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Preparation, characterization, mechanical and barrier properties investigation of chitosan–clay nanocomposites

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ABSTRACT

In the current study the effect of dilution of chitosan acetate solution and of the use of a reflux-solution method on the morphology, the mechanical and water barrier properties of chitosan based nanocomposites is being investigated. Two series of nanocomposite films from two chitosan acetate solutions with 2 w/v% and 1 w/v% in chitosan were prepared, with 3, 5 and 10 wt% Na-montmorillonite (NaMMT) and/or 30 wt% glycerol. Intercalation of NaMMT was more effective in films based on 2 w/v% solutions which presented decreased hydrated crystallinity. Upon NaMMT addition an enhancement was found in stiffness and strength (up to 100%) and a remarkable decrease in the elongation at break (up to 75%) and water vapor permeability (WVP) (up to 65%). This enhancement was less pronounced in 1 w/v% systems. Addition of glycerol had a negative effect on the stiffness, strength and WVP, and a positive effect on the elongation at break and the absorbed water. Compared with the conventional solution cast method, the reflux treatment led to a significant improvement of the tested properties of nanocomposite films.

1. Introduction

Environmental concerns caused by the solid waste after use of petrochemical-based plastic packaging materials have increased the interest in biodegradable packaging materials (Han & Gennadios, 2005). These materials are often formulated with natural biopolymers, such as polysaccharides, proteins, and natural gums, capable of forming a cohesive and continuous matrix (Cuq, Gontard, & Guilbert, 1998; Han & Gennadios, 2005).

Chitosan, the cationic (1-4)-2-amino-2-deoxy-β-D-glucan, is industrially produced in various quality grades from chitin, the second most abundant polysaccharide in nature (Muzzarelli, 2012; Muzzarelli et al., 2012) and has been studied extensively for applications in the packaging industry (Rhim & Ng, 2007) owing to its biodegradability, biocompatibility, and absence of toxicity. However, it's mechanical and water barrier properties should be improved.

A commonly used approach to enhance mechanical and barrier properties of chitosan to meet standards for a wide range of applications is through the introduction of reinforcement at the nanoscale (Jason, Marroquina, Rheea, & Park 2013; Lavorgna et al., 2014; Muzzarelli & Muzzarelli, 2002; Muzzarelli, 2011). The addition of layered silicates and in particular montmorillonite (MMT) in chitosan has been extensively studied (Günister, Pestreli, Unlu, Atici, & Gungor, 2007; Hong et al., 2011; Oguzlu & Tihminlioglu, 2010; Rhim, Hong, Park, & Ng, 2006; Tang et al., 2009; Wang et al., 2005; Wang, Du, Yang, Tang, & Luo, 2006; Xu, Ren, & Hanna, 2006). It was been shown that both the structure of chitosan/MMT nanocomposites and their thermal stability are strongly affected by the solvent-casting procedure used (Günister et al., 2007). In Ref. Wang et al. (2005) the effect of both acetic acid residue and the hydrogen bonds formed between chitosan and MMT on the nanocomposite properties have investigated. They demonstrated that the residual acetic acid accelerates the thermal decomposition of chitosan and decreases its crystallinity level. The effect of the solution's temperature and acidity (e.g. pH 5, 8 and 12) on the MMT dispersion has been also documented (Potarniche et al., 2012). It was found that for pH 5 and high solution temperatures a higher quantity of chitosan was intercalated between the silicate layers compared to the samples processed at room temperature or at other pHs. From this it can be assumed that at pH 5 the chitosan chains are oriented preferentially between the silicate layers.

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Table 1
Amounts (g and wt%) of chitosan, glycerol, NaMMT used for the preparation of chitosan, chitosan/glycerol, chitosan/NaMMT and chitosan/glycerol/NaMMT films via the reflux solution method as well as d_{001}, Young's modulus (E), tensile strength (σ_{uts}), elongation at break (ε_b), and water vapor permeability (WVP) values.

Code name	Chitosan (g)-wt%	Glycerol (g)-wt%	NaMMT (g)-wt%	d_{001} (nm)	E (MPa)	σ_{uts} (MPa)	ε_b (%)	WVP ($g\,h^{-1}\,m^{-2}$)
Chitosan solution 2 w/v% in 1 v/v% acetic acid (HAc)								
CS_2	2–100%	–	–	–	3411 ± 410	123.65 ± 4.55	15.65 ± 2.30	9.5 ± 0.5
CS3MMT_2	2–97%	–	0.0583–3%	–	6940 ± 461	208.50 ± 4.97	6.05 ± 0.53	3.3 ± 0.3
CS5MMT_2	2–95%	–	0.0950–5%	1.66	4866 ± 307	151.00 ± 9.57	5.00 ± 0.85	5.0 ± 0.3
CS10MMT_2	2–90%	–	0.1820–10%	1.74	6156 ± 117	122.50 ± 15.72	3.93 ± 0.83	3.2 ± 0.2
CS30G_2	2–70%	0.857–30%	–		1403 ± 232	118.00 ± 11.90	67.55 ± 6.43	17.9 ± 0.5
CS30G3MMT_2	2–67%	0.896–30%	0.0896–3%	–	416 ± 2	78.00 ± 7.48	82.90 ± 7.40	15.5 ± 0.4
CS30G5MMT_2	2–65%	0.926–30%	0.1540–5%	2.09	1043 ± 58	82.40 ± 12.40	61.85 ± 12.15	14.9 ± 0.4
CS30G10MMT_2	2–60%	1.004–30%	0.3370–10%	2.07	608 ± 37	92.60 ± 6.12	89.25 ± 5.70	13.3 ± 0.3
Chitosan solution 1 w/v% in 0.5 v/v% acetic acid (HAc)								
CS_1	2–100%	–	–	–	3527 ± 247	108.00 ± 6.96	15.38 ± 1.70	16.2 ± 0.4
CS3MMT_1	2–97%	–	0.0583–3%	1.69	4264 ± 202	111.00 ± 2.63	5.15 ± 2.18	14.1 ± 0.3
CS5MMT_1	2–95%	–	0.0950–5%	1.81	4748 ± 78	126.00 ± 11.4	9.58 ± 2.38	12.7 ± 0.3
CS10MMT_1	2–90%	–	0.1820–10%	1.83	4480 ± 402	128.00 ± 8.20	6.13 ± 2.38	11.9 ± 0.2
CS30G_1	2–70%	0.857–30%	–	–	1178 ± 125	67.25 ± 12.04	50.68 ± 9.23	23.8 ± 0.4
CS30G3MMT_1	2–67%	0.896–30%	0.0896–3%	2.05	31 ± 5	25.25 ± 3.34	56.63 ± 0.80	23.6 ± 0.5
CS30G5MMT_1	2–65%	0.926–30%	0.1540–5%	2.69	96 ± 10	58.75 ± 4.20	92.18 ± 5.28	22.8 ± 0.5
CS30G10MMT_1	2–60%	1.004–30%	0.3370–10%	2.03	48 ± 8	10.47 ± 0.65	37.50 ± 4.40	20.9 ± 0.5

