

Biodegradation Behavior and Material Properties of Aliphatic/Aromatic Polyesters of Commercial Importance

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Copolyesters of aliphatic monomers with a defined amount of terephthalic acid recently have been shown to be biodegradable. This group of plastic materials exhibits very interesting material properties with regard to their technical application potential. A tensile strength of 25 N/mm² combined with elongations at break up to 1500% was achieved for BTA materials. Melting points varied from 80 to 140°C. Biodegradation rate under composting conditions were determined, showing typical erosion rates of films, in the range of 5 to 10 μm/week. The material properties and the degradation rate as well can be adjusted by the copolymer composition. Stretching of the polymer in the cold state leads to 10-fold higher mechanical strength of the material. The polyester chain can be extended to high molar masses, resulting in melt viscosities suitable, e.g., for melt below extrusion.

KEY WORDS: Biodegradability; poly(tetramethylene terephthalate)-co-(tetramethylene hexanedioate); 1,4-butanediol; terephthalic acid; adipic acid; use properties; copolyester; compost.

INTRODUCTION

In the last few years a new group of polymers, biodegradable plastics, has been of great interest. These plastics, which undergo controlled degradation by microorganisms present in the natural environment, can be applied, e.g., as packaging materials [1], in solving waste problems, or to provide new advantages during application (e.g., agricultural use). A number of commercial materials are already available on the market, but there are still some serious problems with this new class of plastics. First, the high prices must be mentioned. They range from about \$5 kg to more than \$10 kg for poly(3-hydroxybutyrate) (PHBs) polyesters. Furthermore biodegradable plastics still often do not provide optimal material properties, which is important for their application. Polycaprolactone (PCL)-based materials, for example, exhibit melting points of about 60°C. Hence, these materials are not usable at elevated tem-

peratures (e.g., hot beverages, exposure to sun light). Starch-based materials are often very sensitive to moisture conditions, dramatically reducing the mechanical properties in dry and humid environments, and migration of plasticizers has been observed in some cases.

Recently, we reported on a new group of copolyesters which combine both biodegradability and excellent properties [2, 3]. In addition, their price will be considerably lower compared to other biodegradable materials currently sold on the market. The copolyesters can be synthesized by conventional bulk condensation techniques from various aliphatic diols and a defined mixture of different aliphatic dicarboxylic acids with terephthalic acid as the aromatic component. These copolyesters exhibit acceptable thermal and mechanical properties above 35 mol% terephthalic acid (with regard to the total amounts of acid components), while the rate of biodegradation drops rapidly when more than about 55 mol% terephthalic acid is present. Thus, a range from about 35 to 55 mol% of terephthalic acid offers an optimal compromise between biodegradability and useful properties of the BTA copolyesters (1,4-butanediol/adipic acid/terephthalic acid). It is understood that by

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varying the aromatic fraction, the properties can be altered and thus adapted to desired applications.

Particular attention has been given to the biodegradability of potentially resistant aromatic oligomers which may arise during primary degradation of the polymer chain. Applying aromatic model oligoesters the degradation characteristics of the aromatic component were investigated with regard to its dependence on the polymer microstructure [4, 5]. It was observed that oligomers with more than three aromatic diester units are not attacked by microbes, probably due to their lack of bioavailability (solubility). For the range of compositions given above (e.g., 35 to 55 mol% of aromatic acid) the fraction of blocks having ≤ 2 aromatic repeating units is always above 90%, as a result of the random polycondensation process. At elevated temperatures (e.g., 60°C) larger oligomers have also been shown to degrade, indicating the total degradability of the materials under composting conditions.

This paper reports on some characteristic properties of BTA-copolyesters which are important for their manufacture and application. In addition, data on their biodegradation are provided, which allow the degradation rate of copolyesters of various compositions in a natural compost environment, to be predicted.

GENERAL PROCEDURES

Synthesis of Copolyesters

All copolyesters used in this study were synthesized by a conventional bulk polycondensation process

from 1,4-butanediol, dimethyl adipate, and dimethyl terephthalate, under vacuum in the presence of an acidic catalyst. Weight-average molecular masses of the copolyesters with different stoichiometric compositions were always in the range necessary for commercial applications. All materials were purified carefully by repeated solvent precipitation to remove traces of catalyst and low molecular weight compounds. Characteristic data on the synthesized copolymers are listed in Table I.

Polymer Characterization

Weight-average molecular weight (M_w) and polydispersity (M_w/M_n) were determined by size exclusion chromatography (SEC) using polystyrene standards for calibration. Differential scanning calorimetry (DSC) was applied to characterize the thermal behavior of the copolyesters (melting points (T_m) and heats of fusion (ΔH) were calculated from precipitated materials). Contact angles (Θ) were measured to characterize the hydrophobicity of the surface of the copolyester films.

