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Interactive effects of water-glycerol and water-sorbitol on physical properties of konjac glucomannan films

L.H. Cheng [1], A. Abd Karim [1*], Norziah, M.H., Fazilah, A., C.C. Seow [2]

MAJAL

[1] *Food Biomaterials Science Research Group, Food Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia*

[2] *Food Technology Consultant, 209 Solok Pemancar, 11700 Gelugor, Penang, Malaysia*

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*Corresponding author. Tel.: 60-4-6533888 Ext. 2221; Fax: 60-4-6573678; E-mail address: akarim@usm.my

Abstract

Konjac glucomannan (KGM) edible films were prepared with different amounts of glycerol or sorbitol as a plasticizer. Films were characterized by moisture sorption isotherm, differential scanning calorimetry, and tensile tests after being conditioned at different relative humidities. Moisture and polyols incorporated into KGM films were found to generally plasticize tensile properties of KGM-based films. However, thermal properties and water sorptive capacity (WSC) of polyol-plasticized KGM films were found to vary with water activity (a_w), i.e. at low a_w below 0.6, WSC and melting enthalpy were decreased with increasing in polyol content and the opposite was true at higher a_w (>0.6). This was attributed to extensive interactions between plasticizer and KGM that reduced the available active site (-OH groups) for water adsorption. The presence of polyols at low a_w appeared to suppress crystalline structures due probably to molecular hindrance. These effects were diminished when the moisture content was in excess.

Keywords: Konjac glucomannan; Edible films; Sorption isotherm; Differential scanning calorimetry; Tensile properties

1. Introduction

For certain biopolymer-based edible films, such as wheat gluten and hydrolyzed whey protein films, plasticizers play an important role in conferring workability and flexibility (Gontard, Guilbert & Cuq, 1993; Sothonvit & Krochta, 2000). Plasticizers are capable of reducing film brittleness and modifying the molecular organization of the polymer network because they are able to decrease the cumulative intermolecular forces, increase intermolecular spacing and mobility of polymeric chains, and reduce polymer chain cohesiveness upon incorporation (Banker, 1966; Cuq, Gontard, Cuq & Guilbert, 1997; Lieberman & Gilbert, 1973).

Apart from water, the most usual plasticizers are polyols, mono-, di-, and oligosaccharides (Cuq et al., 1997). The effects of composition, shape, polarity, chain length and number of active functional groups on the ability of plasticizers to plasticize a polymer network has been intensively studied (Cuq et al., 1997; Donhowe & Fennema, 1993; Gueguen, Viroben, Noireaux & Subirade, 1998; Lieberman & Gilbert, 1973; Sothornvit & Krochta, 2001). Plasticizers with characteristics such as small size, high polarity, more number of polar groups per molecule, and greater molecular dimensions between polar groups within a molecule generally impart greater plasticizing effects on a polymeric system. However, the selection of a plasticizer for a specified system is normally based on the compatibility and permanence of the plasticizer, and the desired physical properties of the films one wishes to achieve (Banker, 1966; Donhowe & Fennema, 1993; Sothornvit & Krochta, 2001). When a plasticizer is added to a film, it will generally induce a large decrease in film strength, elasticity, and barrier and thermal properties but increase film flexibility and extensibility (Cuq et al., 1997; Donhowe & Fennema, 1993; Garcia, Martino & Zaritzky, 2000; McHugh & Krochta, 1994; Yang & Paulson, 2000; Sothornvit & Krochta, 2001).

Water, is a ubiquitous natural diluent which plasticizes and/or antiplasticizes some biopolymeric films depending on the amount sorbed onto the films matrix (Chang, Cheah & Seow, 2000; Cheng, Abd Karim, Norziah & Seow, 2002; Gontard et al., 1993; Kumar, Bhandari & Bhat, 1991; Seow, Cheah & Chang, 1999). During initial hydration from the dry state, a biopolymer film experiences improved film elasticity as a result of extensive connections established between water and polymer. With increasing hydration, film elasticity and cohesiveness decrease progressively because water-polymer interactions developed to the detriment of polymer-polymer bonds. In a ternary system, water-plasticizer-polymer, the presence of a second plasticizer normally has a deciding factor on the plasticizing action of the primary one (Lourdin, Coignard, Bizot & Colonna, 1997). This is supported by the work of Gaudin, Lourdin, Forssell and Colonna (2000), in which they reported that the classic plasticizing effect of water (an increase in oxygen permeability) was fading with a low concentration of sorbitol. The similar effect was demonstrated in Kumar et al. (1991), where the thermal properties of starch-polyethylene glycol and starch-polyethylene glycol stearate were reported to be moisture dependent. The nature of this effect was not entirely understood because water content at a given relative humidity results from the combined affinities of the macromolecular network and the characteristics of the plasticizers (Lourdin et al., 1997).

