Hydrolytic Degradation of Melt-Extruded Fibers from Poly(β-Propiolactone)

TORBJÖRN MATHISEN and ANN-CHRISTINE ALBERTSSON*
Department of Polymer Technology, The Royal Institute of Technology, 10044 Stockholm, Sweden

Synopsis

β-Propiolactone was polymerized in bulk at 5°C using pyridine as initiator. The melt spun fibers were drawn at 50°C and subjected to degradation, which was monitored by mechanical, thermal, and molecular weight measurements. The hydrolytic degradation of poly(β-propiolactone) fibers has been investigated in a buffered salt solution (pH 7.2) maintained at 37°C. The degradation was found to be very rapid during the first 90 days of immersion, with respect to mechanical properties and the weight average molecular weight. Between 90 and 180 days there were no significant changes in the mechanical properties which, however, rapidly decreased thereafter and finally reached zero at 240 days. The crystallinity seemed to increase in a linear fashion, during the same period, from about 55 to 70%.

INTRODUCTION

The hydrolysis of polymers containing unstable ester linkages has been studied in a great number of articles over the past 20 years. The great interest for polymers such as poly(glycolic acid),[1] poly(glycolic-co-lactic acid),[2] and polyparadioxanone[3] is mainly due to their expanding use as degradable materials in medical and pharmaceutical applications. Poly(glycolic acid) was the first synthetic degradable polymer used in surgery as a suture, and its kinetics of degradation both *in vitro* and *in vivo* have been widely studied.[4,5] Other materials that have also been given much attention are poly(lactic acid),[6,7] poly(β-hydroxybutyrate),[8] and poly(ε-caprolactone).[9] All these materials are commonly synthesized through ring opening polymerization, except for poly(β-hydroxybutyrate), which is usually extracted from certain bacteria.[10]

From a structural point of view, considering the α-hydroxy acid in poly(glycolic acid) or poly(lactic acid) and the β-hydroxy acid in poly(β-hydroxybutyrate) (PHB), it is logical to turn our view towards poly(β-propiolactone) (PPL). This polymer, with one methylene group more between the ester bonds than poly(glycolic acid), has been shown to polymerize very easily with a vast number of catalysts[11] and it can be obtained with a high molecular weight. Much work has also been devoted to its physical characterization.[12,13] It is, therefore, surprising that no articles, to our knowledge, have discussed the hydrolytic degradation of this polymer in terms of change in crystallinity, decrease in molecular weight, and loss of mechanical strength. In an early patent,[14] claiming the use of poly(β-hydroxybutyrate) (PHB) as implant material, films of PPL and PHB were reported to have been implanted in rabbits. These films were removed after certain periods and the degradation

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was assessed visually (i.e., whether holes or changes in color developed within the specimen). A few years later, PPL was briefly reported to lose mechanical strength over a period of 6 months[15]; no data were given. A few articles about the *in vivo* compatibility of PPL have also been published.[16]

The object of the present work has been to investigate the hydrolytic degradation of melt spun fibers of PPL, which is insufficiently covered in the present literature, and thereafter to contribute with new data. Two different techniques for purification of β-propiolactone have been used in order to study their effect on the polymerization initiated by pyridine.

EXPERIMENTAL

Materials

Pyridine (aristar) was obtained from BDH Chemicals (U.K.) and used as received. β-Propiolactone (pract.) was obtained from Fluka AG, Chemische Fabrik, CH-9470 Buchs, and two different methods of purification were used:

1. β-Propiolactone was dried over sodium sulfate for 3 days at 4°C, rapidly passed through two columns of anhydrous calcium chloride, and then immediately distilled under reduced pressure (32°C, 1.5 mbar).
2. β-Propiolactone was stirred together with finely divided calcium hydride for 4 h at room temperature, and then distilled under reduced pressure.

