DESIGN OF MECHANICAL PROPERTIES OF POLY(BUTYLENE-ADIPATE-TEREPHTHALATE) REINFORCED WITH ZEIN-TIO$_2$ COMPLEX

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Introduction

The realization of composite materials aims to modify the properties of the matrices, besides lowering their costs [1].
Poly (butylene-adipate-terephthalate) (PBAT) is a flexible thermoplastic biodegradable polymer that has gained increasing attention in the last years.
Zein is a protein derived from corn, with film-forming ability but characterized by poor mechanical properties [2].
TiO$_2$ is an amphoteric, inert, non-toxic, and biocompatible metal oxide, widely used as a white pigment in the food industry and recently employed as a reinforcement for zein films [3].
The study of the interactions between matrix and filler is crucial to define the properties of the composites. Several theoretical models allow correlating the tensile properties to the effectiveness of the reinforcement.
In this study, PBAT-based composites are reinforced with a zein-TiO$_2$ complex (ZTC) at different concentrations. The mechanical characterization is carried out through a uniaxial tensile test (UTT) and the obtained properties are modeled through the application of Kerner's and Pukánszky's models.

The composites were realized by solvent casting at 4 different filler concentrations: 0, 5, 10, and 20 wt%, named PBAT, PBAT+5% ZTC, PBAT+10% ZTC and PBAT+20% ZTC, respectively.
Specimens 1BA (standard ISO 527) were obtained by injection molding of the pelletized casted films and subjected to UTT at a constant speed of 100 mm/min up to failure. Averaged values of Young's Modulus (E), yield stress (σ_y), stress at break (σ_B), elongation at break (ε_B), and toughness (T) were calculated.
Generalized Kerner's equation [4, 5] was applied to compare experimental values of E obtained from the mechanical analysis with predicted calculated values.

Pukanszky's model was applied to σ_y and σ_B, respectively [6, 7], to analyze the trend of experimental tensile and to investigate the extension of the interphase interaction through the calculation of the empirical parameters B and B_b, respectively.
The composite microstructure was investigated with scanning electron microscopy (SEM).

Result and discussion

The stress-strain curves obtained by the UTT are reported in Figure 1.

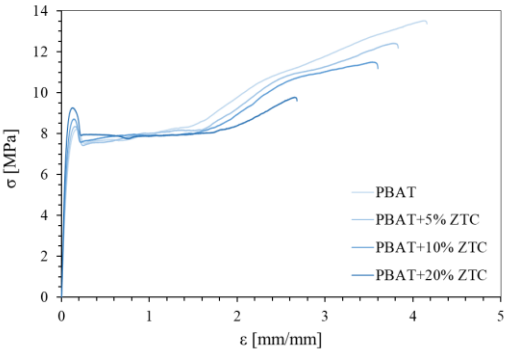

Figure 1: Stress-strain curves of PBAT and PBAT composites obtained by UTT

The composites showed increments of E and σ_y up to 44 and 10%, respectively, besides, the overall reduction of 27, 33, and 42% of respectively σ_B, ε_B, and T, confirming a stiffening effect at expenses of the flexibility of the pristine matrix.
The application of generalized Kerner's model was expressed on the reduced modulus (the ratio between the composite (E') and the neat polymer (E'$_0$)) as a function of the volumetric filler fraction φ_f. Remarkable agreement was found between the experimental and the theoretically predicted values, even at the highest filler concentration (Figure 2).

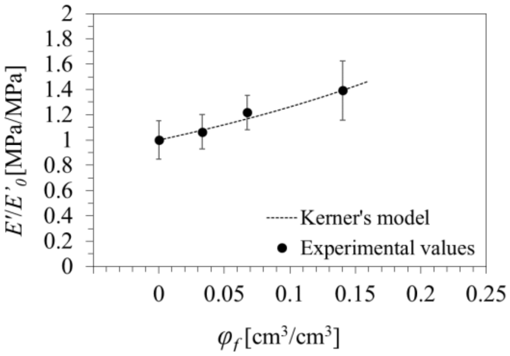

Figure 2: Comparison between experimental reduced E of PBAT composites and the corresponding theoretical values, calculated with Kerner's model.

Pukanszky's model was applied to σ_y and σ_B, and the values were plotted against φ_f. Linear correlations were obtained, whose slope represents the empirical B and B_b values, respectively, representing the goodness of interphase interaction. Generally, B values characterizing efficient reinforcement are included in a wide range, going from 2 to 15 [8], with high values meaning higher goodness of the interaction. For PBAT-ZTC composites in this study, values of $B = 4.06 \pm 0.12$ and $B_b = 2.23 \pm 0.12$ were obtained.

The effectiveness of interfacial interaction is defined by many parameters, including the particle size and size distribution, influencing the surface area, particle shape and orientation, the possible different chemical nature of matrix and filler [1]. In this last case, surface treatments or compatibilization may be performed to enhance adhesion [9]. On the other side, poor adhesion or aggregation of the filler particles, leads to a reduction of the mechanical properties of the composite.

Homogeneous dispersion of the filler within the matrix could be observed through SEM characterization even at high filler concentrations (Figure 3). In particular, the absence of aggregation or phase separation is a further indication of a strong interface.

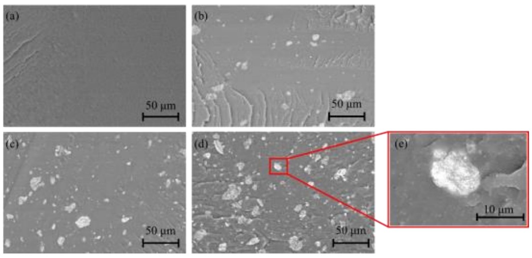

Figure 3: SEM images of PBAT (a), PBAT+5% ZTC (b), PBAT+10% ZTC (c) and PBAT+20% ZTC (d) at a magnification of 1600X and of a single ZTC particle detail at 12000X (e).

Conclusions

The design of the properties of the composites is crucial for tailoring the materials to different needs. Theoretical models allow studying the effect the addition of the filler has on the matrix.

The realization of composites in this study, made of PBAT and ZTC at different concentrations, produced a reinforcing effect, increasing the stiffness and the yield strength. The application of Kerner's model to the experimental E values returned a very good correspondence. Through the application of Pukanszky's model, values of B indicating a good interaction between PBAT and ZTC were obtained. Good interphase adhesion could be furthermore observed through SEM images of the surface of the samples. Overall, these composites, with modulated properties according to the filler content, can represent a sustainable alternative to non-biodegradable plastics currently used in various fields.

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