Supplementary Information
for
Dependency of tensile properties and biodegradation on molecular mass during hydrolysis of poly(butylene succinate)

Felix Eckel, Daniel Van Opdenbosch, Katharina Sophie Schandl, Cordt Zollfrank

Chair for Biogenic Polymers, TUM Campus Straubing for Biotechnology and Sustainability, Technical University of Munich, Schulgasse 16, Straubing, 94315, Germany

Supplementary Note 1 Mathematical models describing the dependency of mechanical properties on molecular mass

1 Introduction

The following quantitative relationships describe the molecular mass dependency of mechanical properties from the literature. They have been used to model the obtained data to provide the interested reader with a quantitative mathematical relationship.

$$P = a_0 + \frac{a_1}{M} \tag{1}$$

Equation 1 (referred to as "Flory") with a_0 and a_1 being variables fitted on experimental data and M as molecular mass has been developed on data for cellulose acetate and vulcanized butyl rubber. It has been used successfully for other polymers such as PS and on properties like tensile strength, elongation at yield, Young's modulus and flexural properties. It has been established as a suitable model for linear and cross-linked polymers. However, it is not useful for different dispersities, which are an indicator for the shape of the molecular mass distribution or a varying degree of cross-links. Usually, M_n gives better results than M_w [1–3]. An adaption is possible by using the geometrical mean of M_n and M_w and has been used for PP (referred to as "Ogawa") [2]. It was possible to describe the Young's modulus, flexural modulus, elongation at yield and the tensile strength at yield but not the tensile strength or the elongation at break [2]. For s-shaped property-molecular-weight relationships a function in the form of

$$P = A + \frac{B}{M^2 + C} \tag{2}$$

with M being the molecular mass and P the respective property and A, B, C experimentally determined constants was suggested and has to be used separately on both sides of the point of inflection of the curve (referred to as "Nakano"). This model was established for amorphous polymers like PS [4]. A different approach was used by Bersted et al. to account for narrow and broad molecular mass distributions since none of the average molecular masses seems to give a satisfying dependency. Therefore, a failure property parameter F_p was created which is multiplied with the estimated property at an infinite molecular mass.

$$F_p = \phi(1 - \frac{M_T}{M_n^*}) \tag{3}$$

with M_T being a threshold molecular mass and M_n^* is the calculated M_n of the remaining molecular mass fractions above M_T. ϕ is the sum of the weight fractions above the threshold molecular mass M_T. The corresponding threshold molecular mass for the experimental data can be found by trial and error. It works for tensile strength data for PS and Bersted proposed that it should work for all amorphous polymers (the equation is referred to as "Bersted") [5]. The use of a multivariable power law was suggested by Dobkowski in order to achieve a correlation between the mechanical properties with the shape of the molecular mass distribution, the molecular mass and the branching of the sample. For linear polymers without a change in the dispersity, this relationship can be simplified and generalized with M being a suitable average molecular mass to

$$P = A * M^b \tag{4}$$

Equation 4 (referred to as "Dobkowski"). P is the respective property, A and b are parameters for fitting the experimental data. Dobkowski used the equation successfully for PS and PC on viscosity properties, glass temperature and tensile strength [3, 6].

2 Results mathematical model of mechanical properties

Young's modulus could be described with the relationships established by Flory, Ogawa and Dobkowski while no fit could be achieved with the models by Nakano and Bersted. Tensile strength

could be characterized by the functions of Flory, Ogawa and Nakano with good coefficients of determination. In contrast, the function by Dobkowski seems unable to describe the property well enough for low molecular masses. For the tensile strength it was also possible to predict the property with the model of Bersted using the failure property parameter instead of the weight average molecular mass with a threshold molecular mass of 94,547 g/mol.