Polymerization

A typical procedure can be described as followed: An empty three-necked round-bottomed flask was maintained at 200°C overnight, and then removed from the oven and immediately sealed with a rubber septum while a stream of dry N_2 was passed through it; allowing it to cool at room temperature. β-Propiolactone 51.6 g (0.72 mol) and pyridine 30 μL (0.37 mmol) were introduced by means of a syringe. To prevent contamination of the reaction vessel, the contents were stirred by a glass shaft fitted with a Teflon blade and a Teflon bearing. The flask was then placed in a water bath at 5°C, controlled by a thermostat, and dry N_2 was passed through the bulk during the time of polymerization, which lasted for 11 days. The polymer was dissolved in 500 mL of chloroform and precipitated in 4 L of methanol. Drying to constant weight gave a yield of 94%. The polymer was stored in a dry N_2 atmosphere.

The polymer used in degradation experiment was prepared from β-propiolactone 250 g (3.5 mol) and pyridine 140 μL (1.73 mmol) in a 500 mL three-necked flask and the polymerization was completed after 12 days. The yield of poly(β-propiolactone) was 92%.

Preparation of Fibers

The fiber was melt spun from an Axon BX-12 extruder equipped with a gateway plasticating screw. The temperature in the first zone was maintained at 50°C, in zones 2 and 3 at 100°C, and in zone 4 (die) at 90°C. The fiber was cooled in an ethanol (initially 99.5%) bath, and the take-up speed was regulated to obtain an appropriate fiber diameter. The fiber produced

was drawn in a 600 mm long pipe maintained at 50°C through which a slight stream of preheated dry N_2 was passed. A suitable neck force was obtained by an electric motor at each end of the pipe; one operating at constant rpm and the other producing a constant momentum. The draw ratio λ was about 5 for all three fibers. The drawn fiber was stored in dry N_2 atmosphere prior to use.

Molecular Weight Measurement

Using an Ubbelohde viscometer, the molecular weight was determined in chloroform at 30°C using the constants, $k = 2.59 \times 10^{-4}$ and $a = 0.72$ at 30°C, previously determined in the Mark–Houwink equation.[12]

Gel permeation chromatography was used in the degradation study to measure the molecular weight. A Waters GPC system, which was run with chloroform in all measurements, consisted of a solvent delivery system (Model 6000A), automatic injector (Wisp 710B), and a differential refractometer. Three columns from Shodex of the type GPC AC-80M/S were used and maintained at 50°C as well as the detector. The columns were calibrated with polystyrene standards.

DSC Measurements

A Perkin-Elmer DSC-2 was used to determine the heat of fusion of the fibers. The melt enthalpy area was calibrated with indium and the heating rate was 10°C/min. The crystallinity of the fibers was estimated using the standard heat of fusion for 100% crystalline PPL.[13]

Mechanical Tests

An Instron Model 1122, equipped with pneumatic grips (No. 2714-002), was used in the mechanical measurements and calibrated with appropriate standard loads prior to use. The gauge length of the fibers was 100 mm in all experiments, and the crosshead speed was set to 10 mm/min.

Degradation Experiment

Fifty fibers, each 500 mm long, with diameters of 0.15–0.20, 0.25–0.30, and 0.35–0.40 mm, respectively, were immersed in three different bottles containing 500 mL of a buffered salt solution,[17] having a pH of 7.2, and placed in a shaking chamber maintained at 37°C. Prior to testing, three fibers from each bottle were removed and rinsed for a few minutes under running water to remove any salt crystals, then rapidly soaked in 99.5% ethanol, and dried in an air stream. Three samples were randomly cut from fibers of each diameter for DSC and GPC measurements prior to mechanical testing.

RESULTS

Polymerization

Table I shows the result of polymerization in terms of yields and viscosity average molecular weights, where different techniques of purification and different initiator concentrations were used.

TABLE I
Polymerization of β-Propiolactone with Pyridine as Initiator at 5°C[a]

Sample	Drying method	β-PL (g)	Pyridine (μL)	M/I	Time (days)	Yield (%)	M_v
1	CaH_2	30.3	13.5	2500	21	62	136,000
2	CaH_2	5.2	3.5	1500	23	52	31,000
3	CaH_2	7.3	5.5	1500	23	73	148,000
4	CaH_2	46.1	20.6	2500	21	—	—
5	$CaCl_2$	42.3	10	4720	11	96	266,000
6	$CaCl_2$	42.6	13	3670	11	93	253,000
7	$CaCl_2$	44.6	16	3110	11	96	224,000
8	$CaCl_2$	43.3	20	2420	11	96	195,000
9	$CaCl_2$	51.6	30	1920	11	94	132,000

[a]Two different methods of purifications were used for the monomer.

