerated caprolactam. The process proceeds in the presence of wa-

was about 260°C and the maximum pressure about 0.6 MPa. The processes were run in three different variants. In variant I, the process time was 6 hours, of which 4 hours was a pressure phase, and 2 hours a non-pressure period during which the polymer was left under streaming oxygen-free nitrogen. Variant II was a 7-hour pressure/vacuum process. The pressure phase lasted 5 hours, while vacuum was applied during the last 2 hours with the final pressure at 0.05 MPa. The entire time in variant III was 9 hours, divided into 6 hours of pressure and 3 hours of vacuum phases, with the final pressure of 0.03 MPa.

### Analytical methods

The relative viscosity ( $\eta_{rel}$ ), the content of low molecular substance ( $\%_{lmc}$ ) and the melting temperature ( $T_m$ ) were estimated for both the degradation product of the PA6 wastes and the synthesised copolyamides [6,7]. An Ubbelohde viscometer with a No II capillary was used for measuring the relative viscosity at 25°C, using a solution of 1g of the degradation product or copolyamide, neither dried nor extracted, in 100 cm<sup>3</sup> of 96% sulphuric acid. The content of low molecular compounds was measured according to the weighting method. The content of extract in water solution was measured after

6 hours' extraction of the degradation product or copolymer with boiling water. A Boetius apparatus was used to measure the melting temperature of the degradation products and copolyamides.

## Results and Discussion

In our research into the degradation of PA6 wastes, conditions were fixed to obtain low molecular oligomeric degradation products, which are useful in the synthesis of genuine copolyamides. The PA6 degradation products obtained were used in the synthesis of selected copolyamides of the **Polmid<sup>1</sup>** type, as developed in the Institute of Chemical Fibres, Łódź [8].

**Table 1.** Properties of PA6 degradation products obtained after 4 hours with the use of various acids.

Type and proportion of components	Acid	Properties of degradation products		
		$\eta_{rel}$	$\%_{lmc}$ , wt. %	$T_m$ , °C
PA6, W (2:1)	phosphoric	1.64	4.7	219 - 221
	adipic	1.40	2.1	218 - 221
	terephthalic	1.42	1.5	217 - 224
	sebacic	1.43	0.9	212 - 216
PA6, CL, W (2:1:1)	phosphoric	1.71	1.4	219 - 221
	adipic	1.46	2.9	216 - 217
	terephthalic	1.43	3.0	213 - 216
	sebacic	1.50	2.4	217 - 219

**Table 2.** Properties of degradation products obtained in different process times at 250°C with the use of adipic acid.

Type and proportion of components	Degradation time, h	Properties of degradation products		
		$\eta_{rel}$	$\%_{lmc}$ , wt. %	$T_m$ , °C
PA6, W (2:1)	2.0	1.41	2.3	216 - 220
	1.0	1.43	2.3	219 - 222
	0.5	1.44	2.0	218 - 222
PA6, CL, W (2:1:1)	2.0	1.42	2.4	212 - 215
	1.0	1.44	2.0	218 - 217
	0.5	1.43	1.9	212 - 215

**Table 3.** Properties of degradation products obtained at different temperatures, during 0.5 hour, in the presence of adipic acid.

Type and proportion of components	Process temperature, °C	Properties of degradation products		
		$\eta_{rel}$	$\%_{lmc}$ , wt. %	$T_m$ , °C
PA6, W (2:1)	230	1.48	1.4	218 - 220
	220	1.61	0.9	216 - 219
PA6, CL, W (2:1:1)	230	1.39	3.0	216 - 219
	220	1.37	2.3	215 - 218

**Table 4.** Properties of degradation products obtained with different concentration of adipic acid during 0.5 hour at 220°C.

Type and proportion of components	Content of adipic acid, wt. % to PA6 or PA6+CL	Properties of degradation products		
		$\eta_{rel}$	$\%_{lmc}$ , wt. %	$T_m$ , °C
PA6, W (2:1)	5	1.24	2.2	215 - 218
	10	1.23	5.7	208 - 211
	20	1.14	14.4	186 - 190
PA6, CL, W (2:1:1)	5	1.18	4.1	210 - 214
	10	1.16	8.6	197 - 202
	20	1.11	20.9	178 - 181

### Investigation on the degradation of PA6 waste

Mixtures of PA6 and water in the weight proportion of 2:1, and of PA6, caprolactam and water in the proportion of 2:1:1, were first prepared. Phosphoric acid and dicarboxylic acids were added to the mixture in the amount of 2.0 wt. % on PA6 or the total quantity of PA6 and CL. The degradation time was 4 hours at about 250°C. The properties of the products obtained are shown in Table 1. The process conditions which were applied effected a distinct change in the PA6 waste subject to degradation. A decrease in the relative viscosity could be seen, an increase in the content of low molecular compounds, and a slight drop in the melting temperature. When dicarboxylic acids were used, the relative viscosity could be lowered from 2.55 to the level of 1.40-1.50, while with phosphoric acid the decrease was only to the values of 1.64 and 1.71.

