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Microstructure transformation due to hydrolytic degradation of ethylene terephthalate/lactic acid copolyesters

Summary — Wide-angle (WAXS) and small-angle (SAXS) X-ray scattering methods have been used to study the supermolecular structure of ethylene terephthalate and lactic acid copolyesters having different chemical structure of macromolecules. The effect of copolymers chemical structure on their microstructure was investigated using crystallized (annealed) polymer samples. It has been found that the crystalline phase in the copolyesters contains mainly PET segments (ET sequences). The degree of crystallinity decreases with lowering the length of $(ET)_x$ sequences (X values). The crystallized copolymers of sufficiently long ET sequences showed lamellar structure (long period reflex) in SAXS studies.

Copolyester specimens in form of monofilaments ("as spun" as well as annealed) were subjected to hydrolytic degradation at pH 7.35 and temp. 60°C over a time period of up to 9 weeks. Intensity of degradation changes (η_{red} and weight of the specimens) as well as intensity and nature of microstructure changes (WAXS and SAXS data) were highly dependent on chemical structure of the copolymers. Microstructure changes, especially SAXS characteristics, were also highly dependent on the initial morphology of the specimens, *i.e.* on whether they were crystallized or not before degradation.

Key words: ethylene terephthalate/lactic acid copolyesters, hydrolytic degradation, microstructure investigation, microstructure changes, SAXS, WAXS.

Copolyesters of ethylene terephthalate (ET) and lactic acid (LA) are hydrolytically degradable polymers that can be obtained by melt polycondensation using different kinds of raw materials [1, 2], *i.e.* by transesterification from poly(ethylene terephthalate) (PET) and poly(lactic acid) (PLA) or PET and lactide or by direct polycondensation (modelled the PET synthesis) from DMT, ethylene glycol and lactic acid. Depending on the synthesis method as well as specific conditions of the process, the copolymers obtained are characterized by different chemical structure.

Because biodegradability of synthetic polyesters is a function of their susceptibility to hydrolysis under environmental conditions [3, 4], well hydrolytically degradable ET/LA copolyesters could become potentially biodegradable plastics for processing by melt techniques.

ET/LA copolyesters have been found to be susceptible to hydrolysis under average conditions, *e.g.* at 60°C [1]. Their hydrolytic degradability is highly dependent on chemical structure of their macromolecules. However, physical structure of the copolyesters and its changes accompanying degradation of macromolecule chains could have significant influence on the course of hydrolytic degradation process.

The aim of the work reported was to study the effects of the copolymer chemical structure on the supermolecular structure ET/LA copolyesters and on change of their microstructure during hydrolytic degradation. The structure of PLA and its copolymers, both before and after hydrolytic degradation, have been studied in recent years by differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR), atomic force microscopy (AFM) and X-ray scattering [5—8]. Relatively few studies have been devoted to the lamellar structure of these polymer systems.

This paper deals primarily with the morphological structures of two types of ET/LA copolymers probed by small-angle scattering (SAXS). Morphological parameters in the lamellar level, such as the long period, are deduced from the SAXS profiles. Results of supplementary investigations performed by means of wide-angle X-ray scattering (WAXS) are also reported.

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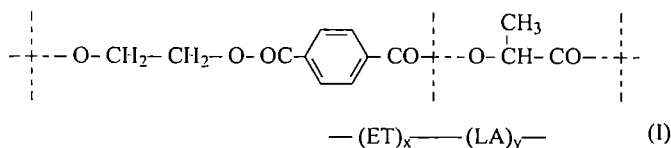[2)] University of Bielsko-Biała, Textile Institute, Willowa 2, 43-309 Bielsko-Biała, Poland.
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EXPERIMENTAL

Materials

The polymers studied were ET/LA copolyesters of general formula (I). Indexes x and y will be further used to denote the lengths of ET and LA sequences, respec-

$$-\!+\!-\!O\!-\!CH_2\!-\!CH_2\!-\!O\!-\!OC\!\!-\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-\!CO\!-\!\!+\!\!-\!O\!-\!\overset{\overset{\displaystyle CH_3}{|}}{CH}\!-\!CO\!-\!\!+\!-$$

$$-\,(ET)_x\!\!-\!\!-\!\!-\!\!(LA)_y\!\!-\qquad\qquad (I)$$

tively. Copolymers investigated in this work were prepared under original conditions.