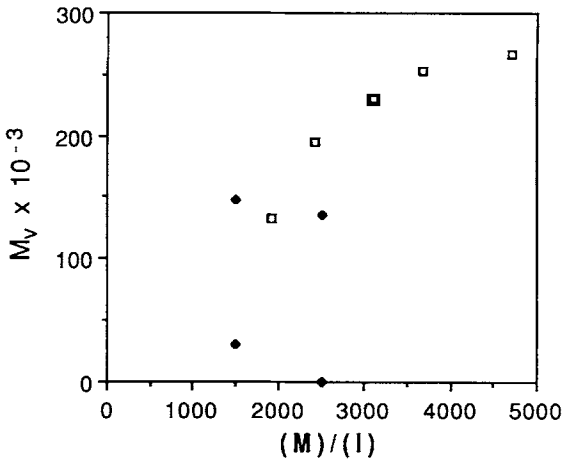

Fig. 1. The relation between M_v of poly(β-propiolactone) and the concentration of pyridine (I), using two different methods of purification: (◆) CaH_2; (□) $Na_2SO_4/CaCl_2$.

In Figure 1 M_v is plotted against [monomer]/[initiator] ([M]/[I]), for two different techniques of purification of the monomer. When $Na_2SO_4/CaCl_2$ was used to purify β-PL, a connection is seen between M_v of the polymer and the ratio [M]/[I]. The curve levels out, indicating that there is a maximum limit of M_v which can be achieved in bulk polymerization under these conditions.

The use of CaH_2 as drying agent for β-propiolactone has been previously questioned,[18] and it has been found to have a lower drying capacity than $Na_2SO_4/CaCl_2$. In the same article, the authors also mentioned that this drying method may remove some of the impurities found in commercial β-PL.

Degradation

In Figures 2(a), (b), and (c), the breaking force, for the three different fiber dimensions, is plotted against time of immersion in the buffered salt solution. All three fiber sizes A, B, and C, corresponding to diameters of 0.15–0.20, 0.25–0.30, and 0.35–0.40 mm, respectively, show a similar relation between the measured load at break vs. time of immersion in the buffer solution, although

