Methylcellulose-Based Edible Films and Coatings: 2. Mechanical and Thermal Properties as a Function of Plasticizer Content

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Several edible films based on methylcellulose and polyethylene glycol 400 (PEG400) were prepared and stored until equilibration at different relative humidities. Tensile stress−strain curves show very different behaviors as a function of PEG400 and relative humidity. Tensile strength strongly depends on relative humidity and then on water content, more than on PEG400 content. On the contrary, elongation is dependent both on water and PEG400. These differences correspond to the glass transition of the polymer, which affects the elongation more than the tensile strength. However, from DSC measurements, it appears that the PEG400 has no or a very low compatibility with the methylcellulose matrix.

INTRODUCTION

Since the 1990s, edible films and coatings from biopolymers have received increasing attention. Edible packagings can be used to reduce water vapor, oxygen, lipid, and flavor migration in multicomponent food products and between food and surrounding atmosphere (Park et al., 1993; Debeaufort and Voilley, 1994). Agricultural origins and application of edible films and coatings were recently reviewed by Greener-Donhowe and Fennema (1994) and Torres (1994). Cellulose is the most abundant renewable resource, and its derivatives have excellent film-forming properties. Cellulose derivative based edible films are very efficient barriers to oxygen and aroma compound barriers (Greener-Donhowe and Fennema, 1993a,b; Debeaufort and Voilley, 1994).

The use of plasticizers is necessary to improve mechanical properties of protein- or polysaccharide-based edible films (Torres, 1994). Plasticization, due to water and plasticizers, such as polyols or lipids, induces an increase of transfer through edible and plastic packaging (Park et al., 1993; Hernandez, 1994; McHugh and Krochta, 1994). The effects of plasticizers on the structure of edible packaging have been little studied (Park *et al.*, 1993; Gontard and Guilbert, 1994).

Previous work has shown that the visual appearence of methylcellulose films is not affected by the addition of polyethylene glycol 400 (PEG400) at concentrations lower than 30% (Greener-Donhowe and Fennema, 1993a,b; Debeaufort and Voilley, 1995a,b). Moreover, methylcellulose-based edible films remain transparent for the same range of water or PEG400 contents. But the addition of PEG400 during the preparation of the film-forming solution and water sorbed after the film drying involves plasticization of the film, which significantly increases the oxygen, water vapor, and aroma transfers and sorption within the films (Debeaufort and Voilley, 1995a,b). These modifications can be attributed to structural changes due to the plasticization process.

Our objectives were to examine the effect of water and polyethylene glycol 400, used as an edible packaging plasticizer, on the thermal and mechanical behavior of methylcellulose-based edible films.

MATERIALS AND METHODS

Casting of Films. Methylcellulose (MC) (Benecel M02, Aqualon France S.A., Alizay, France) is a water soluble hydrocolloid whose characteristics are as follows: molecular weight = 18 000 g·mol^{-1} corresponding to 100 glucose units, methoxy substitution degree = 27.7−31.5, and viscosity range in 2% solution at 25 °C = 15−18 mPa·s^{-1}. Polyethylene glycol 400 (PEG400, Merck, Darmstadt, Germany), used as plasticizer, was infinitely soluble in water, with density = 1.127 kg/dm^3, melting range = 12−14 °C.

To make films, 5.66 g of Benecel was dispersed and solubilized in 100 mL of a water/ethanol (3:1, v/v) mixture at 80 °C with magnetic stirring (600 rpm). After 15 min, PEG400 was added and the mixture was maintained for 10 min under the same conditions before being spread onto glass plates with a thin layer chromatography spreader. Glass plates were previously covered with an adhesive poly(vinyl chloride) sheet to improve detachment of the MC films after drying for 1 h in a ventilated climatic box at 40 °C and 7% relative humidity. The quantities of PEG400 were 0, 10, 20, and 30% of the total dry matter.

The thickness of films was 25 ± 2 μm, and their density (25 °C) ranged between 1.2 and 1.3 kg/dm^3 depending on the PEG400 content.

