

Properties of Biodegradable Poly(butylene adipate-*co*-terephthalate) and Sodium Caseinate Blends

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ABSTRACT: Sodium caseinate (NaCAS) was blended with commercially available biodegradable polyester, poly(butylene adipate-*co*-terephthalate) (PBAT) with the aim to obtain environmentally friendly materials for packaging applications with increased oxygen barrier properties. Mechanical properties (tensile strength, elongation, and Young's modulus) of such blends were determined versus ratio of protein to polyester, plasticizer type and content, and relative humidity conditions. Among the two plasticizers tested, glycerol (Gly) and triethanolamine (TEA), Gly was the most efficient for the improvement of mechanical properties (high strains for low stresses) of PBAT/NaCAS blends. The maximum content of protein in blends to keep interesting mechanical properties was about 30% w/w. At this level, the material still exhibits interesting mechanical properties, that is, maximum tensile

strength of 20–25 MPa for elongation at break about 25%. Protein-specific water solubility was determined from a 280-nm absorbance method. PBAT/NaCAS materials exhibit good resistance to water, and NaCAS specific solubility was kept under 7 wt % after 48 h immersion in water even for samples containing 30% w/w NaCAS. The PBAT/NaCAS materials also showed an increase of oxygen barrier properties as NaCAS content increased, leading to materials with oxygen permeability lower than 40,000 cm³ μm m⁻² d⁻¹ atm⁻¹, which is half the initial value of PBAT. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: sodium caseinate; PBAT; blend; plasticizer; oxygen permeability; solubility; mechanical characterization

INTRODUCTION

Many studies have demonstrated that proteins could be used in the manufacture of plastic goods.^{1–4} Because proteins are renewable and biodegradable, protein-based materials can be used in replacement of synthetic polymers obtained from petroleum resources. Materials made from proteins are interesting for biodegradable applications, but some limitations are attached to such protein-based plastics: they are stiff and moisture (water) sensitive.^{5,6} To overcome such drawbacks, proteins can be blended with plasticizers,³ chemically modified through crosslinking reactions for example,^{6,7} or blended with other biodegradable polymers like synthetic polyesters.⁸ If several studies have dealt with blends of polyesters and starch^{9,10} or so-called thermoplastic starch, few works described blends of proteins with such polyesters.^{11,12}

Among proteins that should have interesting properties for packaging applications,^{5,13–15} casein is a commercially available protein obtained in great quantities and with good purity from acid precipitation of cow's milk. Sodium caseinate (NaCAS) is obtained with good purity (up to 95%) by soda treatment of casein and present thermoplastic and film-forming properties due to its random coil nature and its ability to form weak intermolecular interactions, that is, hydrogen, electrostatic, and hydrophobic bonds. Considering their transparency, biodegradability and good technical properties (high barrier for gases like O₂)^{3,5,16,17} caseinate-based films and materials can find various applications,¹⁸ not only in packaging, but also in edible or protective films and coatings or in mulching films. In a previous work,⁶ caseinate-based films were prepared with improved properties as close as possible to available packaging films based on synthetic polymers like polyethylene or plasticized PVC. Caseinate films were plasticized in order to confer interesting mechanical properties to the material like good elongation at break (about 200%) and a rather low-tensile strength (less than 8 MPa). The incorporation of a minimal content of plasticizers is needed to avoid brittleness and to increase extensibility and

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flexibility. By decreasing intermolecular forces between polymer coils, the plasticizer causes an increase in material flexibility and conversely a decrease in the barrier properties due to the augmentation of the free volume.¹⁹ Plasticizer efficiency is mostly governed by its molecular weight and polarity and its ability to reduce intermolecular hydrogen bonding while increasing intermolecular spacing.

Further, in order to increase mechanical strength and to improve water resistance, caseinate films can be crosslinked: the occurrence of covalent bridges between protein chains allows water-insoluble three-dimensional network to be achieved. The most commonly used techniques for crosslinking protein materials include chemical crosslinking with reactants like formaldehyde or glutaraldehyde,²⁰ enzymatic crosslinking with transglutaminases or peroxydases,²¹ and physical treatments such as irradiation.^{22,23} Radiation of proteins (electron beam,²⁴ γ irradiation²⁵) is a way to induce their crosslinking and to improve their performances like mechanical strength. The radicals formed during irradiation promote a binding between adjacent molecules forming a three-dimensional network. Because of the limited availability of transglutaminases and peroxydases, their high cost, and their limited efficiency at macromolecular level, enzymatic crosslinking is not extensively used in the manufacture in films and coatings.

In this work, NaCAS was blended with commercially available biodegradable polyester, poly(butylene adipate-co-terephthalate) (PBAT)²⁶ in order to improve water resistance and mechanical properties of protein-based materials. In previous studies,^{6,24} NaCAS was already crosslinked with formaldehyde or with electron beam in order to create a three-dimensional network able to increase water resistance of protein films. In this work, the incorporation of PBAT in casein would be a possible way to control water solubility and also an efficient way to reduce the price of the final material considering the initial cost of PBAT (4 €/Kg) is about half the price of NaCAS (7–8 €/kg). Besides, proteins were also blended to PBAT to bring better oxygen barrier properties to final products in order to find further specific uses in food packaging or in any other specific area where barrier properties are required.

NaCAS was first blended with PBAT at different levels, and mechanical properties of materials obtained from these blends were determined by tensile testing. Water resistance of PBAT/NaCAS blends was also evaluated by simple immersion in water using an UV detection method of protein solubilization.

