



Poly(*n*-butyl acrylate)–Casein Nanocomposites as Promising Candidates for Packaging Films

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Abstract

Partially degradable materials, offer an interesting sustainable alternative for short-term use applications where their environmental impact could be importantly reduced. This article investigates the preparation of a series of poly(*n*-butyl acrylate)–casein nanocomposites with varied bio-component content via emulsifier-free emulsion polymerization. The influence of casein content on the morphological and film properties of the natural/synthetic materials is discussed. Film performance was analyzed in terms of water and vapor resistance, biodegradability in composting conditions, mechanical behavior, opacity, and thermal stability. The obtained results suggest that poly(*n*-butyl acrylate)–casein nanocomposites, with grafting of acrylic chains onto protein molecules, have great potential as bio-defragmentable packaging materials.

Keywords Casein–acrylate · Bio-based nanocomposites · Film properties · Food packaging materials · Seed coating

Introduction

Currently, most of the feedstocks employed in the different packaging industries are undegradable fossil-fuels-derived materials [1]. For instance, fossil-based high-density polyethylene (HDPE) films in the form of inner pouches are used as the major raw materials for dry-food packaging and their global consumption is growing everyday. Thus, packaging materials of short-term use have devastating impacts on the environment. For this reason, during the few last years research attention has been focused on the replacement of petroleum-based polymers by new degradable bio-based materials [2, 3]. According to the European Bioplastics Association the term “biopolymer” includes all those

bio-based polymers fully made on renewable sources, and also those partially made from non-renewable ones. Nowadays, there is no agreement or a clear definition about which would be the minimum percentage of renewable raw material that should have a polymer to be classified as a biopolymer. However, it is clear that partially bio-based materials, although they only have a certain percentage of renewable raw materials, could also provide an important environmental benefit [4]. In this way natural/synthetic hybrid materials could be an interesting sustainable platform for packaging applications.

On the other hand, recently film-coating has gained increasing acceptance in the seed industry as a reliable approach to uniformly apply active ingredients to seeds such as fungicides and/or insecticides. In addition to being able to remain adherent to the seed surface, important requirements of film-coating materials include good barrier properties for preservation of the final product until the application time. Once planted in the soil, seed coatings should be easily degraded (by moisture and/or microorganism action) thus ensuring uniform germination and successful crop establishment [5].

Among the different renewable sources, polysaccharides, proteins and vegetable oils constitute the main starting materials for the current generation of bio-based products [6]. In this sense, bovine casein is a completely biodegradable and harmless natural polymer which has

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certain film properties that make it interesting for a wide range of industrial applications [7]. However, some of its properties such as mechanical behavior and moisture sensitivity should be enhanced to obtain useful and competitive products [8]. Most research efforts have been focused on improving the moisture tolerance of casein films. This certainly plays an important role, especially in dry-food packaging such as that for cereals or nuts [9]. A widely explored approach to correct these weaknesses consists in introducing new hydrophobic segments onto protein molecules via graft polymerization of acrylic monomers [10–19]. In this sense, González and Alvarez [20] have recently reported the preparation of soy protein-methyl methacrylate graft copolymers for packaging applications. Although both the bio- and synthetic components have a high T_g , films were formed by heat compression. Film-forming dispersions could have certain advantages in comparison with thermo-forming materials such as lower energy consumption upon their manufacturing. Thus the use of film-forming polymers, such as poly(*n*-butyl acrylate) (PBA), appear as an interesting alternative in the preparation of protein-based packaging materials.

Graft copolymerization of *n*-butyl acrylate, has been previously studied in aqueous media using persulfate initiators [8, 10, 11]. However, such initiators promote the oxidative degradation of casein and the production of yellowish products, which are undesirable for packaging application, since the lack of transparency negatively influences consumers quality perceptions [21]. Li et al. [18, 19] have reported a synthesis method that overcomes such oxidative problems, which consists of using redox initiation between a hydroperoxide and the amine groups of casein. Although hydroperoxide has been used to produce chitosan–PBA latex [22], there were no reports on using this kind of initiation to synthesize casein–PBA copolymers. Additionally, very few efforts have been made to investigate the correlation between protein content and structure/performance of acrylic–casein films in depth [16, 17]. To the best of our knowledge, the use of acrylic–casein materials for packaging applications has hardly been researched; thus representing these film-forming dispersions a potential alternative in such field.

In this work, PBA–casein nanocomposites were prepared via emulsifier-free emulsion polymerization using tert-butyl hydroperoxide (TBHP) as initiator. The performance of these nanocomposites was analyzed in terms of sensitive properties for food and/or packaging films including water and vapor resistance, biodegradation in composting conditions, film formation, mechanical behavior, opacity and thermal stability. The influence of the bio-component content of synthesized materials on their morphological and film properties was also discussed.