The monomer composition of the BTA copolyesters was calculated from the appropriate peak integrals of the 600-MHz ^{13}C -NMR spectra. Details of the determination of the stoichiometric composition of BTA copolyesters were described earlier [4].

Tensile strength at break (σ_R) and elongation at break (ϵ_R) of polyester films were measured to characterize their mechanical properties, and melt flow indices (MFI) were determined as a measure of the melt viscosity, which is important for different processing techniques.

Table I. Compositions and Characteristic Properties of the Copolyesters

Polyester ^a	M_w (g/mol) ^b	M_w/M_n	T_m (°C)	σ_R (N/mm ²) ^c	ϵ_R (%) ^c	ΔH (J/g)	Θ (deg) ^c
BTA 31/69	43,100	1.9	79	7.8 ± 0.2	650 ± 50	7.7	57.9 ± 1.8
BTA 34/66	45,500	1.9	89	7.8 ± 1.6	440 ± 140	9.1	62.9 ± 1.2
BTA 36/64	43,800	2.0	93	8.9 ± 0.9	500 ± 130	12.0	68.3 ± 1.1
BTA 38/62	51,000	1.8	106	9.8 ± 0.8	430 ± 100	13.1	70.5 ± 1.4
BTA 39/61	47,100	1.9	110	12.1 ± 1.6	470 ± 100	15.6	71.6 ± 1.5
BTA 42/58	48,900	1.8	115	12.3 ± 1.3	450 ± 150	16.0	71.8 ± 2.2
BTA 44/56	45,000	1.9	119	13.9 ± 0.2	550 ± 100	17.5	74.3 ± 1.8
BTA 45/55	50,500	1.8	122	12.2 ± 1.2	380 ± 170	17.2	75.9 ± 2.2
BTA 47/53	49,500	1.8	129	11.7 ± 1.6	320 ± 120	21.4	79.6 ± 1.5
BTA 48/52	54,000	2.1	137	12.3 ± 0.1	180 ± 50	24.9	81.4 ± 0.9

^aStoichiometric compositions according to ^{13}C -NMR analysis [4]. The copolyesters are abbreviated BTA (1,4-butanediol, terephthalic acid, adipic acid). Their nomenclature is as follows: poly(tetramethylene terephthalate)-co-(tetramethylene hexandioate). The ratio of the two acid components (mol%) is noted after the abbreviation (e.g., BTA 39/61: 39 mol% terephthalic acid and 61 mol% adipic acid).

^bBased on polystyrene calibration.

^cDetermined by use of melt pressed films.

Biodegradation

To investigate the effect of aromatic content on microbial accessibility of BTA copolyesters, materials with different compositions were synthesized. The degradation experiments were carried out on melt-pressed polyester films 25 mm in diameter of different thicknesses. Two test systems were used: (a) a compost simulation test at elevated temperatures and (b) a solid-medium agar-plate test at elevated temperatures using an adapted microbial population.

MATERIALS AND METHODS

Synthesis of Copolyesters

1,4-Butanediol (Riedel de Haën), dimethyl adipate (Fluka), dimethyl terephthalate (DMT; Fluka), and zinc acetate (Fluka) were used without further purification. The highest available purities were used.

BTA copolyesters were obtained by transesterification polycondensation in the bulk state using dimethyl terephthalate, dimethyl adipate, 1,4-butanediol, and 0.1 wt% zinc acetate as the catalyst. The polymerization reactor was a 100-ml and round-bottom flask equipped with a leakproof stirrer, a nitrogen inlet, and a condensate collector with an air-locked vacuum system. Dicarboxylic acids were added in the appropriate stoichiometric compositions with an excess of 20 mol% 1,4-butanediol. The system was purged with nitrogen and the bath temperature was raised to 150°C to liquefy the monomer mixture. The bath was then heated gradually to 190°C and the pressure was reduced to 0.01 hPa within 8 h and maintained under those conditions for about 36 h with stirring. Copolyesters were purified by repeated dissolution in chloroform and precipitation in a 10-fold amount of ice-cold methanol. They were filtered, washed with methanol (p.a.), and dried under reduced pressure at room temperature for 48 h. The polyesters were obtained as white fibrous materials.

Other Polymers

PCL was used as unmodified material (Polyscience, Inc., Warrington, PA). The molar mass was determined to M_n 43,000 g/mol and the T_m to 59°C. PHB/V (charge: PO27) was kindly supplied by ICI Bioproducts and Fine Chemicals, Billingham, UK. The material had a HV content of 11.6 mol% and a molar mass of M_w 400,000 g/mol (data supplied by producer).