Table 1. Characteristics of chemical structure of ethylene terephthalate and L-lactic acid copolyesters

Copolyester samples[*]	LA contents mol %	Average sequences lengths	
		$(ET)_x; \overline{X}$	$(LA)_y; \overline{Y}$
PET/LA:			
A	18.4	4.2	~ 1.0
B	21.9	3.6	~ 1.05
C	26.7	3.4	~ 1.15
D	30.4	3.2	~ 1.2
PET/PLA:			
E	40.7	8.6	6.1
F	36.3	5.6	3.2
G	38.2	4.6	2.9
H	41.0	3.4	2.4

[*] Further informations see text

Two different types of copolyesters, characterized in Table 1, were selected for analysis:

— copolyesters denoted as PET/LA (samples A—D), obtained by direct melt polycondensation from monomeric substrates: DMT, ethylene glycol and L-lactic acid. Those copolymers contained mainly individual LA monomeric units; $\overline{Y} < 1.25$. In this case, copolymers containing higher amounts of LA are characterized with shorter $(ET)_x$ sequences.

— copolyesters denoted as PET/PLA, obtained by transesterification of PET and PLA (samples E—G) or by transesterification PET and L-lactide (sample H). These copolyesters differed in the lengths of $(ET)_x$ and $(LA)_y$ sequences at a similar level of LA content, about 40 mol % (i.e. about 20 wt. %). Sample E had the longest and sample H the shortest ET and LA sequences.

Note that average lengths of sequences, especially values of $\overline{X}$, highly influenced copolymer properties including ability to hydrolysis.

Samples preparation

To study supermolecular structure, the copolyesters were annealed (crystallized) at 140°C during one hour

(samples A—C and E—H) or at 100°C during 4 h (sample D having the shortest ET sequences and the lowest melting temperature range).

Before hydrolytic degradation studies, the copolymers were melt spun into monofilaments 0.3—0.4 mm in diameter. Monofilament specimens, "as spun" — not crystallized, as well as crystallized — annealed at 140°C or at 100°C, were used in degradation tests.

Methods of copolymer examination

Hydrolytic degradation tests were carried out using a phosphate—citric buffer solution of pH 7.35. Monofilament specimens (50 mm long) weighing ca. 0.4 g, each, were kept in 200 mL of buffer at 60°C during time periods of from 1 to 9 weeks. Degradation progress was assessed on the basis of changes in reduced viscosity and in weight of the specimens, as described in [1] (solvent — mixture phenol: tetrachloroethane = 1:1 w/w, temperature 25°C).

Supermolecular structure of the copolymers was investigated by means of X-ray methods [9] (using monochromatized Cu K_α radiation):

— wide-angle X-ray scattering (WAXS) method, performed by using HZG-4 type diffractometer (Seifert, Germany);

— small-angle X-ray scattering (SAXS) method, performed by using Kratky camera (MBraun, Austria).

RESULTS AND DISCUSSION

Crystallinity and morphology of copolyesters

Figure 1 shows a WAXS pattern typical for the investigated copolyesters. Sample A diffractogram is given by example. Experimental diffractogram (denoted by
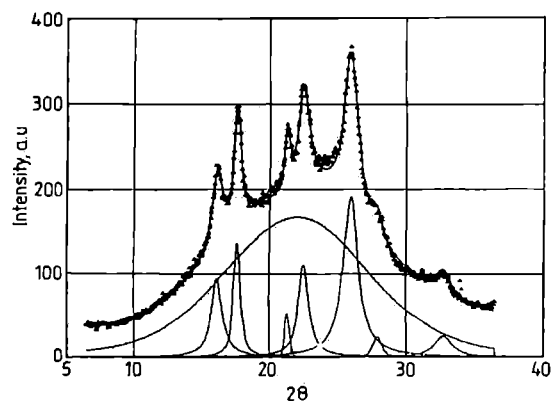

Fig. 1. The WAXS diffractogram of sample A (see Table 1): ▲ — experimental, solid line — amorphous halo

points) was separated into seven interference maxima and amorphous halo (solid lines). The angular positions

and the interplanar distances calculated from Bragg's law [10], were the same as for semicrystalline PET homopolymer [11]. No significant differences in interplanar distances were observed for other copolyester samples. So, it can be concluded that crystalline phase in the copolyesters was formed by monomeric ET units. These units were arranged in macromolecule chains in form of sequences with different lenghts ($\overline{X}$ data, Table 1).

As it is known [12], PET homopolymer crystallizes in a triclinic system with edges of the elementary cell being the single ET units. PET chains assume an approximately planar configuration with the chain plane being almost parallel to the (100) lattice plane.

