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High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: thermal characterization and physical properties

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The miscibility of high molecular weight poly(L-lactide) (PLLA) with high molecular weight poly(ethylene oxide) (PEO) was studied by differential scanning calorimetry. All blends containing up to 50 weight% PEO showed single glass transition temperatures. The PLLA and PEO melting temperatures were found to decrease on blending, the equilibrium melting points of PLLA in these blends decreased with increasing PEO fractions. These results suggest the miscibility of PLLA and PEO in the amorphous phase. Mechanical properties of blends with up to 20 weight% PEO were also studied. Changes in mechanical properties were small in blends with less than 10 weight% PEO. At higher PEO concentrations the materials became very flexible, an elongation at break of more than 500% was observed for a blend with 20 weight% PEO. Hydrolytic degradation up to 30 days of the blends showed only a small variation in tensile strength at PEO concentrations less than 15 weight%. As a result of the increased hydrophilicity, however, the blends swelled. Mass loss upon degradation was attributed to partial dissolution of the PEO fraction and to an increased rate of degradation of the PLLA fraction. Significant differences in degradation behaviour between PLLA/PEO blends and PLLA/PEO/PLLA triblock-copolymers were observed. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Polymer blends containing biodegradable or hydrolytically unstable components have received much interest because of the ease with which their physical properties and degradation characteristics can be tailored[1–6]. These materials have attracted much attention[7,8] especially in relation to applications in disposables and biomedical uses.

With respect to polymer blends with biodegradable or hydrolytically unstable components we can distinguish two main types:

(1) Blends composed of degradable polymers. Examples are blends of poly(ε-caprolactone) with poly(L-lactide) (PLLA) or with poly(D(-)3-hydroxybutyrate). The degradation characteristics of these blends are not necessarily intermediate to the properties of the constituent polymers. It has been shown that mixtures of degradable polymers can be used to obtain materials with new degradation characteristics[1,2] and improved mechanical properties.

(2) Blends of a degradable polymer and a non-degradable polymer. Here the hydrophobicity of the nondegradable polymer and the miscibility of the polymers has great influence on the blend properties. Two examples of nonmiscible blends with hydro-

phobic nondegradable polymers are poly(propylene) with poly(ε-caprolactone) and poly(ethylene-*co*-vinyl alcohol) with plasticized starch. In these blends the nondegradable polymer disintegrates when the fraction of the degradable component is large enough. A different situation arises when the nondegradable polymer is very hydrophilic or even water soluble. Some blends of this type have been described, for instance mixtures of poly(ethylene oxide) (PEO) with PLLA or poly(D(-)3-hydroxybutyrate)[9,10]. However, no mechanical properties and degradation characteristics of these two blends were presented. In the case of PEO/PLLA blends, no conclusive evidence was given for their miscibility in the amorphous phase.

In this paper we present degradation characteristics, mechanical properties and thermal behaviour of blends of PEO and PLLA. PEO is a hydrophilic nondegradable polymer, while PLLA is a hydrolytically degradable but rather hydrophobic polymer. Both polymers are semicrystalline polymers. The glass transition temperatures of PEO and PLLA are, respectively, −54°C and 57°C, while the melting temperatures are close to 74°C and 186°C, respectively. As a result of blending PLLA with PEO, it is expected that the degradation rate of PLLA will be accelerated and the mechanical properties further improved.

In biomedical applications the use of PEO is of

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special interest because of its good biocompatibility[11,12] and its very low toxicity[13]. Blending with PEO could therefore also increase the biocompatibility of L-lactide polymers[14,15]

EXPERIMENTAL

Chemicals

All solvents were dried before use. Dichloromethane was dried and stored over calcium chloride, diethyl ether was dried and stored over sodium wire,

L-Lactide (Purac Biochem, The Netherlands) was recrystallized from dry toluene prior to use. High molecular weight PEO (MW 4×10^6) was purchased from Aldrich Chemie, Belgium. Poly(ethylene glycol) (PEG) with MW 20 000 was purchased from Merck, Germany. Drying was done by dissolving the polymers in a tenfold amount of dry benzene, followed by slow (azeotropic) distillation of benzene. After complete removal of benzene the polymer was further dried under vacuum for several hours at 100°C.

Polymerization

High molecular weight poly(L-lactide) (PLLA) with $M_v = 8 \times 10^5$ was synthesized by polymerization of 50 g L-lactide at 110°C for 100 h with tin(II)-2-ethyl-hexano-ate (Sigma, USA) as a catalyst. The monomer to catalyst ratio was 15 000. The polymerizations were carried out in vacuum-sealed and silanized glass ampoules. A PLLA/PEO/PLLA triblock-copolymer was prepared by polym-erization of a solution of 10 g poly(ethylene glycol) (PEG) with a molecular weight of 2×10^4 in 40 g of L-lactide for 180 h under the same conditions as the PLLA homopolymer.

Blend preparation

All blends were prepared in a nitrogen atmosphere. PLLA and PEO were dissolved separately in dichloro-methane to form 1 w/v % solutions. Predetermined amounts of the solutions were mixed and precipitated into a magnetically stirred five-fold volume of dry diethyl ether. After decanting, the polymer was dried in vacuum for several hours. The blends were stored under nitrogen over Sicapent® (Merck, Germany). Yields were between 95 and 98 weight%. The PEO/PLLA ratio in the blend was determined by n.m.r. Spectra were recorded on a 90 MHz Bruker WH90 with TMS as an internal reference.

Samples ($50 \times 6 \times 1\,\mathrm{mm}^3$) for mechanical testing and degradation experiments were machined from compression-moulded sheets ($50 \times 50 \times 1\,\mathrm{mm}^3$), moulded at 200°C for 7 min. The sheets were quenched in cold water and stored at 40°C under vacuum. Samples of the block copolymer of L-lactide and poly(ethylene glycol) were prepared in the same manner as the blends.