Characterization Methods

SEC was performed at room temperature with PL Phenogel columns (M_w range approx. 2000–80,000

g/mol—PL-Gel $5 \cdot 10^3$ Å, 7.5×300 mm; M_w range approx. 30,000–1,000,000 g/mol—PL-Gel $5 \cdot 10^4$ Å, 7.5×300 mm) at a flow rate of 1 ml/min HPLC-grade chloroform (Fluka) and a concentration of 1 mg/ml (100- μ l injection volume). A SDK Shodex RI SE-51 refractive index detector and a Gynkotek 300C HPLC pump were used. The system was calibrated with polystyrene standards from Polymer Laboratories (ranges of calibration were 710–85,000 and 23,000–990,000 g/mol when using the column PL $5 \cdot 10^3$ and PL $5 \cdot 10^4$ Å, respectively).

DSC was carried out at a heating rate of 10°C/min using a Perkin Elmer DSC 2C instrument.

^{13}C -NMR spectra were recorded at 300 K on a Bruker DMX 600 NMR spectrometer locked to the deuterium resonance of the solvent CDCl_3 . Spectral widths of 190.4 ppm were acquired at a digital resolution of 0.44 Hz with 30° pulse widths and 2-s relaxation delays. FIDs were multiplied with a Gaussian window function, chosen to give suitable resolution of signals at ca. 25 ppm before signal integration.

Contact angle measurements were performed using a Krüss G40 contact angle device with automatical video recording and program software version 6.1. Before performing the measurements the copolymer films were washed with ethanol and vacuum-dried for 24 h at room temperature. Each measurement was repeated 10 times.

Mechanical properties (tensile strength at break and elongation at break) were measured according to DIN 53455 using a Zwick 1425 universal test machine. Measurement of melt flow indices (MFI) was carried out according to DIN 53735 using a Zwick 4105 melt index device.

Film Preparation

Films of different thicknesses were prepared by melt-pressing using a constant-thickness film maker P/N 15620 (Sepatec). Disks of 25-mm diameter were obtained by punching out. The pressing temperature was chosen about 5°C below the melting temperature of the respective copolymer. Blown film production of BTA 39/61 and BTA 39/61-HMDI(II) used a Dr. Collin lab-melt below equipment filled with an extruder Y 30 mm \times 25 D and a three-zone screw with mixing and shearing aggregates. Blowup rates of BTA 39/61 and BTA 39/61-HMDI(II) were 1:1.5 and 1:2, respectively.

Biodegradation Tests

Microorganisms. Populations of microorganisms which grew on BTA 39/61 films during a 6-week compost simulation test were isolated from the polymer surface and used for preparation of an inoculum as follows.

Inoculum. The population of microorganisms grown on one BTA 39/61 film (diameter: 25 mm) was mechanically removed from the polymer surface and suspended in 2 ml sterilized buffer (0.7 g KH_2PO_4 , 0.7 g K_2HPO_4 , 1 L deionized water).

Solid Test Medium. Mineral salt medium according to DIN 53739 used for preparation of agar plates contained the following components (per liter): KH_2PO_4 , 0.7 g; K_2HPO_4 , 0.7 g; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.7 g; NH_4NO_3 , 1.0 g; NaCl , 0.005 g; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.002 g; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.002 g; and $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.001 g. Twenty grams of agar was added to 1 L of mineral salt medium. The suspension was autoclaved for 30 min at 120°C , then agar plates were cast.

Solid-Medium Agar-Plate Test. On each agar plate a 100- μl drop of the suspension of the population of adapted microorganisms was added, and on it one polymer film was placed. The plate was incubated for 2 weeks at 55°C . Afterward the partially degraded polymer film including a thin layer of agar was placed on a fresh agar plate and incubated again. This process was repeated once more. A change of agar plates after approximately 2 weeks was necessary because of drying-up of the agar.

Compost Simulation Test. For the compost simulation tests externally thermostated 3-L reactors were used. Each reactor was filled with 2 L of compost (approx. 4 months old, composting plant, Watenbüttel, Germany) and maintained at 60°C . Humidity of the compost was adjusted to 60% [6]. The test specimens were enclosed in small polyethylene nets, thus allowing better recovery of disintegrated samples. The system was aerated with preheated and water-saturated pressurized air.

After recovery from the test systems, the samples were washed with deionized water and dried under vacuum at room temperature for 24 h. Weight loss of the partly degraded materials was determined and calculated as specific degradation rates ($\text{mg}/\text{week} \times \text{cm}^2$).