Materials and Methods

Materials

Technical grade casein from bovine milk (Sigma), and butyl acrylate (BA) monomer containing traces of mono methyl ether hydroquinone as inhibitor (Aldrich) were used. The employed initiator was TBHP (Aldrich). Sodium carbonate (Na_2CO_3 , Cicarelli) was used to regulate the pH. Calcium chloride (CaCl_2 , Cicarelli) was used as desiccant and glycerol (Taurus) was used as plasticizer in casein pure films used for the water vapor permeability test. All reagents were used as received without purification. Distilled and deionized water was used throughout the work.

Synthesis of Casein–PBA Nanocomposites

Polymerizations of BA in the presence of casein were carried out in a 0.5 L glass jacketed reactor equipped with thermostatic bath, digital thermometer, condenser, stirrer, N_2 inlet and sampling device. Five experiments of 20% of solid content (only BA and casein were considered for solid calculation) were carried out with variable casein concentration from 3 to 50% weight based on monomer (% wbm), with the following procedure. Casein was first dissolved in the reactor, in a water solution containing 2.5% wbm of Na_2CO_3 (pH 11) and at 50 °C. Then, the solution temperature was raised up to the polymerization temperature (80 °C) and the monomer was loaded under stirring (200 rpm). The resulting dispersion was purged with N_2 for 30 min before injecting 0.2% wbm of TBHP, and it was left to polymerize for 180 min.

Characterization

The fraction of casein grafted to the acrylic polymer (casein grafting efficiency, CGE) was determined following a procedure previously reported [13]. Shortly, ungrafted casein was first extracted from latex through multiple centrifugation and redispersion steps and quantified by UV spectroscopy after calibration with neat casein. Grafted casein was then calculated as the difference between initially loaded and ungrafted protein.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to confirm the formation of PBA-grafted-casein (PBA-g-casein), using a Nicolet 8700 spectrometer equipped with a MCT detector. ATR-FTIR analysis was carried out onto the dried sample latex without containing the ungrafted casein, resulted from extraction procedure used to determine CGE. Additionally, ATR-FTIR spectra from pure PBA and casein were recorded.

Morphology of films obtained from PBA–casein nanocomposites was determined by atomic force microscopy (AFM) using a commercial Nanotec Electronic equipment operating in tapping mode. To this effect, thin films were prepared by casting the latexes onto seal paper using a 120 μm wet-thickness frame applicator and drying it at room temperature during 24 h. Silicon cantilevers (All-In-One, Budget Sensors, Bulgaria) with a nominal spring constant of $k = 40 \text{ N/m}$ and a resonance frequency of 350 kHz were used. AFM experiments were carried out in air at room temperature. Acquisition and image processing were performed using the WSXM free software [23].

For water resistance analysis, film specimens of 1 mm of thickness and 20 mm in diameter were immersed in distilled water at room temperature. Specimens were removed from the medium at a regular time, dried with filter paper, and immediately weighed before being immersed again. This procedure was repeated during 7 days or until the film exhibited damage, measuring the degree of swelling (DS) and the total soluble matter (TSM) (i.e., the percentage of dissolved mass of the dry film). Water vapor permeability (WVP) of films was determined following the ASTM E96M-10 standard method. Films (without physical defects) were placed onto circular aluminum permeation cups (50 mm in diameter and 17 mm in depth) containing dry CaCl_2 . Then, they were located in a humidity chamber at $75 (\pm 2) \% \text{ RH}$ and $25 \text{ }^\circ\text{C}$. The permeation cups containing the analyzed film were weighted at intervals of 24 h during 9 days. Linear regression was used to calculate the slope of a fitted straight line in a graph of variation of mass versus time. The water vapor transmission rate (WVTR) ($\text{g m}^{-2} \text{ s}^{-1}$) and the WVP ($\text{g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) were calculated from duplicate assays according to Eqs. (1) and (2), respectively:

$$\text{WVTR} = F/A \quad (1)$$

$$\text{WVP} = \text{WVTR} \times e / (S_p \times \text{RH}) \quad (2)$$

where F is the slope of the mass versus time curve (g s^{-1}), A is the test area (m^2), e is the film thickness (m), S_p is the water vapor saturation pressure (Pa) at the test temperature, and RH is the relative humidity in the humidity chamber.

The biodegradation ability of the PBA–casein films was qualitatively determined as the materials weight loss (W_{loss}) under composting conditions [8, 16]. To this effect, soil burial experiments were carried out onto films of 1 mm of thickness and 20 mm in diameter. Film samples were buried 14 days in a moisturized commercial compost with the following characteristics: total dry solid = 45% of the wet solids; pH 6.5; and non volatile-solids content = 40% of the wet solids. Then, samples were removed, carefully cleaned to ensure stopping degradation and dried in oven at $60 \text{ }^\circ\text{C}$ up to a constant weight. Finally, W_{loss} was calculated on the basis of the dry films weight as the percentage of the lost mass.

