Bio-Hybrid Nanocomposite Coatings from Polysaccharides and Nanoclay

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Abstract: In recent years a lot of effort has been aimed at developing new bio-hybrid nanocomposite barrier packaging materials for foods. Nanocomposite films and coatings with improved properties were produced from nanoclay and polysaccharides such as ultrasonic dispersed chitosan and high pressure fluidized pectin. The intercalation of chitosan in the silicate layers was confirmed by the decrease of diffraction angles while the chitosan/nanoclay ratio increased. Nanocomposite films and multilayer coatings had improved barrier properties against oxygen, water vapor, grease and UV-light transmission. Oxygen transmission was significantly reduced under all humidity conditions. In dry conditions, over 99% reduction and at 80% relative humidity almost 75% reduction in oxygen transmission rates was obtained. All chitosan coating raw materials were "generally recognized as safe" (GRAS) and the calculated total migration was in all cases ≤ 6 mg/dm^2, thus the coatings met the requirements set by the packaging legislation. Processing of the developed bio-hybrid nanocomposite coated materials was safe as the amounts of released particles under rubbing conditions were comparable to the particle concentrations in a normal office environment. Nanoclay-pectin hybrid film formation and high shear induced orientation of nanoclay platelets were investigated by means of model surfaces which were prepared using high shear spincoating. After fluidization, the nanoclay formed uniform and laterally oriented stacks consisting of approximately 15 individual nanoclay layers. Pectin films with different nanoclay concentrations were prepared by casting. Nanocomposite films made of pectin and nanoclay showed improved barrier properties against oxygen and water vapor. Films were also totally impermeable to grease. The developed bio-hybrid nanocomposite packaging materials can be potentially exploited as a safe and environmentally sound alternative for synthetic barrier packaging materials.

Keywords: Barrier, Chitosan, Coating, Film, Nanocomposite, Nanoclay, Montmorillonite, Packaging, Pectin

1. Introduction

There is a growing interest in utilization of by-products of agriculture and food industry in order to develop biodegradable materials to replace petroleum based polymers in packaging applications. In addition, nanotechnology in food packaging is expected to grow strongly over the next five years as the increased globalization sets demands for shelf life enhancing packaging [1]. Recently, a lot of effort has been aimed at developing new biobased polymer containing films and nanocomposites which can act as e.g. barriers in packaging materials [2-5]. Unlike synthetic plastics, in dry conditions, the films and coatings from natural polymers exhibit good barrier properties against oxygen and grease due to the high amount of hydrogen bonds in their structure. However, natural polymers are hydrophilic in nature, thus films and coatings produced from these materials are often hygroscopic, resulting in partial loss of their barrier properties at high humidity [6]. A major challenge for the packaging developers is to overcome the inherent hydrophilic behaviour of biomaterials. Among the potential fillers for nanocomposites, clay platelets have attracted a particular interest due to their high performance at low filler loadings, rich intercalation chemistry, high surface area, high strength and stiffness, high aspect ratio of individual platelets, abundance in nature, and low cost [7]. Clays are naturally occurring materials composed primarily of fine-grained minerals. Nanoclays (or nanolayered silicates) such as hectorite, saponite and montmorillonite are promising materials with high aspect ratio and surface area [8-10]. Because of their unique platelet-like structure nanoclays have been widely studied as regards the barrier properties. Such nanoclays can be very effective at increasing the tortuosity of the diffusion path of the diffusing molecules, thus significant improvement in barrier properties can be achieved with the addition of relatively small amounts of clays [11] When the nanoclay layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained. Full exfoliation (single platelet dispersion) of nanoclay by using existing/traditional compounding techniques is very difficult due to the large lateral dimensions of the layers, high intrinsic viscosity of the polymer and a strong tendency of clay platelets to agglomerate [12]. Most of the clays are hydrophilic, thus mixing in water with water-soluble polymers results good dispersion, especially when the sufficient amount of mixing energy is used. The degree of exfoliation can be improved by the use of conventional shear devices such as extruders, mixers, ultrasonicators, ball milling, fluidizators, etc. The main goal of this work was to study the effects of nanosized montmorillonite on the barrier properties of polysaccharides as a function of relative humidity.

