Effects of Hydrophilic Plasticizers on Mechanical, Thermal, and Surface Properties of Chitosan Films

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Chitosan films were plasticized with four hydrophilic compounds, namely, glycerol (GLY), ethylene glycol (EG), poly(ethylene glycol) (PEG), and propylene glycol (PG). Our objective was to investigate the effect of plasticizers on mechanical and surface properties of chitosan films. The stability of plasticized films was observed by storage for 3 and 20 weeks in an environmental chamber at 50 ± 5% RH and 23 ± 2 °C. Plasticization improves the chitosan ductility, and typical stress–strain curves of plasticized films have the features of ductile materials, except the film made with 5% PG that exhibits as a brittle polymer and shows an antiplasticization effect. In most cases, the elongation of plasticized films decreases with the storage time, which might be due to the recrystallization of chitosan and the loss of moisture and plasticizer from the film matrix. Although at the beginning the mechanical properties of films made with PG, at high plasticizer concentration, are comparable to those of films made with EG, GLY, and PEG, their stability is poor and they tend to become brittle materials. The surface properties, analyzed by contact angle measurement, reveal that plasticization increases film hydrophilicity. It is found that GLY and PEG are more suitable as chitosan plasticizers than EG and PG by taking into account their plasticization efficiency and storage stability. Furthermore, a plasticizer concentration of 20% (w/w) with GLY or PEG seemingly is sufficient to obtain flexible chitosan film with a good stability for 5 months of storage.

KEYWORDS: Chitosan; plasticizers; edible film; mechanical properties; surface properties

INTRODUCTION

The concept of employing edible films as protective coatings for food is not novel. Patents on edible films to extend the shelf life of foods date back to the 1950s (*1*). However, there has been a resurgence of interest in recent years in the development of edible films and coatings for food due to the increased consumer demand for food quality, long shelf life, convenience, and reducing the environmental impact of packaging wastes (*2*). Edible films and coatings are thin films prepared from edible material that act as a barrier to the external elements (factors such as moisture, oil, and vapor) and thus protect the product and extend its shelf life. The major benefit of the edible films and coatings is that they can be consumed along with the food, can provide additional nutrients, may enhance sensory characteristics, and may include quality-enhancing antimicrobials. Biopolymer films and coatings are generally designed using biological materials such as polysaccharides, proteins, lipids, and derivatives (*1*).

Chitosan [β-(1,4)-2-amino-2-deoxy-D-GLUCOPYRANOSE] is a natural polymer derived by deacetylation of chitin, which is the second most abundant biopolymer in nature after cellulose (*3*). Chitin is present in the exoskeleton of arthropods such as insects, crabs, shrimps, lobsters, and certain fungal cell walls. The production of chitosan from crustacean shells, wastes of the seafood industry, is economically feasible (*4*). Compared with other polysaccharides, chitosan has several important advantages, including biocompatibility, biodegradability, and no toxicity. Moreover, several studies have indicated the bacteriostatic (*5–10*) and fongistatic (*11*) activities of chitosan.

Thanks to its film-forming properties, chitosan has been reported as a potential material of food packaging, especially as edible films and coatings (*12*). Furthermore, the potential of chitosan as antimicrobial films and coatings for extending shelf life of foodstuffs has been reported in several publications, e.g., in the storage of fruits and vegetables (*13–15*), meat products

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(*16*, *17*), and seafood products (*18*, *19*). Unfortunately, chitosan film is brittle (*20*, *21*); thus it needs a plasticizer to increase film flexibility.

Plasticizers are additives used to increase the flexibility or plasticity of polymers, and occasionally they are used only to facilitate the polymer processing (*22*). Several theories have been proposed to explain the mechanisms of plasticization action (*23*). The lubrication theory postulates that plasticizers, by interspersing themselves, act as internal lubricants by reducing frictional forces between polymer chains. The gel theory postulates that the rigidity of polymer comes from three-dimensional structures, and plasticizers take effect by breaking polymer−polymer interactions (e.g., hydrogen bonds and van der Waals or ionic forces). The free volume theory states a plasticization as a study of ways to increase free volume and is useful in explaining the lowering of the glass transition temperature (T_g) by a plasticizer. Ideal plasticizers are miscible and compatible in all proportions with plastic components, and they may be added to polymers in solution (dispersion technique) or after solvents have been removed (absorption technique) (*24*). Water, oligosaccharides, polyols, and lipids are different types of plasticizers widely used in hydrocolloid-based films.

Several studies on plasticization of chitosan films revealed that poly(ethylene glycol) (PEG) could improve the elastic properties of chitosan (*25*−*27*). Caner et al. (*28*) observed that chitosan plasticization using PEG was stable until 9 weeks of storage. On the contrary, Butler et al. (*29*) found the water barrier and mechanical properties of plasticized chitosan films with glycerol changed during storage. Other authors used plasticizers in chitosan blends. Hosokawa et al. (*30*) used glycerol to plasticize chitosan/cellulose composites, whereas Arvanitoyannis et al. (*31*) used sorbitol and sucrose to plasticize chitosan/poly(vinyl alcohol) blends. They stated that the elongation of blended films increased with increasing plasticizer contents, but at high plasticizer contents there were decreases in both tensile strength and modulus. From these studies, the film aging and the amount and type of plasticizer would be important issues in the application of chitosan as edible films and coatings. However, the comparisons among plasticizer efficiencies have not been studied for chitosan films.