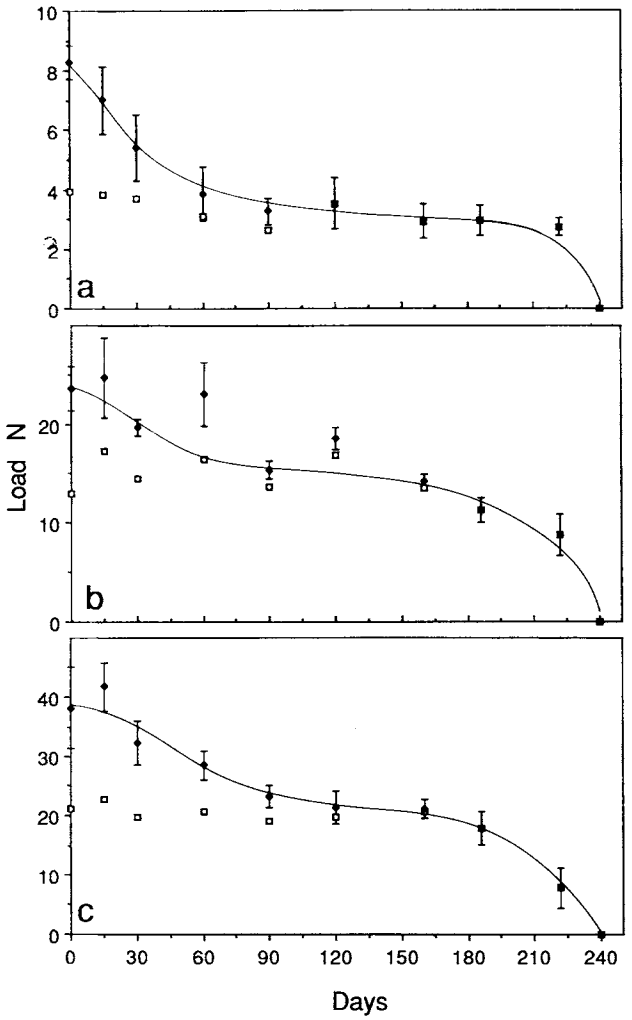

Fig. 2. The load at break (◆) and load at yield (□) vs. the degradation time in days. The three diagrams represent fiber diameters of (a) 0.15–0.20, (b) 0.25–0.30, and (c) 0.35–0.40 mm. Error bars represent the standard deviation.

the relationship is less apparent for fiber B. For fibers B and C there seems to be a small induction period in the beginning of the degradation. All the fibers lost about 50% of their total strength within 90 days. In the interval from 90 to 180 days the fiber strength remained almost constant and coincided with the load at yield. After 180 days it rapidly declined and finally reached zero at 240 days.

The strain at yield and strain at break are plotted vs. time of immersion in Figures 3(a), (b), and (c). The strain at yield was constant for all fibers up to about 180 days while the strain at break decreased. Approximately 80% was lost for fibers A and B and 70% for C during the first period of 90 days.

M_n and M_w are plotted against time of immersion in Figures 4(a), (b), and (c). There was a rapid decrease in M_w and a smaller decrease in M_n during the first period of degradation. The values obtained should not be taken to be

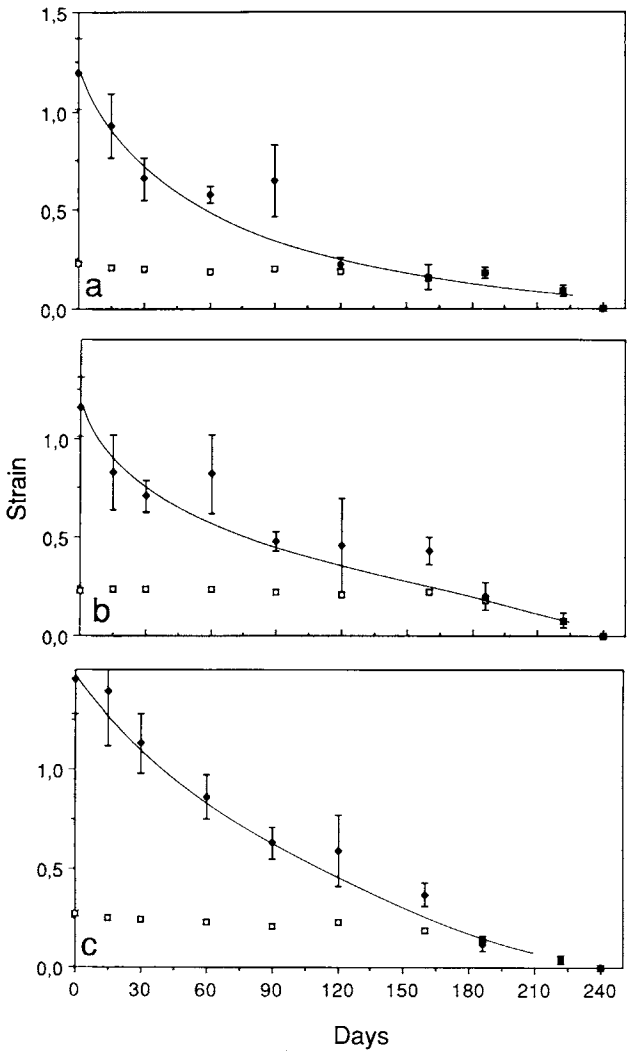

Fig. 3. The strain at break (◆) and strain at yield (□) vs. the degradation time in days. The three diagrams represent fiber diameters of (a) 0.15–0.20, (b) 0.25–0.30, and (c) 0.35–0.40 mm. Error bars represent the standard deviation.

absolute values, because the GPC columns were calibrated against polystyrene standards, but simply as the relative change in M_n and M_w. After 30 days the molecular weight distribution taken as M_w/M_n approached a value near 2.