Differential scanning calorimetry

The samples for differential scanning calorimetry (d.s.c.) were sealed in aluminium pans under an argon atmosphere. Samples of 15–20 mg were used in the determination of the PEO/PLLA phase diagram. These samples were heated in a Perkin–Elmer DSC-2 to 220°C and kept at this temperature for 5 min. Subsequently, they were quenched in stirred, liquid nitrogen. At these low temperatures the quenched samples were transferred

to a Perkin–Elmer DSC-7 and stabilized at −150°C for 10 min. In the first run (run 1) the samples were heated from −150°C to 220°C at a rate of $20°\mathrm{C\,min}^{-1}$. After 5 min at 220°C, a non-isothermal crystallization run (run 2) was obtained at a cooling rate of $20°\mathrm{C\,min}^{-1}$ to 0°C.

In the isothermal crystallization experiments PLLA/PEO blend samples of 3–10 mg were used. Starting at room temperature, the samples were rapidly heated to 220°C. After 5 min at this temperature, the samples were cooled at the maximum cooling rate of $500°\mathrm{C\,min}^{-1}$ to a predetermined crystallization temperature (T_c) ranging from 90°C to 150°C. After 30 min at T_c the crystallized blends were again heated to 200°C at a rate of $5°\mathrm{C\,min}^{-1}$.

In vitro degradation

Test bars ($50 \times 6 \times 1\,\mathrm{mm}^3$) were degraded by hydro-lysis in physiological salt solutions at 37°C for periods of up to 60 days. Every two days the salt solution was changed. After a predetermined time the dimensions of the samples were carefully measured, after which they were dried to constant weight at 40°C.

Tensile testing

An Instron 4301 tensile tester was used to determine the mechanical properties of the blends. Tensile tests were performed at room temperature with a cross-head speed of $10\,\mathrm{mm\,min}^{-1}$ and a gauge length of 25 mm.

RESULTS AND DISCUSSION

Thermal properties of PLLA/PEO blends

Homogeneous blends were obtained by precipitating combined solutions in dichloromethane of high mole-cular weight PLLA and PEO into diethyl ether. This quenching technique has been shown to give good results with other polymers[16] and is comparable to rapid freezing of a combined solution[17]. We avoided preparing our PLLA/PEO blends by solution casting techniques as these methods can induce crystallization, even in systems that are normally amorphous[18]. PEO and PLLA are semicrystalline polymers. Because the PEO melting peak and the PLLA glass transition are located close to 60°C, calorimetric miscibility studies are somewhat complicated[19]. This is illustrated in *Figure 1*, where the thermograms of a number of these PLLA/PEO blends are shown.

Blends containing less than 20 weight% PEO prepared by this quenching procedure were found to be completely amorphous. In these samples no melting endotherm corresponding to the PEO fraction could be detected. Comparison of the heat of crystallization and the heat of fusion of the PLLA fraction, revealed the absence of a crystalline PLLA fraction also. In these amorphous samples, only single glass transition temperatures, T_g, intermediate between the glass transition temperatures of PLLA and PEO, could be determined.

The thermal characteristics of PLLA and PEO blends obtained by differential scanning calorimetry (d.s.c.) are summarized in the phase diagram presented in *Figure 2*.

In blends with 20–30 weight% PEO, no clear glass transition temperature could be distinguished owing to the recrystallization and melting process of the PEO fraction in the blend. Because of overlap of the PEO melting peak and the PLLA crystallization exotherm no accurate

PLLA crystallization temperatures could be determined for blends containing more than 20 weight% PEO.

The phase diagram of PLLA/PEO blends shows similarities to other miscible blends of semicrystalline polymers such as blends of poly(D(-)3-hydroxybutyrate) and poly(ethylene oxide) and blends of poly(ε-caprolactone) and poly(3,3-bis(chloromethyl)oxetane)[10,20]. The decrease in PLLA and PEO melting temperatures on blending and the uneventful change of T_g with blend composition of PLLA/PEO blends is comparable to that of these other systems.

The PLLA peak melting temperature shows a slight shift to lower temperatures when its proportion in the
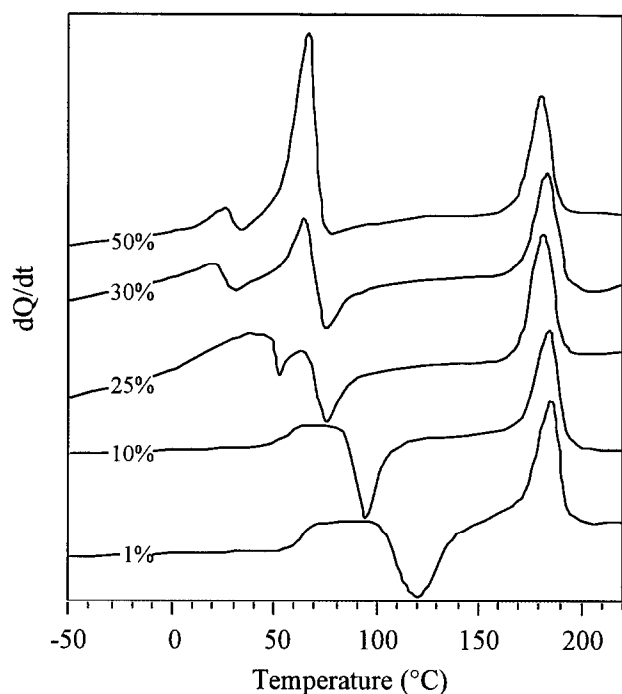
Figure 1 Thermograms of PLLA/PEO blends. The PEO concentration (weight%) is shown on the left of the figure. The curves are scaled to the PLLA melting peak
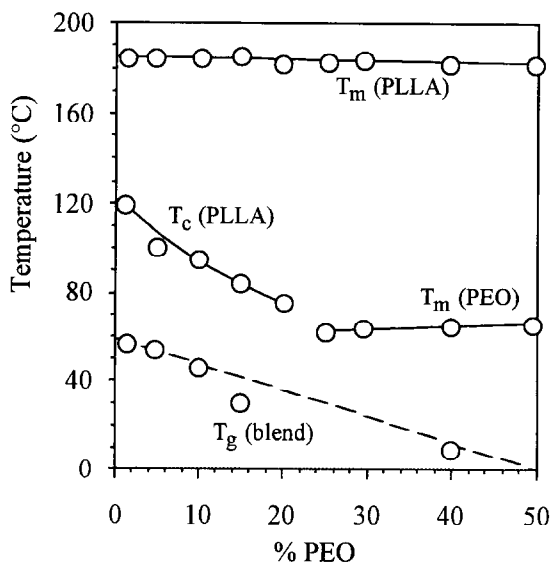
Figure 2 Phase diagram of PLLA/PEO blends. The dotted line shows the proportional dependence of T_g with the blend composition