Two different plasticizers, glycerol (Gly) and triethanolamine (TEA), were also incorporated in

blends in order to increase mechanical properties of NaCAS/PBAT blends through plasticization of the protein part. Indeed, it was already demonstrated⁶ that these two plasticizers were the most efficient among different polyol type plasticizers for plasticizing NaCAS. Gly and TEA are both mentioned in the list of the authorized substances that can be used in the manufacture of plastic materials and articles intended to come in contact with food as mentioned in food contact material registration (registration EU no. 10/2011), though they both have specific migration limitations.²⁷ The efficiency of TEA and Gly was evaluated considering their ability to increase maximum elongation and to decrease tensile strengths as well as elastic modulus of NaCAS/PBAT materials.

Finally, oxygen permeability of PBAT/NaCAS blends was determined and compared to the initial values of plasticized NaCAS films, PBAT alone and also of other synthetic polymers commonly used in packaging materials. Usually, oxygen barrier layers are obtained from synthetic polymers including ethylene vinyl alcohol copolymers, polyvinylidene chloride, or polyamide-6 (nylon).^{28–31} Such polymers are commonly used in the form of coextruded or laminated films and coatings. In this study, the protein is simply blended with the PBAT in order to enhance its oxygen barrier properties. This simple process was efficient for increasing oxygen barrier properties: the initial oxygen permeability of PBAT can be divided by more than two by the simple incorporation of 30% w/w of NaCAS.

EXPERIMENTAL

Materials and reagents

NaCAS was purchased from Epi ingredients (France). Its composition according to manufacturer was proteins 90.2%, water 5.7%, minerals 3.5%, and fat <1%. TEA and Gly are of analytical grade (purity 99+%, Acros Organics). Poly(butylene adipate-co-terephthalate) (PBAT) under the trade name of Ecoflex FBX7011 was purchased from BASF corporation and used as received.

Blend preparation

The blends were prepared using a laboratory-scale internal mixer Haake Polydrive (ThermoScientific) equipped with two contra-rotating rotors. The temperature was controlled in three different zones: back, front, and middle. The rotor speed was fixed at 60 rpm. The residence time of 10 min was the same for all the blends and corresponds to the time necessary to obtain a stabilization of the torque. The fill factor in the blending chamber was 0.7, and the

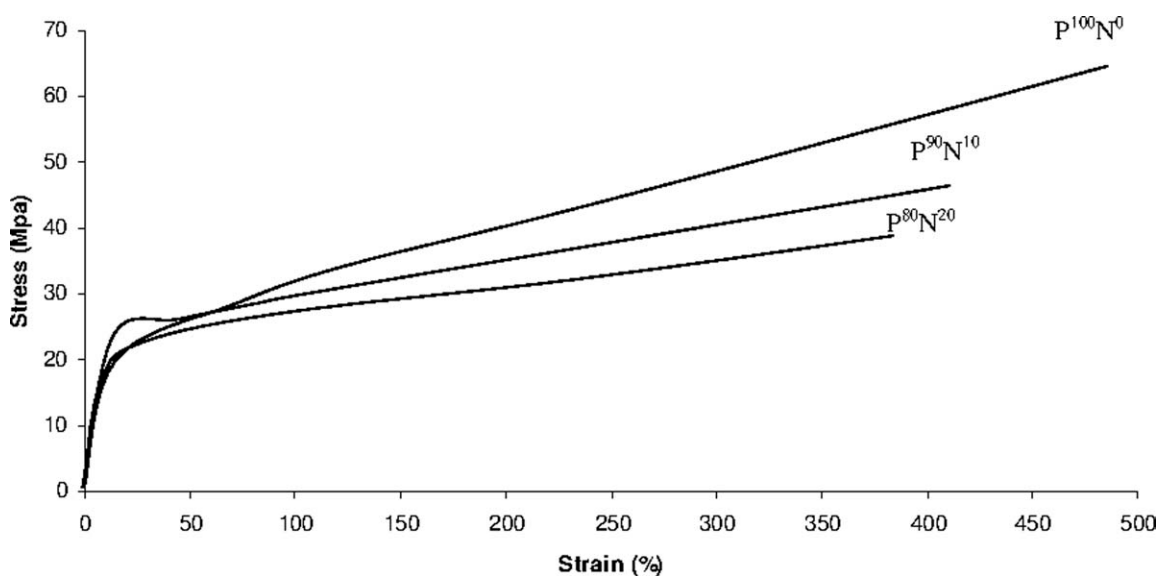


Figure 1 Stress–strain curves of PBAT/*NaCAS* blends containing from 0 to 20% *NaCAS*. Blend composition is indicated on each curve.

mixing was carried out at temperature between 100 and 170°C. Compression-molded plaques were prepared from the compound stocks at 120°C. After cooling, dumbbell specimens with an active portion of 5 mm wide and 2 mm thick according to the standard Iso 527-2 type 1BA were cut in the plaques. The dumbbells were equilibrated for 2 weeks at 53% RH or 0% RH, 23°C before testing. About 53% RH conditions were obtained in closed tanks containing saturated solutions of $Mg(NO_3)_2$. About 0% RH conditions were obtained in vacuum desiccators over P_2O_5 . OTR measurements were performed on 500- μm thick films prepared in the same conditions.

Stress–strain testing

Tensile strength, elongation at break, and Young's modulus were obtained using a model 1011 testing system (Instron, Engineering Corp., Canton, MA). Uniaxial stress–strain and ultimate properties were performed onto normalized samples (dumbbell specimens according to the standard iso 527-2 type 1BA) using rubber jaws and a cross-head speed of 10 or 50 $mm\ min^{-1}$. Data were the average of five samples. Stress–strain curves plotted on Figures 1 and 2 were obtained from experimental data as close as possible to the mean mechanical properties.