RESULTS AND DISCUSSION

The purpose of modifying aliphatic polyesters by introducing an aromatic component (terephthalic acid) was to improve the thermal and mechanical properties of the materials, particularly with regard to their technical application. In Fig. 1 two important mechanical parameters, the tensile strength and the elongation at

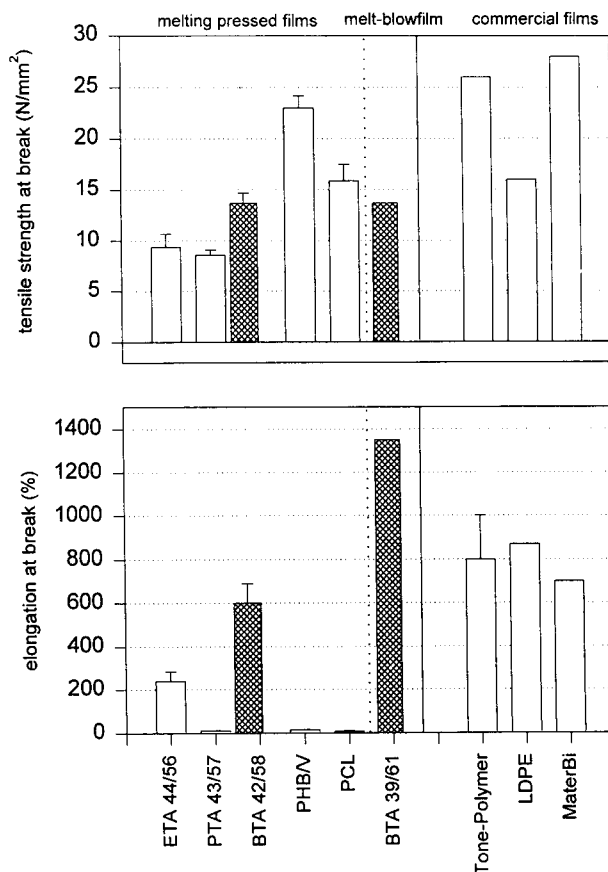


Fig. 1. Comparison of mechanical properties of selected aliphatic/aromatic copolyesters with commercial biodegradable plastics. Data for TONE polymer: TONE P-767, technical data sheet, Union Carbide, Danbury, CT, USA. Data for LDPE and MaterBi: MaterBi ZF02U, MaterBi-info, Novamont Group Montedison, Italy. All data for technically processed film in machine direction.

break, of three aliphatic/aromatic copolyesters with comparable contents of terephthalic acid but different diol components [1,2-ethanediol (ETA), 1,3-propanediol (PTA), 1,4-butanediol (BTA)] are shown. These copolyesters are compared with other biodegradable plastic materials and, additionally, LDPE as the most used conventional plastic.

In the left part of the plot the properties of laboratory melt pressed films, which usually do not reach the optimal properties of technically produced films, are compared. At a tensile strength of 10–15 N/mm^2 the copolyesters are comparable with the PCL sample. PHB/V, a bacterial polyester, exhibits a higher mechanical strength but, as shown by the elongation at break, is a rather stiff material. The flexibility of pure PCL is comparable with that of PHB/V. However, commercial PCL materials like the TONE polymers (Union Carbide, Danbury, CT) exhibit high tensile strengths (up to

40 MPa) and elongations at break in the range of 600 to 1000%. Probably this increase in material properties is achieved by compounding PCL with additives (M_w of TONE P-787, 58,000 g/mol; M_w of TONE P-676, 62,000 g/mol). Despite these improved mechanical properties, the melting point of the TONE polymers remains at about 60°C.

Within the copolyesters investigated, the best mechanical properties are found for BTA polymers. ETA and PTA have somewhat lower tensile strengths and significantly lower elongations at break. Therefore, the properties and biodegradability of BTA polymers were investigated in more detail. In the middle part of Fig. 1 material properties of a melt blow film (pilot scale) of BTA 39/61 are shown. The tensile strength is comparable to that of the laboratory-made samples; the elongation at break is much higher due to the more homogeneous material structure.

The right side in Fig. 1 presents selected data for commercial products, as given in the information sheets of the producers. The mechanical strength of the BTA copolyester is only somewhat lower than that of LDPE, but the PCL-based materials TONE-767 and MaterBi ZF02U exhibit a significantly higher tensile strength, which is about twice that of the BTA 39/61 copolymer. However, it can be supposed that this value can still be enhanced by optimization of the preliminary extrusion experiments with BTA and an optimized formulation with other components. Remarkable is the very high elongation at break of BTA copolyester, about two times higher than that of the other commercial products compared here.