blend decreases. The PLLA melting point decreases from 186°C for pure PLLA to 182°C for a blend containing 50 weight% PEO. The PEO peak melting temperature displays similar behaviour. The PEO melting temperature decreases from 74°C for pure PEO to 63°C for a blending containing 25 weight% PEO. (The high melting temperature found for pure PEO, 74°C, is indicative of very high molecular weight PEO and agrees well with literature data[21,22].) On blending semicrystalline polymers with other polymers, a decrease in melting temperature is indicative of miscibility of the polymers in the amorphous phase. The behaviour of the PLLA and PEO melting temperatures in the blends, therefore suggests miscibility of these polymers.

This phenomenon alone is not absolute proof of miscibility. For instance, isotactic polystyrene and poly(methyl methacrylate) are nonmiscible, isotactic polystyrene single crystals, however, do show a melting point depression when embedded in PMMA[23]. Conversely, miscible blends of PEO with M_n 13 000 and PMMA do not show a clear decrease in PEO melting temperature[22].

More direct proof of polymer miscibility in blends, can be obtained by observing the behaviour of the T_g with the blend composition. The glass transition temperatures of the pure polymers are 57°C for PLLA and −54°C for PEO[24]. In the blends only a single T_g, intermediate between T_g of PLLA and PEO was observed. The location of the blend T_g appears to be more or less proportional to the composition of the blend. This is a clear indication of miscibility of the two polymers[25,26].

The phase diagram in *Figure 2* also shows that the crystallization temperature (T_c) of PLLA decreases with an increase in the proportion of PEO. Crystallization of the initially amorphous PLLA fraction can take place only at temperatures above T_g (*Figure 1*), where the mobility of the PLLA chain is sufficiently high to reorganize into a new crystalline conformation. This shift of crystallization temperature parallelling the glass transition temperature is also observed with other miscible semicrystalline polymers. In mixtures of poly(ε-caprolactone) and poly(3,3-bis(chloromethyl)oxetane) the change in T_c with composition was shown to be parallel to T_g[20].

Similar effects are reported in semicrystalline polymers where the T_g is lowered by the presence of a solvent. The plasticizing action of the solvent results in increased crystallization at temperatures where normally crystallization is suppressed by the T_g of the amorphous phase[18].

Isothermal crystallization of PLLA/PEO blends

Further evidence of miscibility of PLLA and PEO in the amorphous phase was obtained by studying the melting point depression of the PLLA fraction according to the method of Hoffman and Weeks. The results are shown in *Figure 3*. The equilibrium melting point determined by the Hoffman–Weeks method is the melting point of an infinitely large crystal. By crystallizing the polymer at different crystallization temperatures the melting point of crystals with different fold lengths can be determined. Extrapolation to $T_m = T_c$ gives the equilibrium melting point of a perfect polymer crystal with infinite large fold length melting in a homogeneous matrix.

The equilibrium melting points of the PLLA fraction of these blends were determined to be 196°C for pure PLLA, 193°C for a PLLA/PEO blend containing 5 weight% PEO, 192°C for a blend containing 10 weight% PEO and 190°C for a blend containing 18 weight% PEO. The equilibrium melting point of PLLA determined here (196°C) is lower than a previously reported value[27], most likely owing to the very high molecular weight of the used PLLA polymer and the short crystallization time of 30 min.

The determination of the melting temperature at different crystallization temperatures can be complicated by a lamellar reorganization[18,22,28-32]. The thermograms in *Figure 4* indicate that some form of rearrangement also takes place in our PLLA/PEO system.

Lamellar rearrangement is a process that takes place during heating to high temperatures of a specimen crystallized at T_c. The dual melting peaks that result from this process were observed for our PLLA/PEO blends and also for pure PLLA. Lamellar rearrangement has been discussed extensively by Rim and Runt[18,19].

That the dual melting peaks observed in our blends are a result of lamellar rearrangement could be demonstrated by heating in the d.s.c. PLLA/PEO blends containing 20 weight% PEO and crystallized at 120°C at heating rates of 10, 20 and 40°C min⁻¹. At increasing scan rates, the lower temperature melting peak showed a strong shift to the higher temperatures, while the shift of the high temperature melting peak to higher temperatures was only marginal. This is in agreement with what is to be expected if rearrangement takes place.