In the present study, an attempt has been made to explore in much greater detail the effect of equilibrium moisture content on konjac glucomannan (KGM) film properties in a ternary system. Attention has been focused on the sorption isotherms, thermal and tensile properties of the plasticized KGM films.

2. Materials and methods

2.1. *Materials*

Purified KGM (PROPOL A) was obtained from Shimizu Chemical Corporation, Japan. Glycerol-anhydrous (86-88% purity) from R&M Chemicals and D-Sorbitol (98% purity) from Fluka were used in this study.

2.2. *Film preparation*

Films were obtained by the casting method described by Cheng et al. (2002), where KGM (7 g on dry basis) and glycerol or sorbitol (0, 0.7, 1.4, 2.1, 2.8 or 3.5 g) was added to 1 l of distilled water in a National® home blender (Model MX-595N). Blending was carried out for 15 min. The mixture was then left to stand for 1 h at 30 °C, after which 90 g portions were poured and spread onto a level, square perspex plate fitted with rims around the edge to give a 16 × 16 cm film-forming area. The solutions were allowed to dry at room temperature for ~20 h. Films that formed were peeled off and kept in a desiccator over phosphorus pentoxide before being subjected to analysis. The thickness of the films produced ranged from 0.03-0.04 mm. Where necessary, analysis of variance (ANOVA) on the experimental data obtained was performed with General Linear Model using Minitab For Windows, Release 10.1 (Minitab Inc., State College, PA).

2.3. *Film characterization*

Films were characterized in terms of sorptive and tensile properties as described by Cheng et al. (2002). Differential scanning calorimetry (DSC) was performed using a DuPont 2910 differential scanning calorimeter (E.I. DuPont de Nemours & Co., Inc.,Wilmington, Del., U.S.A.). Films were cut into small pieces. The cut sample pieces were equilibrated under vacuum for approximately 7 d over specified saturated salt solution of known relative humidities (32, 43, 56, 69, 75, 84%) at 30 °C (Greenspan 1977). Samples (8-10 mg each) were hermetically sealed in aluminium sample pans using an inverted lid configuration. Samples were heated from room temperature (~25 °C) to 270 °C at a heating rate of 20 °C min^{-1} and an oxygen-free nitrogen flow rate of 30 mL min^{-1}. The transition temperatures (onset, T_o; and peak, T_p) and enthalpy of melting (ΔH) were determined from the thermograms obtained.

3. Results and discussion

3.1. Sorption isotherms

Fig. 1 and Fig. 2 show the moisture sorption isotherms of the glycerol- and sorbitol-plasticized konjac glucomannan (KGM) films, respectively. The sigmoidal-shaped moisture sorption isotherms associated with complex or polymeric foods (Coupland, Shaw, Monahan, O'Riordan & O'Sullivan, 2000) were evident for all film types studied. Moisture content of the film increased slowly with progressive increase in water activity (a_w) up to ~0.5, after which it increased drastically with a small increase in a_w.

The effect of polyol concentration on the water sorptive capcity (WSC) of polyol-plasticized KGM films was a_w dependent. Over the range of a_w from 0 - 0.6, water sorption generally decreased when the polyol content was increased. Such an effect was more clearly shown in sorbitol-plasticized KGM films than in glycerol-plasticized ones (Fig. 1 vs Fig. 2). Above a_w 0.6, WSC increased drastically when the plasticizer concentration was progressively increased. Similar observations have been reported for methylcellulose-based films (Debeaufort & Voilley, 1995), pullulan-based films (Diab, Biliaderis, Gerasopoulos &

Sfakiotakis, 2001), gluten-based films (Gontard et al., 1993), and starch-based films (Lourdin et al., 1997).