The synergistic effect of plasticizer and layer silicate on the properties of chitosan based films has been reported in Ref. Lavorgna, Piscitelli, Mangiacapra, and Buonocore (2010). It was concluded that there is a competition between local structure and long-range order in self-associated chitosan and chitosan based nanocomposite films, controlled by electrostatic interactions, hydrogen bonding and crystallization processes, which has not been yet fully understood.

Based on the above the aim of the current study is to elaborate on the solution casting method in order to enhance intercalation/exfoliation and thus improve the performance of the NaMMT reinforced chitosan films. Since the temperature, the acidity of the chitosan solution and the amount of acetic acid residues are of key importance for the degree of intercalation, the amount of hydrogen bonding and the crystallinity level of the final films, a reflux-solution methodology has been introduced for the preparation of chitosan based nanocomposites. The reflux condenser does not allow any water or acetic acid to evaporate during processing, and is expected to result in higher mobility and more homogenous charge of the chitosan's amine groups and thus more effective interaction between chitosan and NaMMT. The reflux-solution methodology is applied on two different chitosan acetate dilution levels (2 w/v% and 1 w/v% in chitosan) in order to define the required acetate concentration for effective charge of the chitosan's chains with limited residues. Selected films were prepared with the conventional solution cast method for comparison. Also the effect of the: (i) addition of different amounts of NaMMT varying from 3 wt% to 10 wt% and (ii) addition of both glycerol (in a standard content of 30 wt%) and clay were studied. The obtained morphology as well as the mechanical and barrier properties of the nanocomposite films was investigated.

2. Experimental

2.1. Materials

Medium molecular weight chitosan with viscosity of 200–800 cP, 1 wt% in 1% acetic acid at 25 °C (Cat. No. 448877) with a deacetylation degree 75–85% was purchased from Sigma–Aldrich. The pristine clay Na-montmorillonite (NaMMT) (Nanomer® PGV – hydrophilic betonite nanoclay) and glacial acetic acid (HAc) was bought from Sigma–Aldrich. Glycerol used as plasticizer was purchased from Carlo Erba.

2.2. Preparation of chitosan nanocomposite films

2 w/v% chitosan solution was prepared by dissolving 20 g of chitosan powder in 1000 ml of 1 v/v% aqueous HAc solution, under vigorous stirring for 24 h at 70 °C. Then the mixture (pH ≈ 4.4) was left to cool down at room temperature. 500 ml of the as above prepared chitosan solution was diluted in 500 ml distilled water to make a second chitosan solution with concentration of 1 w/v% (pH ≈ 4.7). The two chitosan solutions were stored for further use.

(i) 100 ml of 2 w/v% and (ii) 200 ml of 1 w/v% chitosan solution were respectively mixed with the appropriate amounts of NaMMT and glycerol in order to reach a final clay concentration of 3, 5 and 10 wt% and glycerol concentration of 30 wt%. The amounts of chitosan, clay and plasticizer used for each sample are listed in Table 1. The chitosan–clay and chitosan–glycerol–clay mixtures were refluxed for 1 h, spread onto plastic dishes (14 cm diameter), dried at ambient conditions (≈22 °C) for 5 days and finally the plastic films were peeled off.

2.3. XRD analysis

The X-ray diffraction analysis of the obtained films was performed on a D8 Advanced Brüker diffractometer with CuK_a radiation ($\lambda = 1.5418$ Å) and the d-spacing of the clay containing samples was estimated from the 0 0 1 reflection.

2.4. Tensile measurements

Tensile tests were performed according to ASTM D882 using a miniature material tester with a 1000 N load cell. Three to five samples of each formulation were clamped between the grips (30 mm initial distance) and tensioned at a crosshead speed of 10 mm/min. The shape of the samples was dumbbell with gauge dimensions of 15 mm × 3 mm × 0.22 mm. Force (N) and deformation (mm) where recorded during the test. The results obtained from the mini-tester can only be used for comparison, because the strain values are based on the rotational movement of the drive shaft. Baseline samples (not containing nanoclay or glycerol) were tested at the beginning of each set of samples for comparison.

2.5. Water sorption

Selected films were cut in small pieces (12 mm × 12 mm), desiccated overnight under vacuum and weighed to determine their