The marginal shift of the high temperature peak is a thermal conductivity effect, intrinsic to d.s.c. The shift of the low temperature melting endotherm results from the rearrangement processes: when the scanning rate is low enough, lamellar rearrangement or recrystallization starts after the first original crystals are molten. The evolved heat of crystallization compensates the heat of fusion of the original crystallites and decreases the slope
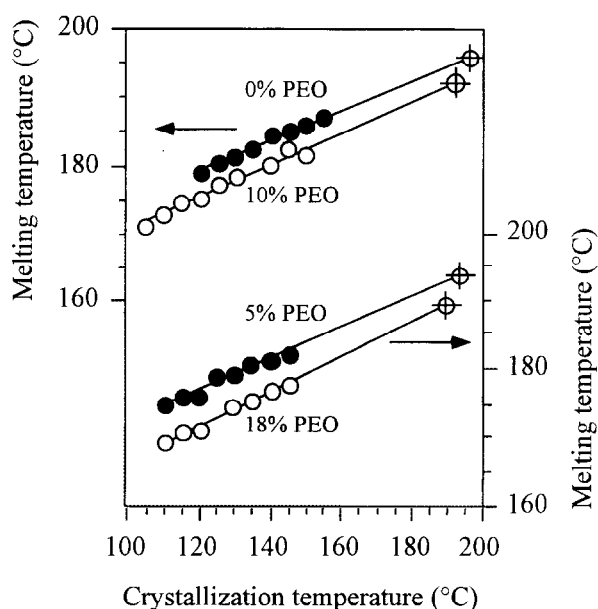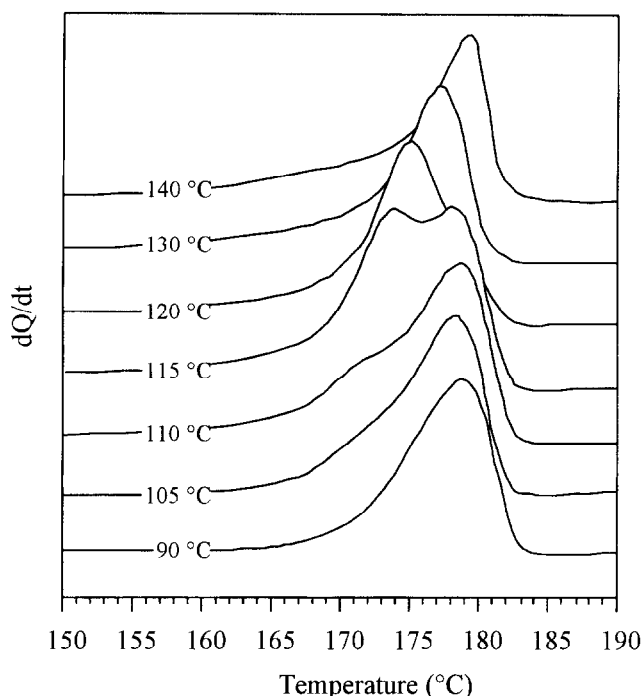
of the melting endotherm. In this way, a shoulder is formed on the melting endotherm of the original crystallites or an apparent low-temperature melting endotherm is formed. This lamellar rearrangement is a relatively slow process and shows a strong shift to higher temperatures when the scanning rate is increased[18,19] as observed for our PLLA/PEO blends. At higher scanning rates the high temperature endotherm decreases relative to the low temperature endotherm because the crystalline fraction is given less time to reorganize. The total heat of fusion of both endotherms does not change with scanning rate, during reorganization there is no change in the amount of crystalline material.

The heat of fusion of PLLA in PLLA/PEO blends depends on the crystallization temperature. In *Figure 5* the heat of fusion is plotted as a function of the crystallization temperature.

The maximum heat of fusion of pure PLLA is obtained at a crystallization temperature of 135°C, close to the maximum spherulitic growth rate at 130°C, determined by optical microscopy[27]. At higher temperatures, the heat of fusion decreases sharply. At these high temperatures, the undercooling is relatively low and the negative dependence of the rate of crystallization with temperature is controlled mainly by the secondary nucleation rate[10]. High crystallization temperatures or lower degrees of undercooling ($\Delta T = T_m^\circ - T_c$) result in a decrease in the secondary nucleation rate[33].

At high crystallization temperatures and low undercoolings, *Figure 5* shows that PLLA/PEO blends with increasing amounts of PEO show the lowest heats of fusion. Because it was shown that at low undercoolings the rate of secondary nucleation in a system of miscible polymers is smaller than that for the homo-polymers[33,34], it follows that PLLA and PEO are miscible polymers.

Figure 3 Hoffman–Weeks plots of PLLA/PEO blends. The equilibrium melting temperatures on the right of the figure are obtained by extrapolation to $T_m = T_c$

Figure 4 Representative thermograms of melt crystallized PLLA/PEO blend containing 10 weight% PEO. The crystallization temperature is shown on the left of the figure. The PLLA melting peaks are scaled to the same height

Figure 5 also shows that at higher undercoolings, before the maxima in the heat of fusion, the PLLA fraction becomes more crystalline with increasing PEO content. This is the result of the decrease of the T_g of the blend compared with T_g of PLLA. Because the factor $(T_c - T_g)$ becomes larger with increasing PEO concentration, the PLLA crystallization rate becomes higher at high undercoolings[35]. On a molecular scale one could also argue that dilution of PLLA will decrease the number of trapped entanglements or intercrystalline links and so enhance the rate of crystallization[36].

Mechanical properties and hydrolytic degradation of PLLA/PEO blends

The mechanical properties of PLLA/PEO blends containing up to 20 weight% of PEO were studied. Test samples were obtained by compression moulding at 200°C and subsequently quenching in ice water. This moulding procedure resulted in slightly yellowish, crystal clear sheets. The transparency of the sheets is indicative of the absence of significant amounts of crystalline material and the miscibility of the polymers in the melt. The tensile strength and elongation at break are shown in *Figure 6*.