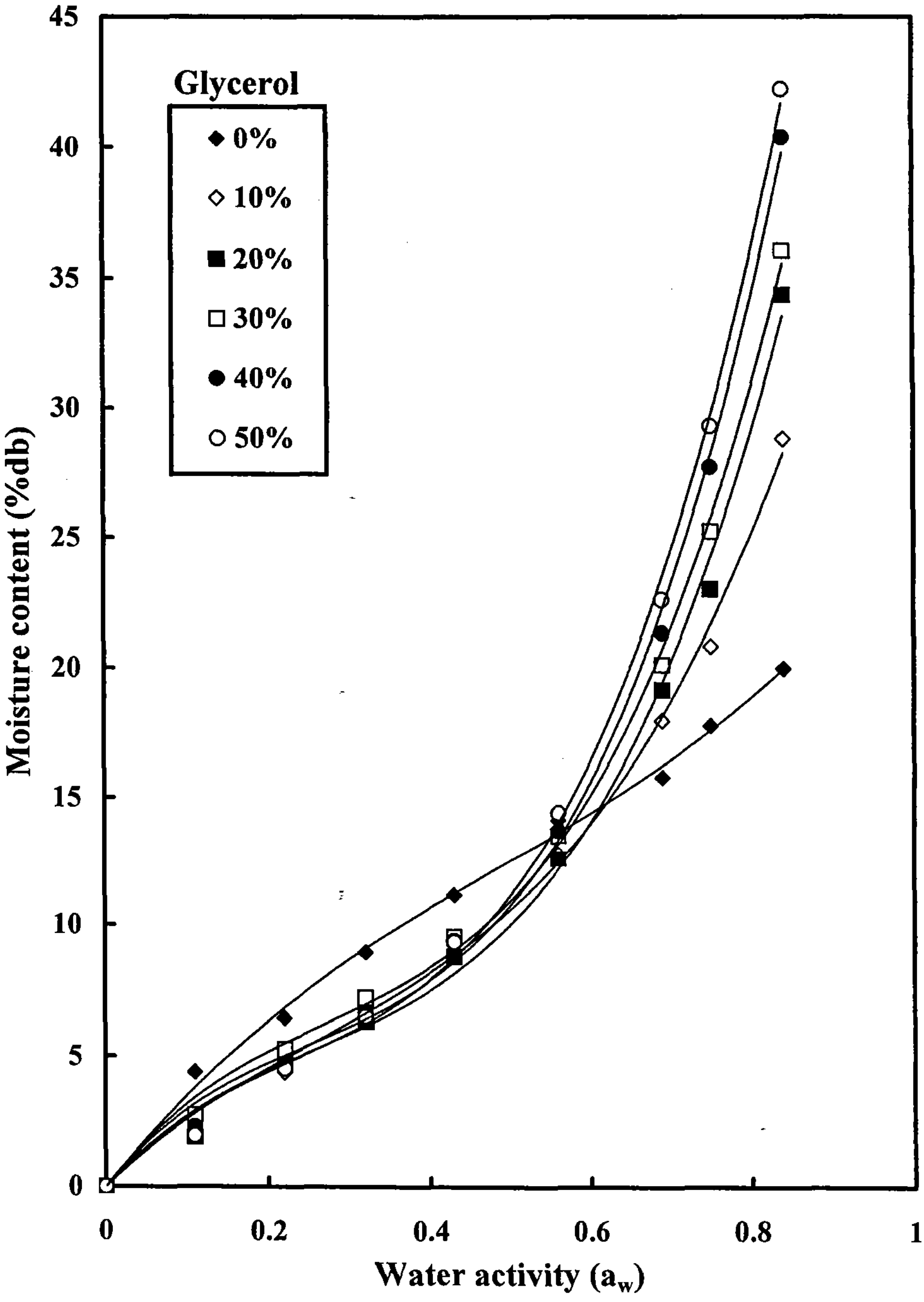

Fig.1. Moisture sorption isotherms of native and glycerol plasticized konjac glucomannan films at 30 °C. [Typical coefficient of variation (C.V.) for quadruplicate measurements did not exceed 12%.].