For this reason, in further investigations, one of the dicarboxylic acids was used: adipic acid. For both blends: PA6+W (2:1) and PA6+CL+W (2:1:1), the reaction time was shortened and the process temperature was lowered. Table 2 shows the properties of PA6 degradation products, obtained at the temperature of 250°C over shorter periods. The degradation process proceeded quickly, and as soon as after 30 minutes a degraded product was obtained with a quality close to the products attained at longer process times. In further trials, the 30-minute reaction time was applied and the process temperature was reduced to 230 and 220°C. The results of the trials are presented in Table 3. Comparing the respective figures in Tables 2 and 3 reveals that from the PA6+W blend, as a result of the temperature reduction to 230

and 220°C, degradation products were obtained which were characterised by higher relative viscosities than those for the 250°C temperature. In the case of PA6+CL+W mixtures, the process at lower temperature proceeded as did that at 250°C, and the products' properties were similar.

The influence of the amount of adipic acid introduced on the properties of the final products was investigated for 30 minute hydrolysis at 220°C. The amount of the added acid was increased to 5, 10 and 20 wt.%. The results of the investigation are compiled in Table 4.

The addition of adipic acid in amounts above 5% profoundly altered the properties of the degraded PA6. A distinct decrease in the relative viscosity can be seen, as well as an increase in the content of low molecular compounds and lower melting temperatures of the degradation products. The degradation products obtained were characterised by relative viscosity in the 1.24-1.11 range.

In the investigation concerning PA6 degradation, a smaller amount of water was eventually used. The degradation temperature was 220°C, the time was 30 minutes, the adipic acid content amounted to 20%, and the proportions between the components PA6+W and PA6+CL+W were changed. Table 5 presents the results of the investigations.

It can be seen from the results presented that the decrease in the amount of used water has no distinct impact on the process course. The properties of the obtained products were close to those of the products made earlier with a higher amount of water (Table 4).

### Synthesis of copolyamides

For the syntheses of copolyamide type Polmid with the composition CL/AH (80:20) and CL/6T/AH (60:15:25), oligoamides were prepared in two series of degradation under the following process conditions: temperature - 220°C, pressure - 0.6 MPa, weight proportion of the PA6 waste to water - 10:1. Adipic acid was used in an amount which corresponded to the weight proportions between caprolactam and adipic acid in the composition of the actual Polmid copolyamide. Accordingly, the adipic acid content was 13.93% and 23.22% on the PA6 waste. The properties of the obtained oligoamides are presented in Table 6.

The composition of the reaction mixes for the synthesis of copolyamides CL/AH (80:20) and CL/6T/AH (60:15:25) was adopted while taking into account the proportions between the PA6 waste and the adipic acid applied during degradation. To the degraded PA6, blocked with adipic acid molecules, hexamethylenediamine was added in an equimolar amount with the adipic acid (the equimolar proportion of adipic acid and hexamethylenediamine appears in the AH salt). In the case of the synthesis of copolyamide CL/6T/AH (60:15:25), the 6T salt was also added except hexamethylenediamine. Water was used as a reaction activator in the amount of 5% on the polyamide-generating substances.

The copolyamides were produced with various properties, applying the process methods described above. The results are compiled in Table 7. The properties of the same Polmids made from standard raw materials, i.e. CL, AH salt and 6T salt, are also given for comparison.

The copolyamides obtained were different mainly in respect of their relative viscosity. The copolyamides made of the

degradation products according to process variant I revealed lower viscosity in comparison to copolymers obtained from standard raw materials. The extended synthesis process and the additional vacuum phase according to variants II and III resulted in the higher relative viscosity of the copolyamides. In the process according to variant III, copolymers were obtained which corresponded to that of copolymers from standard raw materials. The content of low molecular compounds was very close in all the copolyamides obtained. The melting characteristics for copolyamides of the same kind were similar.

