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Evaluation of the Suitability of Some Biodegradable Polymers for the Forming of Fibres

Abstract
Commercially available biodegradable, thermoplastic resins were evaluated as candidates raw material in the melt spinning of fibres. The aliphatic copolyester Bionolle made by Showa Co and the aliphatic-aromatic copolyester Easter Bio made by Eastman were investigated. Both materials revealed good fibre-forming properties. The basic mechanical features were evaluated and the susceptibility to biodegradation of the fibres obtained was estimated.

Key words: biodegradable copolyesters, fibre-grade copolyesters, biodegradable fibres, mechanical properties.

Introduction

When analysing the present supply of fibrous raw materials for the textile industry, it is evident that any substantial replacement of chemical fibres with eco-friendly natural fibres is in truth impossible. The introduction of entirely biodegradable resins into the manufacture of chemical fibres is seen as a way of solving the problems of environmental protection. Such resins should ideally be made from renewable raw materials available in nature.

Of the known methods to produce chemical fibres, melt spinning is favoured thanks to its inherent high processing speeds and capacities, which in turn provide economic advantages. The absence of both gaseous and solid by-products, as well as of wastes, speaks for the environmental advantages of the method. Aliphatic polyesters, both homo- and copolyesters, belong to the known thermoplastic polymers which are susceptible to degradation. In the search for useful biodegradable resins, attention has also been paid to investigations into aromatic-aliphatic copolyesters containing terephthalate units, e.g. PET; aliphatic polyester units, e.g. polyethylenadypinate; and other polyester segments based on aliphatic dicarboxylic acids [1-3].

Of the aliphatic polyesters, the poly(lacitic acid) (PLA) has long attracted attention. It was discovered in 1932 by Carothers, and in the 1960s it was considered as a potential, entirely biodegradable resin for medical use. Since that time, investigations into the material have been intensified in many world-wide renowned chemical companies. The leader in the production of PLA nowadays is the US company Cargill Dow Polymers [4,5]. Beyond its principal application in fibres, other uses of the resin have also been explored, notably film, thermobonding and injection moulding.

The features of fibres made from the Cargill Dow trial PLA polymer are very attractive. Its tenacity is about 60 cN/tex; the fibres are highly elastic and resistant to UV radiation, and produce much fewer fumes during combustion than PET fibres. The density of the material (1.24 g/cm^3) is distinctly lower than that of standard polyester fibres. Under normal wearing conditions, the fibres are resistant to atmospheric factors. At high temperature and moisture, specifically for waste composting, the PLA products undergo complete degradation to carbon dioxide and water [6,7].

Apart from PLA, which has already been tested in textiles, some other biodegradable polyesters have appeared on the world markets: Biomax by DuPont, Bionolle by Showa, Eco ex by BASF and Easter Bio of Eastman [8-11]. The resins are used mainly in the manufacture of package film.

In this article, our works are described in relation to the use of commercially available biodegradable thermoplastic resins for the manufacture of fibres. The assessment of the structure of fibres from biodegradable thermoplastic polymers, namely Bionolle from the family of aliphatic polyesters and Eastar Bio from the aromatic-aliphatic polyesters, is the subject of further investigations. In 2002, when research devoted to the use of such polymers for fibre manufacture was begun [12], information concerning the subject was not available in the technical literature. The first results of investigation on the use of Eastar Bio for the manufacture of POY fibres and nonwovens were published in the second half of 2003 by German scientists [13,14].

Experimental

Materials used

- Bionolle made by Show Highpolymer Co. Ltd., a trade product type 3001, an aliphatic polyester of buthylene glycol and succinic and adypic acids: polybuthylene succinate adipate, random copolymer;
- Eastar Bio made by Eastman Chemical Corp., a trade product, an aliphatic-aromatic polyester of buthylene glycol and adypic and terephthalic acids.