Mechanical Properties of Films. The mechanical resistance of the films, including tensile strength (TS, MPa) and percentage elongation (*E*, %) at breakpoint, was measured uniaxially by stretching the specimen (size stretched = 50 mm × 20 mm) in one direction at 5 mm·min^{-1} using an Instron apparatus (model UTTI 1122, Instron Universal Tensile Testing Instrument Ltd., Bucks, U.K.). Tensile strength and elongation were computer recorded. Before and during measurements, films were maintained at constant temperature (25 ± 1 °C) and relative humidity (RH) using saturated salt solutions (22% RH, potassium acetate; 53% RH, magnesium nitrate; 75% RH, sodium chloride; and 84% RH, potassium chloride).

Calorimetry Analysis. The calorimetric behavior of methylcellulose powder, PEG400, and methylcellulose-based edible films was analyzed by differential scanning calorimetry (DSC). A Perkin-Elmer DSC2 microcalorimeter apparatus was used. Samples of 15−20 mg, corresponding to 50−70 3 mm

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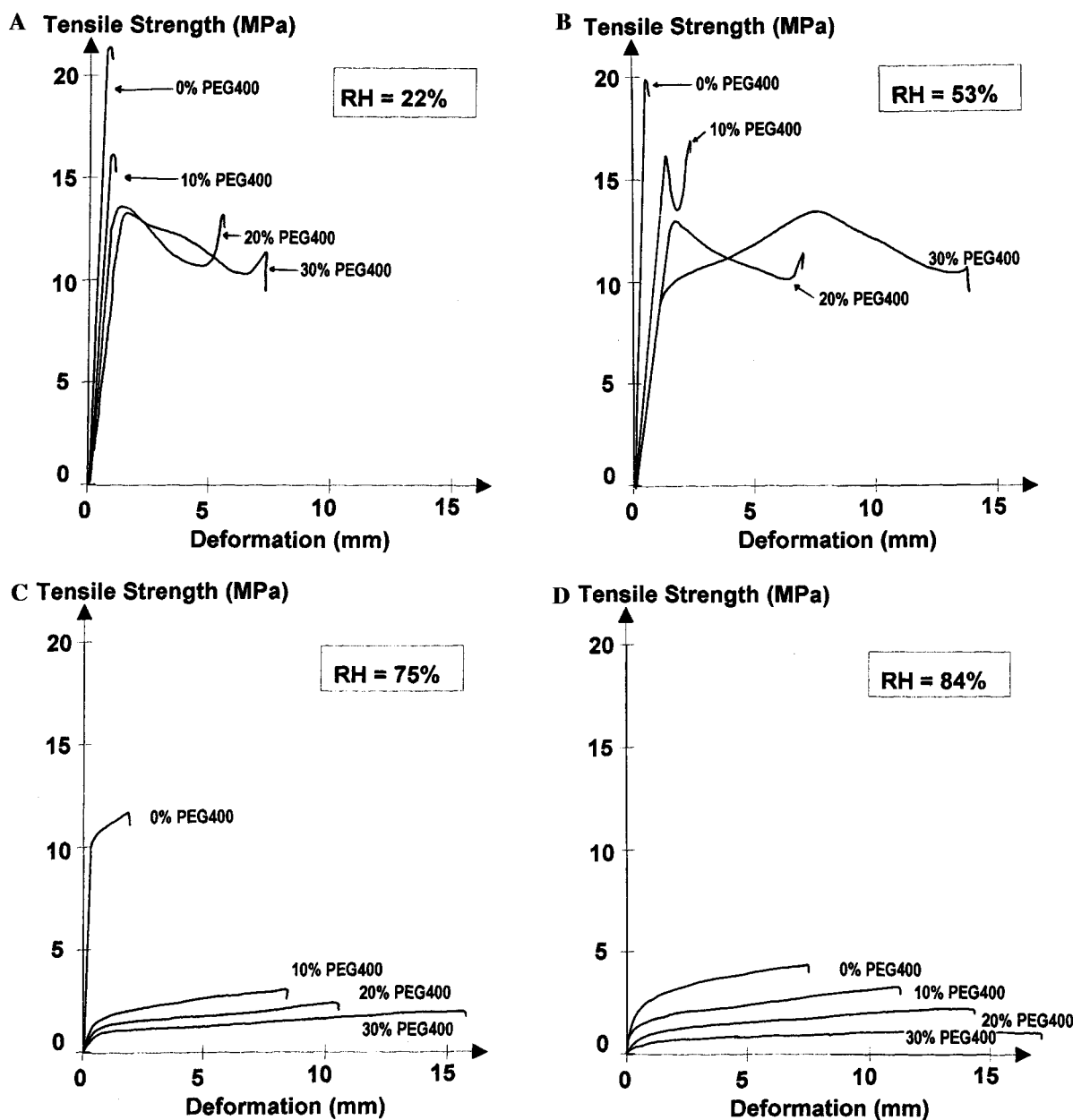
Figure 1. Tensile stress—strain curves of methylcellulose—PEG400 films as a function of relative humidity (25 °C): A, 22% RH; B, 53% RH, C, 75% RH; D, 84% RH.

