

Biodegradability of Non-Wovens Made of Aliphatic-Aromatic Polyester

Abstract

Non-wovens made of a thermoplastic aliphatic-aromatic polyester of butylene glycol and adipic & terephthalic acids were evaluated in respect of their susceptibility to biodegradation. Eastar Bio made by Eastman Chemical Corp. was used to prepare a non-woven with a nominal surface density of 100 g/m² which was then used to evaluate its susceptibility to biodegradation. The course of biodegradation was traced by loss of mass, changes in mechanical properties and the non-woven's appearance. IR spectrophotometry was also employed to detect changes proceeding in the polymeric material of the non-woven.

Key words: biodegradable polyester, aliphatic-aromatic polyester, melt-blown non-woven, biodegradable non-woven.

Introduction

Synthetic biodegradable polymers are a new group of polymers that offer a wide range of possible applications. Aromatic-aliphatic polyester containing structural units of typical terephthalic polyesters (PET), aliphatic polyesters like poly(ethylene adipate) and other polyesters based on dicarboxylic acids are members of this family [1-4]. Aliphatic-aromatic polyesters that display favourable behaviour during processing and good application properties have already found their way into commercial production [5,6]. They carry the potential of a modern raw material for the manufacture of man-made fibres designed both for apparel and technical textiles. The results of investigations on the fibre-forming properties of the fibre-grade aliphatic-aromatic polyester of butylene glycol, and adipic and terephthalic acids, carried out in the Institute of Chemical Fibres, Łódź, indicate that this polymer is a good starting material for the preparation of disposable textiles [7]. A very considerable demand for such comparatively cheap materials is emerging in medicine and agriculture. Spun-bond and melt-blown non-wovens respond with their quality indices to the expectations of the consumers; with biodegradability being a highly desired feature.

The aim of the work conducted was to assess the susceptibility of non-wovens made of the thermoplastic polyester derived from butylene glycol and adipic & terephthalic acids to biodegradation in water and compost medium.

The biodegradability of polymers depends not only upon their chemical configuration but also their internal structure. As an individual feature of polymeric products, biodegradability can not be predicted. For this reason, every new product should be tested separately.

Experimental

Materials used

Eastar Bio, made by Eastman Chemical Corp, is an aliphatic-aromatic polyester of butylene glycol and adipic & terephthalic acids. The producer does not reveal the percentage content of the individual acids in the polymer composition. The polymer is designed for packaging film. Recent research conducted in the Institute of Chemical Fibres and in other units have revealed the fibre-forming properties of the resin.

Preparation of the non-woven

The non-woven was formed directly from the melt using an experimental melt-blow stand in the Central Institute for Labour Protection (in Polish: Centralny Instytut Ochrony Pracy [CIOP]). The stand is equipped with two extruders (screw diameter D=12 mm) made by Axon Co., an air heater, a forming head and a take-up unit to form the non-woven into sheets. The take-up unit constitutes a drum covered with a net. The temperature of both the polymers in the extruder and the blown air was 200°C; the throughput

of each single extruder was 8 g/min. The non-woven was prepared with a nominal surface density of 100 g/m².

Test methods

- The physico-mechanical properties of the non-wovens were measured using an Instron 5540 apparatus, according to the following Polish-EN standards:
 - surface density - PN-EN 29073-1
 - tenacity - PN-EN 29073-3
 - elongation at break - PN-EN 29073-3.
- The thickness was measured with a mechanical thickness gauge used for flat textiles. 8 measurements were made for each sample.
- The mass loss was estimated by weighing 2×10^{-2} m² samples on an analytical balance before and after biodegradation.
- Photos of the non-woven surface were made using the Quanta 200 scanning electron microscope, FEI.
- IR spectrophotometric spectra were obtained using the FTIR ATI Mattson apparatus with wave numbers in the range of 500-4000 cm⁻¹. Moulded pieces were prepared from the tested material in constant amounts: 1 mg of powdered non-woven and 300 mg of KBr.