Compared with compression moulded PLLA, blends containing up to 10 weight% PEO do not show large differences in mechanical properties. A small increase in the elongation at break and a small decrease in tensile strength can be observed. These properties change significantly when the PEO concentration is increased to 15 weight%. The elongation at break increases to 50% and the tensile strength decreases further to 35 MPa. Neck formation during elongation is observed in blends with a PEO concentration greater than 10 weight%. Blends containing more than 15 weight% PEO are very flexible and tough materials.

In the phase diagram of *Figure 2* it can be seen that at

20 weight% PEO, the glass transition temperature of the blend is close to room temperature. This blend has an elongation at break of more than 500%, and has a rubbery character.

Just as important as the initial mechanical properties, is the change in properties upon hydrolytic degradation. The change in tensile strength for several PLLA/PEO blends is shown in *Figure 7*. For comparison the behaviour of as-polymerized PLLA is also shown[37].
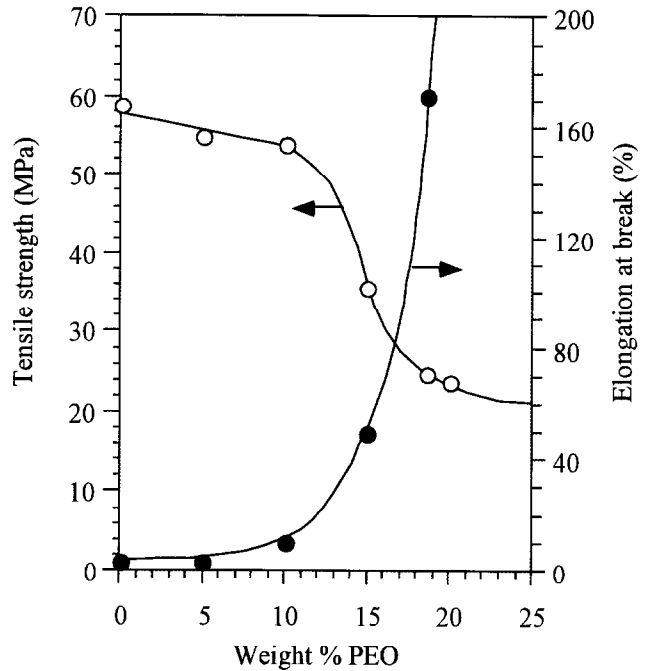
Figure 6 Tensile strength and elongation at break of compression-moulded high molecular weight PLLA/PEO blends
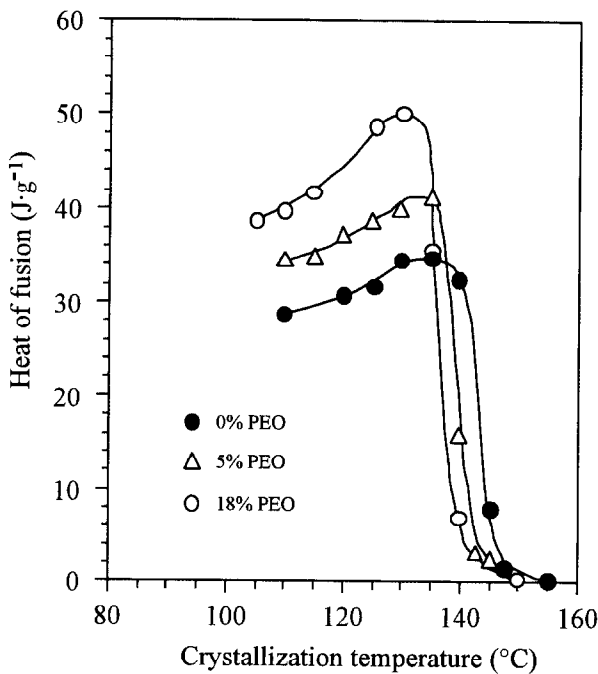
Figure 5 The heat of fusion of the crystalline PLLA fraction in PLLA/PEO blends as a function of the crystallization temperature. The crystallization time was 30 min
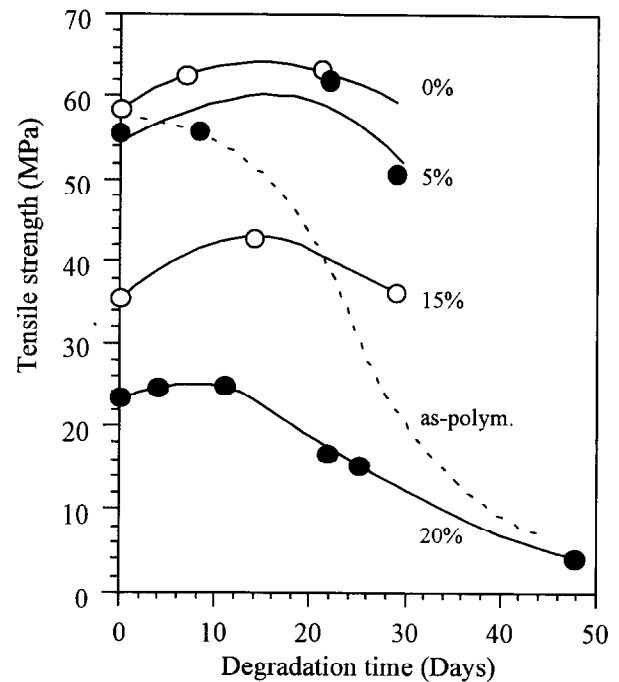
Figure 7 The tensile strength of compression-moulded PLLA and PLLA/PEO blends during hydrolytic degradation at 37°C. The dotted line shows the behaviour of as-polymerized PLLA (ref. 37)

