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Degradation Kinetics of Biodegradable Fiber Composites

A. Keller,[1,5] D. Bruggmann,[1] A. Neff,[2] B. Müller,[3] and E. Wintermantel[3,4]

In a composite, fast degradable fibers determine the degradation of the slowly degradable matrix. Such biodegradable composites consisting of degummed hemp fibers and a polyester amide matrix were produced with fiber mass fractions between 0 and 0.48. The hot-pressed plates, 1-mm thick, were incubated in a standard soil. The degradation kinetics was quantified by the measurement of CO_2 production. Furthermore, after termination of experiment, the carbon balance was uncovered. The results were fitted to an exponential law taking into account the degradation of fibers. The increased amount of pores realized by high fiber contents induces pronounced degradation. The degradation is fully characterized by the time constant τ, which is correlated to the fiber mass fraction. The model allows to predict the degradation kinetics of composites with a few well-defined experiments.

KEY WORDS: Polyester amide; hemp fiber; composite; biodegradation; carbon balance.

INTRODUCTION

Increasing environmental awareness and decreasing dump space lead to the search for new polymer recycling and disposal possibilities [1, 2]. Regarding the reduction of polymer waste, compostable, biologically degradable polymers represent a promising alternative to conventional plastics. Recently developed biodegradable polymers are used to produce compostable bags and packaging materials [3, 4]. If fiber reinforcement is applied, these materials have sufficient mechanical properties to be used as lightweight construction materials. In particular, bast fibers, such as hemp or flax, are suitable for polymer reinforcement without the loss of materials' biodegradability. Their weight specific mechanical properties are comparable to those of glass fibers [5–8]. With respect to glass fibers, however, the bast fibers are less abrasive, which results in reduced tooling equipment costs and higher productivity. For applications of biodegradable polymers, where the material has to be disintegrated in soil, a well-defined degradation behavior is generally required. Biodegradable plant pots and cultivating pots used in horticulture, for example, have to fulfill standards regarding mechanical properties, surface quality, water permeability, and degradation kinetics. To adapt their degradation behavior perfectly to these standards, further research and development is required [9]. One possibility to influence the degradation is to incorporate natural fibers into the polymer pots. These fibers should accelerate the disintegration if they degrade much faster than the matrix polymer. Here, the fibers create an increased effective surface accessible to microorganisms. Consequently, the fiber content controls the disintegration. The present communication elucidates the relation between fiber mass fraction and degradation velocity using the polyester amide hemp–fiber composite. The results are the basis of a model, which precisely predicts the degradation on the basis of a few well-defined experiments.

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[1] Swiss Federal Research Station for Agricultural Economics and Engineering, CH-8356 Taenikon, Switzerland.

[2] Swiss Federal Laboratories for Materials Testing and Research, CH-9014 St. Gallen, Switzerland.

[3] ETH Zurich, Biocompatible Materials Science and Engineering, Wagistrasse 23, CH-8952 Schlieren, Switzerland.

[4] Technical University of Munich, Central Institute for Medical Engineering, Boltzmannstr. 15, D-85748 Garching, Germany.

[5] To whom all correspondence should be addressed. Telephone +41-52-368-3131; fax: +41-52-365-1190; email: andreas.keller@fat.admin.ch

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MATERIALS AND METHODS

Composites

The degradable polyesteramide, BAK 2195, manufactured by Bayer AG (Germany), was chosen as the matrix material. For reinforcement, hemp fibers degummed by steam explosion were supplied by Institut f. Angewandte Forschung (Reutlingen, Germany). Both, the fibers and the polymer were vacuum dried ($p = 100$ mbar) at a temperature of 60°C during 16 h. Subsequently, they were compounded with a corotating twin-screw extruder (Brabender PL 2100-6). Table I gives the processing parameters. The extruded composites were air cooled and granulated. The composite granules were formed to plates of 1-mm thickness in a standard hot-pressing process. These plates were cut into specimens 65-mm long and 10-mm wide. The fiber mass fraction X_{fiber} of the specimens was calculated using the nitrogen mass content X_N measured by means of elementary analysis (LECO CHN-900) according to Eq. (1):

$$X_{fiber} = \frac{X_{Ncomposite} - X_{Nmatrix}}{X_{Nfiber} - X_{Nmatrix}} \tag{1}$$

Besides the bare fibers, fiber mass fractions between 0 and 0.48 were obtained. The fiber lengths and their distribution in the composites were determined after dissolving the samples in meta-cresol at room temperature [10]. The fiber lengths varied between 0.3 and 1.6 mm for all samples with a mean value of 0.74 mm. Powder of glucose and regenerated cellulose (Avicel) were selected as reference material.