2. Materials and Methods

Chitosan was obtained from Fluka BioChemika (low-viscous with a molecular weight of 150 kDa), sugar beet pectin from Danisco Sugar A/S and hydrophilic bentonite nanoclay (Nanomer PGV) from Aldrich. Chitosan and pectin were used as continuous natural polymeric matrixes in which an inorganic nanosized material, >98% montmorillonite, was dispersed. In order to ensure the sufficiently defoliated and nanosized structure of the nanoclay platelets, the ultrasonication and high pressure fluidization were used for homogenization polysaccharide-nanoclay dispersions. Coatings and films were prepared by wet coating of chitosan onto plasma-activated LDPE coated paper (coatings) and solvent casting of pectin on Petri dishes (films). Oxygen transmission rates were measured with Oxygen Permeation Analyser Model 8001 (Systech Instruments Ltd.). The oxygen transmission tests were carried out at 23°C and 0%, 50% and 80% relative humidity. A new test method was also developed for testing particle release from planar materials. Particle measurements were performed with Met One R4815 optical particle sensor. Particle sensor counts 500 nm size particles. The sensor was attached to a moving nozzle. Nozzle had an automated reciprocating motion, motion length and repetition were computer controlled. When nozzle was moving forward, sample surface was flushed with clean pressurized air and particles were absorbed from the sample surface. When nozzle was moving backward, sample surface was rubbed with the nozzle bottom and particles were absorbed from the sample surface after rubbing. Measurements were performed in the clean room to avoid deposition of normal air particles to the sample surface.

3. Chitosan coatings

Nanoclay (0.2, 1, and 2 wt%) was swelled in 30 mL of distilled water and dispersed using ultrasonification tip (Branson Digital Sonifier) for 10 min. The dispersion was added into 30 mL of 1% chitosan in 1% acetic acid, followed by sonication for 10 min. For reducing the surface tension and increasing the wettability, 60 mL of ethanol was added and mixed under rigorous mixing. For coated multilayer structures, the solutions were applied onto plasma-activated LDPE coated paper using the standard coating bar no. 6 (wet film deposit of 60 µm). Chitosan solutions with initial nanoclay concentrations of 0, 17, 50, and 67 wt%, and total coating dry weight of 0.2–0.6 g/m^2 were used.

4. Pectin Films

Aqueous solutions of pectin were prepared into distilled water by mixing pectin and glycerol at final concentrations of 5 and 1.75 wt%, respectively. pH of the mixture was adjusted to pH 4.5 and the mixture was heated at 60°C for 2h to increase fluidity. 0.5, 1 or 2wt% nanoclay was added to pectin solutions and immersed for two days under constant mixing. Fluidizer (Microfluidics M110Y) was used for homogenization of nanoclay/pectin dispersions. Feed solutions were pumped from inlet reservoir and pressurized by an intensifier pump to high pressure (900–1350 bars) and fed through fixed geometry chambers with inside microchannel diameter varying between 100 and 400 µm. Films of pectin and nanoclay were prepared by casting 15 mL of each solution in polystyrene Petri dish (Ø 8.5 cm) and dried for two days at room temperature. Final nanoclay concentrations in the solvent cast hybrid films were 10, 20 and 30 wt%.

5. Results and Discussion

Nanoclay was delivered as dry powder with particle size of 2–15 µm. Nanoclays typically tend to be agglomerated when mixed into water. The agglomerates are held together by attraction forces of various physical and chemical nature, including van der Waals forces and water surface tension. These attraction forces must be overcome in order to deagglomerate and disperse the clays into water. Ultrasonication and high pressure fluidization were used to create alternating pressure cycles, which overcome the bonding forces and break the agglomerates. As can be seen in Fig. 1a, dry nanoclay powder consisted of round particles with coarse and platelety surface. By ultrasonic dispersing (Fig. 1b), and high pressure fluidization (Fig. 1c) the nanoclay platelets were effectively ripped off and distributed on the surface. The diameter of the intercalated nanoplatelets varied between 100 and 500 nm. Nanocomposite chitosan coatings effectively decreased the oxygen transmission of LDPE coated paper under all humidity conditions (Fig. 2). In dry conditions, over 99% reduction and, at 80% relative humidity, almost 75% reduction in oxygen transmission rates were obtained. Highest concentration of nanoclay (67 wt%) offered the best barrier against oxygen, whereas the 17 wt% concentration of nanoclay performed almost as good as 50 wt% of nanoclay. Barrier effects of nanoclay became less evident in dry conditions. Presumably higher nanoclay concentrations were partly agglomerated, which hindered the crystallization and hydrogen bonding formation between chitosan chains, especially in dry conditions. Nanoclay addi-