The mechanical properties can be adjusted by the content of terephthalic acid in the copolymer (Fig. 2). In the range of compositions investigated, the tensile strength increases from about 8 N/mm² for BTA 31/69 to about 12 N/mm² for a material containing 39% terephthalic acid (laboratory melt pressed films). A further increase in the aromatic component up to 48% does not influence the tensile strength significantly. The behavior of the elongation at break is opposite. Up to 45 mol% terephthalic acid, the elongation at break is relatively constant, leveling off at about 500%, but drops rapidly when more than 45% aromatic compound is present; hence, the material becomes stiffer.

Other material properties are also affected by the copolymer composition. In Fig. 3 the melting point, heat of fusion, and contact angle are plotted against the composition of BTA copolyesters. All BTA materials are partially crystalline materials. The maximum of the crystallite melt peak in the DSC shifts from about 80°C for BTA 31/69 to 137°C for BTA 48/52. Thus, melting

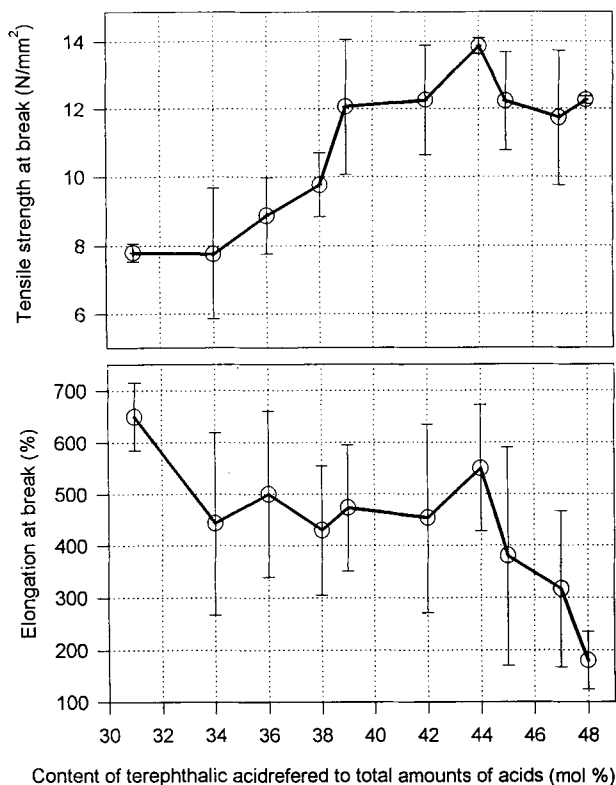


Fig. 2. Tensile strength and elongation at break of BTA copolyesters (melt pressed films); dependence on the terephthalic acid content.

temperatures are noticeably higher than, e.g., that of PCL and are in the range of PE. In parallel, the heat of fusion (peak area of the melt peak) increases linearly with the terephthalic acid content. The glass transition temperature of BTA 39/61 has been determined as -40°C. According to the rule of Boyer-Beaman [7] a range of T_g from -61°C (BTA 31/69) to -23°C (BTA 48/52) can be estimated for the BTA copolyesters.

Substituting the aliphatic acid partially by an aromatic acid increases the hydrophobicity of the plastic materials as measured by the contact angle, which increases linearly with the content of terephthalic acid (Fig. 3).

Optimizing the material properties by altering the copolymer composition, one has also to take into account the biodegradability behavior, because the rate of biodegradation also strongly depends on the fraction of aromatic compound in the material. Figure 4 demonstrates the behavior of three BTA copolyesters with different stoichiometric compositions in a compost environment (left side). The rate of biodegradation, expressed as weight loss per week and surface area, first increases with the degradation time and then tends to stabilize at a constant level. This can be explained by