Measurement of Carbon Dioxide Production

In order to characterize biodegradation kinetics, the production of carbon dioxide during degradation was quantified. Figure 1 shows the scheme of the experimental set up. The soil columns were filled with 300 g of soil mixture and 15 g of specimens. The soil mixture was composed of 10% ripe compost and 90% peat (FRUX ED 72). This mixture was passed through a sieve (mesh size 3 mm) and stored at a constant temperature of 28°C and a relative humidity of 97% for 30 days. The water content of the soil was adjusted to 60% of its maximal water absorption capacity. Most active biodegradation is observed at a C/N ratio between 20/1 and 10/1 [11, 12]. The carbon content of the specimens investigated by means of elementary analyses was found to be 42.6–58.5 wt.%, depending on the fiber mass fraction. To adjust the C/N ratio, 21.8 g 2.6 *M* sodium nitrate was added to the soil of each column. The columns were continuously ventilated with humidified oxygen with a gas flow of 10 ml min^{-1}. The exhaust was passed through sodium hydroxide solutions (first bottle 0.8 *M*, second bottle 0.25 *M*), which adsorbed the carbon dioxide produced during biodegradation (Eq. 2).

Table I. Compounding parameters of the co-rotating twinscrew extruder.

Screw diameter	25 mm
L/d ratio	22 D
Die diameter [mm]	6
Temperatures [°C] (zone 1–5)	190/185/180/180/180
Screw speed [min^{-1}]	60–90

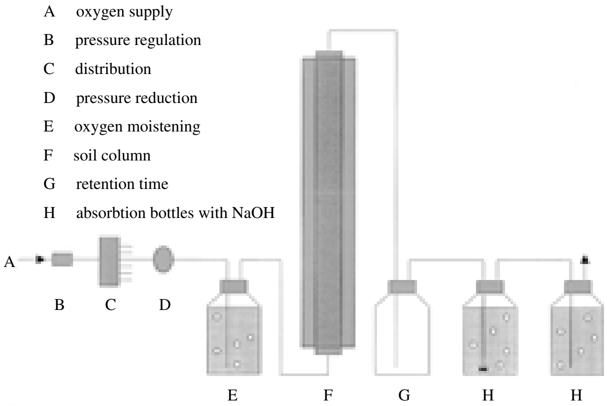

Fig. 1. Experimental set up for the measurement of carbon dioxide production during degradation.

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \tag{2}$$

The carbonate content of the sodium hydroxide solutions was measured periodically by titration with 0.5 *M* hydrochloric acid. To be able to distinguish between the protonation of the carbonate ions and the neutralization of the sodium hydroxide, barium chloride was added to build barium carbonate (Eq. 3)

$$2Na^+ + CO_3^{2-} + BaCl_2 \rightarrow BaCO_3 + 2\ NaCl \tag{3}$$

At a pH value higher than 6, barium carbonate is insoluble and, therefore, precipitates. Hence, up to the first transition point EP1, the added hydrochloric acid is absorbed by the sodium hydroxide (Eq. 4, Fig. 2).

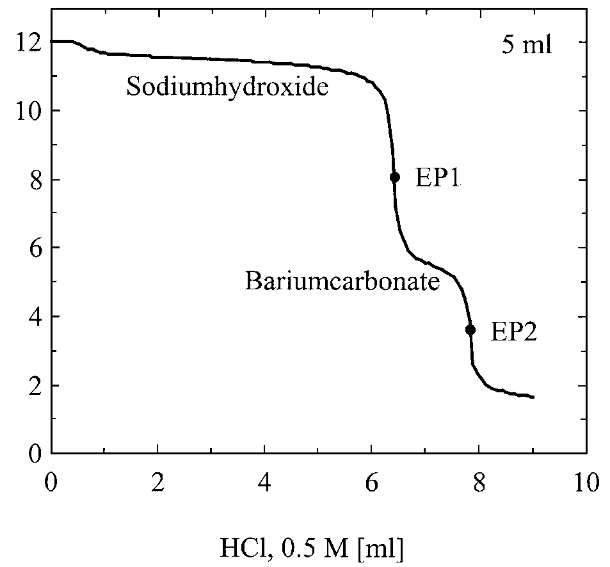

Fig. 2. Titration of the sodium hydroxide solution with adsorbed CO_2 after addition of barium carbonate. The hydrochloric acid added between the transition points EP1 and EP2 is used to protonize the carbonate ions.