The aim of this study is to investigate the influence of four hydrophilic plasticizers, namely, glycerol (GLY), ethylene glycol (EG), poly(ethylene glycol) (PEG), and propylene glycol (PG), on chitosan films. The plasticizer efficiencies of four hydrophilic compounds and their stability during storage were compared using the same conditions.

MATERIALS AND METHODS

Materials. Chitosan powder (No. 234), food grade with a degree of deacetylation of 98%, was kindly provided by France Chitine (Marseille, France). Ethylene glycol (MW = 62), poly(ethylene glycol) (MW = 200), propylene glycol (MW = 76), and glycerol (MW = 92) were purchased from Sigma-Aldrich Co. (St. Louis, MO).

Preparation of Plasticized Chitosan Films. Plasticized chitosan films were prepared with some modifications of the method of Kolhe and Kannan (*27*). A 2% chitosan or chitosan/plasticizer solution was prepared by adding 10 g of chitosan powder or chitosan/plasticizer in 500 mL of 1% acetic acid aqueous solution by vigorously stirring the chitosan suspension. The chitosan and chitosan/plasticizer solutions were filtered through a coarse sintered glass filter to remove undissolved impurities. The compositions of chitosan/plasticizer blends were 100/0; 95/5; 80/20, and 60/40 by weight. Films were cast on a poly-(methyl methacrylate) plate and dried at ambient conditions. The obtained films were conditioned in humidity chamber (CIAT, France) at 50 ± 5% relative humidity (RH) and 23 ± 2 °C.

Film Characterization. *Thickness Measurements.* Film thickness was measured with a thickness tester (Thwing-Albert Instrument Co., Philadelphia, PA). Five values were randomly taken at different locations for each specimen of tensile tests, and the mean value was used in the determination of mechanical properties.

Moisture Content. To determine the moisture content of films stored for 3 and 20 weeks (23 ± 2 °C and 50 ± 5% RH), about 100 mg of film samples was dried in a vacuum oven at 60 °C until an equilibrium weight was reached. This method was adopted from Hulleman et al. (*32*). At these conditions, evaporation of plasticizers from matrix film was negligible. The weight loss of the sample was determined, from which the moisture content was calculated using the equation $WC = (M_i - M_d)/M_d \times 100$, where M_i and M_d are the masses of initial and dried samples, respectively.

Mechanical Properties. Tensile tests were performed on a tensile testing machine (model TEST 108 from GTTest, France, equipped with the software Test Winner 920), with a crosshead speed of 10 mm/min and a 2 kN static load cell. The films were cut into standard tensile samples from a dumbbell-shaped knife (H3 type) with a dimension 17 mm × 4 mm × 0.08 mm (length × width × thickness). At least five samples of each type of film were tested after a suitable storage period (3 and 20 weeks) at 50 ± 3% RH and 23 ± 2 °C in a humidity chamber (CIAT, France). We started the film characterizations after 3 weeks because in our experiments the materials did not achieve the moisture equilibrium before this time. The maximal tensile stress (TS) was calculated by dividing the maximum load for breaking film by cross-sectional area and elongation at break (E_b) by dividing film elongation at rupture by the initial gauge length.

Surface Hydrophobicity. Contact angle measurements were performed with a goniometer (Kruss G23, Germany). A drop of distilled water (5 μL) was placed on the film surface. The evolution of the droplet shape was recorded. A CCD video camera and image analysis software were used to determine the contact angle evolution, which may be used to determine the initial contact angle and the kinetics of the water sorption (slope of the curve contact angle = f(time)). A minimum of seven measurements, taken at different positions on the film, was carried out. The contact angles were measured on both sides of the drop and averaged.

Moisture Uptake. Moisture uptake were measured by following the method of Anglès and Dufresne (*33*) instead of the classical technique (immersion in water), because chitosan is very sensitive to liquid water and can partially dissolve after long time exposure to water. The dried sheets of 20 mm × 20 mm were first conditioned at 0% RH (P_2O_5) for 1 week. After weighing, they were conditioned at 20−25 °C in a desiccator containing $CuSO_4 \cdot 5H_2O$ saturated solution to ensure a relative humidity of 98%. The samples were removed at desired intervals and weighed until the equilibrium state was reached. The moisture uptake of the samples was calculated as follows:

$$\text{moisture uptake (\%)} = \frac{W_t - W_0}{W_0} \times 100$$

where W_t and W_0 are the weights of the sample after t time in 98% RH and the initial weight of the sample, respectively.

Thermal Analysis. The thermal characteristics of the films were determined using a differential scanning calorimeter (TA instrument) cooled with liquid nitrogen circulation. Samples (∼10 mg) were cut from a sample specimen after conditioning and placed in sealed aluminum pans. For each sample, the following thermal cycle was applied: a first scan was made from −30 to +190 °C, conditions were isothermal for 1 min at 190 °C, then the sample was cooled rapidly to 0 °C and kept isothermal for 5 min at 0 °C, and then there was a second heating to 300 °C. The heating rate used was 5 °C/min, and an empty pan was used as the reference. With two cycles of heating and cooling runs, the effect of moisture is eliminated, and we observed the thermal properties of films just once in the middle of the storage time.