The crystallinity of the fibers, shown in Figures 5(a), (b), and (c), increased, however, in an almost linear fashion. There was a vague tendency for a more rapid increase during the first 60 days.

DISCUSSION

During a period of 240 days over which the mechanical properties were recorded, the fibers showed a steady increase in crystallinity. The deterioration of mechanical properties in this period is assumed to be due to degrada-

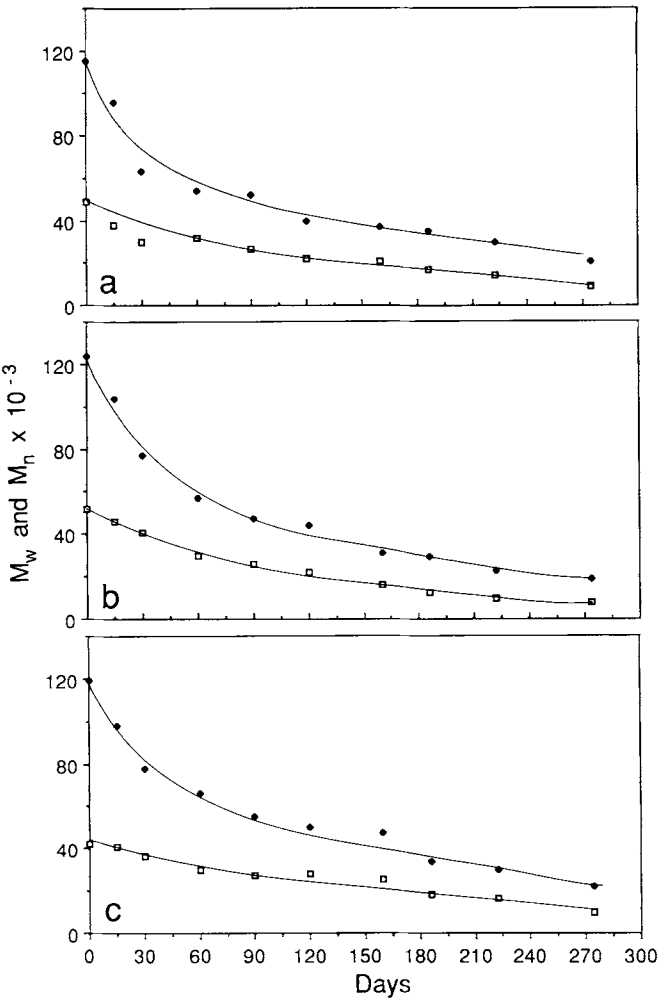

Fig. 4. M_w (◆) and M_n (□) vs. the degradation time in days. The three diagrams represent fiber diameters of (a) 0.15–0.20, (b) 0.25–0.30, and (c) 0.35–0.40 mm.

tion only in the amorphous phase. The relative low crystallinity of the oriented fibers (55–60%) results in about 40–45% of amorphous phase which consists of inter- and intrafibrillar tie chains, loops, and loose chain ends. Because of this high content of amorphous phase, the fiber structure can be assumed to be more "open" than in the usual picture of highly crystalline fibers.[19] At the temperature of degradation (37°C), the polymer is well above its T_g, reported to be −15°C,[12] which facilitates the diffusion of water into the amorphous areas.