The research conducted proved that new copolyamide resins can be obtained from the degradation products of polymer wastes in the manufacture of polyamide fibres. Differences in the properties attained can be corrected by adjustments in the process procedure.

### Conclusions

- The polymer waste of the manufacture of polyamide fibres can be degraded in a controlled way by adequate selec-

**Table 5.** Properties of degradation products obtained in processes with a smaller amount of water, with the addition of 20 wt.% of adipic acid at 220°C and reaction time of 0.5 hour.

Type and proportion of components	Properties of degradation products		
	$\eta_{rel}$	% <sub>lmc</sub> , wt.%	T <sub>m</sub> , °C
PA6, W (5:1)	1.13	14.3	186 - 189
PA6, W (10:1)	1.12	16.1	185 - 189
PA6, CL, W (10:5:2)	1.12	20.2	187 - 194
PA6, CL, W (10:5:1)	1.12	20.8	189 - 195

**Table 6.** Conditions of the degradation and properties of oligoamides prepared for the synthesis of copolyamides.

Type and proportion of components	Content of adipic acid, wt.% on PA6	Properties of degradation products		
		$\eta_{rel}$	% <sub>lmc</sub> , wt.%	T <sub>m</sub> , °C
PA 6, W (10:1)	13.93	1.18	10.9	194 - 202
		1.18	10.4	196 - 205
	23.22	1.12	20.7	178 - 183
		1.14	17.5	183 - 189

**Table 7.** Properties of Polmid-type copolyamides made of oligoamides and standard raw materials.

Type of copolyamide	Type of raw material	Process variant	Copolyamide properties		
			$\eta_{rel}$	% <sub>lmc</sub> , wt.%	T <sub>m</sub> , °C
CL/AH (80:20)	degradation product	I	2.28	1.8	184 - 197
	degradation product	II	2.26	1.4	185 - 202
	degradation product	III	2.39	1.6	188 - 200
	standard	I	2.45	1.5	190 - 195
CL/6T/AH (60:15:25)	degradation product	I	2.18	1.9	164 - 168
	degradation product	II	2.23	1.3	165 - 174
	degradation product	III	2.65	1.1	169 - 179
	standard	I	2.57	2.2	173 - 179

tion of the kind and proportion of the components used in the degradation, as well as by the process conditions.

- The degradation can be accomplished on laboratory scale in an autoclave, in the presence of water and adipic acid with a 10:1 weight proportion of waste to water. The use of adipic acid is most favourable in the amount of above 5 wt.%. Recommended process conditions are as follows: degradation time - 30 minutes, temperature - 220°C, pressure - 0.6 MPa.
- A novel types of copolyamide can be produced by utilising the oligoamides obtained from the degradation of clean PA6 waste. Copolyamides with tailored composition and properties could be manufactured from the degradation products obtained in the presence of an adequate amount of hexamethenediamine and 6T salt.
- The properties of the copolyamides obtained may be tailored by selecting adequate synthesis conditions.

#### Footnote:

1. *Polmid - a registered trade name of a group of commercial copolyamides produced in the Institute of Chemical Fibres, Łódź, Poland, obtained from caprolactam and salts of dicarboxylic acids with diamines.*

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#### References

1. E. Taeger et al; *Chemiefasern/Textilindustrie*, 1993, 43/95, p. 526.
2. J. Seelig; *Chemiefasern/Textilindustrie*, 1994, 44/96, p. 32.
3. A.K. Błedzki, K. Pawelczyk; *Polimery - Tworzywa wielkocząsteczkowe*, 1994, 39(4), 206.
4. L.A Dmitrieva et al; *Khim. Volokna*, 4, 1985, p. 5.
5. J. Wesółowski, K. Grzebieniak; 'Pro-ecological production, use, and utilisation of fibres and textile products', Part 2: 'Chemical recycling of wastes', Research report, Institute of Chemical Fibres, Łódź, Poland, 2002.
6. 'Conducting the manufacturing process of polyamide fibres. Description of analytic methods', Research report, 1974, Institute of Chemical Fibres, Łódź, Poland.
7. J. Majewska, S. Urbanowicz; *Polimery - Tworzywa wielkocząsteczkowe*, 1964, 1, 18.
8. J. Śmigielski; *Włókna Chemiczne*, 1990, 3, 286.

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