$$NaOH + HCl \longrightarrow H_2O + NaCl \qquad (4)$$

At a pH value lower than 6, the carbonic ions are titrated (Eq. 5)

$$BaCO_3 + 2\ HCl \longrightarrow H_2O + BaCl_2 + CO_2 \qquad (5)$$

The total amount of absorbed CO_2 can be described according to Eq. (6):

$$CO_2[\mathrm{mol}] = (\mathrm{EP2} - \mathrm{EP1})^* M_a{}^* V_s^{-1} V_b{}^* 0.5 \qquad (6)$$

EP1 and EP2 are the HCl volumes added at the titration transition points, M_a represents the molarity of the hydrochloric acid, V_s is the titrated volume, and V_b is the total volume of the absorbing sodiumhydroxide solution.

Carbon Balance

During incubation, the carbon of the specimens is not only converted to CO_2 but also incorporated into the biomass [13, 15]. Furthermore, a certain amount of organic carbon in the soil substrate has to be taken into consideration for the carbon balance (Eq. 7).

$$C_{c\text{-}b} + C_{s\text{-}b} + C_{b\text{-}b} = C_{CO_2} + C_{c\text{-}e} + C_{s\text{-}e} + C_{b\text{-}e} \qquad (7)$$

The carbon contents of the specimens before and after the experiment ($C_{c\text{-}b}$ and $C_{c\text{-}e}$) were measured by means of elementary analysis (LECO CHN-900). To investigate the content of organic material of the soil substrate ($C_{s\text{-}b}$ and $C_{s\text{-}e}$), the soil was completely burned at a temperature of 650°C in air. The residue represents the inorganic components. The carbon content of the organic matter was calculated assuming that the C/H/O ratio is identical to the one of the carbohydrates (CH_2O, resulting in a carbon content of 40 wt.%. In order to evaluate the carbon of the biomass ($C_{b\text{-}b}$ and $C_{b\text{-}e}$), the organic nitrogen content was first evaluated on the basis of the Kjeldahl technique [15]. The C/N ratio of the microorganisms in the soil environment was determined as follows: The microorganisms from the soil were incubated on agar plates, then kept for 3 days in deionized water, and subsequently dried. The carbon and nitrogen contents were determined by means of elementary analyses resulting in a C/N ratio of 3.9 ± 0.1.

RESULTS AND DISCUSSION

Figure 3 shows the percentage of carbon of the samples converted to CO_2 for different fiber mass fractions. Note that the CO_2 production of the soil itself is subtracted. Contrary to the bare polymer, as well as to the polymer composites, the CO_2 production of the hemp fibers reached the plateau. The higher the fiber mass fraction, the faster the composites disintegrate. The disintegration behavior is described by an exponential law (Eq. 8):

$$C_{CO_2} = P^* \left\{ 1 - \exp - \left(\frac{t - t_0}{\tau} \right) \right\} \qquad (8)$$

C_{CO_2} is the percentage of carbon of the samples converted to CO_2 and t is the incubation time. The time required by the microorganisms to adapt to the specific carbon source (t_0), was set to 5 days, a reasonable value found by fitting the most appropriate data sets. For the data where a reliable fit was impossible, this value is also applicable. P is the value of the asymptotic reached plateau, which corresponds to the C_{CO_2} that can be achieved at maximum. The characteristic time constant τ describes the kinetics of biodegradation.

The time evolution of the fiber degradation was fitted to Eq. (8) using the Levenberg–Marquardt algorithm. The fit of P gives rise to (61.5 ± 0.8)%. Two-parameter fits of the bare matrix and the composites are difficult. Therefore, we have used the knowledge that the matrix