Film formation ability of latexes was characterized by measuring the minimal temperature at which homogenous films are obtained (MFFT). For this purpose, an optical method involving the observation of the clarity of a cast film (120 μm thickness) on a large metal table with a temperature gradient was used [24]. The minimum temperature on the table, where the film was judged to be clear, was considered as the MFFT value.

Dynamic mechanical thermal analysis (DMTA) was employed to determine the glass transition temperature (T_g) of the polymer–casein nanocomposites. From DMTA data as a function of temperature, T_g can be taken as the maximum in $\tan \delta$. To this effect, a film of 0.5 mm thick was presented in the single cantilever-bending mode at a frequency of 1 Hz between -80 and $0 \text{ }^\circ\text{C}$ at a heating rate of $4 \text{ }^\circ\text{C/min}$, using a Tritec 2000 equipment from Triton Technology.

Tensile tests of films with bone shape of length 9.53 mm and cross section $3.18 \text{ mm} \times 1.00 \text{ mm}$ were carried out with an elongation rate of 25 mm/min. Analysis were carried out in a universal testing machine (INSTRON 3344), at $23 \text{ }^\circ\text{C}$ and 50% relative humidity and the average values of testing five specimens of each sample were reported.

Film opacity was evaluated through the method proposed by Irissin-Mangata et al. [25], which is based on the determination of the sample absorption spectrum in the 400–800 nm range. Then, film opacity was determined as the area under the absorption spectrum divided by the sample thickness. Measurements were taken by triplicate for each sample and average values were reported.

Thermal stability of materials was analyzed by thermogravimetric analysis (TGA). For this purpose, samples of 10 mg were heated from 40 to $600 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C/min}$ under nitrogen atmosphere using a Mettler-Toledo Thermogravimetric Analyzer, model TG-50. The temperature at maximal decomposition rate ($T_{d,\text{max}}$) was determined as the temperature at main peak of the derivative weight loss curve. The resistance of materials against heating–cooling cycles was investigated by DMTA. To this effect, film samples were kept at $90 \text{ }^\circ\text{C}$ for 2 h and then at room temperature for the same period of time. After each cycle, DMTA measurements were carried out in tension mode, with a frequency sweeps from 1 to 100 Hz, at fixed amplitude of 15 μm and $30 \text{ }^\circ\text{C}$.

Results and Discussion

PBA-g-Casein in Nanocomposites

Figure 1 presents the final values of CGE of the nanocomposites synthesized with different amounts of casein. The experiment codes contain the abbreviation NC with a subscript that indicates the protein concentration (% wbm)

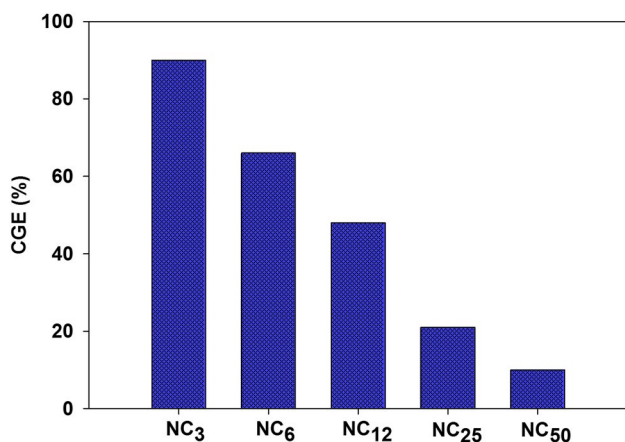


Fig. 1 Casein grafting efficiency of nanocomposites with varied protein content

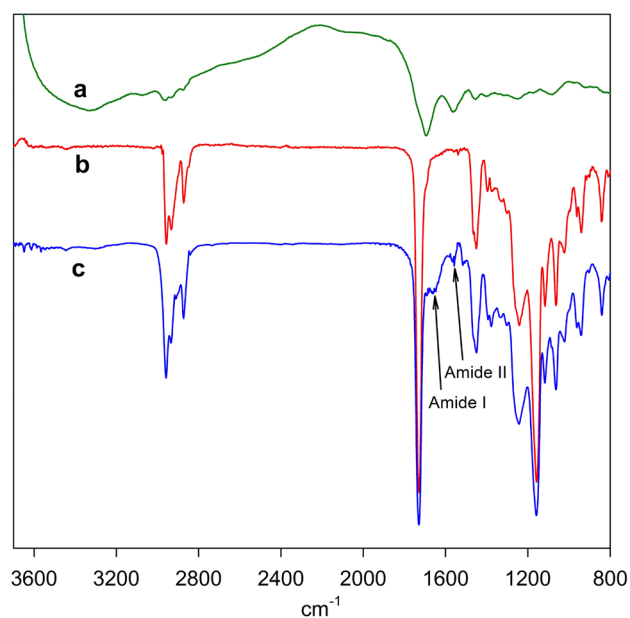


Fig. 2 ATR-FTIR spectra of pure casein (a), pure PBA (b) and PBA-g-casein corresponding to NC₅₀ nanocomposite (c)

used for synthesizing each nanocomposite. As it can be observed, CGE continuously decreases with casein concentration, indicating that high protein contents promote the formation of non-compatibilized nanoparticles (i.e., containing ungrafted casein and PBA). Similar results were previously reported in the graft polymerization of methyl methacrylate and casein [13]. In such case, the generation of uncompatibilized particles was attributed to secondary ways of nucleation (through micellar and/or homogenous mechanisms instead of self-assembling of grafted casein) which were favored by the increase in protein concentration.