Solubility

The specific solubility of *NaCAS* was determined by assaying for protein using the 280-nm absorbance method. *NaCAS* and PBAT/*NaCAS*-based materials were immersed in distilled water (75 mL) at 20°C and magnetically stirred at 250 rpm. From absorb-

ance at 280 nm of the supernatant, the remaining soluble protein was determined. The specific solubility is expressed in weight percentage of initial amount of dry casein in the film. Absorbance at 280 nm of *NaCAS* solutions in distilled water was first measured. It was also checked that Gly and TEA absorbance was negligible at 280 nm. The calibration straight line ($y = 1.457x + 0.016$) of the absorbance of *NaCAS* solutions versus *NaCAS* concentration is obtained with a correlation coefficient $r = 0.9981$. The calculated molar extinction coefficient was $\epsilon = 32,920\ L\ mol^{-1}\ cm^{-1}$. *NaCAS* content in film can be determined with accuracy better than 5%. The solubility of materials was determined after 2, 5, 10, 20, 40, 60 min, 24, and 48 h immersion in water from the 280 nm absorbance of the supernatant.

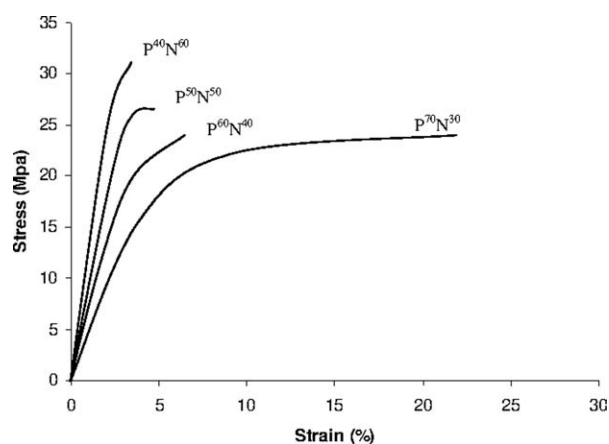


Figure 2 Stress–strain curves of PBAT/*NaCAS* blends containing from 30 to 60% *NaCAS*. Blend composition is indicated on each curve.

Oxygen Transmission Rate

The oxygen transmission rate (OTR) was determined with a MOCON OX-TRAN® 2/21 (Modern Controls, Minneapolis, MN) at 0% RH and 23°C, 760 mm Hg pressure, on 50 cm² films and in standard test mode. Oxygen permeability was calculated by dividing the OTR by oxygen partial pressure and multiplying by the film thickness.

RESULTS AND DISCUSSION

Blends of PBAT and NaCAS

The purpose of the first part of this work was to find the optimum sodium caseinate (NaCAS) content in poly(butylene adipate-*co*-terephthalate) (PBAT) to obtain materials with enough elongation at break (up to 100%) and good elastic modulus, as close as possible to the mechanical properties of commonly used packaging materials. Table I gives the detailed compositions of studied blends as well as blending conditions for each one. Homogeneity of blends was simply determined from their visual aspect. For simple PBAT/NaCAS blends, the blending temperature raised with the increase of NaCAS content, from 120°C for 100% PBAT samples to 170°C for PBAT/NaCAS blends containing 80% NaCAS. However, it was observed that blend containing 60% *w/w* and more NaCAS were inhomogeneous, leading to materials that were impossible to handle.

In a first time, only blends of PBAT and NaCAS alone were studied, with different proportions of NaCAS. The purpose was to find the maximum NaCAS that could be incorporated in blends. Stress–strain curves obtained for such PBAT/NaCAS

blends are represented in Figures 1 and 2. Two important parameters were recorded from tensile stress–strain curves: elongation (strain) at break and Young's (elastic) modulus.

For blends containing from 0 to 20% *w/w* NaCAS (Fig. 1), load raised continuously with the increase of strain until the sample breaks. About 100% PBAT material exhibit very good elongation at break (about 500% and more for some specimens) for maximum stress about 65 MPa. The incorporation of NaCAS caused a decrease in both maximum elongation and stress at break. Nevertheless, for NaCAS contents up to 20% *w/w* in blends (Fig. 1), stress–strain properties are still very interesting for packaging applications. For upper contents of NaCAS in PBAT/NaCAS blends, ultimate mechanical properties were drastically reduced (Fig. 2). When the NaCAS content exceed 40% *w/w* in the blend, the resulting material became brittle exhibiting poor elongation at break, from 3 to 6% only, for tensile strength comprised between 23 and 32 MPa. Thus, the maximum NaCAS that could be incorporated in blend with keeping interesting mechanical properties seems to lie about 30% *w/w*. In such blends, that is, P⁷⁰N³⁰, the maximum elongation is superior to 20%, and maximum stress is about 23 MPa.

From stress–strain testings performed on blends described in Table I, elongation (strain) at break and Young's (elastic) modulus were recorded. Figures 3 and 4 represent the evolution of the elastic modulus and the stress at break as a function of NaCAS content in PBAT/NaCAS blends, respectively. It clearly appears that the incorporation of NaCAS in PBAT caused an increase of the elastic modulus from 173 MPa for PBAT specimens, to about 1560 MPa