Statistical Analysis. All experiments were measured in triplicate, with individually prepared and cast films as replicated experimental units. STATGRAPHICS Plus for Windows (Statistical Graphic Corp, Rockville, MD) was used for multifactor analysis of variance. Differences in the properties of the film samples were determined by Fisher's least
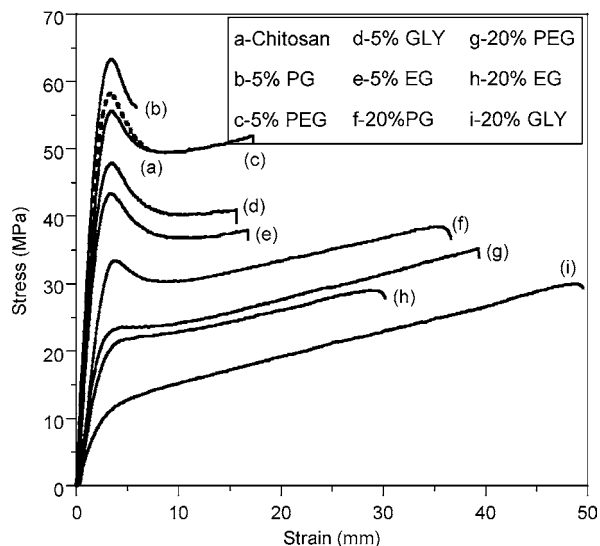
Figure 1. Stress–strain curves of plasticized films after storage for 3 weeks.

significant difference (LSD) mean discrimination test, using a $P < 0.05$ level of significance.

RESULTS AND DISCUSSION

Mechanical Properties and Moisture Contents. The stress–strain curves of plasticized chitosan films aged for 3 weeks are plotted in **Figure 1**. The stress–strain diagrams of films with 40% plasticizer are not shown since their behaviors are close with those of films containing 20% plasticizer. The stress–strain curves of pure chitosan film and film with 5% PG show the typical pattern of brittle materials. The other plasticized films exhibit the stress–strain behavior of ductile polymers. From these stress–strain curves, the maximal tensile stress (TS) and the percentage of elongation at the break point (E_b) are calculated and summarized in **Table 1**. For all plasticization systems, the expected effect on mechanical properties (increase in strain and decrease in stress with increasing plasticizer amount) is observed except plasticization with 5% PG. In this plasticization system, a contrary result was observed, i.e., an increase in stress and a decrease in strain compared with the pure chitosan. It means PG does not exhibit the conventional effect of common plasticizers at low concentration, but for higher concentrations (20 and 40% PG), its plasticizer action was observed. This behavior is well-known as "antiplasticization" effect, which has also been observed in the case of starch–glycerol (*34*) and starch–sorbitol (*35*) systems. Glycerol and sorbitol contents less than 12 and 27%, respectively, lead to a decrease in elongation at the break, corresponding to an antiplasticization phenomenon. The mechanism of antiplasticization is not yet perfectly known. However, Lourdin et al. (*34*) have well discussed it. They stated that a strong interaction might be occurring between the polymer and the small quantity of plasticizer, producing a "cross-linker" effect, which decreases the free volume and the molecular mobility of the polymer. Moreover, a small amount of plasticizer could improve the reorganization of the material and increase its crystallinity, thus decreasing the strain of the material.

Figure 2 presents the strain–stress curves of films stored for 20 weeks. By comparing **Figures 1 and 2**, it is observed that the stress–strain curves of films with 20 and 40% (not shown) PG change their pattern from ductile to brittle material. The characteristics of stress–strain curves of other plasticized films do not change. For simplicity, we can assume that one plasticizer is considered to be more efficient than another, if

the film made with the first one presents higher strain, lower stress, and better stability during storage than the film containing the second one at the same mass ratio. According to **Figure 1** and **Figure 2**, at 20% plasticizer content, GLY and PEG show higher plasticization efficiency than EG and PG. Indeed, films plasticized by 20% GLY and PEG show better stability during storage, higher strain, and lower tensile stress than films plasticized by PG. Films made with EG have high strain and low stress comparable to films made with GLY and PEG, but they are not stable during storage. Mangavel et al. (*36*) stated that plasticizer efficiency depends on its molecular weight; i.e., plasticizer efficiency increases with increasing molecular weight. In our study, the plasticizer efficiency follows the order PEG > GLY > EG > PG, whereas the molecular weight diminishes following the order PEG (200) > GLY (92) > PG (76) > EG (62). Films made with EG present higher elongation and lower tensile stress than films made with PG, although EG has lower molecular weight than PG. To explain this phenomenon, Mangavel et al. (*36*) reported that molecular features other than the molecular weight may also influence the plasticizer efficiency. Moreover, the molecular weight difference between PG and EG is slightly small, and their influence might be negligible.

As shown in **Table 1**, the tensile stress and elongation of plasticized films change after storage for 20 weeks compared to those of films stored for 3 weeks. Tensile strength increases and elongation at break decreases significantly except films made with 20% GLY and 20 and 40% PEG (table of ANOVA for the storage time effect is not presented). This might be attributed to the recrystallization of chitosan during the storage. Indeed, the crystallinity development is well-known to increase the rigidity and brittleness of the film. Moreover, Cervera et al. (*37*) observed the storage has a tendency to increase the crystallinity of the chitosan–amylose corn starch (Hylon VII) films. There are also possibilities such as the evaporation of water and the loss of plasticizers from the film matrix during the storage, thus leading to the decrease in strain and the increase in tensile strength.