The models above did not fit for elongation at break, uniform elongation and work of fracture. We found that these measurements could be well described by using the function

$$P = P_{max} * M^n/(k^n * M^n) \quad (5)$$

(referred to as 'Hill') with P being the respective property, $P_{\max}$ the hypothetical property value at an infinite molecular mass, M being the molecular mass and k and n fitted variables based on the data.

Uniform elongation shows a fast decline around a M_{w} of 100,000 g/mol while work of fracture declines with degrading molecular mass rapidly until about 80,000 g/mol.

3 Discussion of the functions used for modelling mechanical data

3.1 Choice of the fit function

The choice of a model to fit the data on has to be based on the kind of polymer, the branching degree, the shape of the molecular mass distribution and the property investigated. The degradation pathway can be another important factor, considering the different behaviours observed for mechanical properties found for different molecular weights of hydrolysed and synthesized PBS in this study and a similar study by Jin et al.[7]. The investigated relationship proposed by Dobkowski might be useful if a different dispersity and crosslinking density is to be accounted for but for PBS, which is a linear polymer and had a similar dispersity of all samples, other models like the one from Flory gave the same (Young's modulus) or better results like for the tensile strength. The linear fit with the suggested failure property parameter instead of a molecular mass average gave good results for the tensile strength but was not suitable for other properties. For the uniform elongation, the elongation at break and the work of fracture, which showed a rapid rise after a long plateau at low values, a sigmoidal fit, which has been used for a sigmoidal data distribution before, was useful (referred to as "Hill") [8]. All used equations except the one from Dobkowski include a variable corresponding to a material specific maximum value of the investigated material.

3.2 M_{n}, M_{w} or geometrical mean

Since it is difficult to compare the whole molecular mass distribution between samples, one has to choose appropriate measures like central tendencies. If the tail ends of the distribution are especially important for the investigated properties, binning of the molecular mass distribution or the use of averages for the central tendency, variance, skew and kurtosis of the distribution can be utilized [9–11]. In this study, the shapes of the distribution curves do not differ drastically from each other with a dispersity of 1.83+-0.05 for all molecular weights during tensile testing. Since the ratio of M_{n} to M_{w} stays the same over the whole range of the studied degradation, both averages are pretty much interchangeable for modelling the molecular mass dependency. The same is true for the geometric mean of both values. Therefore, we did not analyse the results by the M_{n} and used the M_{w}, which is usually considered more robust against changes in the dispersity of the sample [3, 12]. The geometric mean was used nonetheless, but was only useful for the Young's modulus and tensile strength but showed no advantage over M_{w} with the fitted models being very close to the one by Flory using M_{w}. The choice of measure has therefore no influence on the analysis of the samples in this study.