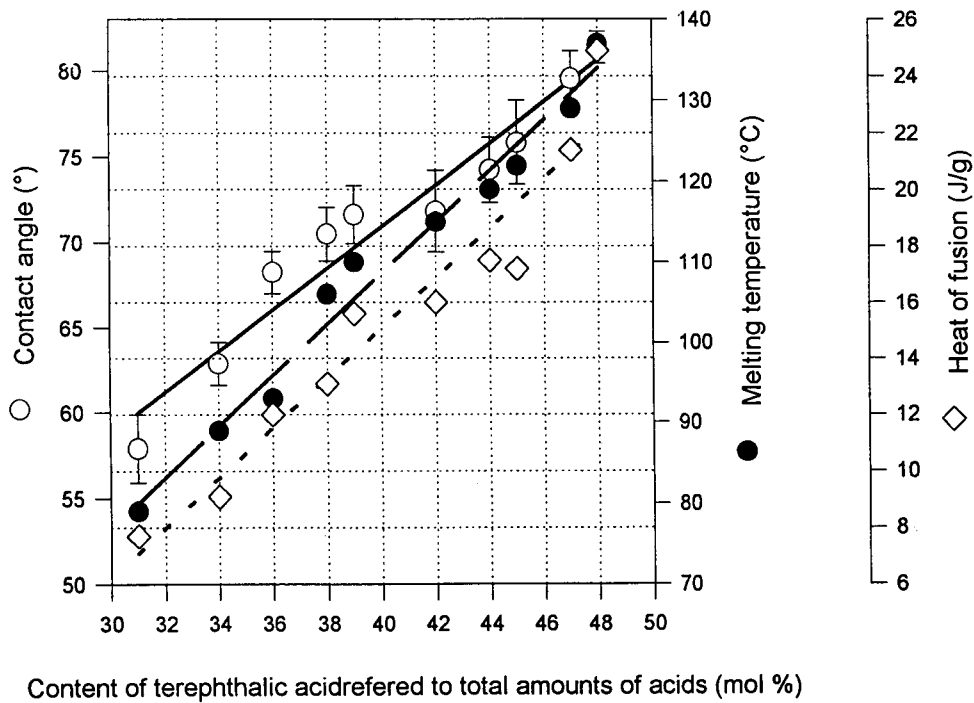


Fig. 3. Contact angle (hydrophobicity), melting point, and heat of fusion for BTA copolyesters; dependence on the terephthalic acid content.

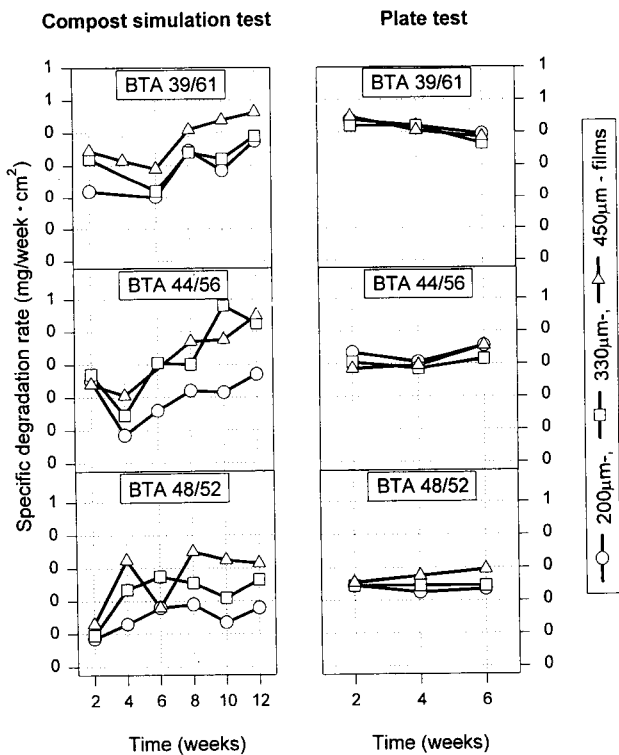


Fig. 4. Rates of biodegradation of BTA copolyesters in a compost simulation test and agar-plate test with preadapted microorganisms.

an adaption phase of the microbial population around the films. Microorganisms able to degrade the BTA material have to multiply and finally dominate the rest of the population. The average rate of biodegradation decreases with increasing terephthalic acid content. A clear influence of the film thickness could not be observed and was also not expected because the enzymatic degradation of solid materials usually is a surface erosion process. Some deviations between the different films may be caused by differences in the contact of films and compost. On the right side of Fig. 4 results of biodegradation tests on agar plates with a prescreened consortium of microorganisms are shown. The reproducibility of these tests is much better than that of the compost simulation tests. The degradation rates achieved were approximately constant over the time investigated and had comparable values to the compost simulation test after the adaption phase (for the plate tests, it was assumed that degradation takes place only on the one side of the film that has contact to the agar). The corresponding average degradation rates are listed in Table II. The agar-plate tests with prescreened organisms from a compost environment reflect the degradation behavior in a real compost system very well but offer much better reproducibility of the results. Additionally, recovery and

Table II. Average Specific Degradation Rates During Compost Simulation Test and Plate Test of BTA Copolyester Films of 200, 330, and 450 μm in Thickness

Polyester	Specific degradation rates ($\text{mg}/\text{week} \times \text{cm}^2$)	
	Compost simulation test ^a	Plate test ^b
BTA 39/61	0.75 ± 0.12	0.82 ± 0.06
BTA 44/56	0.69 ± 0.20	0.63 ± 0.06
BTA 48/52	0.49 ± 0.15	0.50 ± 0.05

^aRates between the 8th and the 12th week.

