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U. Witt^a; R. J. Müller^a; W. -D. Deckwer^a

^a Biochemical Engineering, GBF, Gesellschaft für Biotechnologische Forschung mbH, Braunschweig, Germany

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BIODEGRADATION OF POLYESTER COPOLYMERS CONTAINING AROMATIC COMPOUNDS

U. WITT, R.-J. MÜLLER, and W.-D. DECKWER

Biochemical Engineering
GBF, Gesellschaft für Biotechnologische Forschung mbH
Mascheroder Weg 1, D-38124 Braunschweig, Germany

ABSTRACT

For investigation of the microbial accessibility of polyesters based on 1,3-propanediol, a series of different polymer structures (homo, random, and block copolymers) were synthesized by polycondensation of terephthalic acid, adipic acid, sebacic acid, and 1,3-propanediol. The alcohol component, 1,3-propanediol, can be obtained from a biotechnological process from glycerol, a surplus product of the oleochemical industry. Aliphatic dicarbonic acids can be derived from vegetable oils. Biodegradation was performed in different test systems. 1) Polyester films were exposed to an aerated liquid medium inoculated with eluates from soil. 2) For this test system, polymer films were buried in soil. Copolyesters exhibited significant differences in both tests. Furthermore, a clear influence of the polymeric structure as well as of the chain length of the aliphatic dicarbonic acids on the microbial accessibility was observed.

INTRODUCTION

Due to increasing problems in waste management, biodegradable polymers have become of new interest. In particular, a combination of biodegradability and the application of renewable sources offers the chance to make plastics part of natural cycles. Biologically synthesized and degradable polymers such as PHB show very specific properties; however, these are of limited variability. Preparation of

plastics from different monomers, on the other hand, offers the possibility to create biodegradable polymers with tailor-made properties. At GBF, a series of polyesters based on renewable sources has been synthesized [1]. For example, 1,3-propanediol, exclusively used as a diol component, is obtained from a biotechnological process using glycerol, a surplus product of the oleochemical industry (> 1 million tons per year) [2–4]. Aliphatic dicarboxylic acids can be derived from vegetable oils; for instance, by ozonolysis [5]. These types of polyesters, biodegradable through cleavage of ester bonds by hydrolysis, are especially appropriate to detect correlations between the structure of polyesters and their biodegradability.

BIOLOGICAL TEST SYSTEMS

In order to investigate the microbial accessibility of such polyesters, different polymer structures (homo, random, and block copolymers) were synthesized [1]. The degradation tests were carried out with polyester films of 100 μm thickness by 25 mm in diameter. The films were exposed to an aerated liquid medium at 30°C for 8 weeks. This medium contained only mineral salts to guarantee appropriate physiological conditions. Test media were inoculated with 1% (v/v) eluate from soil. Sterile blank tests were carried out to evaluate the resistance of the polymers against (chemical) hydrolysis. Figure 1 illustrates the correlation between melting temperatures (T_m) and weight losses after biodegradation of synthesized aliphatic polyesters based on 1,3-propanediol. A decrease of weight loss with increasing melting points of aliphatic dicarboxylic acids was observed for the homopolyesters synthesized from dicarboxylic acids with a carbon chain length larger than 2. However, these homopolyesters showed only limited applicability (brittle films, low melting temperatures), even though weight-average molecular weights were in the range of technical relevant polycondensates (approximately 25,000 g/mol). As an exception, the aliphatic polyester with an oxalic acid as the dicarboxylic component showed a surprisingly high melting point and good mechanical properties. In this case, further investigations with regard to the influence of chemical hydrolysis are in preparation. In order to improve the poor material properties of aliphatic poly-

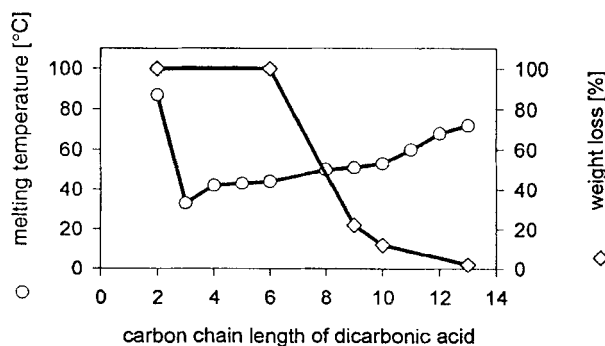


FIG. 1. Melting points and weight losses of aliphatic dicarboxylic acids based on 1,3-propanediol.