The producers do not reveal the percentage content of the individual acids in the polymer composition. The polymers were pre-dried in a shelf-dryer under conditions recommended by the manufacturers:

- Bionolle at 70°C for 2 hours,
- Eastar Bio at 60°C for 8 hours.

Estimation of the rheological properties of biodegradable thermoplastic polymers

To estimate the fibre-forming properties of the two resins, the melt ow index (MFI) was measured at different temperatures:

- Bionolle in the range of 240-280°C,
- Eastar Bio in the range of 160-210°C.

The MFIs were also measured after annealing for 30 and 60 minutes, at 240°C for Bionolle and 200°C for Eastar Bio.

Forming of fibres

Fibres were spun from the melts of Eastar Bio and Bionolle polymers using an extruder spinning bank equipped with a 20 mm diameter Barmag extruder. The spinning temperature was 200-203°C for

Eastar Bio and 240-250°C for Bionolle. The take-up speed was variable within the range of 500-1500 m/min at a constant extrusion rate of about 10 g/min. A twelve-orifice spinneret was used with the openings dimensions of D=0.3 mm, L=0.4 mm. The spun fibres were drawn using the SZ-16 Barmag draw-twister with the draw ratio of 1.2-4.5 at a speed of 230 m/min.

Test methods

Melt ow index (MFI) of polymers was measured using a plastometer according to Polish standard PN-93/C-89069 adapted for fibre-forming polymers. The piston load was 2.16 kG and the orifice diameter 0.5 mm. The temperature was selected adequately to the tested polymer. The measurements were made after a 6-minute annealing of the polymer in the cylinder.

Thermal properties of the polymers
The DSC-2 Perkin-Elmer differential scanning calorimeter and the TGS-1 thermobalance equipped with a Perkin-Elmer programmer were used. The measurements were made at the heating rate of 20°C/min and a nitrogen ow of about 20 cm^3/min.

Photos of the fibres' outer surface were made using the JEOL JSM 35C electron microscope.

Physico-mechanical properties of the fibres were measured using the Instron 5540 apparatus, according to the following Polish-ISO standards for filaments:
- tenacity - PN-EN ISO 2062,
- elongation at break - PN-EN ISO 2062,
- linear density - PN-EN ISO 2060,

and for staple fibres:
- tenacity - PN-EN ISO 5079,
- elongation at break - PN-EN ISO 5079,
- linear density - PN ISO 1973.

Biodegradation of fibres
The biodegradation testing was conducted in an aqueous medium at 35°C and 55°C for 3, 13 and 28 weeks.Strains of microorganisms were introduced into the degradation medium in the amount of 7×10^6 units/ml taken from garden soil and from a decanter in the waste-water treatment plant of the cellulose-pulping mill in Świecie. The medium with a pH of 7.2 was continuously aerated and agitated. After 3, 13 and 28 weeks the fibre samples were removed from the reactor, disinfected and deproteinised in 0.5% NaOH, washed with distilled water and dried to constant weight. The weight loss was estimated in comparison with the starting samples.

Test Results

The objective of the work was to evaluate the possibility of using biodegradable thermoplastic resins in the forming of fibres by melt-spinning. The basic mechanical properties of the obtained fibres were estimated, as well as the susceptibility to biodegradation. The evaluation of the structure of fibres made from biodegradable thermoplastic polymers will be the subject of further studies.

Estimation of the thermal and rheological properties of the thermoplastic, biodegradable polymers

In Table 1, the thermal resistance results are presented for Bionolle and Eastar Bio. The aliphatic copolyester Bionolle manifests a lower thermal resistance, with the decomposition beginning at 320°C.

The DSC analyses were conducted in the cycle of heating (I), cooling and heating (II). The temperatures of the thermal transitions evaluated from the thermographs DSC are compiled in Table 2, notably glass transition T_g, melting T_m and crystallisation T_c.