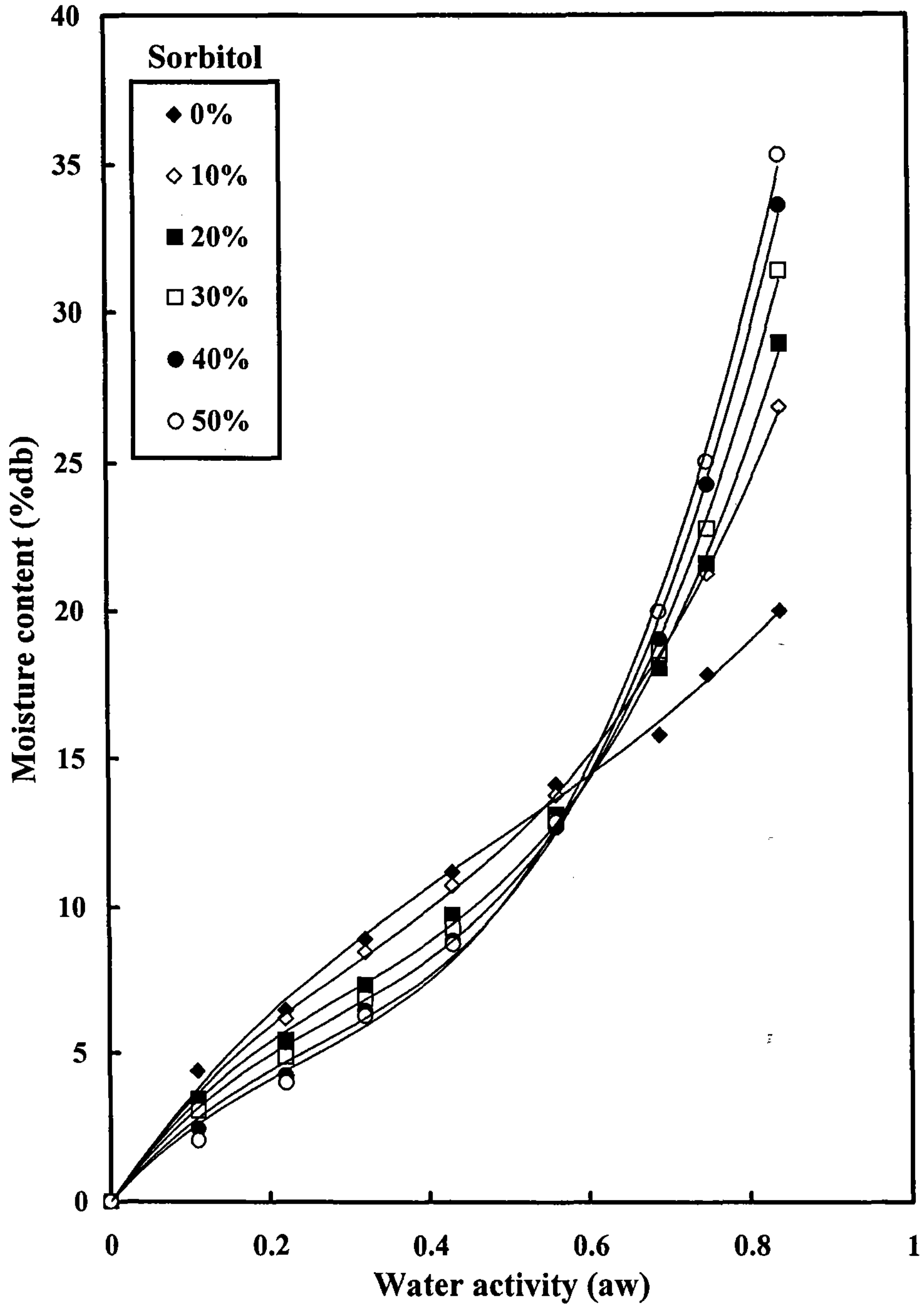

Fig.2. Moisture sorption isotherms of native and sorbitol plasticized konjac glucomannan films at 30 °C. [Typical coefficient of variation (C.V.) for quadruplicate measurements did not exceed 12%.].

The reason for such a phenomenon might lie in the polar nature of polyols, which compete with water for active sites on the biopolymer chains, thus reducing the adsorption surface for water sorption (Debeaufort & Voilley, 1995; Lieberman & Gilbert, 1973). At higher a_w levels, WSC was enhanced with increasing plasticizer contents. This could be attributed to the creation of hydrogen bonds between the plasticizer and water (Lourdin et al., 1997). Low molecular mass polyols with hygroscopic nature have a relatively greater ability to associate with water as compared with biopolymers (Chinachoti & Steinberg, 1984, 1988; Baik & Chinachoti, 2001). Consequently, plasticizer-polymer interactions were diminished at high moisture content (Gontard et al., 1993) and greater free volume was created, allowing the matrix to absorb more water and promoting water clustering at successively higher hydration levels. This suggests that glycerol- and sorbitol- plasticized KGM films could serve as a reasonably good protective layer against moisture sorption for food products only if a_w is less than 0.6.

Upon incorporation, the effect of glycerol and sorbitol on the WSC of KGM films was a_w and concentration dependent. This is clearly shown in Fig. 3 and Fig. 4. At low polyol concentration (10 and 20%) and a_w (0 – 0.6) level (Fig. 3), glycerol-plasticized KGM films sorbed relatively lower moisture content as compared to sorbitol-plasticized KGM films. This could be attributed to the smaller molecular size of glycerol as compared with sorbitol, which facilitated the penetration of glycerols into the amorphous regions of the KGM network (Donhowe & Fennema, 1993; McHugh & Krochta, 1994). Thus, reducing a larger number of available –OH groups for water adsorption. In addition, according to Lieberman & Gilbert (1973), an increase in the molecular dimensions of the plasticizer between polar groups would increase the free volume upon incorporation between polymer chains. This explains why the addition of sorbitol greatly enhanced the WSC of KGM films at low moisture levels.

