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Preparation and characterisation of PBAT-based biocomposite materials reinforced by protein complex microparticles

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Abstract: In this work new biodegradable composite materials based on poly (butylene adipate terephthalate) (PBAT) reinforced with zein-TiO_2 complex microparticles were prepared and characterised by electron microscopy, tensile and dynamic-mechanical tests. The composite pellets were prepared by solvent casting with different filler contents (0, 5, 10 and 20 wt%) to modify and modulate the properties of the final materials. Scanning electron microscopy (SEM) images showed homogeneous dispersion of the filler, without microparticles aggregation nor phase separation between filler and matrix, suggesting a good interphase adhesion. According to tensile tests, the Young's modulus showed an improvement of the rigidity and the yield stress presented an increasing trend, with opposite behaviour compared to other composites. Dynamic-mechanical analysis (DMA) results exhibited increasing storage modulus values, confirming a greater rigidity with higher filler percentage. The glass transition temperature showed a slightly increasing trend, meaning the presence of an interaction between the two phases of the composite materials. Overall, the produced PBAT composites showed similar properties to low density polyethylene (LDPE), proving to be promising and more sustainable alternatives to traditional polymers commonly adopted in agri-food fields.

Keywords: biopolymers; biocomposites; poly (butylene adipate terephthalate); protein complex; characterisation

1. Introduction

Among materials for packaging, plastics are most widely used thanks to their lightness, good mechanical behaviour, barrier properties and, among the others, their low cost [1]. Amongst traditional plastics, the most employed are polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephtalate (PET) and polystirene (PS), which however are not very eco-sustainable due to the problems related to their end-of-life disposal [2].

In the last decades, although, increasing attention has been devoted to the study and the employement of bioplastics in order to reduce the environmental impact and increase sustainability. Since bioplastics generally present poorer properties when compared to traditional plastics, the realisation of composite materials represents a valid way to improve and modulate their characteristics. The major downside of biopolymers being their high cost [3], the use of natural biodegradable fillers is a possible solution to reduce the production costs and at the same time to preserve their degradability [4].

Poly (butylene adipate therephtalate) (PBAT) is a 100% biodegradable polymer produced from fossil resources [5], although recently it has been reported that its monomers can be obtained from renewable sources [6–8]. PBAT presents similar properties and processability to polyethylene (PE), especially high flexibility [9,10].

Zein is a prolammine protein which can be extracted in pure form from corn. Its use in polymers has been studied since the 20th century [11] as it is considered a safe biocompatible and biodegradable material [12]. Zein can be formed into films and displays good barrier properties, thanks to its hydrophobic nature [13]. However, protein films are usually very though and brittle and can not be used as are, but protein in the form of particles can be used as reinforcing phase in the realization of composites which are based on a flexible polymer matrix [14], as in this case PBAT.

As of late, zein has been functionalised in protein-TiO_2 complexes for packaging, environmental and medical applications [15].

The aim of this work is to design and fabricate biocomposites based on PBAT loaded with microparticles of a zein-TiO_2 complex. The so obtained composites have been characterized in terms of their mechanical and dynamic-mechanical properties. .

2. Materials and Methods

PBAT (MAgMa Spa) pellets were dissolved into pure chloroform. Then zein (Sigma Aldrich)-TiO_2 complex, previously milled and sieved at 25 µm, was homogeneously dispersed into the polymer solution at the concentrations of 0, 5, 10 and 20 wt%. After solvent evaporation, obtained films were used for the production of different loaded composite samples named PBAT, PBAT+5%P, PBAT+10%P and PBAT+20%P, respectively.

Dumbbell specimens, model 1BA according to UNI EN ISO 527 standard, of each composite were produced by injection moulding and their mechanical properties were characterised.

Uniaxial tensile test (UTT) results allowed the evaluation of the characteristic parameters, such as Young's modulus E, yield stress σ_y, elongation at break ε_B, stress at break σ_B and toughness T.

DMA measurements were carried out according to ASTM D7028 standard with a single cantilever clamp, for the determination of the storage modulus (E'), the loss modulus (E'') and the loss factor ($\tan\delta$).

SEM images were acquired to investigate the internal microstructure of the composites.

3. Results and Discussion

In Figure 1, SEM images at different magnifications of PBAT and PBAT+20%P are reported as representative samples. The morphology of the filler particles emphasized the protein-TiO_2 complex nature, showing bright white areas corresponding to the TiO_2 portion and a more grey part representing the zein protein.

The images displayed homogeneous dispersion of the protein complex within the polymer matrix, even at high concentration of filler, with no aggregation of the particles and no phase separation. Indeed, a region with an intermediate shade of grey is visible at the grain boundaries. This suggests the formation of an actual interfacial layer bonding the PBAT matrix to the protein, due to the presence in the protein structure of both polar and non-polar functional groups [16], able to interact with the polymer macromolecules. Therefore, good adhesion and interaction between the phases can be supposed.