The stress–strain curves in Figure 6 show a large plastic deformation after the yield point for the nondegraded fiber. In an attempt to explain this behavior, we use the frequently accepted fiber model mentioned earlier to illustrate what takes place within the amorphous phase when the fiber is subjected to an increasing deformation. The tie chains connecting the crystalline blocks can be assumed to consist of a broad distribution of short and

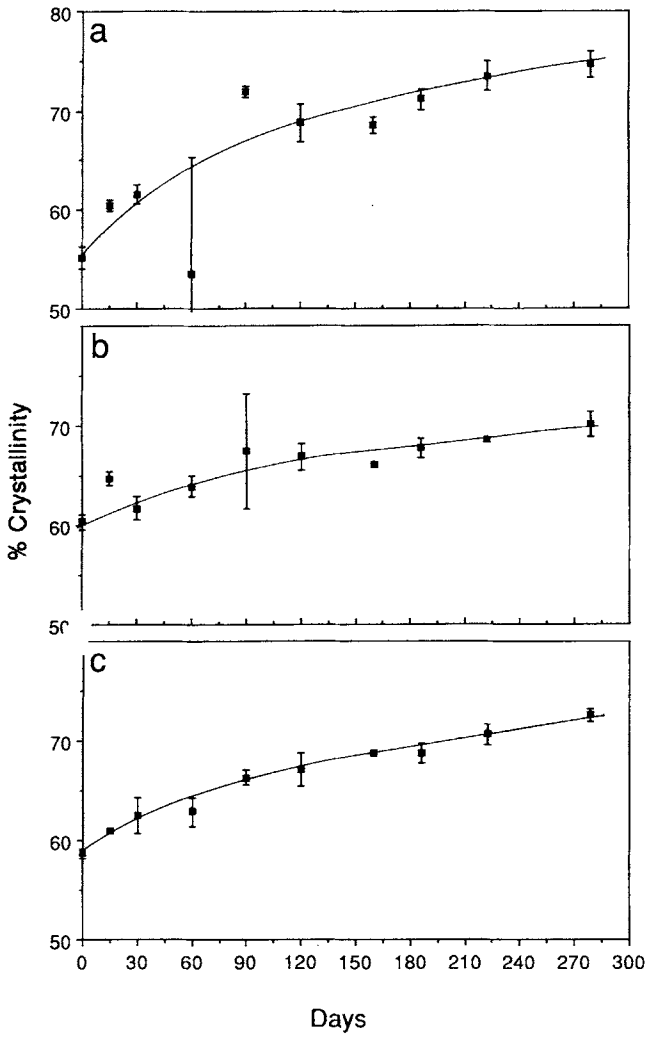

Fig. 5. The crystallinity (%) vs. the degradation time in days. The three diagrams represent fiber diameters of (a) 0.15–0.20, (b) 0.25–0.30, and (c) 0.35–0.40 mm. Error bars represent the standard deviation.

long chains which are more or less entangled. The randomly arranged amorphous chains are hindered from freely moving past one another, even above T_g, due to dipole–dipole interactions between the ester groups. When a load is applied on the fiber, the dipole–dipole interactions and the taut tie chains between crystallites start to break,[20] whereupon the bulk of the amorphous chains start to extend. The strength and number of these bonds account for the initial modulus. The breaking of the taut tie chains results in transfer of the load to not fully extended tie chains and consequently increases the elongation of the fiber.

It is assumed, in this discussion, that overstrained taut tie chains are being ruptured and that no deformation of the crystalline areas is taking place as the fiber is exposed to axial deformation. According to Peterlin,[19] we can also