diameter disks in the case of films, were placed in aluminum pans and stored for equilibration at 0, 53, or 84% relative humidity for 1 month. Aluminum pans were then hermetically closed and weighed before DSC measurements.

Samples were first chilled to −120 °C, heated to 80 °C, and then cooled a second time to −120 °C before being warmed to 120 °C. In all cases, heating and cooling rates were 10 °C/min. The measurement chamber was temperature regulated using both liquid nitrogen and helium gas. The calorimetric flow ($\partial H/\partial t$) was computer recorded as a function of temperature.

RESULTS AND DISCUSSION

Mechanical Properties of Films. Tensile strength and elongation can be used to describe how the mechanical properties of film materials relate to their chemical structure.

Figure 1 presents the tensile data of methylcellulose—PEG400-based edible films at four relative humidities. Plasticizers, both PEG400 and water, make films more flexible, but the plasticizing efficiency of each strongly depends on the concentration of the other. Thus, mechanical properties of methylcellulose-based edible films were compared as a function of plasticizer content.

Whatever the relative humidity, tensile strength decreases with PEG400 content at almost any given deformation. Furthermore, tensile strength increases from 2 to 10 times as the concentration of PEG400 is decreased from 30 to 0%, but the magnitude of the decrease strongly depends on the ambient relative humidity and thus on the water content. The hydration behavior of methylcellulose—PEG400 edible films as a function of ambient relative humidity was studied in a previous work (Debeaufort and Voilley, 1995b). The effect of PEG400 concentration on the TS appears to be more important when ambient relative humidity is lower than or equal to 75%.

Between 22% and 53% relative humidity, TS remains relatively constant, even for a high concentration of PEG400, as shown in Figure 2. However, the higher the PEG400 concentration, the smaller the change in TS with incremental increases in PEG400, whatever the
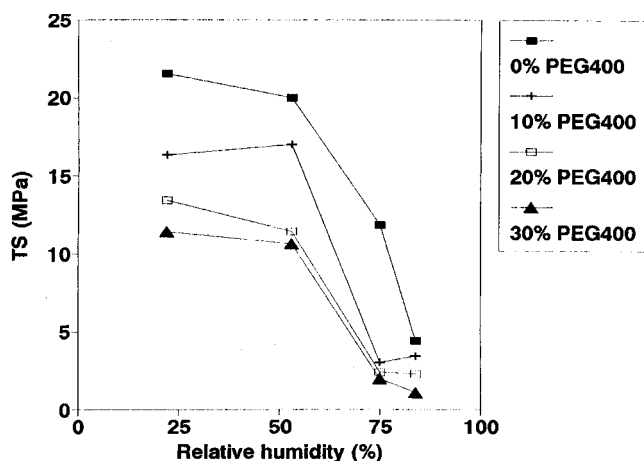
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Figure 2. Tensile strength of methylcellulose-based edible films containing various proportions of PEG400 *vs* relative humidity (25 °C).

Table 1. Classification[a] of Mechanical Properties and Film Structures as a Function of Ambient Relative Humidity and PEG400 Content

PEG content (%)	22% RH	53% RH	75% RH	84% RH
0	A	A	B	D
10	A	C	D	D
20	C	C	D	D
30	C	C	D	D

[a] A: brittle fracture, glassy polymer, $T < 0.8T_g$. B: onset of plasticity, pseudoductile polymer, $T \simeq 0.8T_g$. C: extensive cold drawing, ductile polymer, $T \simeq T_g$. D: uniform viscous flow, rubbery polymer, $T > 1.05T_g$.

relative humidity. Park et al. (1993) observed the same behavior of TS when plasticizer content (PEG400 or glycerin) is higher than 15% in methylcellulose and (hydroxypropyl)cellulose, mechanical properties determined at 25 °C and 50% relative humidity.