TABLE I
Composition of PBAT/NaCAS Blends and Blending Conditions

Blend name	PBAT [% (w/w)]	NaCAS [% (w/w)]	Plasticizer (phr)		T (°C) ^a	Homogeneity
			TEA	Gly		
P ¹⁰⁰ N ⁰	100	0	–	–	120	+++
P ⁹⁰ N ¹⁰	90	10	–	–	130	+++
P ⁸⁰ N ²⁰	80	20	–	–	130	+++
P ⁷⁰ N ³⁰	70	30	–	–	140	++
P ⁶⁰ N ⁴⁰	60	40	–	–	140	+
P ⁵⁰ N ⁵⁰	50	50	–	–	160	+
P ⁴⁰ N ⁶⁰	40	60	–	–	160	+
P ²⁰ N ⁸⁰	20	80	–	–	170	–
P ⁸⁰ N ²⁰ G ¹⁰	80	20	–	10	130	+++
P ⁶⁰ N ⁴⁰ G ¹⁰	60	40	–	10	150	+
P ⁸⁰ N ²⁰ G ²⁰	80	20	–	20	150	+++
P ⁸⁰ N ²⁰ T ¹⁰	80	20	10	–	140	+++
P ⁸⁰ N ²⁰ T ²⁰	80	20	20	–	150	+++
N ¹⁰⁰ G ⁵⁰	0	100	–	50	120	+++

PBAT and NaCAS content is expressed in weight percentage. Plasticizer content corresponds to weights per hundred parts (phr) of resin (PBAT/NaCAS polymer blend).

^a Material temperature recorded in the mixing chamber.

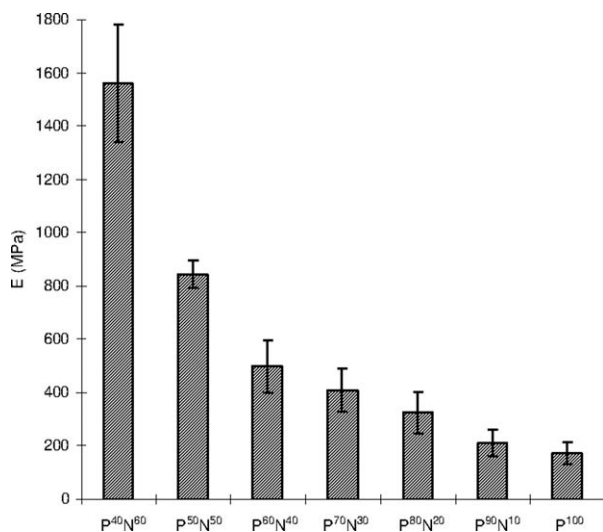


Figure 3 Elastic modulus of PBAT/NaCAS blends.

for blends containing 60% w/w NaCAS. Figure 4 illustrates the drastic reduction of mechanical properties observed for blends containing 30% w/w NaCAS and particularly the fall down of strain observed between 20 and 30% w/w NaCAS in blends: maximum elongations were all inferior to 30% in all these cases. As a partial conclusion to the first part of this work, it clearly appears that maximum NaCAS content in PBAT is comprised between 20 and 30% w/w. Thus, for the following of the study, only two blends were selected, that is, P⁷⁰N³⁰ and P⁸⁰N²⁰, corresponding to the maximum contents of NaCAS that can be incorporated in PBAT keeping mechanical properties interesting enough for packaging applications for example. The loss of mechanical properties for higher contents of NaCAS could be correlated to the increase of the heterogeneity in the material.

Blends of PBAT and plasticized NaCAS

Plasticizers were incorporated in poly(butylene adipate-*co*-terephthalate)/sodium caseinate (PBAT/NaCAS) blends in order to increase elongation at break and decrease mechanical strength. Effect of relative humidity conditions on mechanical properties of such blends was also studied. Tensile properties of 80/20 w/w PBAT/NaCAS blends versus plasticizer type and content were performed under constant given relative humidity conditions. Figures 5 and 6 represent the evolution of the elastic modulus of 80/20 w/w PBAT/NaCAS blends containing Gly and TEA as plasticizers at 53% RH and 0% RH, respectively. The plasticizing effects of both TEA and Gly are both confirmed by the decrease of the elastic modulus with plasticizer content. At 53% RH (Fig. 5), Young's modulus dropped from 325 MPa

for unplasticized blend to less than 100 MPa for P⁸⁰N²⁰T²⁰ or P⁸⁰N²⁰G²⁰ blends plasticized with 20 phr TEA or Gly, respectively. Even for 10 phr plasticizer content, a decrease by more than half of the elastic modulus is observed.

The same tendency (i.e., the decrease of the elastic modulus with plasticizer content) can be observed on Figure 6 where tensile tests were performed at 0% RH this time. Only small differences can be noticed between the elastic modulus recorded at 0% RH (Fig. 6) or at 53% RH (Fig. 5) even if the same tendency is observed, that is, the decrease of elastic modulus as the plasticizer content increase. It can also be noticed that E values are higher at 0% RH than at 53% RH, whatever the plasticizer content and elastic modulus of samples containing TEA are always superior to those of samples plasticized with Gly.

Figures 7 and 8 represent the evolution of the maximum elongation (in %) of P⁸⁰N²⁰T^x and P⁸⁰N²⁰G^x blends containing TEA and Gly as plasticizer at 53% RH and 0% RH, respectively. In the case of Gly, no significant changes of strain were obtained for 10 and 20 phr of plasticizer in the blend whatever the RH conditions (53% or 0% RH) and in all cases maximum elongations were kept about 400% or slightly over. For TEA-plasticized samples, it was very different: even for low-plasticizer content (10 phr), the strain was drastically reduced from about 400% to values inferior to less than 20%, whatever the RH conditions (Figs. 7 and 8). From these results, TEA does not seem to be a good plasticizer for PBAT/NaCAS blends, contrary to Gly. In a previous study dealing with plasticization of NaCAS films, it was demonstrated that between different polyol-type plasticizers, TEA and Gly were the most efficient plasticizers for NaCAS alone. Plasticizer