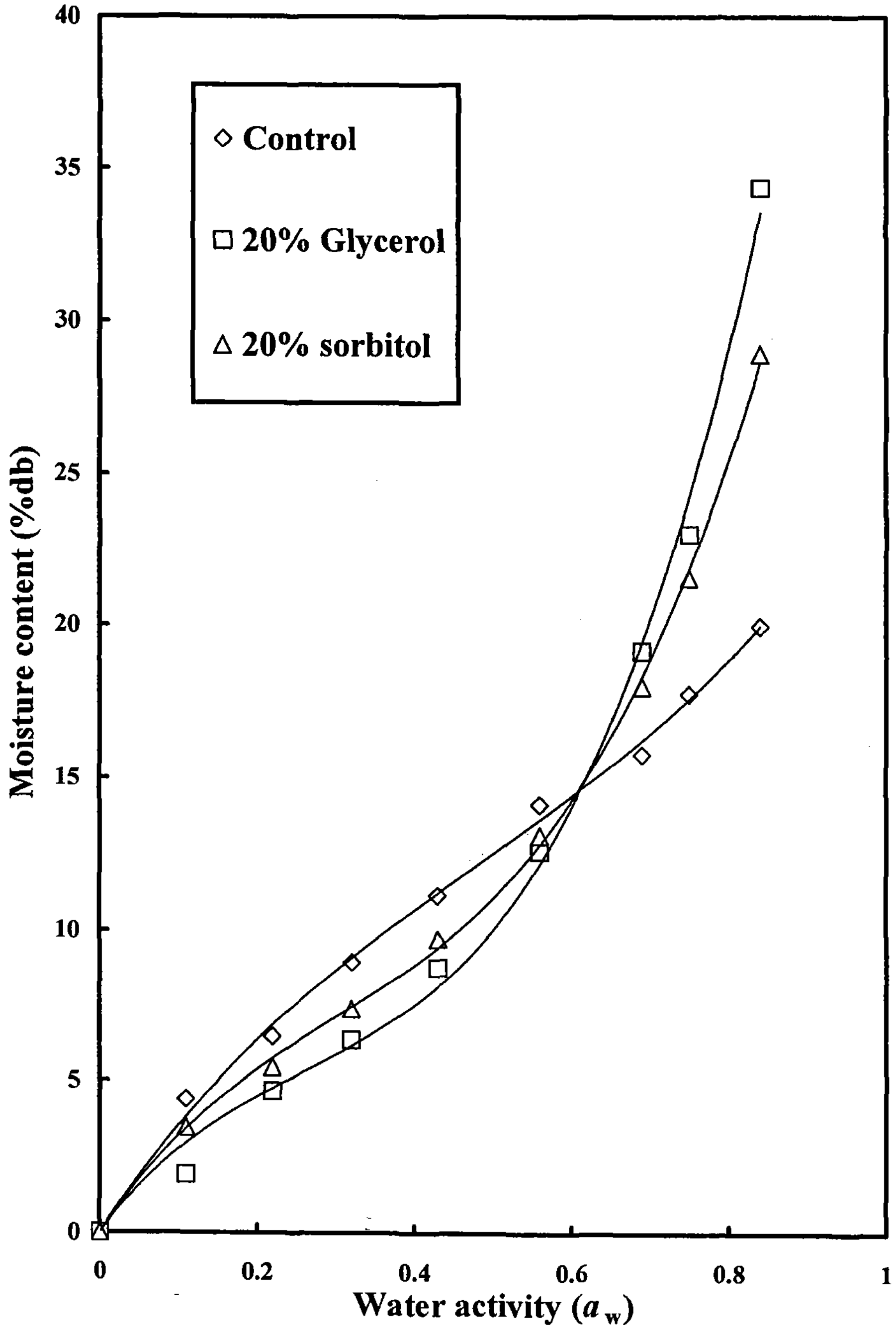

Fig.3. Moisture sorption isotherms of the control and 20% polyol (glycerol and sorbitol) KGM films. The same variation trend was observed in 10% polyol containing KGM films as compared to the control.