These effects could be explained by the glass transition of polymers inducing the structure change from glassy to rubbery, which can be estimated from the shape of stress–strain representations of the tensile curves. The work of Gibson and Ashby (1988) on the mechanical properties of synthetic polymers such as poly(vinyl chloride) shows that the shapes of tensile stress–strain curves are directly correlated to the structure characteristics of the polymer, and particularly to the glass transition. On the basis of the work of Gibson and Ashby (1988), we classified the methylcellulose film behaviors in four groups (A, B, C, and D) as a function of both ambient relative humidity and PEG400 concentration (Table 1). The increase of plasticizer content decreases the glass transition temperature of the polymer. When ambient or measurement temperature is lower than $0.8T_g$ (glass temperature of the film), polymers are linear-elastic to fracture, brittle, and in a glassy state (group A). At higher temperature ($T \simeq 0.8\ T_g$) the mode of failure changes from brittle to ductile, characterized by a yield point followed by rapid drop in load, with small overall extension (group B). A further increase in temperature ($T \simeq T_g$) leads to inhomogeneous cold drawing, with extensions which are now large (group C). Finally, at higher temperatures still ($T > 1.05T_g$), the polymer deforms homogeneously by viscous processes, giving a large extension to failure. It appears from Figure 1 that methylcellulose film behavior follows the same evolution as a temperature increase when the PEG400 content and relative humidity increase.

As observed by several authors in the case of edible polymers such as gluten or starch, the more the plasticizer content in the film increases, the more the glass transition temperature of the polymer decreases (Gontard et al., 1992; Le Meste *et al.*, 1996).

Elongation increases significantly with the PEG400 content, particularly when the relative humidity is higher than 75% (Figure 3). Elongation increases mainly when films becomes rubbery, *i.e.*, when structure changes from ductile (C) to elastic (D).

Using Table 1, it appears from Figures 2 and 3 that elongation increases when the glass transition temperature of the polymer equals or is lower than the measurement temperature. Moreover, the glass transition depends on both water and PEG400 content. On the contrary, the TS increase seems to be more sensitive to the relative humidity than to the PEG400 content because, at high relative humidity, the TS value is not affected by the PEG400 content.

Thermal Behavior of Films and Film Components. During both cooling and heating, thermograms of methylcellulose powder display neither glass transition nor melting or crystallization peaks in the temperature range studied (data not shown). When water is added to methylcellulose powder, a melting peak appears near 0 °C corresponding to the melting of ice. Moreover, methylcellulose shows on a wide range of temperature (45–65 °C) a weak endothermic peak which disappears at the second heating. This phenomenon should correspond either to the evaporation of water sorbed within the polymer or to a reorganization or a destruction of the methylcellulose gel network. Indeed, the gelation temperature of methylcellulose in water is between 55 and 60 °C (Sarkar, 1979; Haque, 1993). In the absence of PEG400, films obtained after drying of the hydroalcoholic solution of methylcellulose have the same behavior as the powder. Thus, ethanol only allows a reduction in drying time but does not remain in the film after drying. Therefore, it cannot act as a plasticizer of methylcellulose edible films. Therefore, solubilization and drying of methylcellulose does not strongly modify the structure and thermal properties of this polymer.

When PEG400 (25%) is added within the methylcellulose films, the temperature range and magnitude of the endothermic peak increase weakly as the water content increases (Figure 4). The thermal behavior of methylcellulose is relatively independent of the plasticizer concentration.

Methylcellulose–PEG400-based edible films show a change of the base line in the temperature range −100 to −50 °C, which can be interpreted as a specific heat variation due to the glass transition (Figure 4). This phenomenon is repeated when the sample is heated and cooled sucessively. The temperature corresponding to this transition decreases from −57 °C to −82 °C when the water content increases. This behavior was observed by Gontard (1991) on gluten-based edible films, and by Koelsch and Labuza (1992) for film-forming solutions containing methylcellulose, PEG400, and ethyl alcohol after drying at several relative humidities. The glass transition temperatures they found as a function of relative humidity are similar to those we obtained.