Biodegradation of the non-woven in water medium

Microbe strains from two different sources were introduced to the degradation bath: from the clarifier in the water treatment plant of the pulp and paper mill in Świecie, and from garden soil. The process was conducted over 4, 10, and 14 weeks at the temperature of 55°C. When conducting the process, the bath contained 7×10^6 units/cm³. The bath, maintained at pH 7.2, was steadily agitated and aerated. After the assumed time

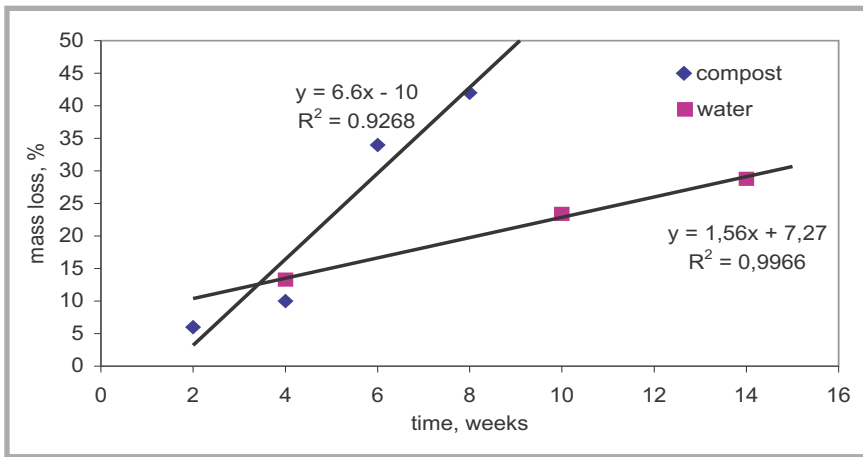


Figure 1. Mass loss of non-woven made of Eastar-Bio after compost and water degradation.

of the experiment, the samples of the non-woven were taken out of the reactor, disinfected with a 3% perhydrol solution, deproteinated with a 0.5% NaOH, washed with distilled water and dried to constant weight.

Biodegradation of the non-woven in compost

The compost used in the experiment was taken from a municipal compost dump in the city of Łódź after 3 months' turbulent maturing. The process was conducted on lab-scale in a container of 120 l, at 55°C, 65% RH with periodic aeration. Air was introduced once a day at a capacity of 10 l/min for 1 hour. Samples were removed after 2, 4, 6 and 8 weeks. After

the experiment, the non-woven sample was handled as in the water test.

Test Results

The mechanism by which biodegradation proceeds in aliphatic-aromatic polyesters consists mainly in the splitting of the medium-sensitive aliphatic ester bonds. The issue is still open to heated discussion amongst scientists [1,8,9]. It is well known that every kind of degradation process of polymers (including the biological process) involves a decrease of the degree of polymerisation. In this work, when evaluating the susceptibility of textiles of synthetic polymers to biodegradation, the useful properties of

the non-woven were mainly taken into consideration, and not the physical properties of the polymer.

The non-woven obtained from the new polymer Eastar Bio was produced by a direct melt-blowing process. The process temperature was selected on the basis of our own investigations [7]. Other parameters of the non-woven production were adopted as for polypropylene filter non-woven [10].

The product, with a nominal surface density of 100 g/m², was used to investigate the biodegradation in both water and compost media. The compost tests proceed differently compared to those in other media, such as water and soil. Compost testing has the virtue of high temperature, resulting from the exothermic character of the process. To assure standard conditions, the pile must have adequate dimensions, which are unattainable on lab-scale. The testing stand is thermally isolated from the environment, although additional warming may appear necessary [11]. The micro-organisms participating in the process are resistant to the elevated temperature. The compost used in the experiment was taken from a municipal compost dump in the city of Łódź after 3 months' turbulent maturing. It can be assumed that the dump formed in autumn from waste collected in parks (leaves and twigs from trees) constitute a homogeneous, repeated material.