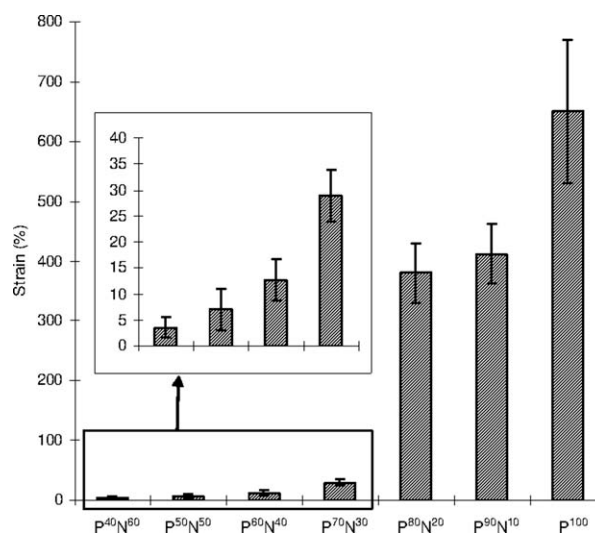


Figure 4 Strain of PBAT/NaCAS blends.

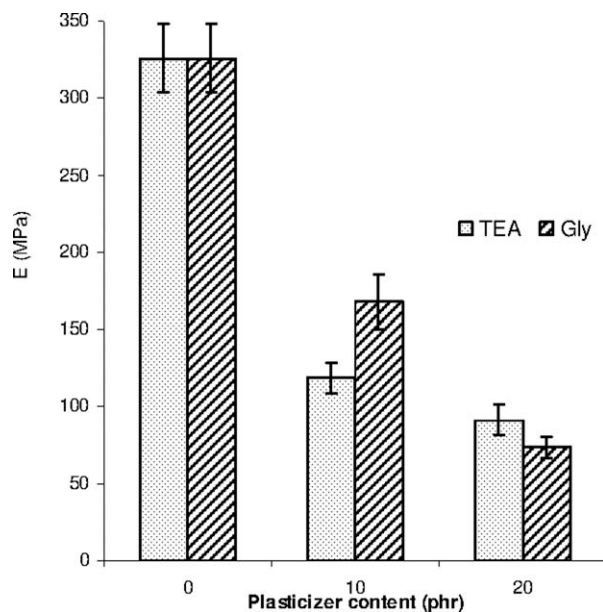


Figure 5 Elastic modulus of PBAT/plasticized NaCAS blends (80/20 w/w) at 53% RH as a function of plasticizer type and content.

efficiency was correlated to a certain extent to the chemical structure of the plasticizer. The increased plasticizing ability of Gly and TEA could likely result from the asymmetry of the Gly and TEA molecules and the presence three hydroxyl group for each molecule leading to polar compounds with good affinity with NaCAS. Both an increase in steric hindrance of plasticizer and asymmetry seems to afford an increase in the NaCAS free volume. Never-

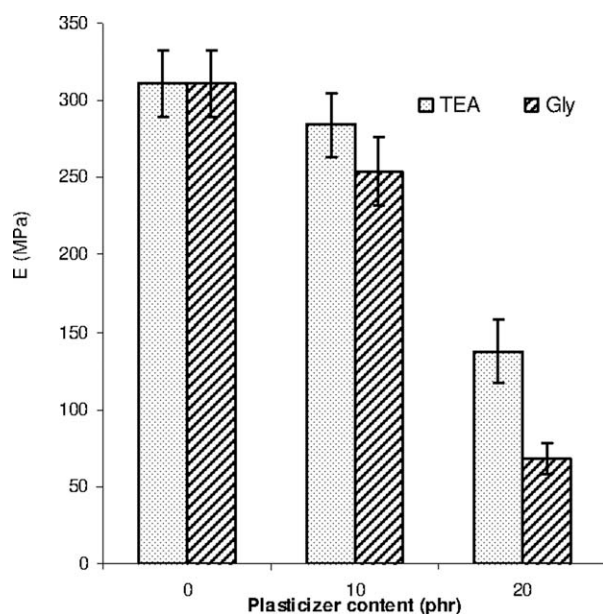


Figure 6 Elastic modulus of PBAT/plasticized NaCAS blends (80/20 w/w) at 0% RH as a function of plasticizer type and content.

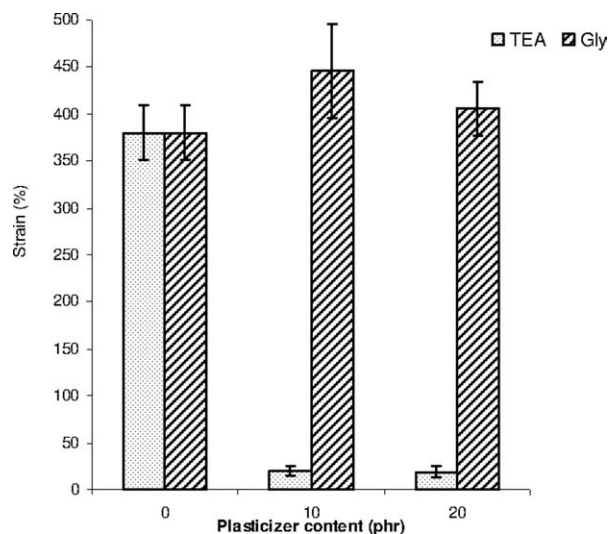


Figure 7 Strain of PBAT/plasticized NaCAS blends (80/20 w/w) at 53% RH as a function of plasticizer type and content.

theless, in the presence of PBAT, TEA does not appear as a good plasticizer any longer. This could be due to a lower compatibility of TEA with PBAT. As a result of the incompatibility of TEA with PBAT, the plasticizer should exude out of the material causing a decrease of the mechanical properties of the blend.