It appears that pure PEG400 presents the same transition (glass transition between −80 and −65 °C) as methylcellulose–PEG400-based films for similar water content (Figure 5). Without water, PEG400 is liquid at ambient temperature and has a glass transi-
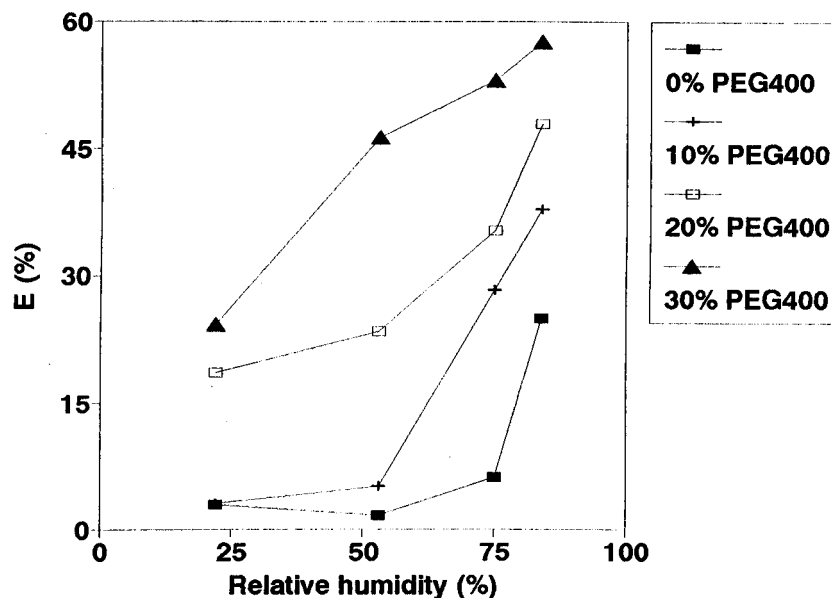
Figure 3. Elongation of methylcellulose-based edible films containing various proportions of PEG400 *vs* relative humidity (25 °C).
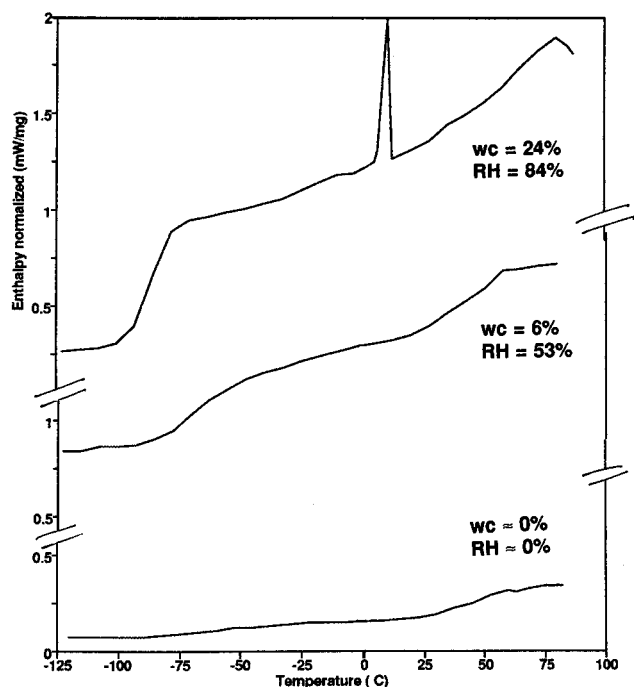

Figure 4. Thermograms of 25% PEG400–methylcellulose films as a function of water content (wc) and relative humidity (RH) at 25 °C.

Figure 5. Thermograms of pure PEG400 as a function of water content (wc) and relative humidity (RH) at 25 °C.

tion close to −70 °C and only one peak of melting at 14 °C during heating. In the presence of water, two peaks of melting appear. Indeed, Blond and Arbogast (1984) observed the same behavior of PEG600 for water content similar to that of methylcellulose–PEG400 films. This phenomenon corresponds to the behavior of a eutectic solution for which only a fraction of PEG is amorphous and can undergo a glass transition.