ters, statistical as well as block copolyesters were synthesized by polycondensation of 1,3-*propanediol*, *terephthalic acid dimethyl ester*, and the dimethylesters of aliphatic dicarbonic acid such as (*sebacic acid* and *adipic acid*, respectively). The melting temperatures of the statistical polyesters with *sebacic acid* as the aliphatic acid component (hereinafter called PTS) and the weight losses of the films after degradation are shown to depend on the composition in Fig. 2(a). Corresponding to the aliphatic materials, the rate of degradation decreases with an increase in melting temperatures. Indeed, from values of the molar fraction approximately larger than 0.3, the melting points and the mechanical properties drastically increased and no weight loss for the statistical polyester PTS 44:56 (molar ratio of *terephthalic acid*:*sebacic acid*) was observed. For a second set of statistical polyesters containing *adipic acid* as the aliphatic acid component (hereinafter called PTA), the same behavior with respect to the correlation between T_m and weight loss after biodegradation was observed (see Fig. 2b). In contrast to the statistical copolyester PTS 44:56, a block copolyester having a similar ratio of aromatic and aliphatic acid (48 mol% *terephthalic acid* and 52 mol% *sebacic acid*) showed a significant weight loss although the T_m (131°C) is comparable with that of the statistical polyester PTS 44:56, $T_m = 139^\circ\text{C}$ (see Fig. 3). Therefore, the clear influence of

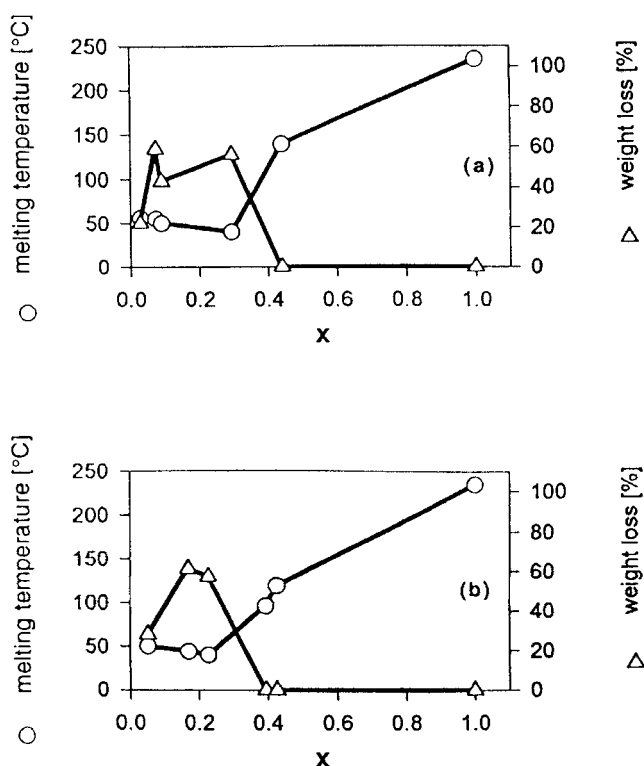


FIG. 2. Melting points and weight losses of statistical copolyesters containing 1,3-propanediol, terephthalic acid, sebacic acid (a), and adipic acid (b), respectively, as a function of molar fraction of terephthalic acid in the copolyester.