To approve the moisture evaporation during storage, the moisture contents of films were measured after 3 and 20 weeks. The result of moisture content measurements is indicated in the **Table 1**. It is well-known that water is the most ubiquitous and uncontrollable plasticizer for most hydrocolloid-based films because of its ability to modify the structure of this natural polymer (*38, 39*). **Table 1** reveals that moisture contents of films made with 40% GLY and 20 and 40% PEG are significantly different from those of unplasticized films. The value is 14.4% (dry basis) for the unplasticized sample stored for 3 weeks and increases significantly to 24.3, 21.9, and 22.1% for films with 40% GLY and 20 and 40% PEG, respectively. Thus, the plasticization effect of moisture could not be negligible for these three films, and their plasticization efficiency does not only come from intrinsic plasticizer action of GLY and PEG. Furthermore, moisture contents of films stored for 20 weeks decreased significantly compared to those of films stored for 3 weeks. This proves that there was an evaporation of moisture from the film matrix during storage.

It is possible that the evaporation of the used plasticizers takes effect in the decreases in elongation and the increase in tensile strength. In the previous study, Sanchez et al. (40) observed that ethylene glycol (boiling point (bp) = 198 °C), diethylene glycol (DEG, bp = 244 °C), triethylene glycol (TEG, bp = 287 °C), and tetraethylene glycol (TEEG, bp = 307 °C) evaporated from wheat gliadin films about 46, 23, 13, and 17%,

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Table 1. Plasticization Effects on Moisture Content (MC), Tensile Strength (TS), and Elongation at the Break (E_b) of Plasticized Chitosan Films (Standard Deviations Given in Parentheses)[a]

film composn (w/w)	3 weeks of storage			20 weeks of storage		
	MC (%)	TS (MPa)	E_b (%)	MC (%)	TS (MPa)	E_b (%)
chitosan (chit) film	14.4(0.3) a	63.1(4.4) a	7.2(1.4) a	12.3(0.4) a	65.4(5.7) a	4.7(0.5) a
chit/GLY: 95/5	13.7(0.3) a	59.5(4.4) a	19.1(2.8) b	11.5(0.4) a	64.2(2.7) a	8.8(1.8) a
chit/GLY: 80/20	15.8(1.4) a	31.8(2.0) b	45.7(3.4) c	13.1(0.4) a	38.4(5.5) b	42.0(5.7) b
chit/GLY: 60/40	24.3(0.2) b	22.0(2.2) c	84.2(6.2) d	21.6(0.2) b	12.6(2.4) c	33.9(5.9) b
chit/EG: 95/5	13.9(0.2) a	53.7(3.7) b	16.8(1.2) b	11.6(0.4) a	60.8(4.3) a	9.4(3.8) a
chit/EG: 80/20	14.5(0.4) a	34.0(1.4) c	38.1(3.6) c	11.9(0.2) a	51.5(4.2) b	19.4(6.6) b
chit/EG: 60/40	14.0(0.6) a	33.2(3.6) c	67.0(5.3) d	11.0(0.6) a	49.1(4.1) b	24.6(4.9) b
chit/PEG: 95/5	13.2(0.6) a	65.1(1.4) a	12.1(1.8) a	11.0(0.1) a	61.0(6.0) a	12.4(1.3) a
chit/PEG: 80/20	21.9(0.9) b	40.6(3.8) b	42.2(2.9) b	19.8(0.9) b	39.0(4.5) b	50.6(0.8) b
chit/PEG: 60/40	22.1(1.8) b	36.6(2.5) b	79.7(6.7) c	19.6(0.9) b	22.9(2.1) c	53.6(2.9) b
chit/PG: 95/5	14.9(0.4) a	74.2(1.7) b	6.4(0.6) a	11.1(0.2) a	69.8(2.9) a	4.3(0.6) a
chit/PG: 80/20	15.5(1.5) a	44.6(1.9) c	36.6(3.9) b	11.0(0.4) a	54.2(4.8) b	8.6(1.7) b
chit/PG: 60/40	14.9(0.7) a	36.3(3.4) c	44.3(4.1) c	11.9(0.1) a	49.6(8.6) b	7.0(0.4) b

[a] Means with different letters within a column indicate significant differences ($P < 0.05$).
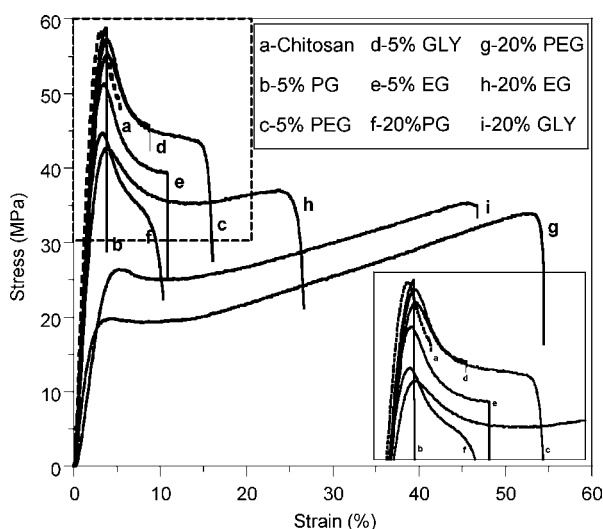
Figure 2. Stress–strain curves of plasticized films after storage for 20 weeks.

respectively, whereas there was no evaporation of glycerol (GLY, bp = 290 °C). Similarly, Guéguen et al. (*41*) reported the aging process of gluten films plasticized with 1,2- or 1,3-propanediol and stated that tensile strength dramatically increased within 1 month as the plasticizers were released from the films.