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tion also clearly improved the oxygen barrier properties of pectin films in high humidity conditions (Fig. 3). Oxygen transmission rate was reduced by 80% with pectin films containing 30 wt% of nanoclay as compared with the pectin film without nanoclay. Water vapor transmission results indicated the improved barrier properties as well. However, the water soluble pectin was lacking the capability of fully preventing the transmission of water vapor, and thus, total barrier effect of films with 30 wt% nanoclay was not more than 23%. Pectin itself formed an excellent barrier property against grease and nanoclay addition did not improve this barrier property anyhow. All films were totally impermeable to grease under the conditions tested. Barrier improvements are explained using tortuous path theory which relates to alignment of the nanoclay platelets. As a result of the sufficient defoliation, the effective path length for molecular diffusion increases and the path becomes highly tortuous to reduce the effect of gas transmission.

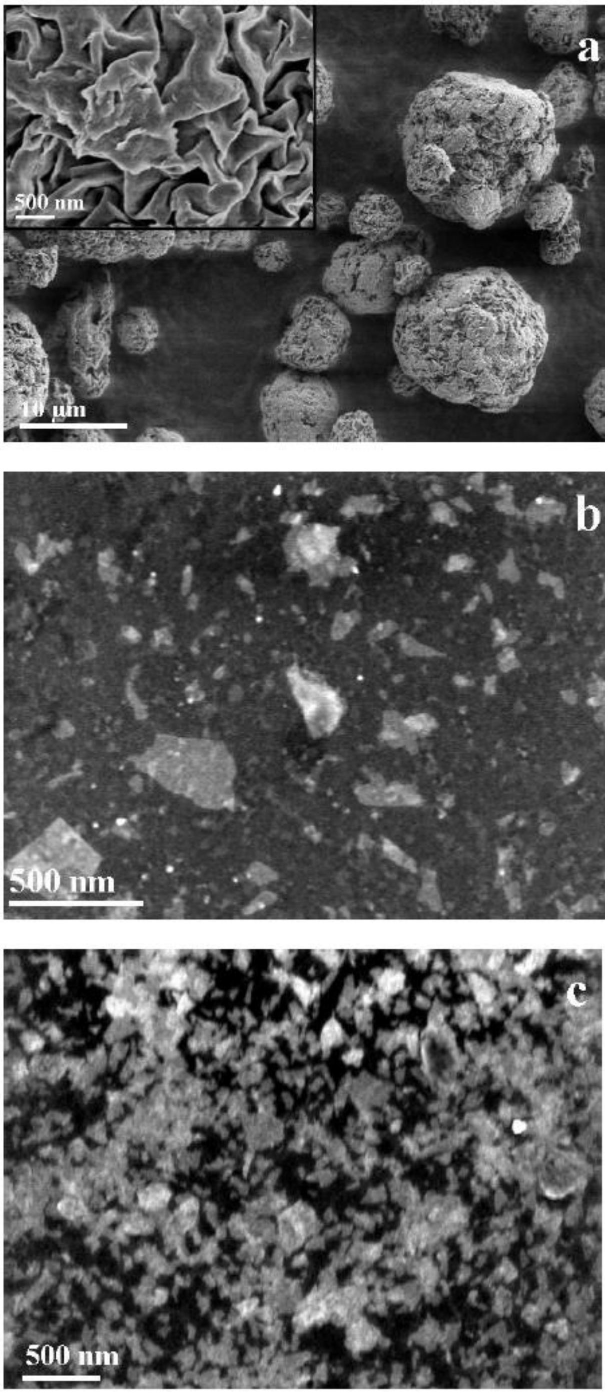

Figure 1. SEM images of (a) large undispersed nanoclay aggregates. The excerpt shows the surface structural features: laminar fine structure can be seen on the aggregate surfaces, (b) spincoated nanoclay platelets after dispersing with the ultrasonic microtip, and (c) spincoated nanoclay platelets after high pressure fluidizer treatment.