Mechanical performances were also performed on plasticized 70/30 w/w PBAT/NaCAS blends. Figures 9 and 10 represent the evolution of the elastic modulus of such blends as a function of plasticizer type and content, at 53% RH and 0% RH, respectively. In 53% RH conditions, for both plasticizers, an increase in plasticizer content caused a decrease of the elastic modulus (Fig. 9). The plasticizing

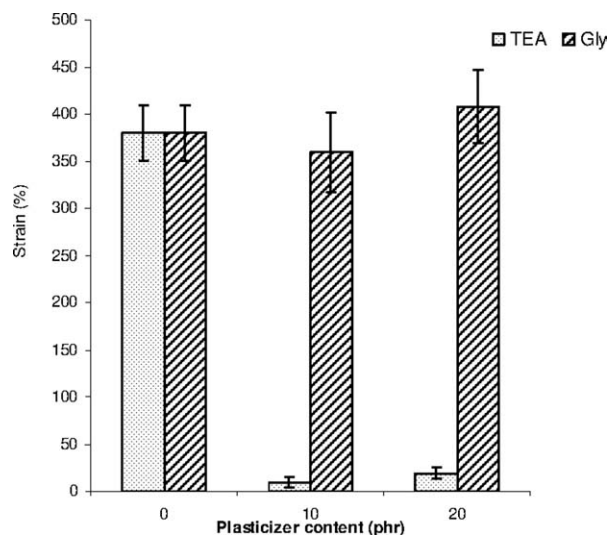


Figure 8 Strain of PBAT/plasticized NaCAS blends (80/20 w/w) at 0% RH as a function of plasticizer type and content.

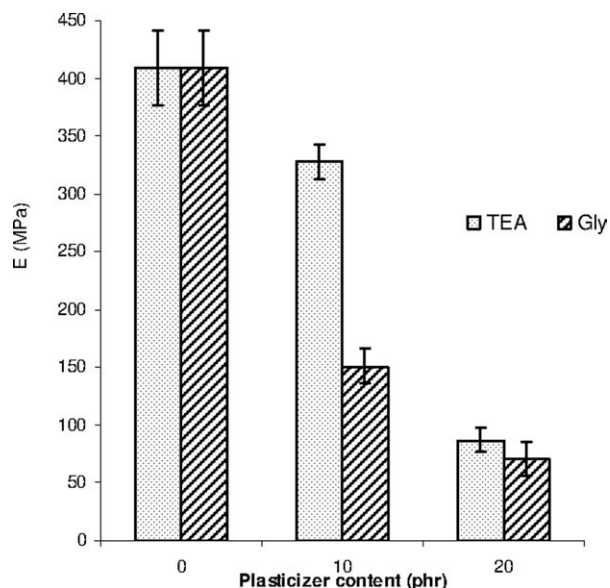


Figure 9 Elastic modulus of PBAT/plasticized *NaCAS* blends (70/30 w/w) at 53% RH as a function of plasticizer type and content.

ability was most pronounced for Gly compared to TEA, especially at 10 phr content, where elastic modulus of 150 and 328 MPa was recorded for Gly and TEA-plasticized samples, respectively. At 20 phr content, elastic modulus was about 87 MPa for TEA-plasticized samples and 71 MPa for Gly-plasticized samples. Once again, TEA was less efficient in plasticizing PBAT/*NaCAS* blends compared to Gly. At 0% RH (Fig. 10), only Gly caused a decrease in Young's modulus when incorporated in blends contrary to TEA, which causes an increase of the elastic modulus indicating its inefficiency as plasticizing

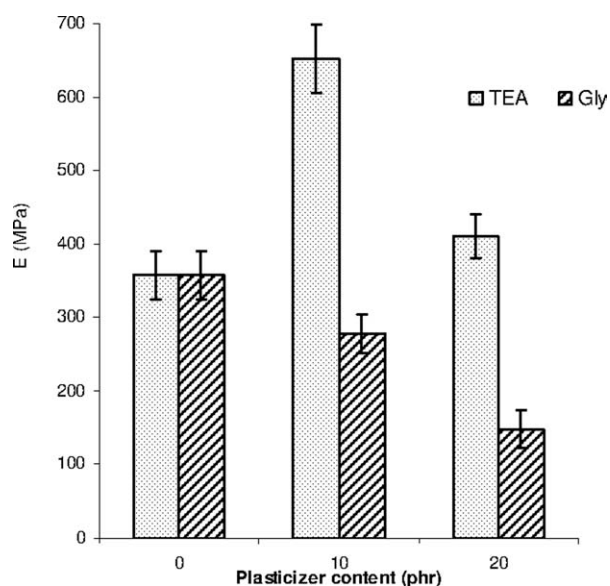


Figure 10 Elastic modulus of PBAT/plasticized *NaCAS* blends (70/30 w/w) at 0% RH as a function of plasticizer type and content.

agent. For Gly-plasticized samples, the elastic modulus decreased from 360 MPa for unplasticized $P^{70}N^{30}$ samples to less than 150 MPa for $P^{70}N^{30}G^{20}$ samples plasticized with 20 phr Gly. On the other hand, for TEA-plasticized samples, the elastic modulus remained high and recorded *E* values were about 700 and 450 MPa for samples containing 10 and 20 phr TEA, respectively. The comparison of the Figures 9 and 10 also shows that plasticizers are more efficient at 53% RH than at 0% RH. This is due to the plasticizing effect of water that was also mentioned in a previous work.⁶ It is well known that water acts as plasticizer for proteins. Thus, equilibrium moisture content affects the mechanical strength of protein-based blends as well through water plasticization. The comparison between Figures 9 and 10 illustrates the plasticizing effect of water: an increase of relative humidity caused a decrease of the elastic modulus, whatever the plasticizer used (TEA or Gly). Equilibrium moisture content enhances plasticizers efficiency.