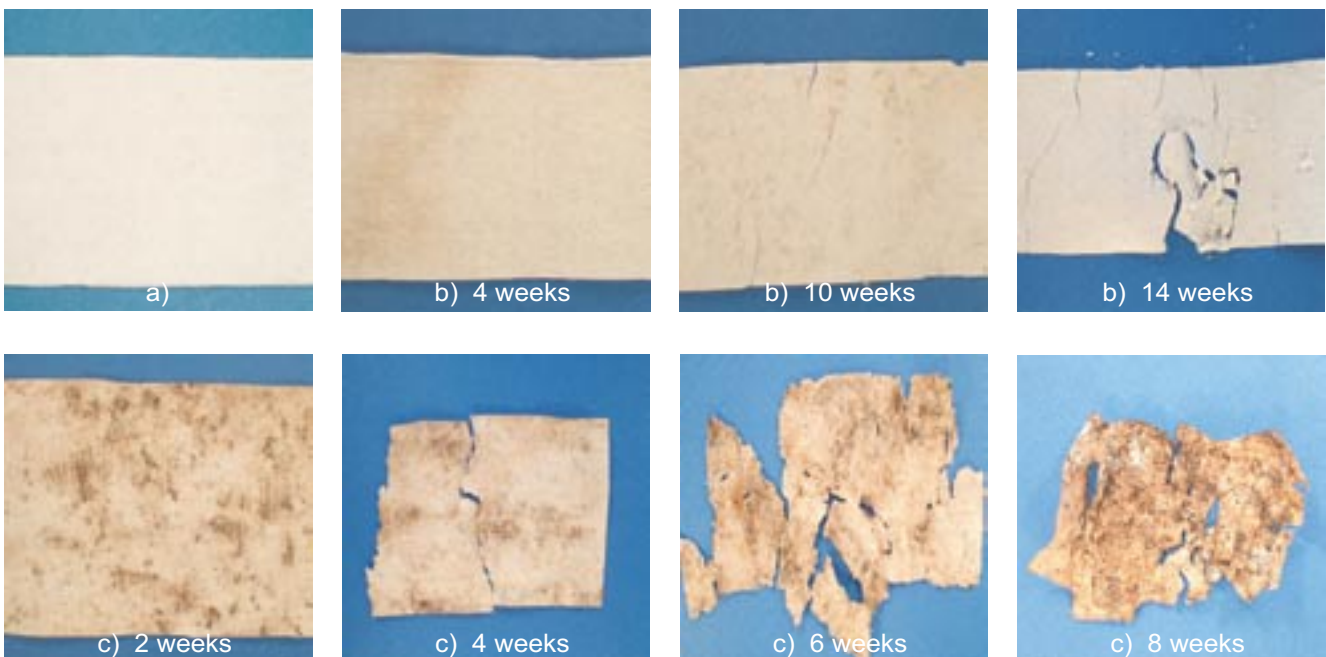


Figure 2. Photos of Eastar-Bio non-woven samples after biodegradation: a - before biodegradation, b - biodegradation in water, c - biodegradation in compost.

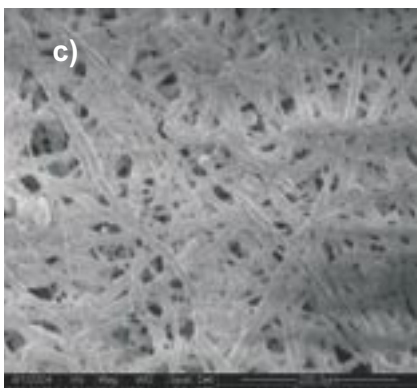
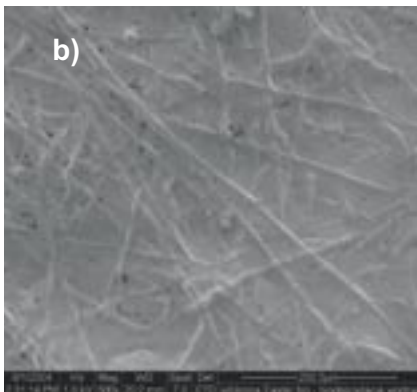
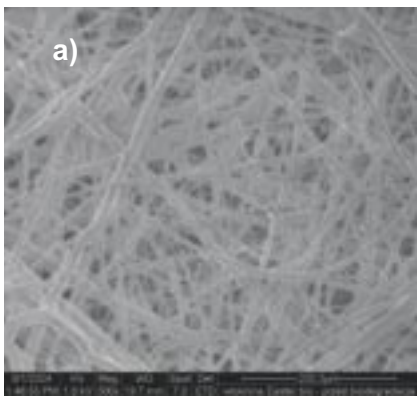


Figure 3. SEM photos of the surface of non-woven made of Eastar-Bio: a) before biodegradation; b) after 4 weeks' biodegradation in water; c) after 4 weeks' biodegradation in compost medium.