Table 1. *Thermal properties of thermoplastic biodegradable polymers.*

Polymer	Temperature at beginning of decomposition, °C	Temperature of weight loss, °C	
		$T_{5\%}$	$T_{50\%}$
Eastar Bio	354	391	424
Bionolle	320	370	416

Both the aliphatic copolyester Bionolle and the aliphatic-aromatic copolyester Eastar Bio reveal crystallisation capacity. The glass transition temperature of both materials are notable below ambient temperature, and so it may be concluded that textiles made from the polymers will be soft and thermally unstable at standard wearing temperature.

Figure 1 presents a comparison of the MFIs of the thermoplastic investigated, biodegradable polymers with fibre grade PP. Eastar Bio shows the lowest melt viscosity of the polymers tested. The MFI=f(Temp) curve for Bionolle resembles that of polypropylene.

Table 2. *Temperature of physical transitions of thermoplastic biodegradable polymers.*

Polymer	Annealing			Cooling	
	Glass transition temperature	Melting temperature	Heat of fusion	Crystallisation temperature	Heat of crystallisation
	T_g, °C	T_m, °C	ΔH_m, J/g	T_c, °C	ΔH_c, J/g
Eastar Bio I II	 -33 -33	 109 111	 18.0 18.0	29	16.7
Bionolle I II	 - -41	 93 93	 48.7 46.7	54	46.7

Table 3. *Spinning conditions and physico-mechanical properties of fibres from Eastar Bio and Bionolle biodegradable polymers.*

Polymer/sample		Spinning conditions			Linear density of as-spun fibres, dtex	Drawn filaments (12f)			
		Melt tempe-rature, °C	Speed, m/min			Draw ratio	Linear density, dtex	Tenacity, cN/tex	Elonga-tion, %
			I godet	take up					
Eastar Bio	I EB	203	500	700	144	2.50	60.9	20.6	55.5
	II EB	200	500	1000	107	1.51	72.0	19.5	80.8
Bionolle	IB	240	~500	500	203	3.28	69.7	24.8	64.5
	IIB	250	500	1000	102	1.51	74.3	22.4	87.5
	IIIB	250	500	1500	62	1.20	68.9	30.2	59.1
PET standard	I	290	~500	500	204	3.53	58.3	26.4	64.9
						4.04	50.6	32.4	45.2
						4.51	45.8	36.1	28.6

Temperature ranges were determined within which the melt viscosities of Easter Bio and Bionolle are close to those of PP under its processing conditions. For both polymers, the spinning temperature ranges predetermined on a base of the MFI values (190-210°C for Eastar Bio and 250-270°C for Bionolle) fall notably below their decomposition temperature. The results obtained indicate that the polymers investigated can be processed according to the melt spinning method.

To estimate the thermostability of the polymers investigated, the MFIs were measured after different annealing times in the cylinder of the plastometer. The results of the measurements can be seen in Figure 2, where data is also given for fibre grade PP and PET for comparison. The annealing temperature for each of the polymers was equal to the spinning temperature. The change of the MFI value after long annealing for Eastar Bio is comparable to that of PP. After 30 minutes of annealing, the MFI value increase amounts to 53% and 47% for Eastar Bio and PP accordingly. The Bionolle's thermostability is much worse; its MFI increase between the 6th and 30th minute of annealing reaches 600%. In this respect, PET is the best of the tested polymers.