Strains at break of 70/30 PBAT/*NaCAS* blends are represented versus plasticizer type and content at different RH conditions on Figures 11 and 12 (53% RH and 0% RH, respectively). The incorporation of Gly in blends (Fig. 11) greatly increased strain at break, leading to materials with 250% elongation for samples containing 20 phr Gly. Even for samples containing 10 phr Gly ($P^{70}N^{30}G^{10}$), 160% elongation was already recorded, which is more than five times the initial elongation at break of unplasticized blend ($P^{70}N^{30}$). TEA also causes an increase in the maximum elongation but in lesser

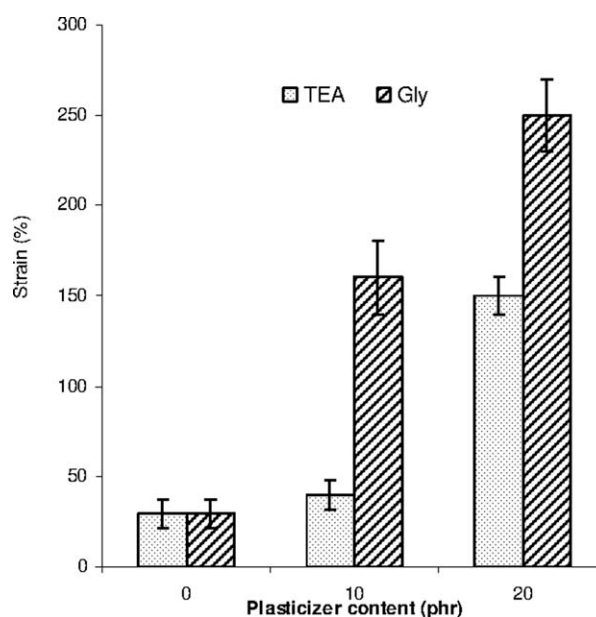


Figure 11 Strain of PBAT/plasticized *NaCAS* blends (70/30 w/w) at 53% RH as a function of plasticizer type and content.

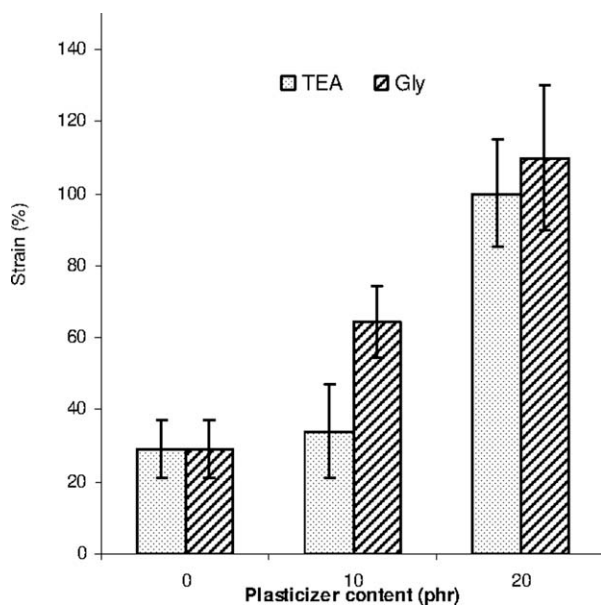


Figure 12 Strain of PBAT/plasticized NaCAS blends (70/30 w/w) at 0% RH as a function of plasticizer type and content.

extend compared to Gly, leading to the same conclusion that once again Gly is most efficient for plasticizing PBAT/NaCAS than TEA. A maximum elongation of only 180% is obtained for 20 phr content of TEA. Figure 12 represents the recorded strains for the same samples (plasticized PBAT/NaCAS 70/30 w/w samples) but at 0% RH. Once more, if the plasticizing efficiency is monitored by an increase of the maximum elongation with the increase of plasticizer content, thus strain values obtained at 0% RH that are inferior to those obtained at 53% RH confirm that water acts as plasticizer and enhances the effect of Gly or TEA. The effect of equilibrium moisture content on mechanical strength of protein-based materials is more visible in 70/30 blends than in 80/20 blends. In fact, mechanical properties of PBAT are not affected by the water content and therefore by relative humidity conditions contrary to NaCAS. Thus, when blends are containing more NaCAS, the only component sensible to water, such blends are more sensible to equilibrium moisture. Thus, materials with higher proportions of NaCAS are also the most affected by RH conditions through water plasticization. At 0% RH, strains were all inferior to 110%, whatever the plasticizer type and content, and Gly is also slightly more efficient than TEA.

Water solubility

Materials obtained from PBAT/NaCAS blends with various contents of NaCAS were immersed into distilled water. The specific water solubility of NaCAS (percentage of initial dry weight of NaCAS in films) versus immersion time is shown in Figure 13. For

the reference sample (N^{100}) only made of protein plasticized with 50 phr Gly, the NaCAS-specific solubility increased rapidly after 10 min, and 45% of the initial content of protein was solubilized in water after only one hour of immersion. A 100% NaCAS, specific solubility was obtained after 48 h immersion in water: the sample was then completely solubilized. For PBAT/NaCAS blends, very low-specific solubilities were only observed after 24 h immersion in water. This solubility increases with NaCAS content in the blend (from $P^{90}N^{10}$ to $P^{70}N^{30}$) but never exceeds 3% of the initial weight content of protein. Even after 48 h immersion in water, the higher specific solubility obtained for $P^{70}N^{30}$ blends remained under 7% of the initial content of NaCAS. Figure 13 pointed out that blending NaCAS with PBAT is an efficient way to increase its water resistance, and PBAT/NaCAS blends are interesting for the manufacture of water resistant goods without any chemical modification of protein by chemical crosslinking or by physical treatment.