The biodegradation process was followed by measuring the loss of mass and observing the changes in the non-woven's mechanical properties and appearance.

Mass loss assessment of the biodegraded non-woven

In Figure 1, the loss of mass is presented occurring during biodegradation in compost and water. In both cases the mass loss is proportional to the degradation time. The figure shows that, although at the beginning of the process the biodegradation in water proceeds more quickly, the biological decomposition generally

Table 1. Change in the physical-mechanical properties of the Eastar Bio non-woven after biodegradation.

Parameter tested	Unit	Before biodegradation	After 4 weeks of biodegradation	
			in water	in compost
Surface density	g/m ²	102	98.2	97.1
Thickness	mm	0.41	0.37	0.36
Variation index of thickness	%	6.05	7.28	27.4
Average breaking force	N	5.81	1.07	1.46
Variation index of force	%	4.54	12.8	11.2
Tenacity	MPa	0.28	0.06	0.08
Elongation at break	%	8.54	1.67	5.35
Variation index of elongation	%	9.3	0	75.3

proceeds much more quickly in the compost. 40% of the initial weight was lost after 8 weeks in compost, while in water the decrease amounted to only 23% after 10 weeks of biodegradation. Such phenomena may be explained by the different mechanisms of biodegradation processes in water and compost. At the beginning (2-3 weeks), hydrolysis proceeds in compost as a dominating process. Just after that time, micro-organisms start to predominate in the degradation process. On the other hand, in water both processes (hydrolysis and biodegradation) constantly take place in parallel. The difference in character of the biodegradation processes in water and compost medium is confirmed by photos. As seen in Figures 2b and 2c, the water degradation proceeds evenly throughout the entire mass of the non-woven, while in the compost local changes prevail, causing fast fragmentation of the material.

Evaluation of the physical-mechanical properties of non-wovens subjected to biodegradation

The physical-mechanical properties of Eastar Bio non-wovens were compared before and after 4 weeks of biodegradation in water and compost. The weight reduction was similar for both samples amounting to 10% for compost and 13% for water biodegradation. Results of the comparison of the physical-mechanical properties are presented in Table 1. The very high variation indexes of elongation and thickness testify the irregularity of the sample resulting from the local changes.

Microscopic inspection of the non-woven degradation

The electron microscope images of the non-woven surface confirm the regular run of water biodegradation. In Figure 3, images are shown of the initial material,

and as it is after 4 weeks of biodegradation in water and compost. As result of the degradation in water, the non-woven becomes evenly smooth, while local pits can be seen on the surface of the composted material.

Spectrophotometric evaluation of the biodegradation of the non-wovens

The changes proceeding in the non-woven material were also traced by IR absorption photometric analysis, which is often used to investigate the degradation processes of polymers [12-14].

Figure 4 presents the comparison between the oscillation bands characteristic for the aliphatic-aromatic polyester derived from butylene glycol, adipic- and terephthalic acids in samples subjected to biodegradation. The following bands were selected to assess the proceeding changes: 3442 cm⁻¹, related to the extension oscillation of the OH groups; 1718 cm⁻¹, related to the extension oscillation of the carbonyl groups C=O; 1274 cm⁻¹, related to the ester groups C-O; and 732 cm⁻¹, related to the bending oscillation of the CH₂ groups arranged close to each other. The intensity of the selected bands characterising the initial and biodegraded material are compared in Table 2. Changes in the spectra can mainly be seen in the reduced intensity of the bands characteristic for the non-woven matter throughout the whole spectra range, thus confirming the polymer's step-wise degradation.

As seen from Figure 4 and Table 2, the lowering of the decrease in intensity of the characteristic bands is observed throughout the whole spectral range. The speed of the changes is different in different areas. Hydroxyl groups are reduced first, and other groups decrease gradually in a systematic way.

Table 2. Comparison of intensity of selected bands characteristic for Eastar Bio polymer in samples subjected to biodegradation in compost.