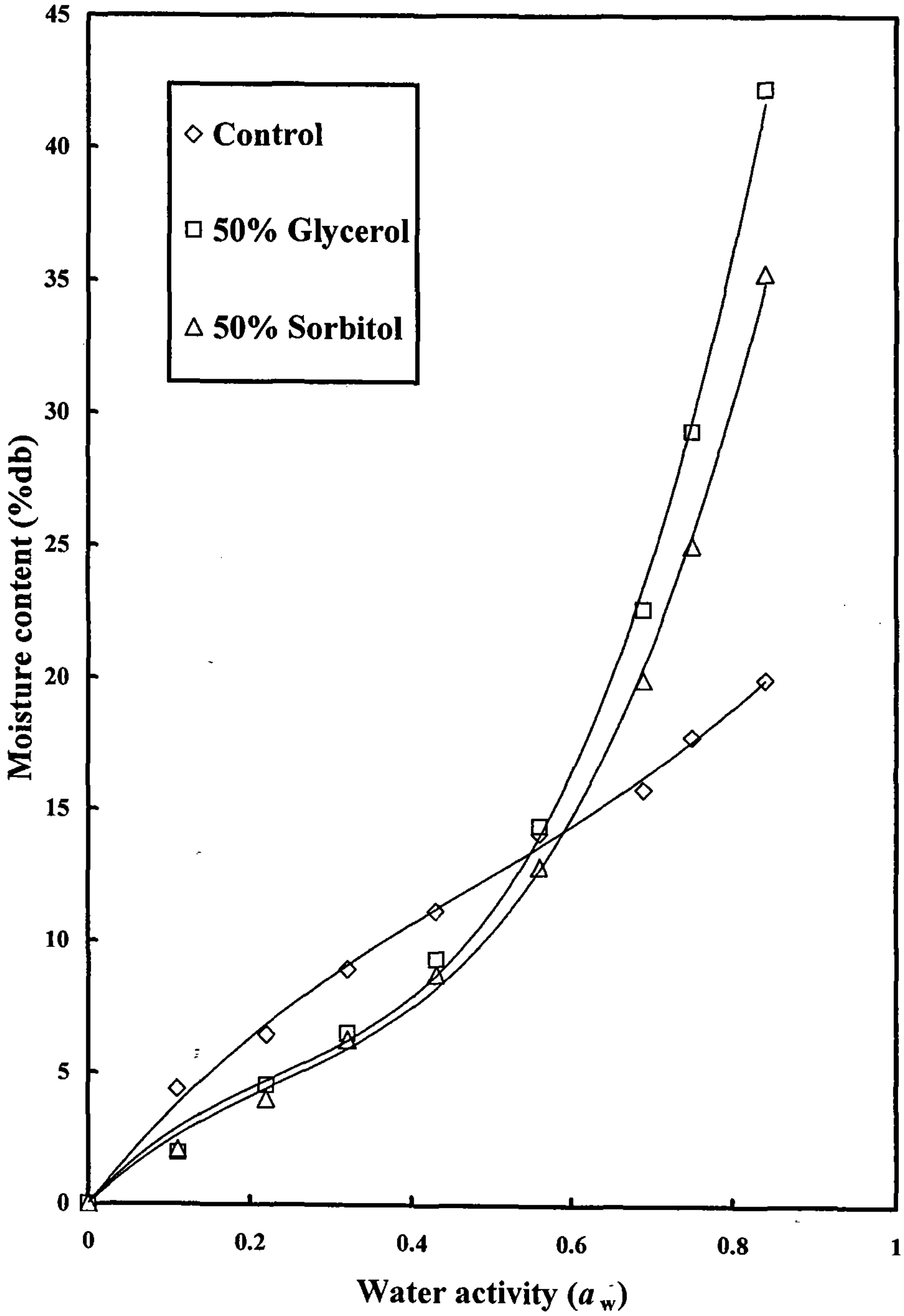

Fig.4. Moisture sorption isotherms of the control and 50% polyol (glycerol and sorbitol) KGM films. The same variation trend was observed in 30% and 40% polyol containing films as compared to the control.

However, this effect was diminished at a higher concentration and/or a_w level. The glycerol-plasticized KGM films at any particular level of incorporation and a_w exhibited a relatively higher WSC than the corresponding sorbitol-plasticized KGM films. This could be attributed to the highly hygroscopic nature of glycerol as compared with sorbitol, which draw relatively more water into the KGM network. In addition, on the same mass basis in both film types (glycerol- and sorbitol- plasticized), those films with the lower molecular weight plasticizer possessed a greater molar content of the plasticizer (Cuq et al., 1997). In other words, glycerol has a larger number of hydroxyl groups per mole or mass unit when compared with sorbitol (Donhowe & Fennema, 1993). Therefore, glycerol-plasticized KGM films sorbed relatively more moisture than sorbitol-plasticized ones, at a higher concentration and a_w level.

3.2. Thermal properties

Statistical analysis of the thermal data obtained revealed that transition temperatures (onset and peak) did not appear to be significantly ($P>0.05$) affected by moisture content and amount of plasticizer added to the system. However, melting enthalpy was significantly ($P<0.01$) affected by moisture and plasticizer contents.

Fig. 5 and 6 illustrate the variations in melting enthalpy as a function of moisture content for glycerol- and sorbitol-plasticized films, respectively. The moisture content of KGM films equilibrated at different relative vapour pressure was determined from the sorption curves obtained previously. Fig. 5 shows that melting enthalpy of the control and glycerol-plasticized films (except those with 40 and 50% glycerol content) increased with increasing moisture content up to a critical point before decreasing, i.e. a peak was evident. The critical point at which a peak was observed appeared to shift to higher moisture content as glycerol content was increased, i.e. shifted from 18 to 26% moisture content as glycerol concentration