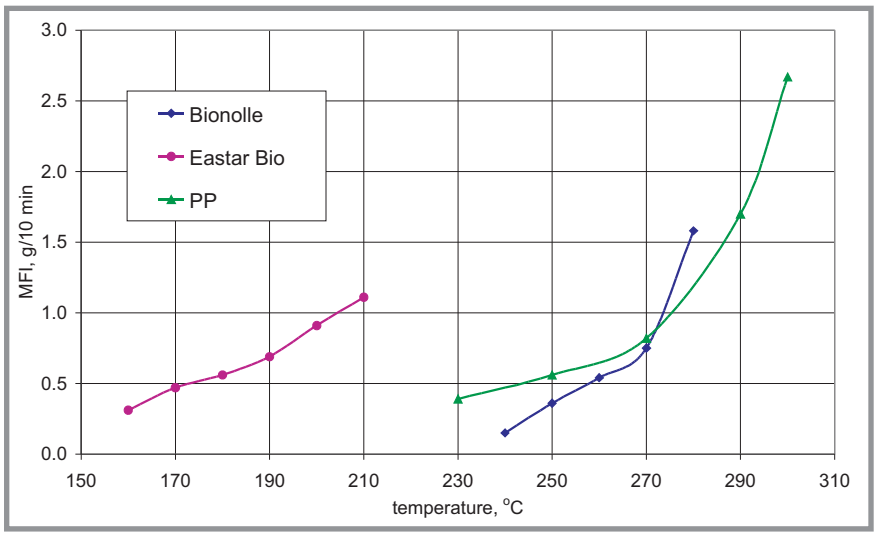

Figure 1. *Melt flow index (MFI) of thermoplastic biodegradable polymers (Bionolle, Eastar Bio) and, for comparison of PP.*

Review of the fibre forming process and properties of fibres made from thermoplastic biodegradable polymers

The properties of continuous fibres obtained from Eastar Bio and Bionolle under different conditions are presented in Table 3. The fibre forming process was accomplished in two steps, spinning and drawing. The properties of PET fibres made in test trials are also shown in Table 3 for comparison. Both Eastar Bio and Bionolle manifested good fibre forming properties. The best fibre spools quality-wise were obtained by increasing the speed difference between the two godets of the spinning bank: the 1st godet 500-700 m/min, the 2nd godet 1000-1500 m/min. The pre-oriented fibre was finally drawn on a draw-twister at draw ratios $\leq$ 2.5. The mechanical properties of Bionolle and Eastar Bio fibres are slightly inferior compared to PET fibres, although they are sufficient for further textile processing.

Fibres from both polymers were tested on biodegradation in an aqueous medium. The biodegradation process was controlled by measuring the weight loss of the fibres tested, changes in their mechanical properties and SEM inspections of the fibres' surface. In Figure 3, the weight loss of the fibres is shown after biodegradation, demonstrating the decomposition of the samples. The decomposition rate increases with the rise in the temperature. At 55°C the aliphatic polyester Bionolle fibres decompose faster then the aliphatic-aromatic Eastar Bio fibres. After 10 weeks the Bionolle fibres were completely decomposed at this temperature. The mechanical properties

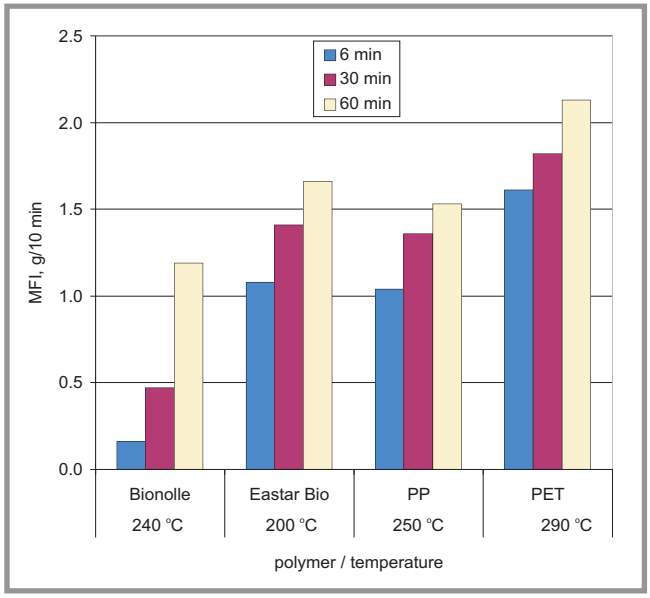

Figure 2. *Changes of melt flow index (MFI) of Bionolle, Eastar Bio and, for comparison, of PP and PET after annealing during 6, 30, 60 minutes.*