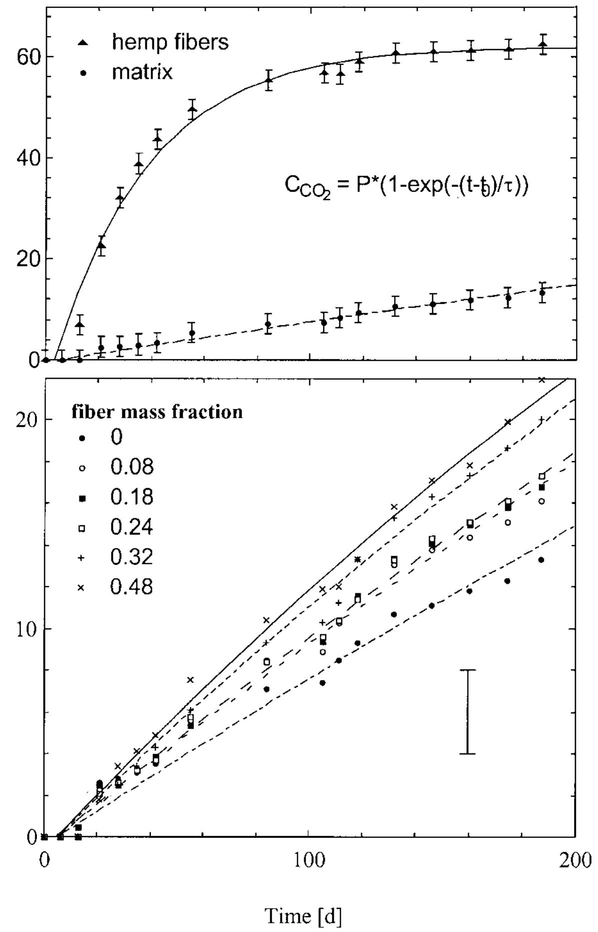

Fig. 3. Degradation of hemp–fiber copolyester amide composites for different fiber mass fractions. The percentage of carbon converted to CO_2 increases much faster for the hemp fiber sample than for the polymer matrix and the composites.

(BAK 2195) is expected to degrade completely to CO_2 within 70 days in a compost environment ($P = 100\%$) [16]. In a soil environment, P reaches only 90% C_{CO_2} since about 10% of the available carbon is integrated into the biomass. This behavior was confirmed by the 100% biodegradable glucose standard. Here, P reaches a value of approximately 90% C_{CO_2}. Therefore, the P value for the polymer matrix was set to 90%. For the composites with fiber mass fractions of $X_{\text{fiber}} = 0.08 - 0.48$, P was chosen by means of linear interpolation between 61.5 and 90%.

Under these boundary conditions (P, t_0), the only fit parameter is the characteristic time constant τ describing the degradation kinetics. It is also fitted using the Levenberg–Marquardt algorithm. The dependence of

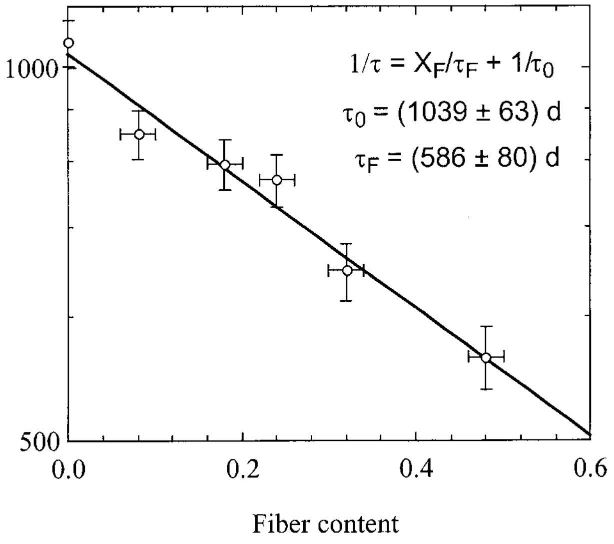

Fig. 4. The time constant τ decreases with increasing fiber mass fraction due to the faster degradation of the fibers. The data were fitted by the power law given. The error bars for the fiber mass fraction are a conservative estimation and, therefore, an upper limit.

these time constants τ, including their error bars, on the fiber mass fraction X_{fiber} is shown in Fig. 4. τ decreases with increasing fiber mass fraction. This indicates that the higher the fiber content, the faster the degradation, which is explained as follows: The fibers degrade much faster than the polymer matrix, creating pores in the material at the surface (Fig. 5). These pores create an increased effective surface, which is accessible to micro-

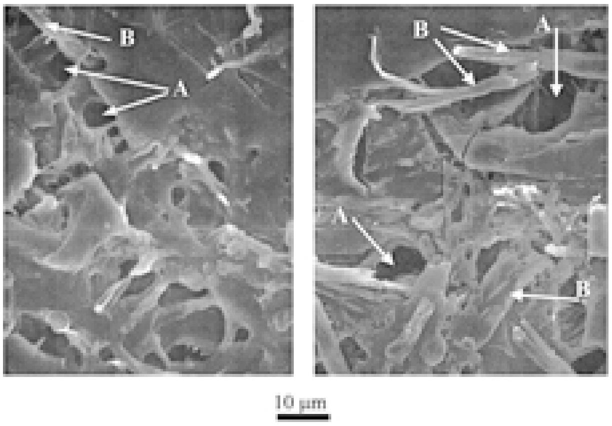

Fig. 5. Surface of a composite with a fiber mass fraction of 0.24 after 187 days of incubation in soil. The fibers near the surface degraded faster than the polymer matrix, creating pores in the composite (A). Remaining fiber fragments (B) are clearly visible.