As a glass transition is not observable on the methylcellulose films which do not contain PEG400, the glass transition observed on methylcellulose–PEG400 films may correspond to the glass transition of the PEG400. As the water content increases in methylcellulose-based edible films or in pure PEG400, the glass transition temperature tends to reach a value equal to −82 °C. The glass transition temperature of films is a little
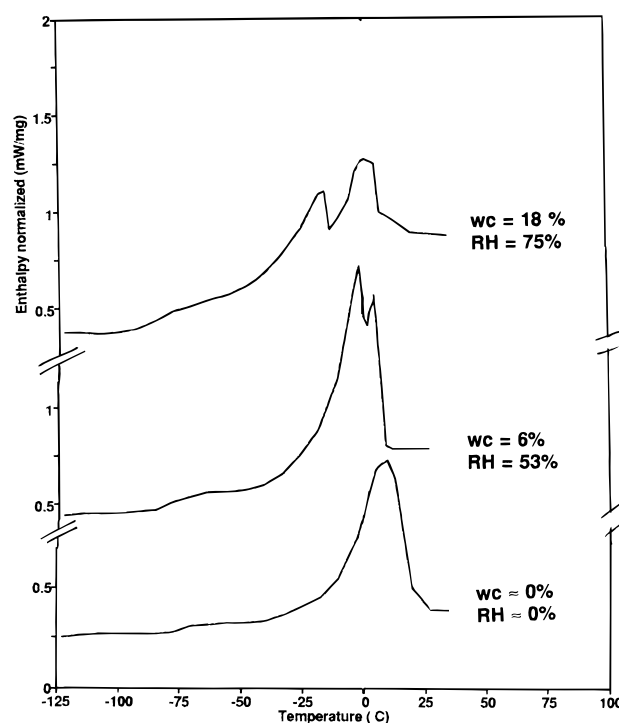
higher than in pure PEG400 for the same water content. This can probably be explained by the fixation of a part of the water molecules by methylcellulose fibers for their gelation (Haque, 1993). These phenomena correspond to the linear part of the sorption isotherm, *i.e.,* for water activities lower than 0.7 (Debeaufort and Voilley, 1995b).

Moreover, melting and crystallization temperatures of PEG400 are the same when it is alone or in films. Thus we can conclude that PEG400 does not have much interaction with the methylcellulose matrix. The plasticizing effect is probably due only to a lubrication phenomenon between the polymer chains because PEG400 has a typical incompatibility behavior (immiscibility) in our films, *i.e.,* the system is composed of two independent phases at 25 °C: liquid phase for the PEG400 and solid for the methylcellulose (Sears and

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Darby, 1982). These conclusions are not in agreement with the work of Greener-Donhowe and Fennema (1993b), who stated from color and transparency observations that PEG400 is compatible with methylcellulose up to a concentration of 30%.

Differential scanning calorimetry measurements do not permit the display of the glass transition of methylcellulose, but it appears that the effect of water and PEG400 on the thermal behavior of films is very different. Thereby, the effects of water and PEG400 on tensile strength and elongation are different. Water involves a swelling of methylcellulose fibers, which allows more deformability of the films due to a decrease of hydrogen bonding (Haque, 1993) between methylcellulose chains. Thus, water has a stronger effect on tensile strength than on elongation whatever the concentration of PEG400.

On the contrary, PEG400 acts more as a lubricant of the polymer chains than as a plasticizer. Thereby, it allows the methylcellulose fibers to slide one over the other, thus increasing the elongation, even for a low relative humidity. Therefore, PEG400 spaces out methylcellulose chains and decreases the interactions between the methylcellulose molecules, which involves a decrease in the tensile strength. However, whatever the parameter, tensile strength or elongation, it appears that all the changes in mechanical properties between 50 and 75% relative humidity correspond to the change of the shape of the sorption isotherm, *i.e.,* the increase of water content *vs* relative humidity change from linear to exponential (Debeaufort and Voilley, 1995). All these modifications of hydration, mechanical, or thermal behavior are correlated to the change of film structure from a glassy state to a rubbery state.

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