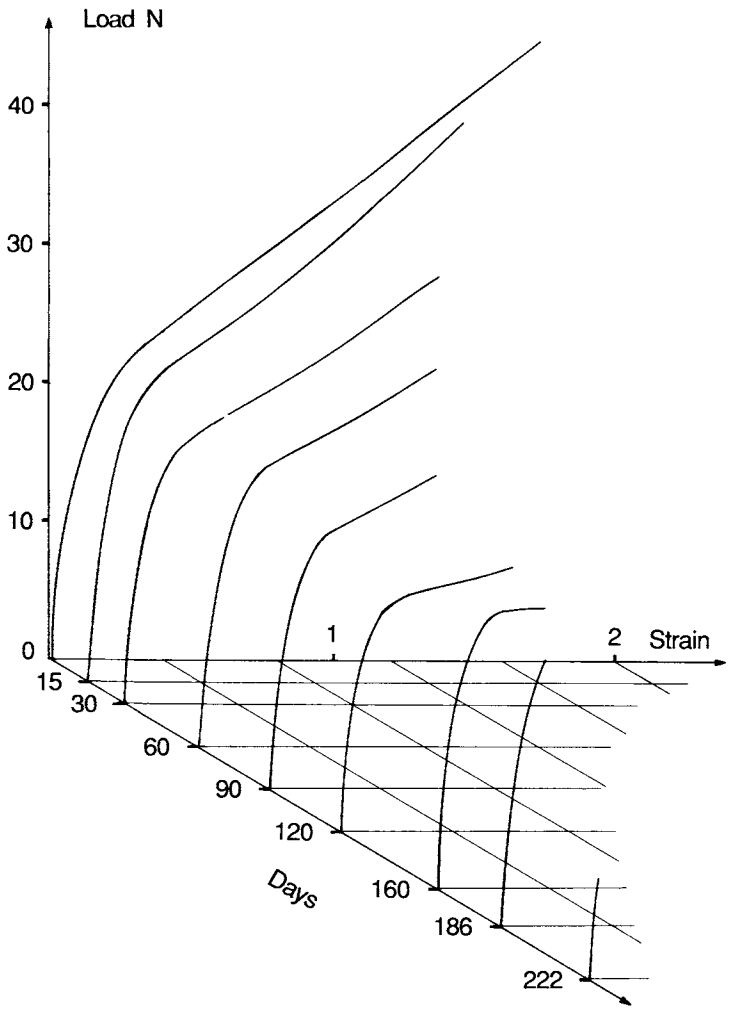

Fig. 6. Load-strain curves vs. the degradation time for an average specimen of the fiber with a diameter of 0.35–0.40 mm. Crosshead speed was set to 10 mm/min and the gauge length to 100 mm (L_0).

expect two other events to occur; a shear displacement of microfibrils and a protrusion of crystalline elements through the amorphous layer within the microfibrils. The shear displacement of microfibrils will, of course, lead to an overall elongation of the fiber, which is related to the length of the interfibrillar tie chains.

Both these aspects of fiber deformation can explain the large elongation after the yield point, which presumably is related to the number of long chains passing through several crystalline lamellas and amorphous regions. The probability of hydrolytic cleavage is higher for longer tie chains because these consist of a greater number of ester bonds than the shorter ones. If we assume this to be true, we can expect a reduction in the elongation after yield point which would also affect the load at break. As can be seen in Figure 4, the weight average molecular weight, sensitive to the fraction of the long polymer

chains, decreases by 50% during the first 60 days, a reduction which has a great effect on the load at break and on the elongation at break (see Figs. 2, 3, and 6).

If the rate of hydrolysis is more or less constant during the degradation, we can assume that the mechanical properties will be retained with only minor changes if it is a nonselective process (i.e., making no difference between loops, loose ends, or tie chains). If a random scission occurs in the amorphous phase, then the probability of hydrolytic cleavage of ester bonds in the tie chains would be less than in non-load-bearing chains because the latter will increase during degradation. This would lead to a lower degree of reduction in the mechanical properties, as can be seen in Figures 2 and 3 within the interval from 90 to 180 days. In the same period, the ratio M_w/M_n lies between 2.1 and 1.7, which probably indicates that random scission is taking place.

At the end of the degradation process, the fibers gradually become more brittle, and after 180 days the load at break rapidly starts to decrease. The number of tie chains has reached a critical minimum level, so that the load cannot be transmitted between the crystalline blocks.

In the early stage of degradation, we can see how the crystallinity slowly increases (Fig. 5), which can be related to the cleavage of ester bonds in the tie chains between the crystalline domains. This would result in a higher mobility which may cause further crystallization.[21]

CONCLUSION

The hydrolytic degradation of melt-spun fibers of PPL shows that the mechanical properties are lost over a period of 240 days, regardless of the three different fiber diameters which have been examined in this article. This shows that the hydrolysis is taking place not only on the surface but also in the interior of the fiber. The rapid loss of fiber strength and loss of elongation during the first stage of the degradation can be connected with the simultaneous decrease in M_w. As the crystallinity constantly increases during this period, we assume that the degradation is mainly taking place in the amorphous phase of the fiber.

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