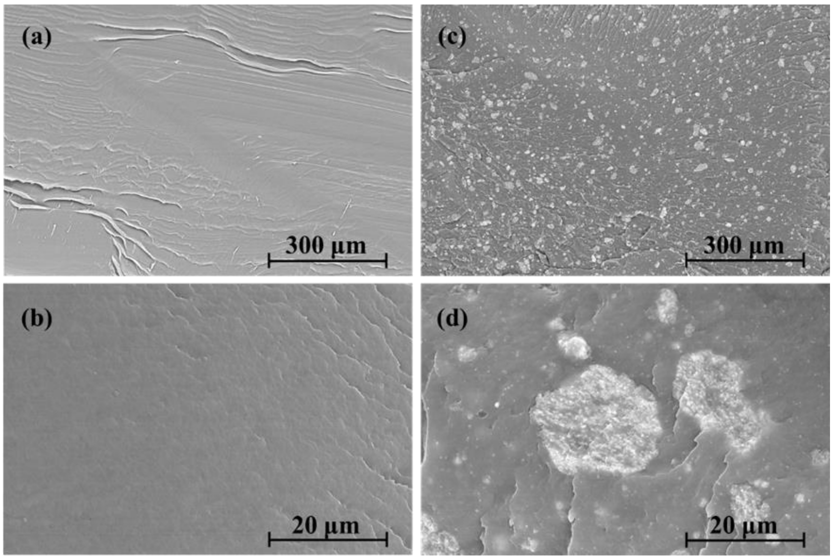

Figure 1. SEM images of PBAT (a, b) and PBAT+20%P (c, d) at different magnifications, as representative samples.

UTT results on the prepared biocomposites indicated a pronounced increase up to 47% in *E* modulus with the increasing the filler content. An important result is the increasing trend showed by σ_Y, significantly different from what traditionally displayed by other composite materials [17]. The obtained results can be interpreted as an additional evidence of the good interaction between the phases involved in the biocomposite [18]. The characteristic parameters ε_B, σ_B and *T* showed a decrease with increasing the filler content, related to the increased stiffening of the composites. The representative values are reported in Table 1.

Table 1. Young's modulus (*E*), yield stress (σ_Y), stress at break (σ_B), elongation at break (ε_B) and toughness (*T*) values of poly (butylene adipate terephthalate) (PBAT) and protein complex composites.

Sample	*E* [MPa]	σ_Y [MPa]	σ_B [MPa]	ε_B [MPa]	*T* [MJ/m³]
PBAT	126 ± 12	8.1 ± 0.2	13 ± 1	4.0 ± 0.8	45 ± 6
PBAT+5%P	131 ± 10	8.4 ± 0.2	12 ± 1	3.7 ± 0.3	35 ± 4
PBAT+10%P	149 ± 4	8.8 ± 0.2	11 ± 1	3.5 ± 0.2	32 ± 3
PBAT+20%P	186 ± 11	8.9 ± 0.1	9 ± 1	2.7 ± 0.2	22 ± 2

The E' modulus obtained from DMA analysis as a function of the temperature exhibited a linear increase with increasing the filler content in the composite, thus confirming the stiffening effect obtained by the addition of high amounts of filler (Figure 1c).

Other authors investigated similar biocomposite systems, based on biopolymers reinforced with natural filler particles at different concentrations [19], finding a similar increasing behaviour of E' compared to the system studied in the present work. The enhanced modulus in composite materials can be attributed to the restricted mobility of the polymer chains, due to the physical presence of the filler particles and to the chemical interaction at the interface between the polymer and the particles [20].

Glass transition temperature (T_g) was calculated as the temperature corresponding to the peak of the tanδ curves, defined by the ratio between E'' and E' moduli. The values of T_g for the different composites show a slight increase as the filler content increases, confirming the interaction between matrix and filler, as observed in other composite systems [21]. Table 2 displays the discussed results of DMA tests.

Table 2. DMA representative results of PBAT and protein complex composites.

Sample	E' @ 0 °C [MPa]	E' @ 20 °C [MPa]	E' @ 40 °C [MPa]	T_g [°C]
PBAT	273 ± 60	202 ± 50	155 ± 50	-20.4 ± 0.9
PBAT+5%P	297 ± 60	224 ± 70	182 ± 60	-20.3 ± 0.8
PBAT+10%P	319 ± 70	239 ± 60	192 ± 70	-18.3 ± 0.5
PBAT+20%P	395 ± 50	294 ± 50	235 ± 60	-17.9 ± 0.5

4. Conclusions

Among the different biopolymers, PBAT is one of the most studied and promising biodegradable plastic materials. In this work it was employed in the fabircation of biocomposites reinforced with zein-TiO_2 complex at different weight percentages. The addition of different amounts of filler allowed to obtain a modulation of the material properties.

The filler particles resulted homogeneously dispersed, as emerged from SEM images of the analysed samples, and with the presence of an interface connecting layer between the protein complex and the polymer matrix. The protein complex appeared to have a stiffening effect on the polymeric matrix, with an increase of the E and σ_Y, suggesting, therefore, an effective good interfacial interaction between the phases.

The stiffening effect was confirmed by the increasing trend observed in the E' modulus calculated from DMA analysis. Moreover, T_g values increased with increasing the filler content, validating the hypotesis of an interface layer bonding the matrix and the reinforcing particles.

According to the obtained results, the biocomposites can be considered a valid and more sustainable alternative to the non-biodegradable, fossil-based plastics generally used in the packaging field, such as LDPE.

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