PBA-g-casein formation was confirmed by ATR-FTIR spectroscopy (Fig. 2). Spectrum of pure casein shows the characteristic broad band at 3400 cm^{-1} attributed to the $-\text{NH}$, $-\text{OH}$ stretching vibrations, and the characteristic peaks of amide I and amide II at 1690 and 1560 cm^{-1} , respectively. On the other hand, spectrum of PBA-g-casein of experiment NC₅₀, where the ungrafted casein was removed, shows a high content of PBA, with the characteristic peak at 1730 cm^{-1} assigned to carbonyl group ($\text{C}=\text{O}$), and the bands of amide I and amide II corresponding to casein, evidencing the formation of PBA-g-casein.

Properties of PBA–Casein Films

The relationship between acrylic/casein compatibility and materials morphology is an important aspect to better understand the films performance. For this reason, morphological study was carried out for the obtained films from nanocomposites NC₃ and NC₅₀ (Fig. 3). For brevity reasons, only phase images of films surface are presented as they provide greater image contrast between the soft phase, corresponding to PBA (in dark color), and the hard domains of casein (in bright color).

When a high compatibility is achieved in the hybrid system, casein is mostly grafted to the polymer particles and therefore phase separation between acrylic and protein components is limited. In NC₃ nanocomposite, most of casein is grafted to PBA polymer (CGE = 90%) forming the shell of polymer nanoparticles [13, 16]. Thus, despite of the low content of protein, its film surface is mainly constituted by hard domains of casein corresponding to the shell of nanoparticles (Fig. 3a). Additionally, soft PBA domains are observed that probably correspond to PBA particles with low content of grafted casein. Meanwhile, when increasing the casein concentration the PBA/casein compatibility is significantly decreased (for NC₅₀ CGE = 10%). Under this circumstance ungrafted protein acts as a mobile phase and its migration could occur during film formation [26]. Therefore a larger amount of free casein was able to cover the film surface, with soft PBA domains of small size (Fig. 3b). This behavior is in agreement with that observed for similar acrylic/casein nanocomposites with varied casein concentration [16].

Roughness of films is an important surface characteristic which could affect sensitive film properties such as gloss, opacity, adhesion, and permeability. In this work the roughness of the nanocomposites was obtained from the AFM height images as the standard deviation of the mean value. Thus, the root mean square (RMS) of roughness for each film resulted 24.04, 11.72, 7.21, and 1.94 nm for NC₃, NC₁₂, NC₂₅ and NC₅₀, respectively. In other words, the increase of casein content in the formulation enhanced the film formation, thus producing smoother and more even films. This result may be due to that casein acts as a rheological additive