Safety aspects of nanomaterials have recently raised many concerns. Chitosan, pectin and bentonite clay have been approved for use as ‘‘generally recognized as safe’’ (GRAS) food additives in the USA. Pectin (E440) and bentonite (E558) have also food additive code numbers meaning, they are approved for use in the European Union. The overall migration limit for the total amount of substances migrating from the packaging material into the food is stipulated in Directive 2002/72/EC. The limit value is 60 mg/kg of packed food or 10 mg/dm^2 of packaging material. Biohybride coatings developed in this study meet the requirements set by the food packaging legislation, as total amount of raw materials including chitosan and nanoclay remain in all cases ≤6 mg/dm^2.

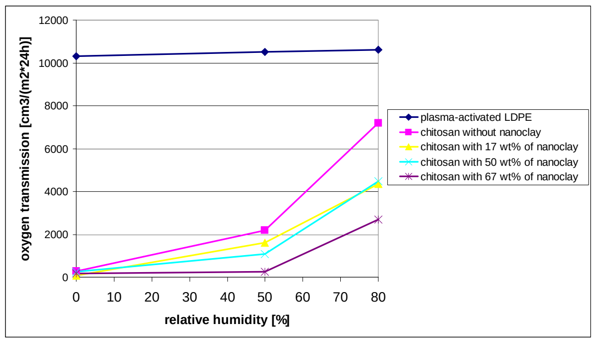

Figure 2. Oxygen transmission rates of different coatings.

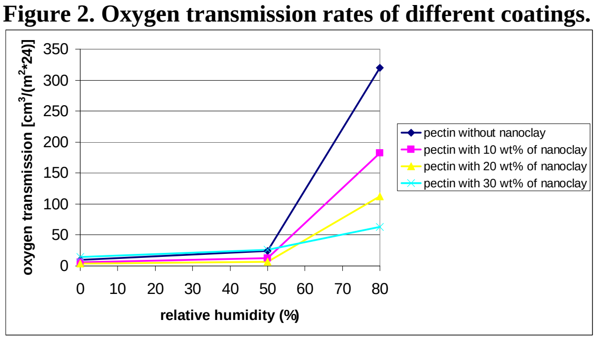

Figure 3. Oxygen transmission rates of solvent cast pectin films (100 μm) with different amounts of nanoclay.

The lungs are the primary route of entry of nanoparticles into the human body. Inhalation of nanoparticles may occur as a consequence of their release into the environment, either during their manufacture or utilization. There is some evidence that long-term occupational exposure to bentonite dust may cause structural and functional damage to the lungs [13]. Also inhaled chitosan microparticles especially in high concentrations can have proinflammatory effects on lung tissues [14].

As particle measurements indicated the amounts of released particles under rubbing conditions were really low. Amounts of 500 nm sized particles were <10,000 particles/cm^3 (Fig. 4). The air in a normal office room typically contains 10,000–20,000 nanoparticles/cm^3, whereas the concentration in urban streets can be as high as 100,000 nanoparticles/cm^3. As expected, the biohybride coatings increased the amounts of released particles as compared with reference LDPE coated paper. However, there were only minor differences between pure chitosan coatings and coatings containing nanoclay. Thus, it seems that chitosan formed an effective binder matrix around both agglomerated nanoclays and intercalated nanoclay sheets.

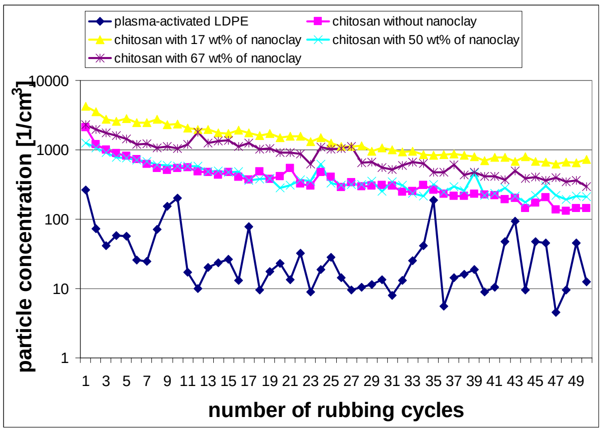

Figure 4. Particle concentration of 500 nm sized particles in air during rubbing of different coatings

6. Conclusions

As a conclusion, montmorillonite nanoclay was successfully dispersed in aqueous polysaccharide solutions using ultrasonication and high pressure fluidization. Nanocomposite coatings and films showed improved barrier properties against oxygen, water vapor and UV-light transmission. Materials were also totally impermeable to grease. The developed biohybrid nanocomposite materials can be potentially exploited as safe and environmentally sound alternative for synthetic barrier packaging materials.

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