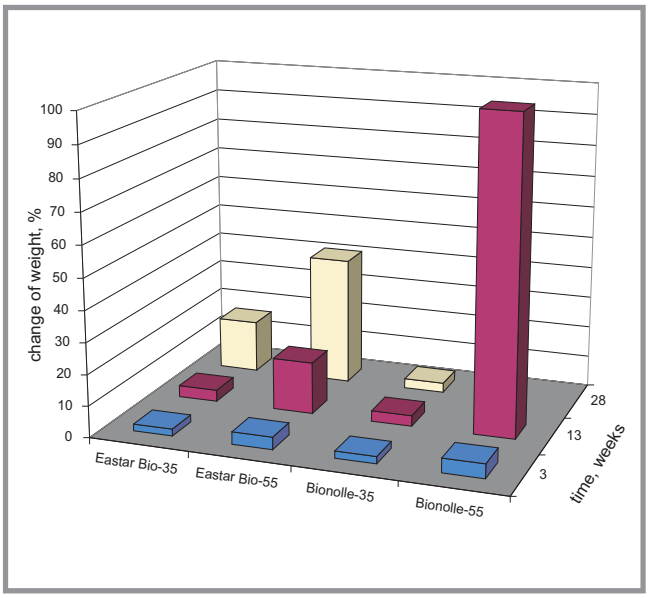

Figure 3. *Weight loss of fibres after biodegradation in an aqueous medium: Eastar Bio-35 and 55 - Eastar Bio fibres after degradation at 35°C and 55°C, Bionolle - 35 and 55 - Bionolle fibres after degradation at 35°C and 55°C.*

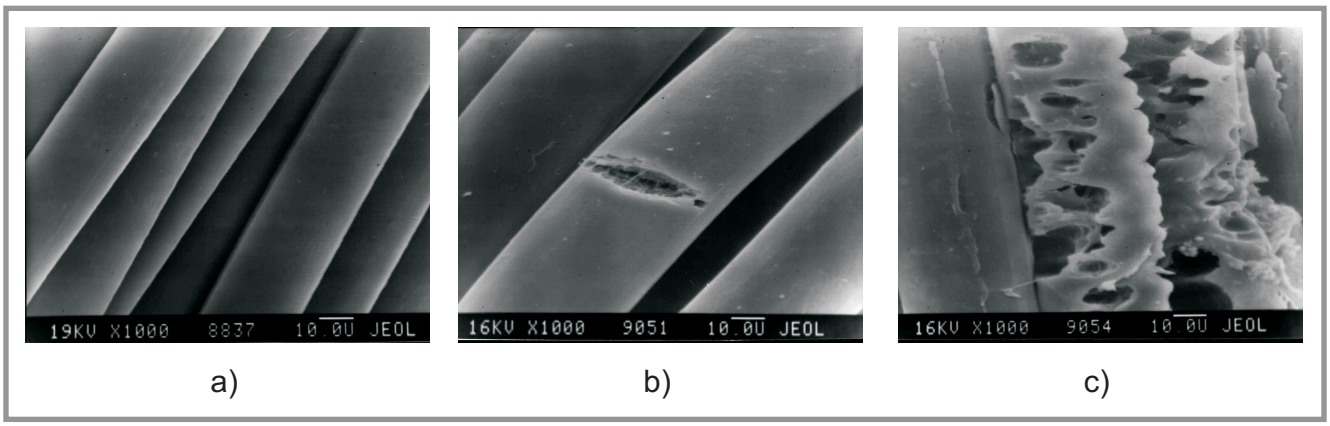

Figure 4. SEM photos of the surface of Eastar Bio fibres: a) before degradation, b) after degradation in aqueous medium - 28 weeks at 35°C, c) after degradation in aqueous medium - 28 weeks at 55°C.

of the biodegraded fibres may be seen in Table 4. The change of the properties of single filaments was estimated in the investigations. The single filaments were taken out of the fibre bundle and tested as staple fibres with 20 mm staple length. With the increase in biodegradation time and temperature, a distinct deterioration can be seen in all of the physico-mechanical properties tested.