Compost biodegradation time, weeks	Intensity of bands in IR spectrum			
	3442 cm ⁻¹	1718 cm ⁻¹	1274 cm ⁻¹	732 cm ⁻¹
0	0.46	0.72	0.65	0.21
2	0.41	0.63	0.60	0.18
6	0.27	0.64	0.59	0.19
8	0.07	0.14	0.11	0.07

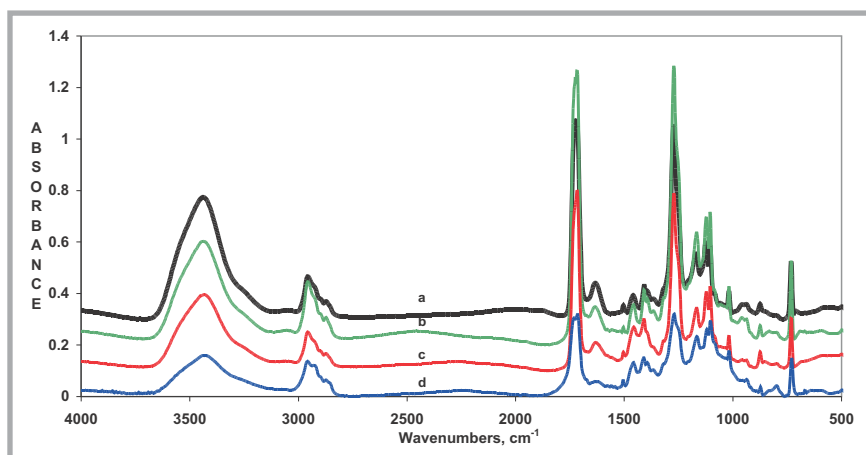


Figure 4. IR spectrum of non-woven made of Eastar-Bio after compost degradation: a - initial, b - after 2 weeks, c - after 6 weeks, d - after 8 weeks of degradation.

The results obtained for the samples biodegraded in water showed similar changes.

Summary/Conclusion

Eastar Bio, constituting an aromatic polyester of butylene glycol and adipic & terephthalic acids, can be processed to obtain melt-blown non-woven that are susceptible to biodegradation.

The biodegradation proceeds more quickly in compost than in water if the process temperature is similar. Biodegradation in water proceeds evenly throughout the entire non-woven mass; in compost, however, local changes emerge which lead to fast fragmentation of the material. The use of a non-woven made of Eastar Bio in the manufacture of disposable products for medicine and agriculture may contribute to the limitation of burdensome waste products.

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References

1. Witt U., Müller R. J., Deckwer W.-D.; *J. Environm. Polymer Degrad.*, 1995, 4 (3), 215.
2. Heidary S., Gordon B., *J. Environm. Polymer Degrad.*, 1994, 1 (2), 19.
3. Witt U., Müller R. J., Deckwer W.-D.; *J. Environm. Polymer Degrad.*, 1996, 4 (1), 9.
4. Grzebieniak K., Ślusarczyk Cz., Włochowicz A., Janicki J., *Polimery*, 2002, 47.
5. Witt U., Einig T., Yamamoto M., Kleeberg I., Deckwer W.-D., Müller R. J., *Chemosphere* 44 (2001) 289.
6. www.eastman.com
7. Twarowska-Schmidt K., *Fibres & Textiles in Eastern Europe*, 2004, Vol. 12, No 2(46), 17.
8. Vlad S., Oprea S., Stanciu A., Ciobanu C., Bulacovschi, *Europ.Polym. J.*2000, 36, 1495.
9. Ki H., C., Park O., *Polymer*, 2001, 42, 1849.
10. Brochocka A., *Fibres & Textiles in Eastern Europe*, 2001, No 4(35), 66.
11. ASTM Standard D 6003-96.
12. Schmidt H., Ratajska M., Brzezińska A., *Przegląd Włókienniczy* 1992, 11, 280.
13. Schmidt H., Twarowska-Schmidt K., *Fibres & Textiles in Eastern Europe*, 1997, Vol. 5, No 1(16), 51.
14. Żenkiewicz M., Rauchfleisch M., Czupryńska J., *Polimery*, 2003, 48, 343.

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4-5 October, 2005, Łódź, Poland



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