In the present study, we performed the evaporation test of plasticizer as an additional experiment. Around 2 g of plasticizers was placed in a desiccator (0% RH) and evaporated under different temperatures: 23 °C in the storage chamber and 50 and 70 °C in the oven during 1 week, 3 days, and 1 day, respectively. The evaporation rates are calculated as the mass loss of plasticizer (%), and the results are presented in **Table 2**. It is obviously observed that PG (bp = 185 °C) and EG (bp = 196 °C) were evaporated rapidly at 50 and 70 °C and evaporated slightly at storage temperature (23 °C), whereas there is no mass loss of GLY (bp = 290 °C) and PEG (bp not known). This observation is in agreement with that of Sanchez et al. (*40*), who showed that differences in evaporation rates of plasticizers might be due to their different boiling points. These results reveal that films plasticized with PG tend to revert to its natural stiffness induced by the migration and the evaporation of the plasticizer from the films.

Thermal Properties. Figure 3 presents differential scanning calorimetry (DSC) thermograms of films made with 20%

Table 2. Evaporation Rates of the Liquid Plasticizer (Standard Deviations Given in Parentheses)

plasticizer	mass losses of the plasticizer[a] (%)		
	after 7 days at 23 °C	after 3 days at 50 °C	after 1 day at 70 °C
GLY	0.0	0.0	0.0
EG	2.6(0.1)	52.0(1.3)	92.2(1.9)
PEG	0.0	0.0	0.0
PG	6.7(0.1)	90.7(2.2)	99.4(2.5)

[a] Values are means from three measurements and corrected by the initial water content of the plasticizers.
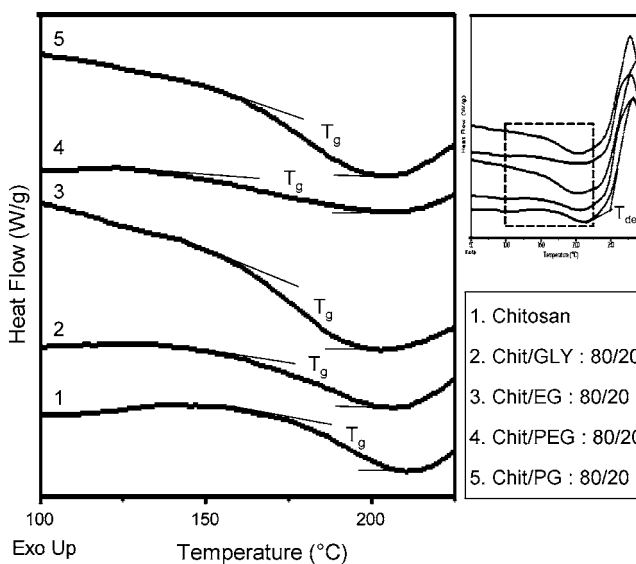
Figure 3. DSC thermograms of films made with 20% plasticizers obtained from the second heating.

plasticizers which were obtained from the second heating. Concerning the glass transition temperature (T_g) of chitosan, it has been reported previously by many authors. Sakurai et al. (*42*) reported the T_g of chitosan, determined by DSC and dynamic mechanical analysis (DMA) measurements, was found to be 203 °C. Cheung et al. (*20*) observed the T_g of chitosan at around 103 °C. Shanta and Harding (*43*) found a sharp glass transition of chitosan at 195 °C. Thus, there are various values of the T_g of chitosan. Recently, Dong et al. (*44*) studied the T_g of chitosan using four different techniques, namely, DSC, dynamic mechanical thermal analysis (DMTA), thermally
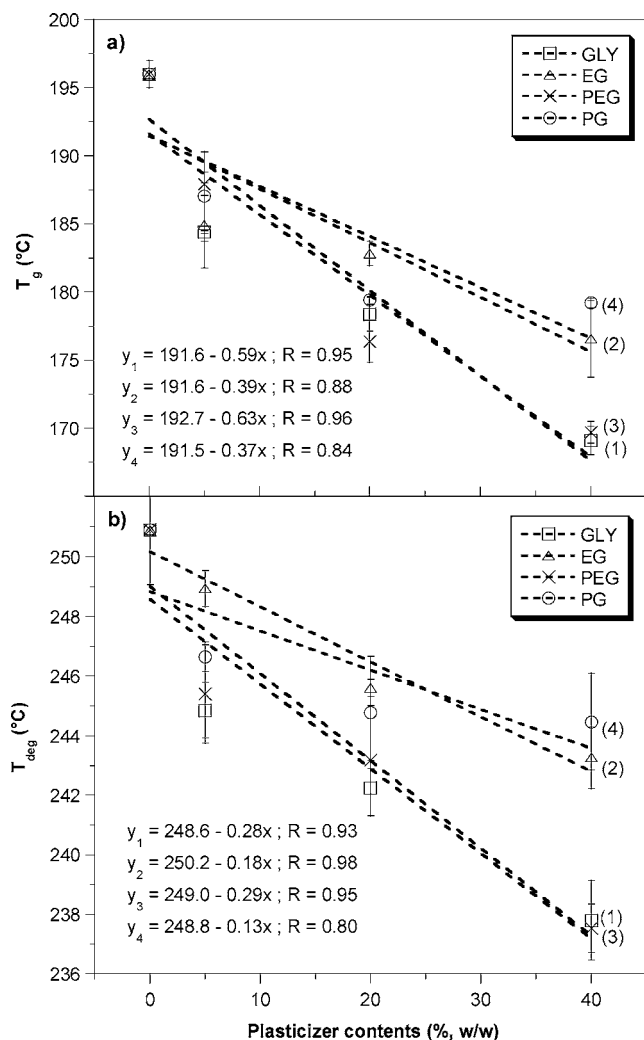
Figure 4. (**a**) Glass transition temperature (T_g) and (**b**) thermal degradation (T_{deg}) versus plasticizer contents. Vertical bars are standard deviations. The slope was calculated from the regression line.