The increase in the linear density of the biodegraded fibres compared to the initial material can be explained by the presence of dead biological material which remains in the fibre despite washing. In case of the rapidly degrading Bionolle fibres, a fast decrease in the residual elongation can be seen along with biodegradation time, even at a temperature as low as 35°C. In Figure 4, the outer surfaces of Eastar Bio fibres are shown before and after biodegradation in an aqueous medium during 28 weeks at 35°C and 55°C. On the surface, and also in the entire cross-section of the fibre, many fractures can be seen testifying to the ongoing biodegradation.

Summary

The trials to form fibres from thermoplastic biodegradable polymers demonstrated that both tested polymers can be formed into fibres by melt spinning. Considering the thermal properties of the polymers, such as their very low glass transition and low melting temperature, the fibres made are prone to deformation and can only be used within a narrow temperature range.

Bionolle and Easter Bio are potential candidates to make staple fibres for various non-woven materials, including spun-bonded and melt-blown, particularly for expendable uses in medicine and agriculture. For such applications, the mechanical properties of fibres from the Bionolle and Eastar polymers are quite sufficient.

Table 4. *Mechanical properties of Eastar Bio and Bionolle fibres after biodegradation (of samples IEB and IB, Table 3).*

Polymer	Biodegradation conditions		Mechanical properties of fibres after biodegradation			
	Temperature, °C	Time, weeks	Linear density, dtex	Breaking force, cN	Tenacity, cN/tex	Elongation, %
Eastar Bio	35	0	6.4	11.3	17.7	122
		3	7.8	9.5	12.2	191
		13	6.7	6.5	9.6	107
		28	6.1	4.5	7.4	68
	55	0	6.4	11.3	17.7	122
		3	7.6	5.4	7.1	87
		13	7.5	1.8	2.4	36
		28	5.1	-	-	-
Bionolle	35	0	7.5	16.2	21.5	148
		3	8.9	11.6	13.0	61
		13	8.4	10.1	12.9	48
		16	8.0	9.4	11.7	46
	55	0	7.5	16.2	21.5	148
		3	7.7	6.9	8.9	33

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References

1. *Grzebieniak K.; Fibres & Textiles in Eastern Europe, 1996, 4 (1), 34-37.*
2. *Grzebieniak K, Wilczek A., Tomaszewski W., Copolymers of ethyleneterephthalate and lactic acid - chemical composition and properties, 12th Scientific Conference: Modification of Polymers, Kudowa Zdrój, Poland, 11-15.09.1995.*
3. *Witt U., Müller R. J., Deckwer W.-D.; J. Environm. Polymer Degrad., 1996, 4 (1), 9-20.*
4. *Dartee M., Lunt J., Shafer A., Chemical Fibres International, vol. 50, December 2000, 546-551.*
5. *author unknown, High Performance Textiles, May 1999, 2.*
6. *author unknown, High Performance Textiles, March 1999, 2.*
7. *author unknown, High Performance Textiles, March 2000, 4.*
8. *www.dupont.com./polyester/resins/products/biomax*
9. *Fujimaki T., Polym.Degrad.Stab., 59, 1998, 209.*
10. *Łabużek S., et al., Polimery, 2002, 47, 4, 256.*
11. *Starke D., Skuoin G., Kunststoffe, 91, 2001 (9), 100.*
12. *Twarowska-Schmidt K., Fibres from biodegradable thermoplastic polymers, Research project, IWCh, Łódź, 2002.*
13. *Schmack G., Tandler B., Vogel R., Haussler L., Blechschmidt D., Lindner R., Chemical Fibres International, vol. 53, October 2003, 350-354.*
14. *Blechschmidt D., Geus H.G., Biologically Degradable Spun-bonded Non-wovens for Technical Application, 42nd International Man-Made Fibres Congress, Dornbirn, 17-18 September 2003.*

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