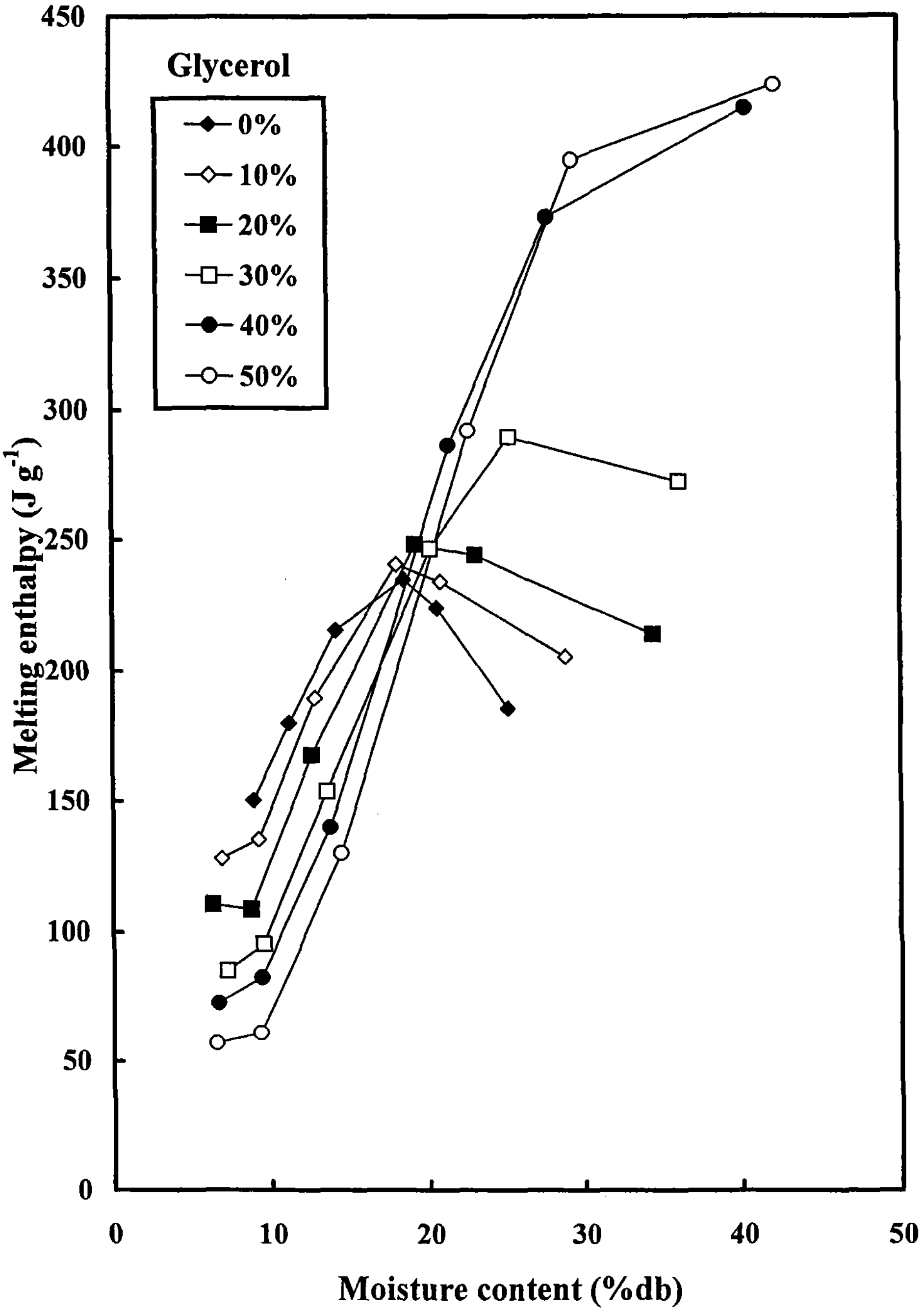

Fig.5. Variations in melting enthalpy as a function of moisture content for konjac glucomannan films plasticized with different glycerol concentrations.