^bRates between the second and the sixth week.

analysis of residual material and intermediates are much easier on agar plates than in the complex compost medium.

Using this improved "compost simulation test on agar plates," the degradation rate in terms of a surface erosion rate ($\mu\text{m}/\text{week}$) was determined for the whole range of BTA copolyesters investigated (Fig. 5). Materials with 31 mol% terephthalic acid exhibit a degradation rate of about $10 \mu\text{m}/\text{week}$, decreasing to $5 \mu\text{m}/\text{week}$ for BTA 48/52. From these results it can be estimated, that a BTA 39/61 film (e.g., $100\text{-}\mu\text{m}$ thickness) which combines a high tensile strength with a high value of elongation at break would be degraded in a compost system within 6 to 7 weeks (assuming an erosion rate of $7.5 \mu\text{m}/\text{week}$ from both surfaces of the film). Usually

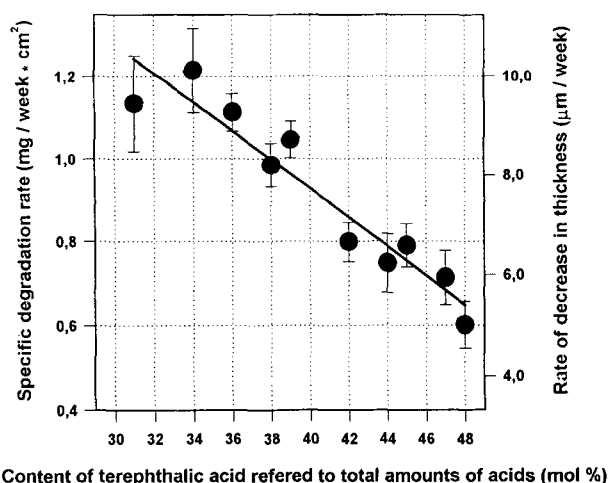


Fig. 5. Biodegradation rate of BTA copolyesters in an agar-plate test with preadapted microorganisms; dependence on the terephthalic acid content.

much thinner films are used, e.g., for packaging purposes.

One outstanding property of the BTA copolyesters is their increase in mechanical strength after elongation [8, 9]. Tensile strength at break can be enhanced dramatically by stretching the material below the melt temperature. In Table III, characteristic mechanical data on fibers which had been stretched at room temperature by hand are given. Tensile strengths of about $160 \text{ N}/\text{mm}^2$ for stretched BTA 39/61 (which is about eightfold the value of the unstretched material) were observed. At these high values of tensile strength the copolyester still exhibits an elongation at break of about 150%. The biodegradability is not affected by the stretching process. This property makes BTA copolyesters extremely interesting for, e.g., fiber applications.

Although molar masses of $50,000 \text{ g}/\text{mol}$ with corresponding MFI ($110^\circ\text{C}/10 \text{ kg}$) values of ca. $5 \text{ g}/10 \text{ min}$ were obtained by conventional polycondensation techniques for the BTA copolyesters, for some applications higher melt viscosities, and hence higher molar masses, are necessary (e.g., for blown film production) [10, 11]. Such an increase in molar masses cannot be achieved by pure polycondensation techniques for technical and economical reasons. One method to increase the molar mass of polyesters is chain extension with diisocyanates as coupling reagent. For the BTA copolyesters it was possible to synthesize materials with weight-average molar masses up to $230,000 \text{ g}/\text{mol}$ by adding hexamethylenediisocyanate to the polymer melt at the end of the polycondensation process without any intermediate recovery of the prepolyesters (Table IV) [12]. This diisocyanate reacts within a few minutes with the hydroxyl end groups of the polyesters. Average molecular mass and molecular mass distribution depend strongly on the mixing characteristics during addition of the diisocyanate to the polyester melt.

In Fig. 6 the size exclusion chromatogram of a chain-extended BTA copolyester is shown. The complete BTA prepolyester is shifted to higher molecular weights; a shoulder of very long polyester chains can be

Table III. Tensile Strength at Break and Elongation at Break of Hand-Stretched Fibers of BTA 39/61

Diameter of handstretched fiber (μm)	σ_R (N/mm^2)	ϵ_R (%)
300 ± 20	88 ± 0	274 ± 29
140 ± 20	164 ± 4	151 ± 15

Table IV. Weight-Average Molecular Weights, Polydispersity, and Melting Points of Chain-Extended BTA Copolyesters Synthesized from BTA Prepolyesters by Addition of Different Amounts of DMDI