Figure 5. DSC thermograms of films made with 20% plasticizers obtained from the first heating.

simulated current spectroscopy (TSC), and dilatometry (DIL) measurements. They reported the T_g of chitosan was found at 140−150 °C and did not depend on the degree of deacetylation. In the most recent study, Cervera et al. (*45*) found the T_g of chitosan, determined by DSC measurement, was 130−139 °C, whereas, in our previous study (*21*), the T_g of chitosan is observed at 194 °C, close to that of the present study. As seen in **Figure 3**, the T_g of chitosan is observed at around 196 °C and the baseline step is broad due to the rigidity of the chitosan molecular structure. In our case, there are no baseline changes in the heat flow signal (associated with T_g) at around 140−160 °C. To explain the variations of chitosan T_g, Cervera et al. (*45*) stated that different properties, such as crystallinity, the amount of water, the degree of deacetylation, and OH or amine groups in the chain of the macromolecule, can be associated with the glass transition and its variability.

Figure 4a presents T_g versus the plasticizer contents. It can be mentioned that the expected plasticizer effects in T_g have been observed. The T_g of plasticized films decreases with the increase in plasticizer contents, which is in agreement with the free volume theory of plasticization. As far as the efficiency of plasticizers is concerned, normally it can be evaluated by comparing the experimental T_g with theoretical models. The Couchman−Karasz model was widely used because it was successfully applied to fit data of various biopolymers (*39*). Due
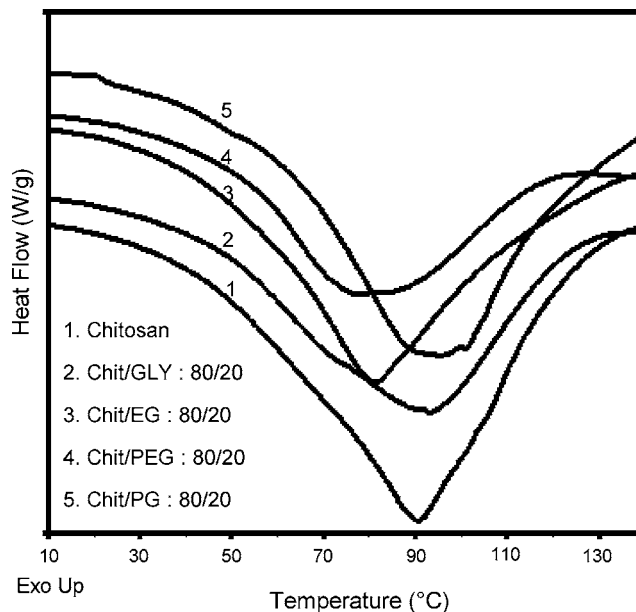
to the limitation in our experiments, the T_g and ΔC_p of the used plasticizers were not obtained in our DSC analysis. Thus, it is not possible to apply this model. However, it is observed that T_g correlates with the plasticizer amounts (**Figure 4a**). The T_g of unplasticized film is found at around 196 °C and shifts to about 184, 178, and 169 °C for the plasticized films containing 5, 20, and 40% GLY, respectively. Similar results are obtained in other plasticized systems. When a linear regression is applied to the T_g versus plasticizer contents curves, it is observed that PEG and GLY have a bigger slope than that of EG and PG. This simple method may be used to compare the efficiency of plasticizers; i.e., PEG and GLY are more efficient as chitosan plasticizer than EG and PG. These observations are in agreement with the mechanical properties obtained previously; i.e., PEG and GLY are more efficient than EG and PG in increasing the ductility of chitosan.