Fig. 2. SAXS diffractogram of PET/LA type copolyesters (samples A, B, C, D)

Table 2. Microstructure of PET/LA and PET/PLA copolyesters (results of WAXS investigations)

Copolyester samples	Degree of crystallinity, mol %	Average size of crystallites, D (100), Å
PET/LA:		
A	33.1	54.2
B	20.6	55.3
C	27.5	50.2
D	10.2	31.5
PET/PLA:		
E	44.0	66.4
F	43.1	64.0
G	41.4	64.0
H	28.0	50.4

Fig. 3. SAXS diffractogram of PET/PLA type copolyesters (samples E, F, G, H)

Table 2 presents numerical data obtained from WAXS measurements, i.e. the degree of crystallinity of copolyesters and the average size of crystallites in direction perpendicular to the (100) planes. Both parameters decreased with decreasing (ET)$_x$ sequences length that is from sample A to sample D for the type PET/LA copolymers and from sample E to sample H for the type PET/PLA copolymers.

In case of sample A, characterized by $\overline{X}$ = 4.2, the average size of crystallites was equal to 54 Å. This corresponds to approx. 12 polymer chains. For sample D having the shortest (ET)$_x$ sequences ($\overline{X}$ = 3.2), the average size of crystallites amounted to 32 Å, which corresponds to about 7 polymer chains. At the same time, a considerable decrease in degree of crystallinity was observed — from 33% for sample A to 10% for sample D. The same tendency is seen for type PET/PLA samples. Note that samples H (PET/PLA) and C (PET/LA), having the same average length of (ET)$_x$ sequences, showed practically the same crystalline structure parameters.

The SAXS curves obtained for crystallized copolyesters investigated are shown in Figures 2 (PET/LA) and 3 (PET/PLA). Most of these curves (samples A—C and E—G) exhibit a distinct interference maximum, so-called long period reflex, which can indicate existence of a lamellar structure in copolyesters, similarly as in case of
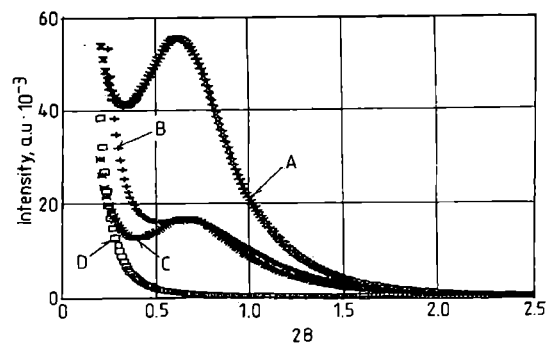
semicrystalline PET homopolymer [13]. The long period reflex gradually disappeared with decreasing $\overline{X}$ parameter value, i.e. in directions from A to D (PET/LA copolyesters) and from E to H (PET/PLA copolyesters). In case of PET/PLA copolyesters lamellar structure was less clearly expressed (less distinct SAXS maximum) than in case of PET/LA copolyesters.

Microstructure changes during hydrolytic degradation

WAXS and SAXS investigations were carried out for both "as spun" (not crystallized) and crystallized monofilament specimens — before and after their degradation.

X-ray examinations, especially SAXS measurements, revealed real changes in supermolecular structure of the copolyesters during degradation. Hydrolytic cleavage of lactic acid ester bonds caused bursting of macromolecular chains into smaller fragments. Once sufficient number of shortened fragments evolve, their aggregation or reaggregation takes place forming a new lamellar structure, generally characterized by smaller value of the long period and higher degree of crystallinity. Initial morphology of the monofilament (specimens not crys-

tallized or crystallized) strongly influenced microstructure transformation.

Of PET/LA type copolyesters, highest susceptibility to hydrolysis was shown by sample D having the shortest ET sequences ($\overline{X}$ = 3.2). In Table 3 this copolyester (specimens not crystallized) is compared with sample B having (ET)$_x$ sequences characterized with ($\overline{X}$ = 3.6). The differences in the paths of these copolyesters degradation are well seen. Specimens D degraded to much deeper degree than specimens B, reaching very low value of η_{red}. After 9 weeks, high weight loss was observed, higher than the initial weight content of LA (18.4% of weight loss compared to 14.1 wt. % of LA content).

Of the PET/LA type copolyesters, copolymer D showed also the most distinct changes in its microstructure according to WAXS and SAXS analyses. Changes in the degree of crystallinity and in the long period values for specimens D, before and after degradation, are illustrated by the adequate data in Table 3.