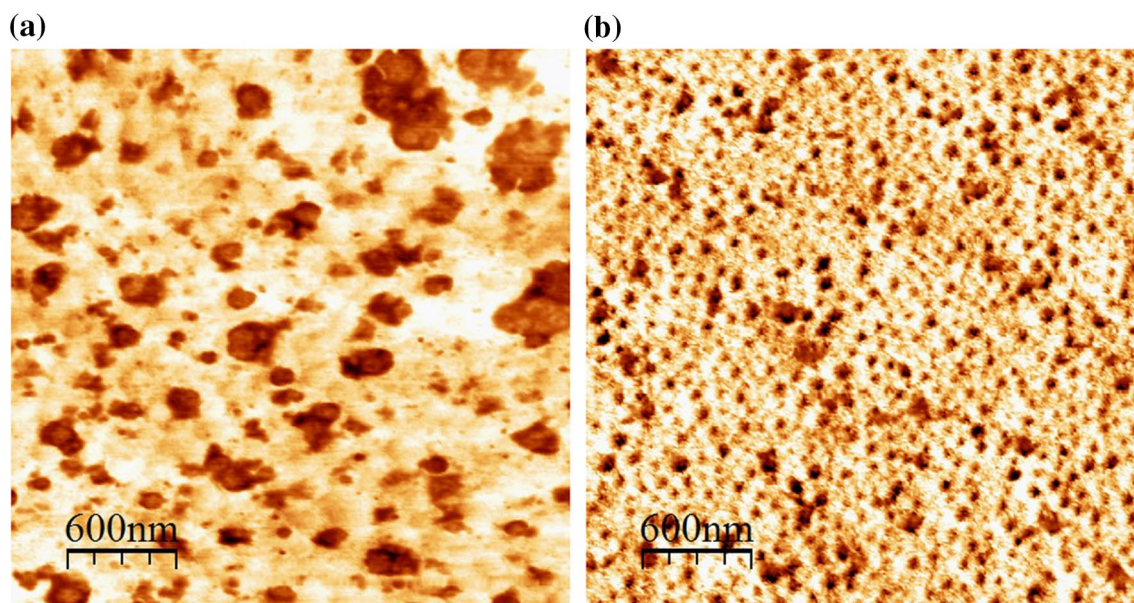


Fig. 3 AFM phase images ($3\ \mu\text{m} \times 3\ \mu\text{m}$) of the film surface of the PBA–casein **a** NC₃ and **b** NC₅₀ nanocomposites

Table 1 Water resistance and vapor permeability of the nanocomposite films

Film	DS (%)	TSM (%)	WVP (g/msPa)
Casein	–	100	1.1×10^{-9}
NC ₃	77.8	6.5	7.6×10^{-10}
NC ₆	116.7	11.7	5.0×10^{-10}
NC ₁₂	165.0	13.1	3.8×10^{-10}
NC ₂₅	–	100	2.3×10^{-10}
NC ₅₀	–	100	1.4×10^{-10}

controlling latex viscosity and delaying water evaporation [27].

Due to the important role of water in deteriorative reactions, WVP and swelling behavior are the most extensively studied properties of films for food packaging [28]. The water resistance and WVP results of nanocomposites and pure casein film are shown in Table 1. Since pure casein film is too brittle to be tested, glycerol (50% based on protein) was used only incorporated in this case as plasticizer with a typical formulation for food packaging applications [29]. Because of proteins are not totally hydrophobic and contain predominantly hydrophilic amino acid residues, they have limited moisture-barrier properties. The grafting of hydrophobic polymers onto casein backbone is expected to reduce its moisture-sensitivity as long as a significant compatibility is reached (i.e., if a great number of both synthetic polymer and protein chains are chemically bonded). Thus, when using low casein concentration (3–12% wbm), compatibilized nanocomposites resisted the water immersion until the

end of the test and presented a very low TSM ranging from 6.5 to 13.1%. Moreover, DS of the films decreased from 165 (NC₁₂) to 77.8% (NC₃) when casein content was reduced and CGE was increased from 48 to 90%. Unfortunately, the use of high casein concentrations (25–50% wbm) and the poor compatibility reached in these cases gave place to the disintegration of films after water immersion, as ungrafted casein was quickly dissolved in the aqueous media.

WVP of the films resulted in all cases lower than that for the pure casein film, indicating that PBA (a hydrophobic polymer) grafted onto protein molecule improve moisture sensitivity. However, according to the above results of water resistance for films, it would be expected that the higher the casein concentration in the nanocomposite film the greater the WVP. Contrary to those expectations, WVP decreased from 7.6×10^{-10} for NC₃ to 1.4×10^{-10} for NC₅₀. Reyes-Mercado and Vazquez [30] have demonstrated that the surface morphology has a strong effect on the WVP of acrylic films. They considered that vapor transfer is carried out mainly through the (micro)voids left between the nanoparticles. As a consequence, the barrier properties are reduced with the increment of the films roughness. RMS roughness results obtained from the AFM height images suggest that nanocomposite films with high casein content have lower values of permeability due to its compact structure and high density, wherein defects as cracks and channels are diminished.

Degradation results of materials after 14 days of burial in composting conditions are shown in Fig. 4. One of the biggest drawbacks of synthetic polymers, as the case of PBA films, is their very low degradability. PBA film exhibits a weight loss of around 0.55% (Fig. 4). However,