In **Figure 3** the exothermic peaks at around 280−300 °C are observed, indicating thermal decomposition of polymers. The onset points, where polymers begin to be degraded, are suggested as thermal degradation temperature (T_{deg}). It appears that the addition of plasticizer diminishes the T_{deg} of films. **Figure 4b** shows the T_{deg} of films versus plasticizer contents. This shows a plasticization promotes a decrease in thermal stability by its action to intersperse itself around polymer and by breaking polymer−polymer interactions, which are predicted in the lubrification and gel theories of plasticization. In fact, according to **Figure 4b**, the slopes of T_{deg} versus plasticizer content curves of PEG and GLY are bigger than that of EG and PG, indicating that PEG and GLY exhibit a better plasticizer action than EG and PG do. This result is good in agreement with previous results.

Figure 5 shows thermograms of chitosan film and films made with 20% plasticizer obtained from the first DSC run. The endothermic peaks, centered about 90−95 °C, are related to the water evaporation. Thus, the enthalpies for this endothermic peak represent the energy required to vaporize the water present in the films. Moreover, Rueda et al. (*46*) reported that the endothermic area of a first DSC run, for starch and chitosan, was correlated to the water content of the sample. In this present
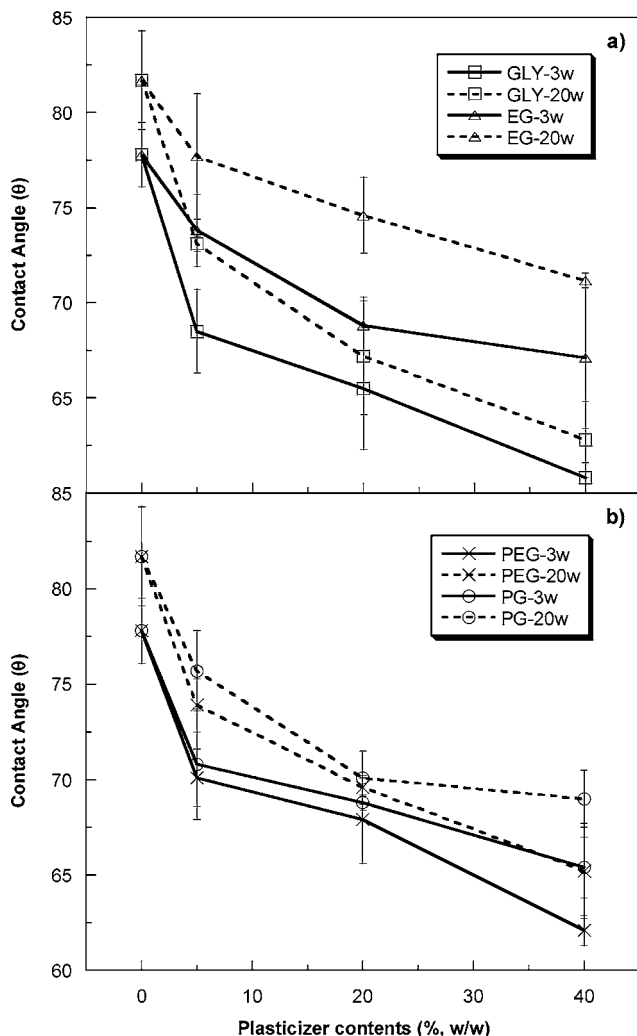
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Figure 6. Contact angles for films plasticized with (**a**) GLY and EG and (**b**) PEG and PG. Vertical bars are standard deviations. The solid and dashed lines represent storage for 3 and 20 weeks, respectively, and serve as a guide to the eye.

Figure 7. Moisture absorption of unplasticized and plasticized films made with 20% plasticizer as a function of exposure time: (**a**) GLY, EG; (**b**) PEG, PG. Vertical bars are standard deviations. The solid and dashed lines represent aging for 3 and 20 weeks, respectively, and serve as a guide to the eye.

study, the evaporation of EG and PG could occur beside the water evaporation, as shown by the evaporation tests (**Table 2**).

Surface Properties and Water Absorption. Contact angle measurements of liquid droplets on material surfaces are used to characterize surface properties of plasticized chitosan films. The contact angle is defined as the angle between the substrate surface and the tangent line at the point of contact of the liquid droplet with the substrate. Parts a and b **Figure 6** show the water contact angles for films made with GLY, EG and PEG, PG, respectively. It is well-known that the water contact angle will increase with increasing surface hydrophobicity. According to the obtained results, the addition of plasticizers diminishes water contact angle of films. Plasticization, therefore, results in decreasing hydrophobicity of the chitosan films. The higher hydrophilicity of the samples is attributable to the hygroscopicity (the water binding capacity) of plasticizer. It appears that the water contact angles of films stored for 20 weeks are higher than those of ones stored for 3 weeks, indicating films are more hydrophobic, which might be due to the loss of plasticizer and moisture content.