Table 3. Changes of η_{red}, weight and microstructure characteristics of copolyesters PET/LA during degradation (samples B and D from Table 1)

Copolyesters*)	Hydrolysis (60°C, pH 7.35)					
	weeks					
	0	1	2	3	5	9
sample D:						
η_{red}, dL/g	0.68	0.54	0.45	0.36	0.22	0.13
weight loss, %	—	0	0	0	0.5	18.4
cryst. deg. (WAXS), %	25	23	24	30	33	35
long period (SAXS)**), Å	—	—	—	—	83	71
sample B:						
η_{red}, dL/g	0.69	0.60	0.53	0.47	0.42	0.21
weight loss, %	—	0	0	0	0	0

*) Specimens not-crystallized before degradation.
**) Values calculated from SAXS curves.

PET/PLA type copolyesters, such as samples E and H compared in Table 4 (data for the specimens initially not crystallized) are good examples of microstructure transformations during hydrolysis. These samples had quite different chemical structure at the same level of LA content (ca. 41 mol %, i.e. 20.5 wt. %).

Specimens H, having much shorter ET sequences ($\overline{X}$ = 3.4) than the copolyester ($\overline{X}$ = 8.6), showed considerably higher susceptibility to hydrolysis (degradation to much lower η_{red} values). Their weight loss started later (in the 4th week), but after 9 weeks it was considerably higher (ca. 25%) than in case of specimens E (beginning of weight loss after 1 week; total weight loss ca. 14%). However, observed much earlier weight changes for specimens E were connected with presence of longer LA sequences ($\overline{Y}$ = 6.1) and delivering low molecular products of their decomposition (e.g. lactic acid).

Table 4. Changes of η_{red}, weight and microstructure characteristics of copolyesters PET/PLA during degradation (samples H and E from Table 1)

Copolyesters*), LA cont. 41 mol % (20.5 wt. %)	Hydrolysis, 60°C, pH 7.35					
	weeks					
	0	1	2	3	5	9
sample H:						
η_{red}, dL/g	0.70	0.51	0.40	0.26	0.19	0.14
weight loss, %	—	0	0	0	7.8	24.9
cryst. deg. (WAXS), %	28	31	29	38	41	43
long period (SAXS)**), Å	—	82	78	77	72	61
sample E:						
η_{red}, dL/g	0.66	0.47	0.37	0.33	0.29	0.26
weight loss, %	—	0	1.4	9.5	12.6	14.1
cryst. deg., %	26	26	31	37	35	34
long period, Å	—	—	—	71	71	71

*) Specimens not-crystallized before degradation.
**) Values calculated from SAXS curves.

High hydrolytic changes in specimens H, led to more pronounced changes in their microstructure as compared with specimens E (data in Table 4 and in Figures 4a and 5a). The initial, not-crystallized monofilament H and E did not show any SAXS maximum. In case of
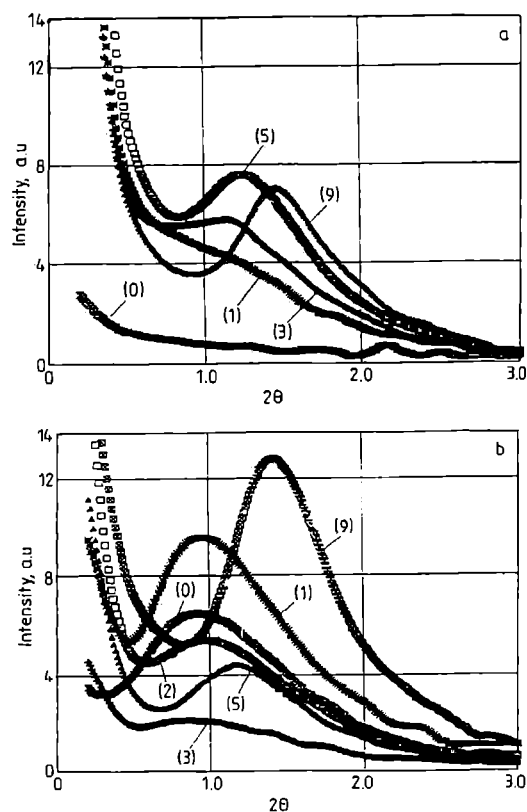