Supplementary References

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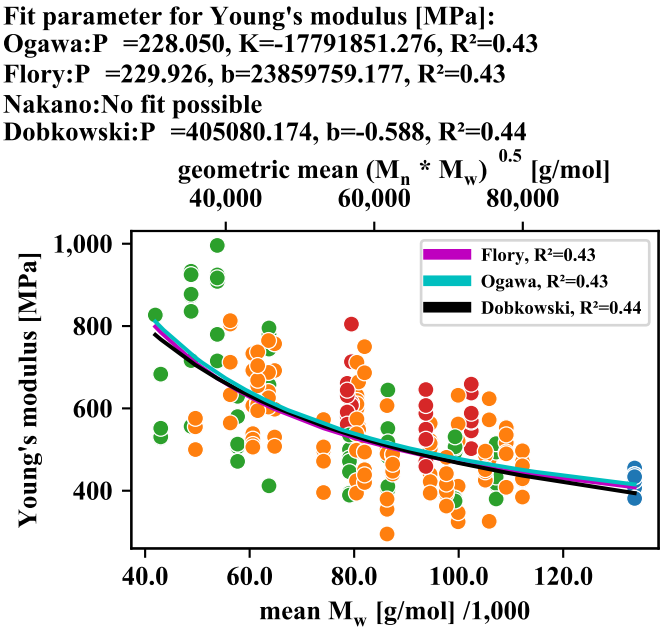
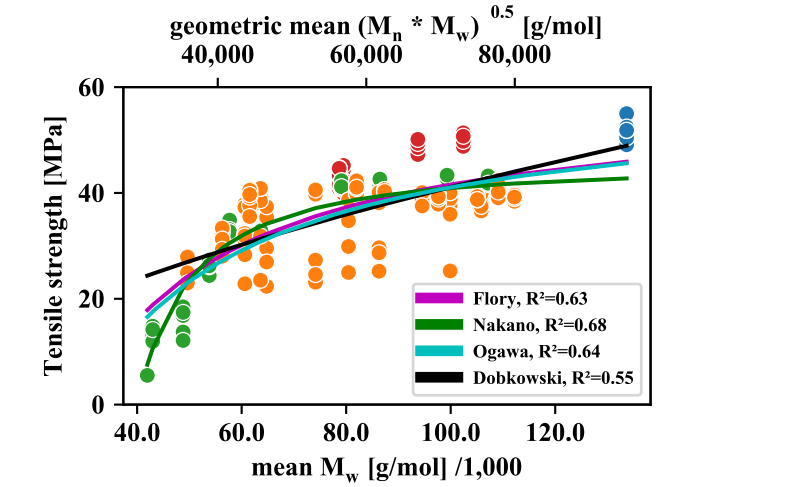
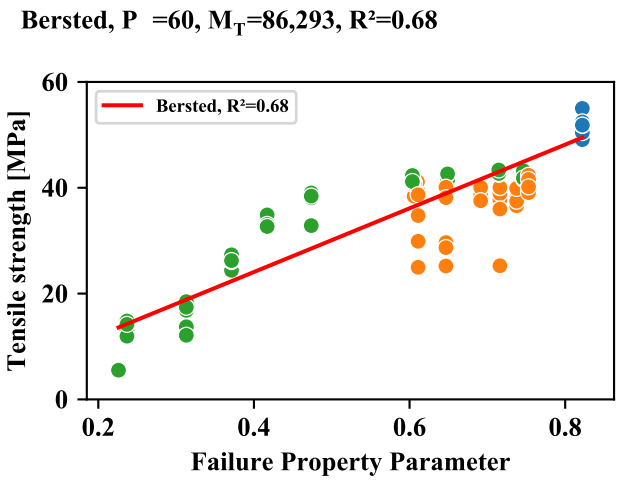


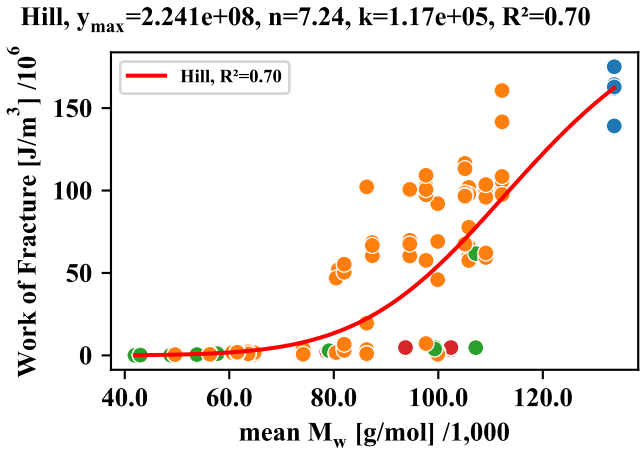
Supplementary Figure 1: Data points and fitted model parameters for Young's modulus fitted with equations from Flory, Ogawa and Dobkowski. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars.