The initial increase of the tensile strength during degradation is characteristic. Recrystallization and water absorption, which have been shown to increase the tensile strength and the toughness in several polymers, both occur during hydrolytic degradation and probably underlie this effect. Because of the very high crystallinity of the as-polymerized polymer, water absorption will be limited and significant recrystallization only takes place after 6 weeks of degradation[37]. This could account for the absence of an initial increase in tensile strength during degradation of as-polymerized PLLA.
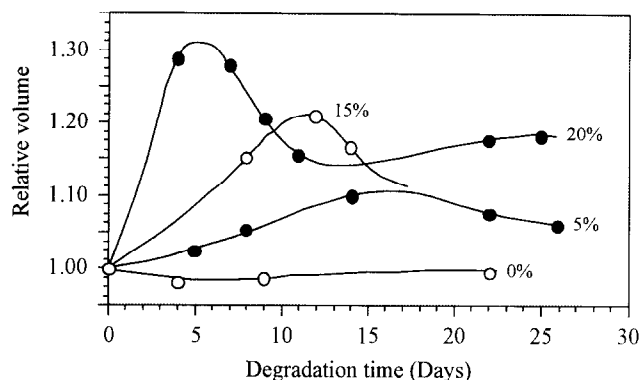

Figure 8 Change in volume during degradation of PLLA and blends of PLLA with PEO in water at 37°C

The change in volume during the first 3 weeks of hydrolytic degradation of PLLA and PLLA/PEO blends is shown in *Figure 8*. High PEO fractions will make the blend more hydrophilic, resulting in faster absorption of larger amounts of water. Absorption of large amounts of water, will result in a more rapid diffusion of PEO out of the blend, causing the relative volume to decrease again. The net result is that with increasing PEO contents in the PLLA/PEO blends, the maximum degree of swelling takes place at lower hydrolysis times.

When water is absorbed a ternary system PEO/water/PLLA will be formed. Although it is initially a miscible system the absorbed water will cause phase separation into a water/PEO-rich phase and a PLLA-rich phase (water being a non-solvent for PLLA). Water absorption of the phase-separated PEO fraction can cause high hydrostatic pressures in the blend material and lead to void formation. This can be observed by comparing the fracture surfaces of an undegraded and a hydrolytically degraded PLLA/PEO blend containing 20 weight% PEO (*Figures 9* and *10*). The undegraded blend shows a smooth, homogeneous and amorphous-like fracture surface, while the hydrolytically degraded blend shows the formation of layered structures with voids in between the layers.

In the hydrolytic degradation experiments, mass loss was observed for all PLLA/PEO blends. Some examples are shown in *Figure 11*. While compression-moulded PLLA and as-polymerized PLLA[37] did not show mass loss over a period of 30 days, all PLLA/PEO blends did.
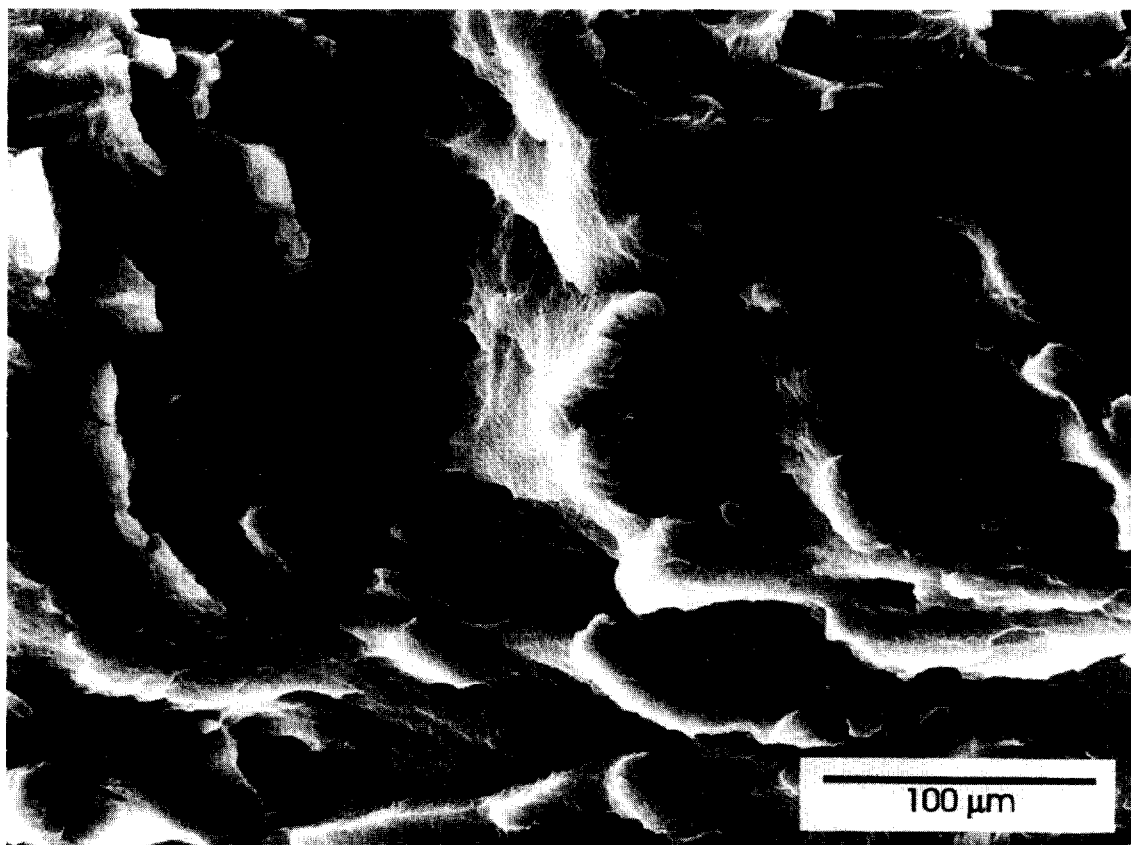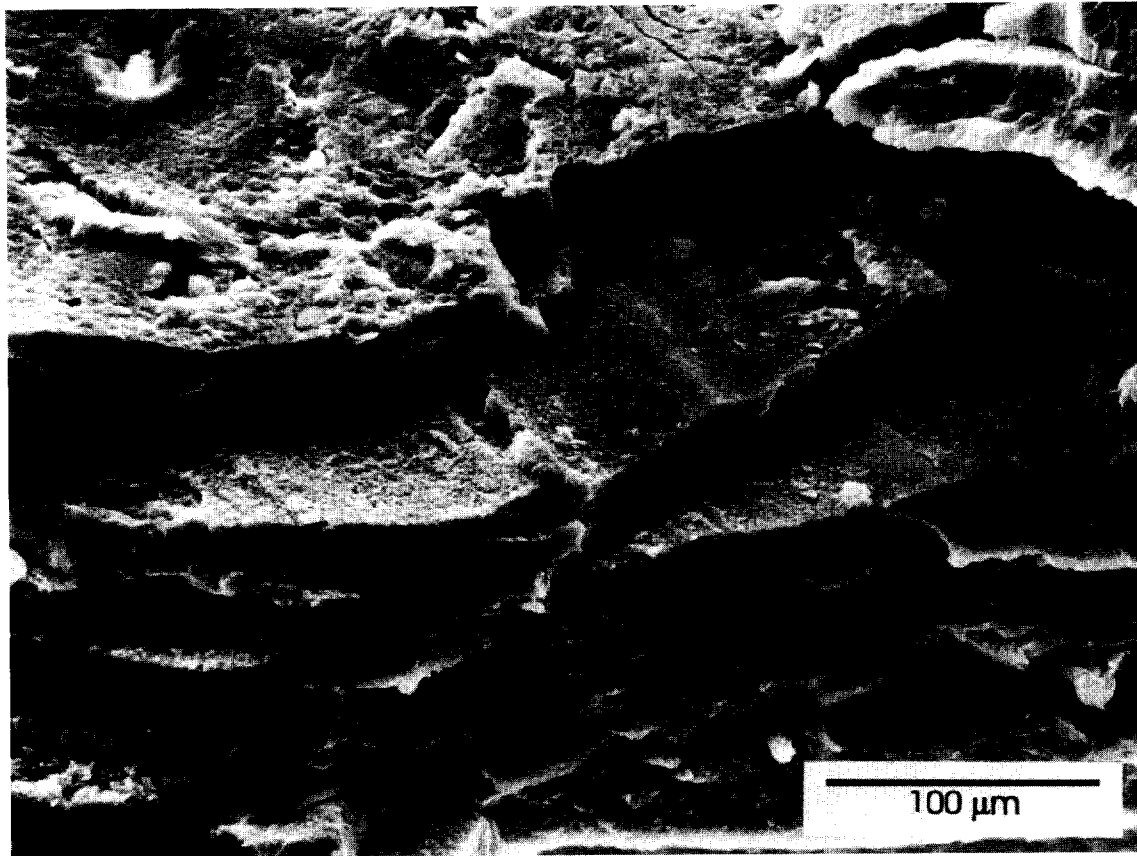