Fig. 4. SAXS diffractogram of the specimens H — before (curve 0) and after different periods of degradation (weeks in brackets); (a) — specimens initially not crystallized; (b) — specimens initially crystallized
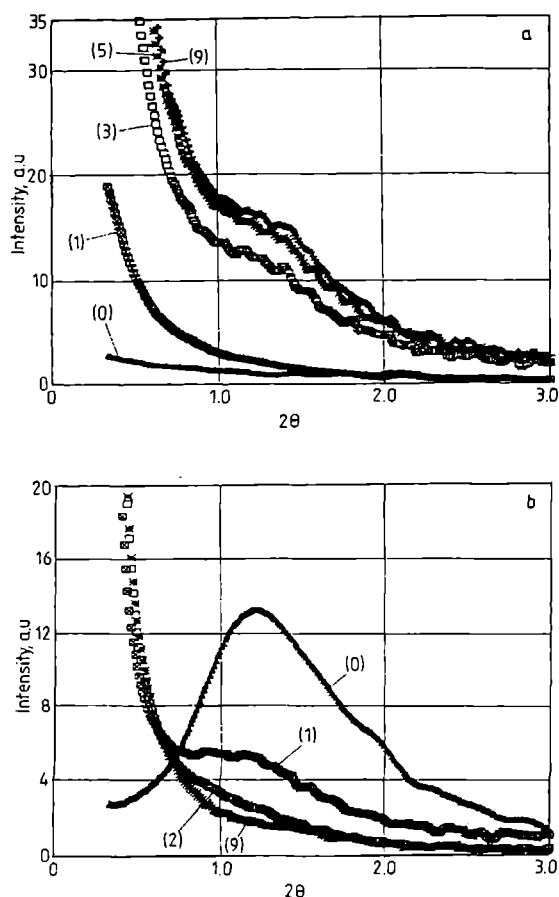
Fig. 5. SAXS diffractogram of the specimens "E" — before (curve 0) and after different periods of degradation (weeks in brackets); (a) — specimens initially not crystallized; (b) — specimens initially crystallized

specimens H such maximum appeared after about a week, indicating development of a lamellar structure (Fig. 4a). Changes deepened in the following degradation periods. As it is seen from the data in Table 4, successive stages of microstructure changes were characterized by decrease in the long period (from 82 Å after a week to 61 Å after 9 weeks; values calculated from SAXS curves). Simultaneously, the degree of crystallinity increased from 28% up to 43%.

Deeply degraded monofilament E showed less distinct microstructure changes. SAXS maximum appeared after about 3 weeks (Fig. 5a) but remained flat and broad in the following stages of degradation, indicating formation of a less perfect lamellar structure. Long period values were 71 Å and did not change. Increase in degree of crystallinity occurred after 3 weeks, but further changes of that parameter were not clear.

The second parts (parts "b") of the Figures 4 and 5 show changes of SAXS curves during hydrolysis for the monofilament H and E which were subjected to crystallization before degradation. It is seen that for initially crystallized specimens changes in the supermolecular

structure had a quite different nature than for not-crystallized specimens. Long period values, calculated from SAXS curves shown in Fig. 4a, 4b and Fig. 5a, 5b, are compared in Table 5 together with values of the degree

Table 5. Comparison of the degree of crystallinity and the long period values for specimens H and E not-crystallized (nk) and crystallized (k) before degradation

Sample	Degradation time week	Degree of crystallinity, %		Long period, Å	
		nk	k	nk	k
H	0	28	48	—	97
	1	31	46	82	94
	2	29	43	78	91
	3	38	41	77	93
	5	41	47	72	75
	9	43	45	61	63
E	0	26	44	—	83
	1	26	40	—	83
	2	31	38	—	—
	3	37	32	71	—
	5	35	30	71	—
	9	34	33	71	—

of crystallinity calculated from WAXS measurements. Lamellar structure (SAXS maximum) was present just before degradation. In case of the monofilament H (Fig. 4b) the initial lamellar structure (with long period of *ca.* 95Å) was considerably destroyed in the time period of 1 to 3 weeks. Next, the "new" lamellar structure developed, characterized by much lower long period (L = 75 Å and 63 Å after 5 and 9 weeks, respectively). The degree of crystallinity changed only slightly (between 40 and 50%). In case of the deeply degraded monofilament E (Fig. 5b), the initial lamellar structure with L = 83 Å was destroyed in time period of 2—3 weeks and no new structure was formed. Degree of crystallinity dropped from 44 to about 30%.

CONCLUSION

The investigated PET/LA and PET/PLA type copolyesters showed crystallization ability owing to existence of sufficiently long crystalline phase forming ET sequences. SAXS studies of the crystallized copolymers showed maximum (long period reflex) characteristic for a lamellar structure.

Hydrolytic degradation process proceeding at temperature as high as 60°C was accompanied by changes of copolymer microstructure. These changes were highly dependent on chemical structure of the macromolecules, especially on the length of $(ET)_x$ sequences. Hydrolysis and transformation of copolyesters structure caused by degradation were more intensive for shorter ET sequences, especially at $\overline{X} \leq 3.4$.

Qualitative and quantitative changes of the copoly-ester microstructure were highly dependent on the su-permolecular structure developed before hydrolysis.

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