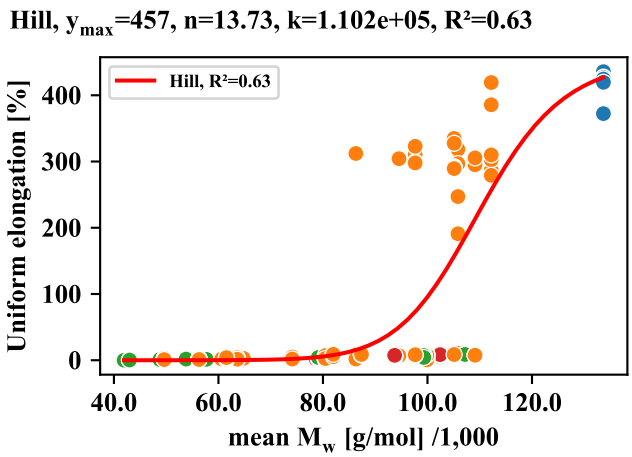
Supplementary Figure 2: Data points and fitted model parameters for tensile strength fitted with equations from Flory, Nakano, Ogawa and Dobkowski. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars.



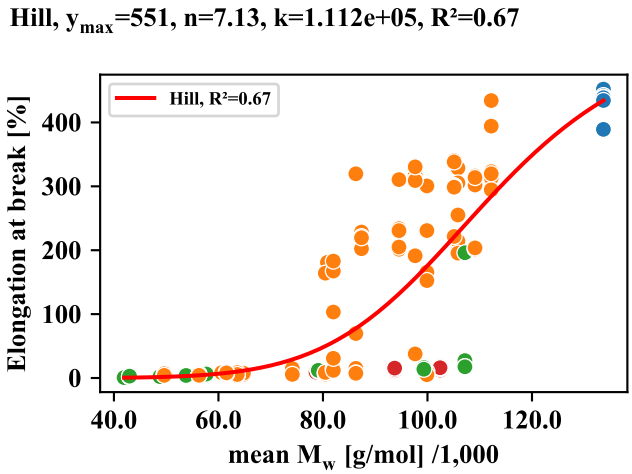
Supplementary Figure 3: Data points and fitted model parameters for tensile strength fitted with the Failure Property Parameter from Bersted with measurements from at 115 degraded tensile bars excluded from the fit. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars.



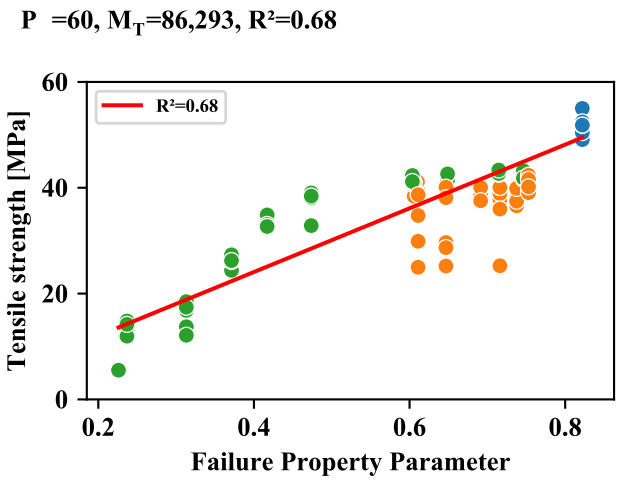
Supplementary Figure 4: Data points and fitted model parameters for work of fracture fitted with the adapted equation after Hill. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars.