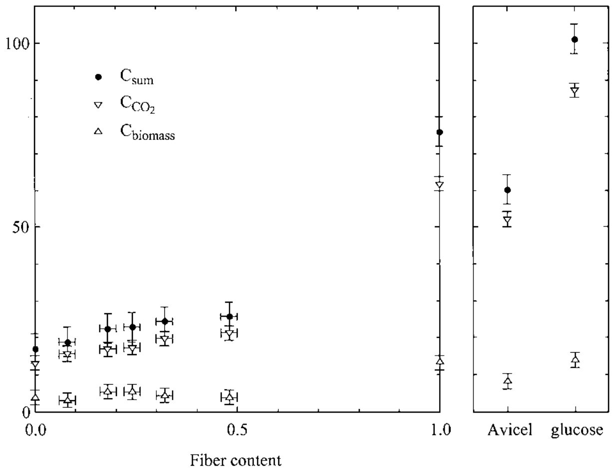

Fig. 6. Degradation after an incubation time of 187 days, composed of the percentage of carbon of the samples converted to CO_2 and incorporated into biomass. The degradation increases continuously with the fiber mass fraction. The degradation of the bare fibers is faster than expected, because its whole surface is accessible. In composites, the fibers are embedded and only a small fraction of the fibers is accessible to microorganisms.

organisms. Since the degradation time of the fibers near the surface can be neglected, τ is inverse proportional to the fiber mass fraction (Eq. 9):

$$\frac{1}{\tau} = \frac{X_F}{\tau_F} + \frac{1}{\tau_0} \tag{9}$$

τ_0 represents the time constant τ of the bare polymer and τ_F is a mean time constant of the fibers surrounded by the matrix polymer. This equation was fitted to the calculated time constants τ using the Levenberg–Marquard algorithm and results in $\tau_F = (586 \pm 80)$ days and $\tau_0 = (1039 \pm 63)$ days.

The considerations discussed above imply that three degradation experiments are enough to qualify the degradation kinetics of composites with different fiber contents.

The difference between the amounts of carbon before and after the experiment has to be zero (Eq. 7). Differences up to ±8% were found, which is within the error bars. Figure 6 illustrates the percentage of converted carbon after an incubation time of 187 days. That is the sum of the percentage of carbon converted to CO_2 and the one incorporated into the biomass. It increases continuously with the fiber mass fraction from 17% ($X_{fiber} = 0$) to 26% ($X_{fiber} = 0.48$). The percentage of converted carbon of the bare fiber sample ($X_{fiber} = 1$) is almost the double than expected. This is due to the fact that bare fibers have a larger effective surface than the fibers embedded into the composites. Hence, they are protected in the matrix material. Therefore, Eq. (9) is only applicable when the fibers are not directly in contact with each other. The percentage of converted carbon of the hemp fibers was 76% compared to 60% for the standard cellulose powder (Avicel). Steam-exploded hemp fibers consist of 16% noncellulosic components [17]. This observation indicates that the noncellulosic components of the hemp fibers degummed by steam explosion degrade faster than the cellulose. We have verified that the glucose standard degrades completely within 187 days. Eighty-six percent of the glucose carbon was converted to CO_2 and 14% was incorporated into biomass. Thus, the amount of carbon incorporated into biomass (in percentage of the total amount of converted carbon) of the other samples was slightly higher (up to 22%). This is because these samples were not yet completely degraded. Therefore, the biomass was still active, whereas the biomass in the glucose sample started to convert itself into CO_2.

CONCLUSIONS

The degradation behavoir of biodegradable materials is important in many applications. Thus, for the design of composites as construction material, the degradation kinetics has to be known. Furthermore, for composites, the kinetics is directly influenced by the fiber content. An experimental investigation of the degradation kinetics is time consuming. Appropriate modeling reduces the experimental work to a few well-defined experiments. Consequently, the proposed model contributes not only to a better understanding of the fundamentals in biodegradation, but also helps to reduce the experimental work for the design of composite materials.

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