Prepolyester			Chain-extended copolyester			
M_w (g/mol)	M_w/M_n	HDMI addition (%)	Sample designation	M_w (g/mol)	M_w/M_n	T_m (°C)
46,000	1.9	1.0	BTA 39/61-HMDI (1)	125,500	3.9	108
50,000	2.1	1.5	BTA 39/61-HMDI (2)	168,500	3.7	109
48,000	2.1	2.0	BTA 39/61-HMDI (3)	232,300	4.2	107

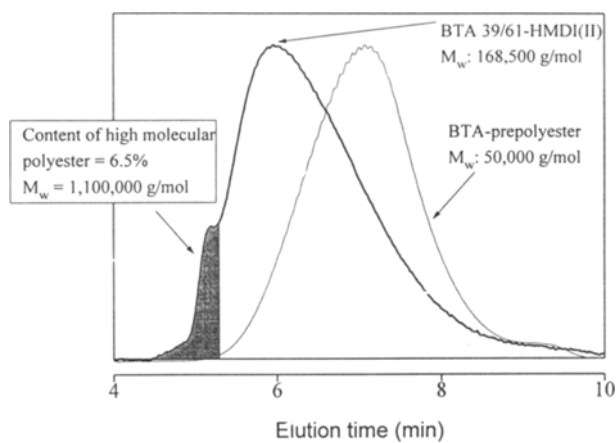


Fig. 6. SEC chromatogram of a BTA copolyesters and a chain-extended BTA copolyester.

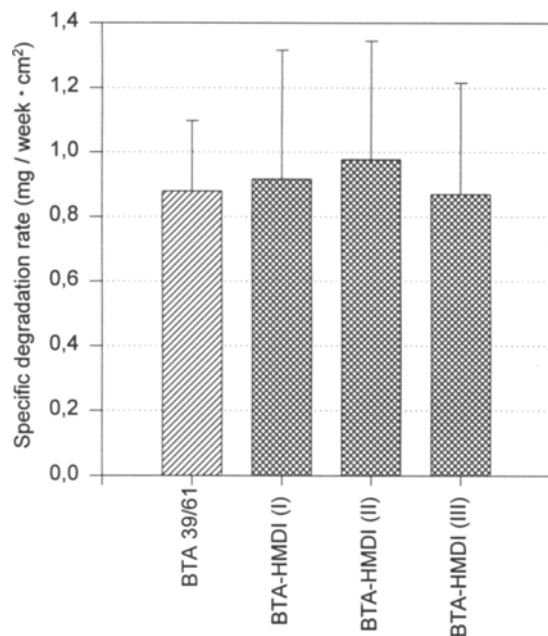


Fig. 7. Biodegradation rates of chain-extended BTA copolyesters in a compost simulation test.

observed. For BTA 39/61-HMDI(II) with an weight average molar mass of 168,500 g/mol a melt flow index MFI (190/5) of 3.1 ± 0.1 g/10 min was achieved, making this material suitable also for blown film production. With this technique a blown film was obtained (pilot experiment; blow ratio, about 1:2) with a tensile strength of 25 N/mm² and an elongation at break of still 900% (extrusion direction).

A very important question was how the chain extension of this aliphatic/aromatic copolyester influences the degradation behavior. The data in Fig. 7 illustrate that no significant change in the degradation behavior is observed for the BTA copolyesters in a compost simulation test. This corresponds with results of Tokiwa *et al.* [13] for pure aliphatic polyester systems.

CONCLUSIONS

BTA copolyesters are a group of new biodegradable plastics of wide commercial application potential. The following facts argue for their successive use as biodegradable materials.

- BTA copolyesters can be synthesized from cheap and widely available bulk chemicals by conventional technical processes. No new investments for production plants are necessary and it is anticipated that the price of the material will be significantly lower than the costs of other biodegradable plastics currently available on the market. Prices of \$2–4/kg are discussed, depending on the production scale.
- Their mechanical and thermal properties can be varied to some extent and are basically comparable to those of polyethylene materials. Melting points from about 80 up to 140°C can be obtained and tensile strengths of unoriented films

reach 20 N/mm². With an elongation at break of up of 1500%, this material is well suited for production of flexible films. The material can be stretched in the cold state, which is important for the production of fibers, tapes, or bidirectionally oriented films. By this treatment the mechanical strength can be increased by a factor of 10. Chain extrusion by polyaddition reactions leads to high molar mass materials with melt viscosities also sufficient for melt blown extrusion.

- The rate of biodegradation can be influenced by the copolyester composition. With degradation rates of up to 10 μm/week (referred to one surface), films will be degraded within the usual composting procedures [14].

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