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Effects of preparation methods on the structure and mechanical properties of wet conditioned starch/montmorillonite nanocomposite films

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ABSTRACT

TPS/Na–montmorillonite nanocomposite films were prepared by solution and melt blending. Clay content changed between 0 and 25 wt% based on the amount of dry starch. Structure, tensile properties, and water content of wet conditioned films were determined as a function of clay content. Intercalated structure and V_H-type crystallinity of starch were found for all the nanocomposites independently of clay and plasticizer content or preparation method, but at larger than 10 wt% clay content nanocomposites prepared by melt intercalation contained aggregated particles as well. In spite of the incomplete exfoliation clay reinforces TPS considerably. Preparation method has a strong influence on mechanical properties of wet conditioned films. Mechanical properties of the conditioned samples prepared by solution homogenization are much better than those of nanocomposites prepared by melt blending. Water, which was either adsorbed or bonded in the composites in conditioning or solution mixing process, respectively, has different effect on mechanical properties.

1. Introduction

Recently growing interest has been shown in the application of biopolymers as packaging materials in order to reduce the environmental pollution caused by plastic waste and to achieve sustainable development. Starch is considered as one of the most promising biopolymer because it is readily available, cheap and biodegradable. Starch is a semicrystalline polymer and it represents the major form of stored carbohydrate in plants. Starch is composed of repeating α-D-glucopyranosyl units, a mixture of two substances, an essentially linear polysaccharide-amylose and a highly branched polysaccharide-amylopectin. In amylose the repeating units are linked by α(1–4) linkages; the amylopectin has an α-(1–4)-linked backbone and ca. 5% of α (1–6)-linked branches (Averous, 2004; Avérous & Pollet, 2012; Hayashi et al., 1981; Zobel, 1988). The relative amounts of amylose and amylopectin depend upon the botanical source. Corn starch granules typically contain approximately 70% amylopectin and 30% amylose (Lambert & Poncelet, 1997). The properties of starch depend strongly on the ratio of these two components. One of the major problems with granular starch is its limited processability, which can be improved by the use of plasticizers, i.e. thermoplastic starch (TPS). TPS can be obtained by the destruction of the starch granules in the presence of plasticizers under specific conditions. Polyols such as glycerol, glycols as well as water are the most widely used plasticizers (Averous, 2004; Avérous & Pollet, 2012; Chivrac, Pollet, & Averous, 2009). The main disadvantages of TPS are its pronounced hydrophilic character and the inadequate mechanical properties. The inferior properties of TPS can be improved by the incorporation of other materials (natural fibers, nanoclays, or other biodegradable polymers) (Averous, 2004; Averous & Boquillon, 2004; Averous & Fringant, 2001; Averous, Fringant, & Moro, 2001a; Averous, Fringant, & Moro, 2001b; Chivrac et al., 2009; Mitrus, 2010; Schwach & Averous, 2004; Vroman & Tighzert, 2009).

Polymer/clay nanocomposites are assumed to exhibit improved barrier, thermal and mechanical properties comparing with traditional composites. Recently several attempts were reported in the literature for the preparation of TPS nanocomposites. In most cases TPS/montmorillonite nanocomposite films were prepared by melt blending (in internal batch mixer or in a twin screw

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extruder) (Avella et al., 2005; Chen & Evans, 2005; Chiou et al., 2007; Chivrac et al., 2009; Chivrac, Pollet, Dole, & Averous, 2010; Dean, Yu, & Wu, 2007; Huang, Yu, & Ma, 2004; Magalhaes & Andrade, 2009; Muller, Laurindo, & Yamashita, 2012; Ray & Bousmina, 2005; Tang, Alavi, & Herald, 2008) or solution mixing (film casting) (Chaudhary & Liu, 2013; Chivrac et al., 2009; Cyras, Manfredi, Ton-That, & Vazquez, 2008; Kampeerapappun, Aht-Ong, Pentrakoon, & Srikulkit, 2007; Kelnar, Kapralkova, Brozova, Hromadkova, & Kotek, 2013; Majdzadeh-Ardakani, Navarchian, & Sadeghi, 2010; Masclaux, Gouanve, & Espuche, 2010; Pandey & Singh, 2005; Ray & Bousmina, 2005; Schlemmer, Angelica, & Sales, 2010). The results clearly demonstrated that the incorporation of organophilic montmorillonite with apolar character led to the formation of conventional microcomposites, while due to the polar nature of both starch and Na–montmorillonite (NaMMT) the application of NaMMT results in an intercalated/exfoliated structure of TPS nanocomposites (Chivrac et al., 2009; Ray & Bousmina, 2005). Large extent of exfoliation was achieved using only water or less than 10 wt% glycerol as plasticizer (Chivrac et al., 2009; Dean et al., 2007; Tang et al., 2008). Several studies proved that the use of glycerol contents larger than 10 wt% led to the formation of intercalated structures with interlayer basal spacing (d_{001}) increasing from 1.2 to 1.8 nm (Chiou et al., 2007; Chivrac et al., 2009; Pandey & Singh, 2005). It is difficult to verify whether the starch or the glycerol molecules intercalate between the clay layers, because both have a tendency to penetrate into the silicate layers, but penetration of glycerol is favored owing to its smaller molecular size (Aouada, Mattoso, & Longo, 2011; Chaudhary & Liu, 2013). Several investigations confirm the strong influence of the polyol plasticizer on the exfoliation process and thus on the resulting morphology. This effect is likely related to the hydrogen bonds established between glycerol and MMT platelets, which could decrease the attractive forces between starch and clay (Chiou et al., 2007; Chivrac et al., 2009; Pandey & Singh, 2005). Exfoliated/intercalated morphology is found to be dependent also on NaMMT content. Exfoliation is the predominant mechanism of clay dispersion at small filler content (Schlemmer et al., 2010), while increasing the clay content above 5 wt% favors the formation of intercalated structure.