Figure 9 Scanning electron micrograph of the fracture surface of a PLLA/PEO blend containing 20 weight% PEO. The specimen was fractured in liquid nitrogen

Figure 10 Scanning electron micrograph of the fracture surface of a hydrolytically degraded PLLA/PEO blend containing 20 weight% PEO. The specimen was hydrolytically degraded at 37°C for 3 weeks and fractured in liquid nitrogen

Degradation time (Days)
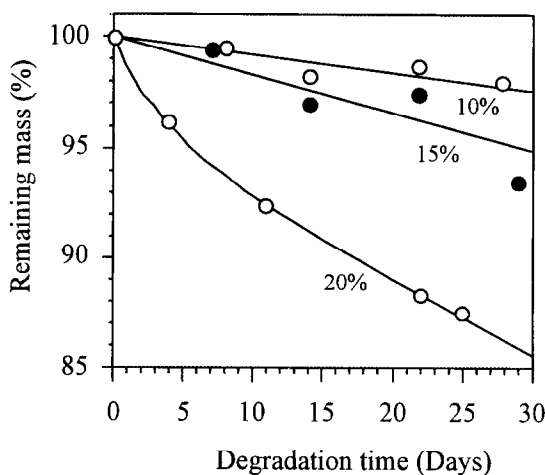
Figure 11 Mass loss of a number of PLLA/PEO blends during hydrolytic degradation. The initial PEO weight% is shown in the figure

Mass loss during hydrolytic degradation could be attributed to both dissolution of the PEO fraction and hydrolysis and subsequent dissolution of the PLLA fraction, as could be shown by n.m.r. analysis of hydrolytically degraded blends. For a PLLA/PEO blend initially containing 20 weight% PEO, the total mass loss after 22 days was 11.6%, it was found that the decrease in mass of the PLLA fraction in the blend was 5.3 weight% at that time. This increase in the rate of PLLA degradation is a result of the increased

hydrophilicity of the blend. PLLA main chain ester bonds in blends with PEO are more susceptible to hydrolysis than in the absence of PEO.

The appearance of the samples changes during degradation. Initially, the materials were completely transparent but turned white after several weeks of degradation. This whitening is the result of recrystallization of the sample, in combination with void formation owing to phase separation and dissolution of PEO.

In order to obtain better insight into the factors that influence the change in properties during degradation, a block copolymer of PEG and PLLA containing 20 weight% PEG was synthesized. Although properties of such block copolymers have been studied previously, the molecular weights of those materials were rather low— less than approximately 10^4. In order to obtain a high molecular weight block copolymer, L-lactide was polymerized with PEG with an MW of 2×10^4 as an initiator. The final block-copolymer had an intrinsic viscosity [η] in chloroform of $1.4 \, dl \, g^{-1}$ at 25°C. Assuming chloroform is a good solvent for this block copolymer, this corresponds to a molecular weight in the range of 5×10^4 to 10^5.