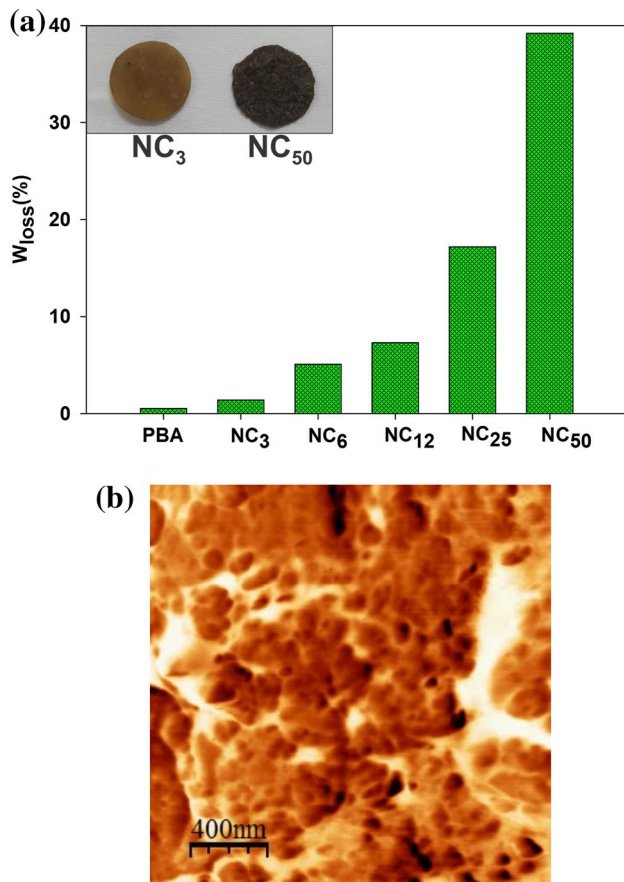


Fig. 4 Soil degradation of the nanocomposite films with different casein content in comparison with PBA film. Picture on the upper left part of the plot shows the films NC₃ and NC₅₀ after 14 days of degradation (a). AFM phase image (2 μm \times 2 μm) of the film surface of NC₅₀ after 14 days of degradation (b)

the incorporation of a highly degradable natural protein to the acrylic formulation, notably improved the biodegradation capability of the films. Thus, the materials weight loss (W_{loss}) was increased from 1.4 to 39.2% for casein contents of 3 and 50% wbm, respectively. Pictures of nanocomposites films NC₃ and NC₅₀ (of 1 mm of thickness) after 14 days of degradation are shown in the left corner of Fig. 4a. Note that despite of film weight loss, films were not disintegrated. However, the AFM-observed surface morphology of NC₅₀ film after degradation (Fig. 4b) shows mainly a PBA coalesced particles phase, containing few hard domains of casein. In comparison with the surface morphology before degradation (Fig. 3b), this observation indicates that casein was mostly degraded.

The low WVP together with the good degradation capability of the high casein content nanocomposites suggest that these materials could be an excellent alternative for dry-food packaging films, where humidity could alter the main characteristics of the packed products (taste and

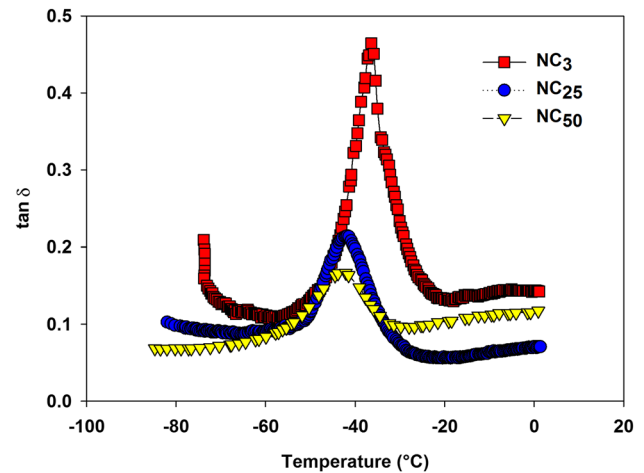


Fig. 5 Tan δ versus temperature for the NC₃, NC₂₅ and NC₅₀ nanocomposites

crunch). Moreover, the combination of good vapor barrier, low water resistance and soil degradation, hardly reached with conventional synthetic polymers, could be very useful in seed coating applications [5].

When focusing on the application of these nanocomposites in food or seed packaging films, a desirable characteristic for this kind of film-forming dispersions is a low MFFT to form smooth films at room temperature. Indeed, casein in aqueous solution can easily form a film (casein MFFT is 11 °C) despite its high T_g (around 180 °C), due to the high plasticization effect of water. Film formation in such protein occurs through intermolecular disulphide bridges and hydrogen bonds accompanied by surface dehydration [31]. A pure PBA latex and the PBA–casein nanocomposites presented a MFFT lower than 2 °C (the minimum temperature able to be recorded with the employed equipment), regardless their casein content. This good film-forming ability of the PBA–casein dispersions is also attributed to the low T_g of PBA and hybrid copolymers.

Figure 5 shows tan δ as a function of temperature for NC₃, NC₂₅ and NC₅₀ nanocomposites. The maximum in the curve of tan δ occurs at -36.4 , -41.7 and -42.9 °C for NC₃, NC₂₅, and NC₅₀ respectively, thus confirming the low T_g of the materials. Furthermore, note that the greater the polymer/protein compatibility (i.e., CGE) the higher the T_g of the nanocomposites. Also, it can be seen that the increase of the casein content yielded a decrease in the maximum value of tan δ (i.e., G''/G'). It was evidenced that the glassy protein has a greater influence on the storage module (G'), increasing it, rather than the loss module (G''), which is mainly determined by the soft acrylic polymer (data not shown for reason of space). Moreover, it is worth to mention that despite the low T_g of the nanocomposites, films were not sticky because of increase in

the bulk storage module reduces the tack adhesion energy [16].