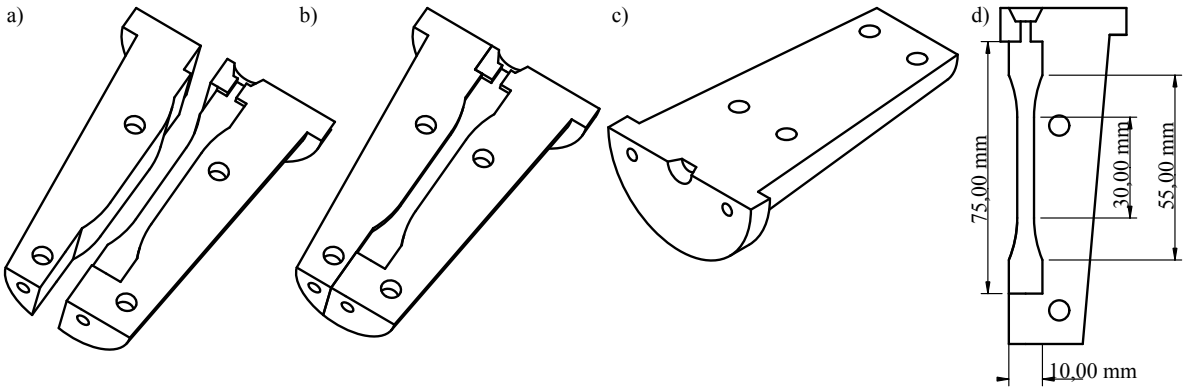
Supplementary Figure 5: Data points and fitted model parameters for uniform elongation fitted with the adapted equation after Hill. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars.



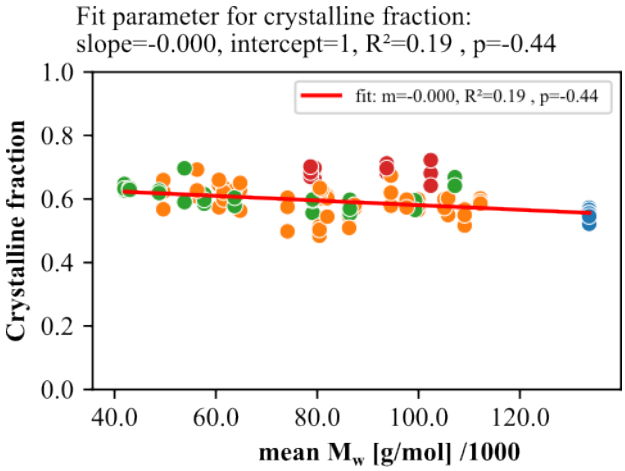
Supplementary Figure 6: Data points and fitted model parameters for elongation at break fitted with the adapted equation after Hill. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars.



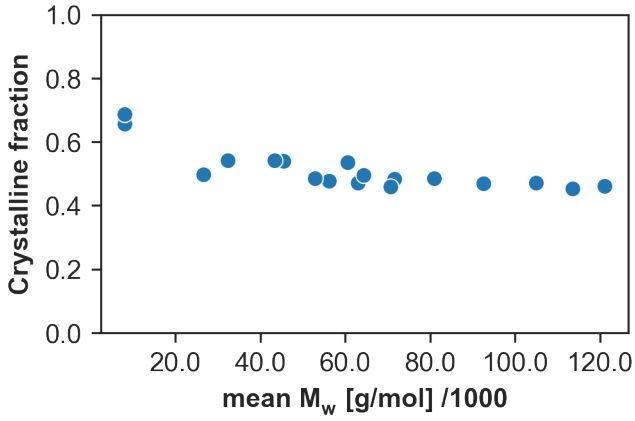
Supplementary Figure 7: Data points and fitted model parameters for tensile strength fitted with the Failure Property Parameter from Bersted with measurements from at 115 °C degraded tensile bars included. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars.



Supplementary Figure 8: Design of the three-part injection mould for type˜1BA-tensile bars. a) the two separated parts forming the mould, b) the two parts forming the mould together like in the original injection mould, c) shows the third part with the surface closing the mould and d) the dimension of the mould for the tensile bars.



Supplementary Figure 9: Crystalline fraction of tensile bars made from degraded granulate as determined with XRD. Blue dots: non-degraded tensile bars, orange dots: tensile bars made from degraded granulates, green dots: at 60 °C degraded tensile bars, red dots: at 115 °C degraded tensile bars. The red dots have not been included in the fit (red line).



Supplementary Figure 10: Crystalline fraction of PBS powder with different molecular masses made from degraded granulate as determined with DSC.