Figure 7 shows the moisture uptake during conditioning at 98% RH versus exposure time: films made with 20% GLY and EG (**Figure 7a**); films made with 20% PEG and PG (**Figure**
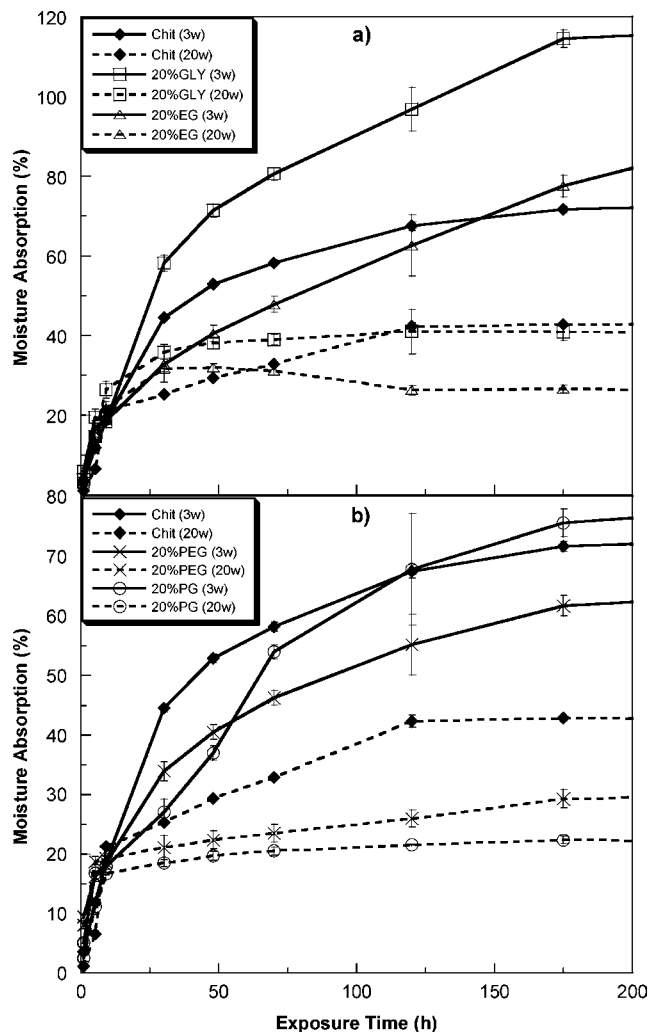
7b). We can differentiate two zones in each curve showing the different kinetics of absorption. For unplasticized film, stored for 3 weeks, it is observed at exposure time below 120 h (zone I) the kinetics of water absorption is fast, whereas at extended exposure times the kinetics of water absorption is slow and reaches a plateau (zone II). The water absorptions at the equilibrium of the films were obtained from **Figure 7** by taking a value at zone II where there was no increase in water absorption against exposure time.

The water uptake at equilibrium versus plasticizer contents is plotted in **Figure 8**. This shows that the swellability of pure chitosan films is affected by the plasticizer content. Furthermore, for the films stored for 3 weeks, plasticization with GLY and EG increases the extent of swelling, whereas plasticization with PEG and PG diminishes slightly the swellability of chitosan film. These observations might be due to the hydrophilicity, and the humectant properties of GLY and EG are higher than those of PEG and PG. Another interesting result is observed: that the swelling of material is reduced by storage. This could have resulted from an increase in film crystallinity and the loss of moisture and plasticizer during storage.

Conclusion. It can be concluded that the addition of GLY, PEG, EG, and PG could improve the ductility of chitosan.
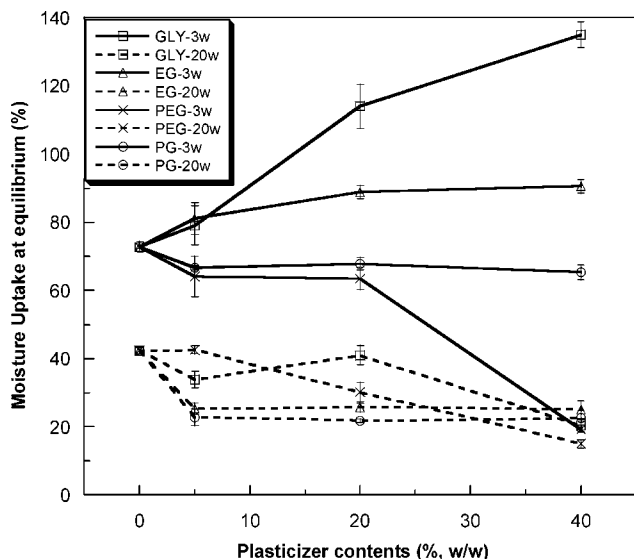
Figure 8. Moisture uptake at equilibrium during exposure at 98% RH for chitosan plasticized films. Vertical bars are standard deviations. The solid and dashed lines represent storage for 3 and 20 weeks, respectively, and serve as a guide to the eye.

Whatever the amount of plasticizers, they show a conventional action of plasticizers (increase in elongation and decrease in tensile strength), except PG at low concentration (5%) which exposes obviously antiplasticization phenomenon. Indeed, the decrease in the strain of the film made with 5% PG is accompanied by an increase in the tensile stress, which is similarly observed in antiplasticized synthetic polymers (*34*). Furthermore, the mechanical properties of plasticized films changed with storage, which might be due to the evaporation of water and the loss of plasticizer from the film matrix. In this study, GLY and PEG are more convenient as chitosan plasticizers than EG and PG because they show a better plasticization efficiency and stability. The present study shows that the volatility of plasticizers must be taken into account in their choice because they influence the stability of film properties during storage and application; i.e., the least volatile plasticizer is better to use. Furthermore, the use of hydrophilic plasticizer has negative effects on water resistance, as shown in the results of surface properties by measuring the water contact angle. However, plasticizer is apparently required as stabilizer by avoiding film cracks during its application, as described by Garcia et al. (*47*).

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