The mechanical properties such as Young's modulus, tensile strength, elongation at break, and toughness of the obtained films are summarized in Table 2. Due to its random coil nature casein can form extensive intermolecular hydrogen, electrostatic and hydrophobic bonds leading to films with high tensile strength and low elongation capability. Somanathan et al. [32] reported values of 45.9 MPa, 7.7% and 1.6 MJ/m³ for the tensile strength, elongation at break and toughness of unplasticized casein films, respectively. As it was expected the grafting of soft acrylic chains onto casein backbone yielded materials with increased elongation capability and toughness in comparison with the pure casein film. As it was also mentioned before, mechanical behavior of nanocomposite films was strongly dependent upon bio-component content, since casein is the glassy component that confers rigidity. PBA film is a soft material with high elongation at break (816%) but with low tensile strength and toughness (0.14 MPa and 0.82 MJ/m³, respectively). Therefore, films containing 3% wbm of casein exhibited an improvement in their mechanical properties with respect to that of pure PBA. For higher casein concentrations, materials presented enhanced Young's modulus, and tensile strength but reduced elongation. Thus, film containing 12% of casein showed the maximum toughness of 12.8 MJ/m³. This behavior may be related to the decrease of the system compatibility with the casein content in the nanocomposite. When the material presents a high amount of non-grafted casein, it could segregate in large hard domains with reduced extensibility, and as a consequence films must fail at lower deformations. However, mechanical performance (elongation at break and toughness) of these films are importantly improved with that observed for pure casein, fulfilling the common service requirements in relation to workability and general handling properties for packaging applications.

In packaging, films aesthetic appearance is a key parameter, which impacts on the ability to visualize the packaged product [33]. Film opacity of the nanocomposites resulted 600.3, 529.5, 379.6, 53.6, and 85.1 AU × nm/mm, for NC₃, NC₆, NC₁₂, NC₂₅, and NC₅₀, respectively. Figure 6 presents a picture of films NC₆ (Fig. 6a) and NC₅₀ (Fig. 6b), with

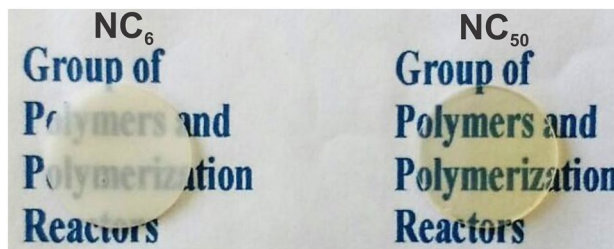


Fig. 6 Appearance of nanocomposite films NC₆ and NC₅₀

different opacity, in order to compare their appearance. The high opacity of the low casein content nanocomposites could be explained based on the film morphology previously discussed. When using low casein concentrations, protein is mostly grafted to the acrylic polymer forming the hard shell of the nanoparticles, which hinders their complete deformation and coalescence. As a consequence, internal large voids and irregularities could be present into the films which promote opacity because of light scattering effects [34]. On the other hand, films containing high casein concentrations (25–50% wbm) present a high transparency. These results are in accordance with the roughness values measured for the nanocomposite films, since such parameter also promotes the surface scattering of light. It represents a good appearance improving of the materials synthesized through the method here proposed, when comparing with films obtained from latex polymerized with potassium persulfate where opacity was 356.9 AU × nm/mm for 25% wbm of casein as a consequence of the protein oxidative degradation.

It is important to carry out studies on the thermal properties and stability of protein-based films for their application in food industry as the materials may be subjected to heat processes during their preparation or processing [35]. Derivative thermogravimetric analysis (DTG) demonstrates the effect of PBA–casein compatibility on the thermal stability of the nanocomposites. For comparison purposes, neat casein was also included in this study. Figure 7 clearly shows that materials displayed similar decomposition patterns with $T_{d,max}$ values ranged from 392 to 404 °C. Also note that $T_{d,max}$ was not significantly affected by the components degree of compatibilization, however the maximum

Table 2 Mechanical properties of the PBA–casein nanocomposite films

Experiment	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Toughness (MJ/m ³)
NC ₃	0.35 ± 0.1	0.89 ± 0.04	1117.6 ± 168	6.4 ± 0.9
NC ₆	5.1 ± 0.8	1.3 ± 0.1	692.9 ± 24	7.4 ± 0.5
NC ₁₂	20.9 ± 3	2.2 ± 0.1	636.3 ± 24	12.8 ± 0.3
NC ₂₅	93.1 ± 4	5.5 ± 0.1	156.2 ± 6	7.5 ± 0.4
NC ₅₀	283.7 ± 21	6.7 ± 0.7	64 ± 2	3.8 ± 0.2