In spite of incomplete exfoliation the TPS/NaMMT nanocomposites have improved properties compared to TPS. Its properties strongly depend on the type of the starch and the montmorillonite used, as well as on the amount of MMT and glycerol. Papers published so far indicate that larger extent of exfoliation results in better properties (Aouada et al., 2011; Chen & Evans, 2005; Chivrac et al., 2009; Dean et al., 2007; Majdzadeh-Ardakani et al., 2010; Muller et al., 2012; Schlemmer et al., 2010; Tang et al., 2008). Besides their barrier properties packaging materials should possess also proper mechanical characteristics. Although several papers discuss the stiffness, strength and deformability of TPS nanocomposite films (Aouada et al., 2011; Avella et al., 2005; Chivrac et al., 2010; Chung et al., 2010; Cyras et al., 2008; Dean et al., 2007; Huang et al., 2004; Majdzadeh-Ardakani et al., 2010; Muller et al., 2012; Schlemmer et al., 2010; Tang et al., 2008), only a limited number of papers reports systematic experiments carried out as a function of filler content in a wide composition range (Aouada et al., 2011; Chen & Evans, 2005; Huang et al., 2004; Majdzadeh-Ardakani et al., 2010), and often very poor mechanical properties are published compared to commodity polymers. Since packaging materials are not usually applied under dry conditions, the mechanical properties of the dry TPS/clay composites investigated generally are not relevant, because it is well known that humidity can strongly influence the strength and the stiffness of TPS nanocomposite films. In spite of this effect, relatively few papers have been published on TPS composites studied under ambient conditions (RH = 30–60%) (Aouada et al., 2011; Chung et al., 2010; Huang et al., 2004). Furthermore the effect of processing technology on the properties of TPS nanocomposites of the same composition has not yet been thoroughly elucidated. Although (Aouada, Mattoso, & Longo, 2013) prepared TPS nanocomposites by the combination of the intercalation from solution and melt-processing preparation methods and they found that the applied method resulted in intercalated/exfoliated structure and good thermal, mechanical properties as well as decreased hydrophobicity and water absorption, indeed, the measured mechanical properties were very poor and the different effect of the individual processes on the morphology and properties of TPS nanonocomposites was not investigated at all.

As a consequence, the goal of our work was to prepare TPS/NaMMT nanocomposite films with different glycerol and clay content using a melt blending as well as a solution mixing procedure and to determine the structure and properties of dry and wet (conditioned) films in a wide composition range. Considerable attention is paid also to interactions developing among the components.

Table 1
Preparation method and composition as well as designation of TPS nanocomposites.

Sample	Method	Glycerol content (g/100 g starch)	Clay content	
			g/100 g starch	(vol%)
S30	Solution	30	0–25	0–8
S40	Solution	40	0–25	0–7
M40	Melt	40	0–25	0–7

2. Experimental

High quality corn starch produced in Hungary (Hungrana Ltd.) was used in the experiments. Glycerol was purchased from Aldrich, Hungary. Sodium montmorillonite (Cloisite Na^+) with a cation exchange capacity (CEC) of 92.6 meq/100 g clay was supplied by Southern Clay Products ((Rockwood Additives Ltd.).

2.1. Preparation of plasticized starch/montmorillonite nanocomposite films

TPS nacomposite films were prepared by solution and melt blending. Solution mixing was carried out in the following way: Native starch was dispersed in the excess amount of distilled water containing 30 and 40 wt% of glycerol. Then the suspension was continuously stirred at 80 °C for 30 min to gelatinize the corn starch granules. The starch concentration of the solution was 4.5 wt%. Sodium montmorillonite (NaMMT) was dispersed in distilled water at concentration of 0.8 wt% by sonication for 30 min at room temperature. The clay dispersion was added to the aqueous gelatinized starch and the mixture was stirred for another 30 min at 90 °C. Films were obtained by casting the hot suspension into Petri dishes covered by a Teflon sheet and dried in an oven at 40 °C for 24 h. Clay content changed between 0 and 25 wt% based on the amount of dry starch. Thickness of the films was 0.10 ± 0.02 mm. Before the tests the films were stored at 23 °C and 52% RH until constant weight was reached. Nanocomposite films were also prepared by melt intercalation. During the process the dry starch was premixed with glycerol (40 wt%) and montmorillonite in a Petri dish and the mixtures were introduced into an internal mixer (Brabender W50 EH) and homogenized at 150 °C for 10 min. 0.10 mm ± 0.02 mm thick plates were compression molded from the melt at 150 °C and 5 min. One part of the films prepared by melt mixing was stored under dry conditions, while the other part was stored at 23 °C and 52% RH until further study. Table 1 contains the list of nanocomposite films, their compositions and the methods used for their preparation.