Oxygen permeability

Many studies have reported^{5,32} that among biopolymers, proteins films present very low oxygen permeability that make them good ingredients for the formulation of barrier films and materials. Figure 14 gives the oxygen permeability of PBAT/NaCAS blends compared to commercial polymers usually used in packaging applications. For the reference film made of NaCAS plasticized with Gly ($N^{100}G^{50}$), the oxygen permeability of $3,300 \text{ cm}^3 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ atm}^{-1}$ measured in this work is actually rather low and close to OP values reported for PA films. On the other hand, the PBAT is not considered as an oxygen barrier polymer, although its OP, about $80,000 \text{ cm}^3 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ atm}^{-1}$, is below OP values of low

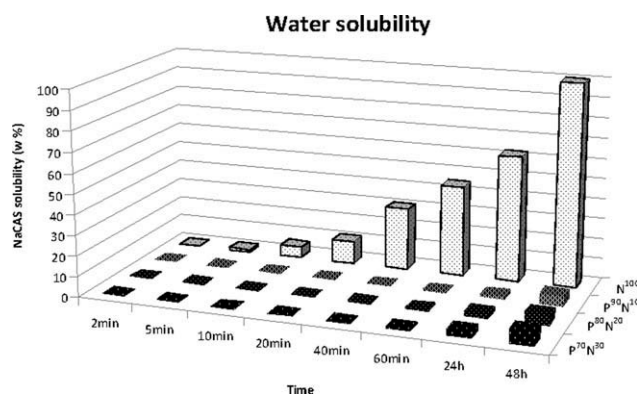


Figure 13 NaCAS specific solubility of PBAT/NaCAS blends in water from the 280 nm absorbance method versus time. PBAT/NaCAS ratios are reported on the right hand side. N^{100} is the reference sample only made of protein plasticized with 50 phr glycerol.

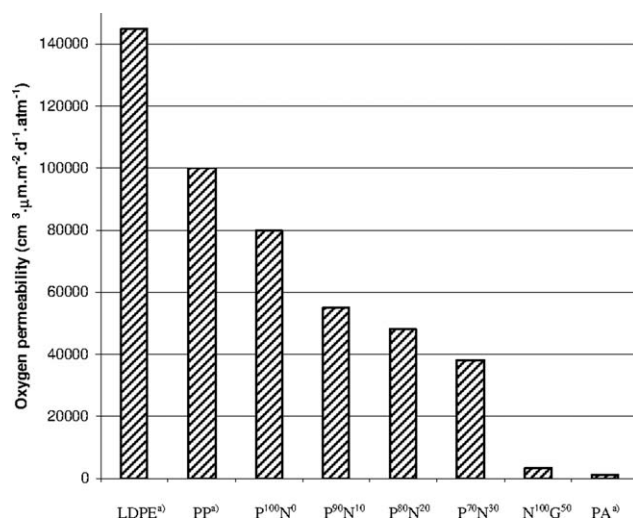


Figure 14 Oxygen permeability of PBAT/NaCAS blends compared to commercial polymers used in packaging applications. LDPE, low-density polyethylene; PP, polypropylene; PA, polyamide-6. ^aAverage OP obtained from different values obtained in the literature.^{28–31}

density polyethylene (LDPE = 145,000 cm³ μm m⁻² d⁻¹ atm⁻¹) and polypropylene (PP = 100,000 cm³ μm m⁻² d⁻¹ atm⁻¹). As expected, the incorporation of NaCAS in PBAT caused a decrease in oxygen permeability proportional to the protein content: the OP of PBAT/NaCAS blends containing 30% NaCAS is thus reduced to less than half of the initial OP value of PBAT alone. These results indicate that protein direct blending with nonbarrier polymers is an efficient and simple way to reduce oxygen permeability of the resulting material.

CONCLUSION

The goal of this work was to obtain biodegradable films with improved oxygen barrier properties, good water resistance, and mechanical properties as close as possible to synthetic polymer films used in packaging applications. NaCAS, a biobased polymer obtained from renewable resources, was first blended with PBAT. From stress-strain testing, it clearly appears that maximum NaCAS content in PBAT to keep mechanical properties interesting enough for packaging applications was comprised between 20 and 30% w/w. Mechanical properties were also increased by the addition of Gly as plasticizer, and the combined efficiency of water acting as another plasticizing agent was also demonstrated. It was also stated that TEA was not convenient for plasticizing NaCAS in blends with PBAT. The resulting material obtained from PBAT/NaCAS blends also showed good water resistance. Finally, it was demonstrated that the incorporation of NaCAS in PBAT causes a decrease in oxygen permeability proportional to the protein content: the OP of PBAT/

NaCAS blends containing 30% NaCAS (OP = 38,000 cm³ μm m⁻² d⁻¹ atm⁻¹) is thus reduced to less than half of the initial OP value of PBAT alone (OP = 80,000 cm³ μm m⁻² d⁻¹ atm⁻¹). These results indicate that protein direct blending with nonbarrier polymers is an efficient and simple way to reduce oxygen permeability of the resulting material. Considering the potential applications in the packaging area of such blends, a part of this work, including supplementary results, was patented (Fr10/02815).

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