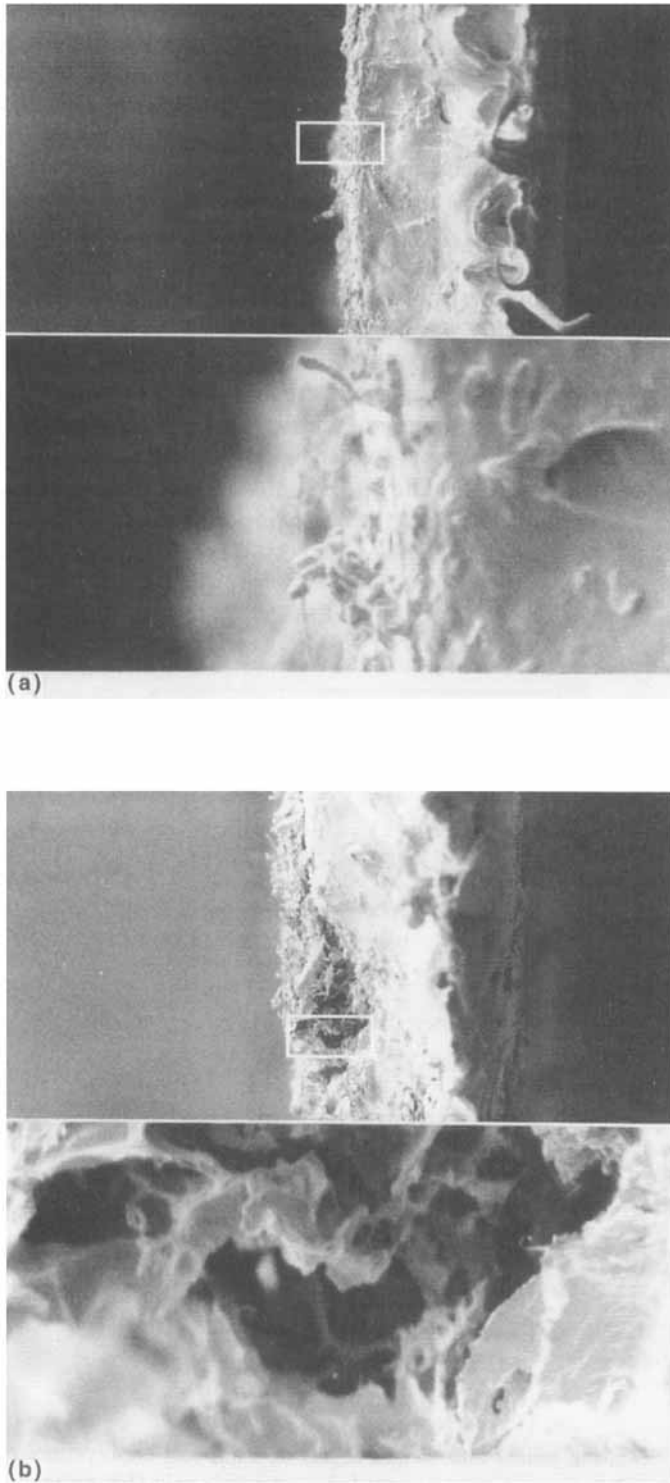


FIG. 3. SEM micrographs of a block copolyester film: (a) original film; (b) film after 4 weeks exposure to a liquid medium containing microorganisms from soil. Enlargement: above, 500-fold; below, 4000-fold.

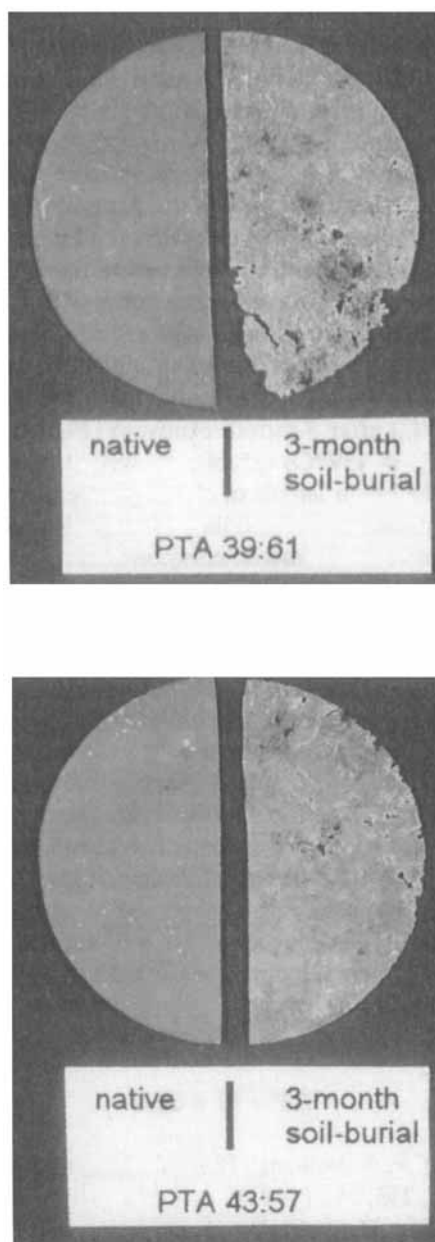


FIG. 4. Photographs of statistical copolyester films PTA 39:61 and (b) PTA 43:57 (native = original films).

polymeric structure on biological resistance becomes evident upon comparison of statistical and block copolyester, both exhibiting similar melting points and similar stoichiometric compositions. These findings show what type of polymer with regard to its sequential structure predominates biodegradability (whether yes or no) whereas the physical properties (e.g., T_m) of the polymers obviously affect the rate of an existing biodegradation (see also Fig. 1). Further investigations will concentrate on the question whether or not only the long aliphatic chains in the block copolyester are exclusively biodegraded and what the fate of the aromatic blocks is. Are they eventually left as a resistant biodegradation residue?

As described before, statistical polyester films with a molar fraction of terephthalic acid approximately larger than 0.3 showed no degradation in the liquid test media. In contrast, the polyester films buried in soil showed a significant weight loss (approximately 20%) for the statistical polyester PTA 39:61 ($T_m = 96^\circ\text{C}$) and PTA 43:57 ($T_m = 119^\circ\text{C}$) after 3-month exposure (Fig. 4), whereas the statistical polyester PTS 44:56 ($T_m = 139^\circ\text{C}$) exhibits no weight loss after soil burial over 6 month. Furthermore, the chain length of the aliphatic dicarbonic acid had an evident influence on the microbial accessibility of statistical copolyesters which have similar melting points and stoichiometric compositions.

CONCLUSION

This study revealed a dependence of biological accessibility on the sequential structure of polyester copolycondensates. For statistical copolyesters with a molar fraction of terephthalic acid approximately larger than 0.3, an adjustment of the optimum between physical properties and biodegradability appears to be feasible. Thus, controlling the biological properties of a plastic material by its chemical structure is a promising subject in the final design of biodegradable polymers. The significant differences in biodegradation observed by application of two different degradation tests elucidates the necessity to use well-defined laboratory tests as well as simulation tests. The latter will help to select natural degradation conditions for a final judgment of biodegradability.

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