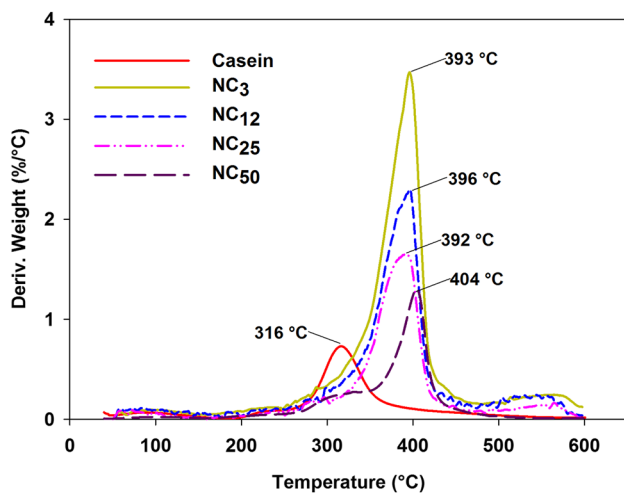


Fig. 7 DTG curves of neat casein and casein–PBA nanocomposites with different protein contents

of the DTG curves at these temperatures decreased as the casein concentration was increased. Similar results were reported by Ma et al. [8] for caprolactam-butylacrylate co-modified casein materials and they attributed this behavior to the heat and mass transport barrier properties of the structured core–shell nanoparticles. The stability and mechanical behavior of films after heating/cooling cycles were also investigated. The DMTA results for nanocomposites NC₆ and NC₅₀ showed that after each heating/cooling treatment the storage moduli (E') of film samples was increased over the range of frequencies analyzed (Fig. 8). This film strengthen could be attributed to casein–casein crosslinking through intermolecular disulfide bonds formed during the heat treatment [36], which is supported by the higher variation of E' when casein content was increased. These results indicated that films were not stable under heating/cooling treatments, but these changes would be less significant in packaging or seed coating applications, where mild processing temperatures are required.

Conclusions

PBA–casein nanocomposites containing varied protein concentrations were successfully synthesized via emulsifier-free emulsion polymerization. PBA–casein compatibility was strongly dependent on the protein amount used in the formulation, so that nanocomposites with low casein concentrations (3–12% wbm) presented high levels of grafted casein. However, for higher casein concentrations (25–50% wbm) most of the casein remained ungrafted, and consequently phase segregation could be produced in the materials. The grafting of PBA hydrophobic chains onto casein backbone also enhanced the water resistance

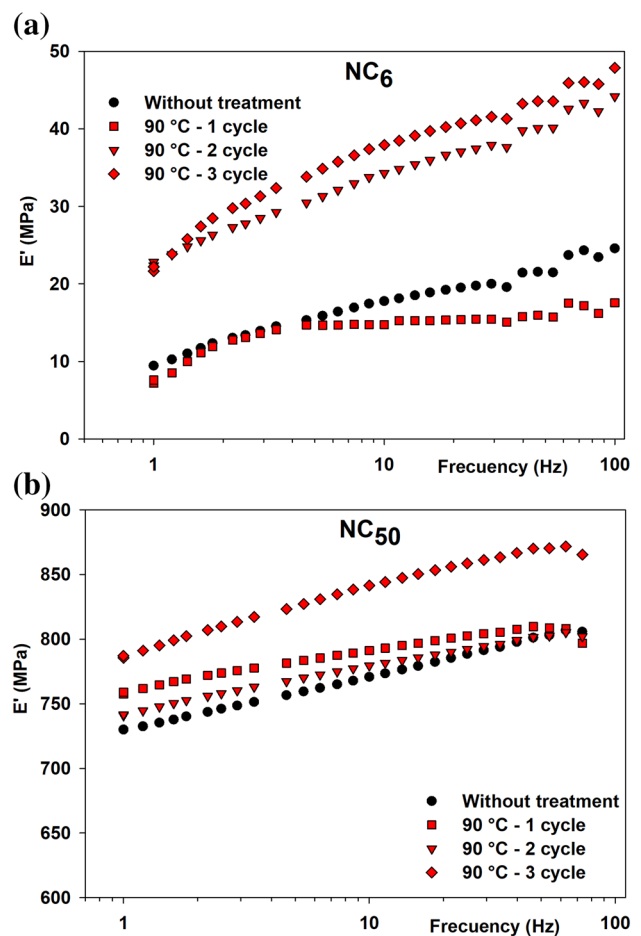


Fig. 8 DMTA results for NC₆ (a) and NC₅₀ (b) nanocomposites after heating/cooling cycles

of the nanocomposites with low casein content. On the other hand, the surface film morphology resulted a key parameter that affected the barrier properties of the nanocomposites films. It was observed that high casein contents led to compact and dense films with lower WVP. Moreover, nanocomposites presented increasing degradation rate in composting conditions as the casein concentration was augmented, obtaining weight losses in 14 days of up 39.2% of the dry film for a casein content of 50%. Also, nanocomposites showed improved mechanical properties, with respect to pure casein films, with higher elongation capability. The above results demonstrate that PBA–casein nanocomposites represent a promising alternative for dry-food packaging films or seed coatings, where moisture barrier and biodegradation after their shelf-life are mainly required characteristics.

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