The thermal properties of this PLLA/PEO block-copolymer resembled very closely those of a PLLA/PEO blend with 20 weight% PEO. Other properties however, showed clear differences. A comparison of the change in tensile strength and elongation at break during degradation is shown in *Figure 12*.

In part, the differences between the PLLA/PEO blend and the PLLA/PEO triblock-copolymer can be attributed

to the lower molecular weight of the triblock-copolymer. However, despite this lower molecular weight, the triblock copolymer has a much higher elongation at break during hydrolytic degradation than the blend. In the block copolymer, the hydrophilic PEO and hydrophobic PLLA blocks are chemically bound together, hindering phase separation during hydrolytic degradation of a PEO/water-rich phase and subsequent loss in integrity, as shown for the PLLA/PEO blend containing 20 weight% PEO in the micrographs of *Figures 9* and *10*.

The difference in chemical structure between the PLLA/PEO blend and the PLLA/PEO triblock-copolymer is also reflected in the mass loss during hydrolytic degradation (*Figure 13*).

Mass loss during hydrolytic degradation of PLLA/PEO blends was, in large part, attributed to dissolution of the PEO fraction. Cohn showed that also in the case of block copolymers, the PEO fraction dissolved during

the first stage of the degradation[38]. The diffusion of PEO out of the triblock-copolymer matrix, however, involves hydrolysis of an ester bond in the PLLA-block closely neighbouring the PEO-block. This delays the diffusion of the PEO fraction when compared to the blend, as illustrated by the rate of mass loss shown in *Figure 13*.

CONCLUSIONS

High molecular weight PEO and PLLA are miscible in the amorphous state. A single T_g, intermediate between the T_g of the pure components, can be observed in all quenched blends. This T_g decreases with increasing PEO content. The equilibrium melting point of PLLA also decreases with increasing PEO concentration in the blend.

In contrast to the behaviour of pure PLLA, the crystallinity of PLLA in blends with PEO increases when crystallized at high undercoolings, and decreases at low undercoolings. Such crystallization behaviour can be expected for miscible blends where the noncrystallizing component has a lower T_g than the crystallizing component.

The mechanical properties of compression-moulded PLLA are significantly influenced by blending with PEO. The elongation at break shows a strong increase with PEO concentration, while the tensile strength decreases. These effects are most pronounced at PEO concentrations higher than 10 weight%. Hydrolytic degradation studies show that the initial degradation of the PLLA fraction in these blends is more rapid than that of unmodified PLLA. A major problem in the use of semicrystalline PLLA in biomedical applications is its very low degradation rate, while amorphous, noncrystallizable poly(D-lactide-co-L-lactide) (PDLLA) is glassy and brittle. Blending amorphous PDLLA with PEO could therefore be a convenient way to improve its mechanical properties and also to realize a more rapid degradation. Suitable applications of these blends could therefore be orbital floor reconstruction, nerve guides or barriers to tissue adhesion.
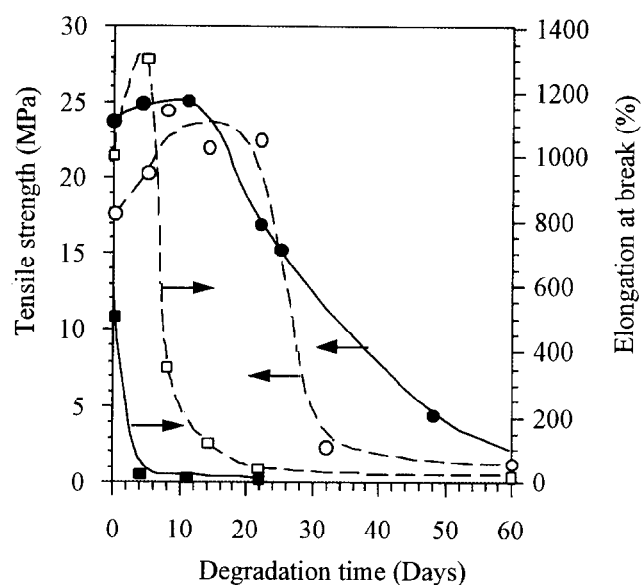

Figure 12 The tensile strength and elongation of a compression moulded PLLA/PEO blend containing 20 weight% PEO (■, ●) and for a PLLA/PEO triblock-copolymer containing 20 weight% PEO (□, ○)
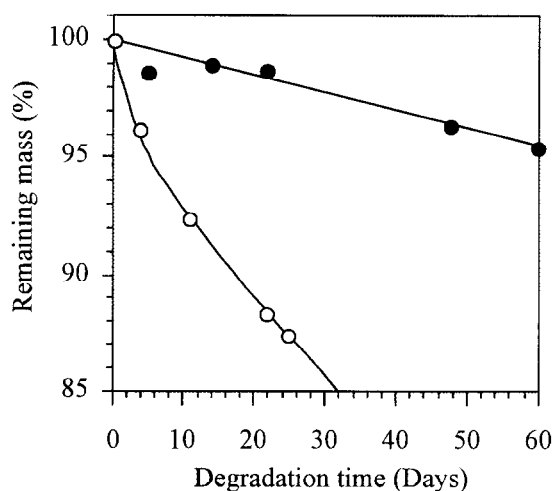
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Figure 13 Mass loss during hydrolytic degradation of a compression moulded PLLA/PEO blend containing 20 weight% PEO (○) and a PLLA/PEO triblock-copolymer containing 20 weight% PEO (●)

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