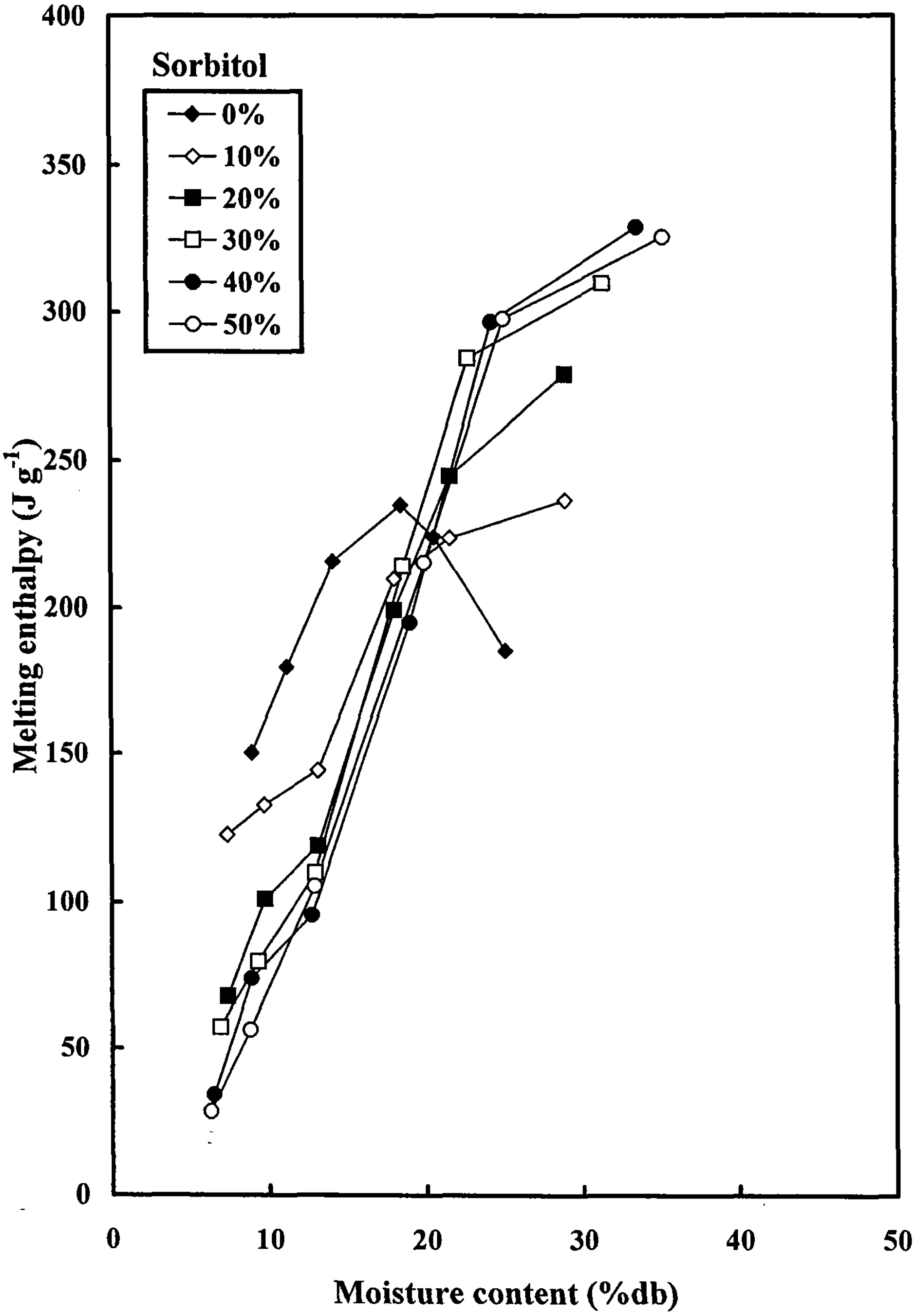

Fig.6. Variations in melting enthalpy as a function of moisture content for konjac glucomannan films plasticized with different sorbitol concentrations.

increased from 0 to 30%. In the case of sorbitol-plasticized films and those containing 40 and 50% glycerol, no peak in melting enthalpy was evident over the range of moisture content studied, but melting enthalpy was increased with a progressive increase in moisture content for all these films.

For both film types (except those with a peak evident), melting enthalpy increased with successive hydration. This appeared to be a direct consequence of enhanced mobility of molecular chain segments brought about by the plasticizing effect of water molecules. This effect reduced the activation energy for the formation of a stable crystalline structure (Arvanitoyannis, Psomiadou, & Nakayama, 1996; Garcia et al., 2000), thus relatively more long-range order crystalline structure was expected.

On the other hand, for those film types with a peak evident, a drop in melting enthalpy was observed with further humidification level (>20% moisture content). In a free-standing polyol-plasticized KGM films, the plasticizer and polymer are generally thought to be held together by intermolecular secondary valence forces (Mellan, 1961). During hydration from the dry state, free polar (-OH) groups that still available within the network were easily hydrated. At successive hydration, mobility of polymer chains was enhanced and better chain alignment was promoted. For those with glycerol, up to a critical level local osmotic dehydration of KGM molecules was expected (Baik & Chinachoti, 2001). This was attributed to the high hygroscopic nature of glycerols as compared to biopolymer, which shows higher affinity to water molecules (Chinachoti & Steinberg, 1984, 1988; Baik & Chinachoti, 2001). According to Baik & Chinachoti (2001), this could subsequently reduce the polymer molecular ability to form a more ordered structure. This explanation accounted for the gradual drop in the increment of melting enthalpy magnitude with a progressive increase in moisture content, until a maximal enthalpy was reached; and also the shift in peak locality to a higher moisture content as glycerol content was increased. At this maximum melting enthalpy, polyols were saturated with water molecules. In the further hydration range, the later-sorbed water fraction in either native or glycerol-plasticized KGM films may exhibit "liquid-like" properties (Arvanitoyannis et al., 1996). The subsequent water-polymer interactions probably developed to the detriment of polymer-polymer bonds (Barie, 1968). Thus, a reduce in melting enthalpy was observed.

Effect of plasticizer content on the melting enthalpy of glycerol- and sorbitol- plasticized films was found to be moisture content dependent. In general, at any particular moisture content within the range of 0 – 20%, a decrease in melting enthalpy was observed with a progressive increase in plasticizer concentration. The opposite trend was observed for those films contained more than 20% moisture content. This suggests that interactions could have occurred between water and polyol molecules.

At any particular moisture content within the range of 0 – 20%, the presence of glycerol or sorbitol interfered with the formation of crystalline structures. According to Baik and Chinachoti (2001), the ability of a polyol to inhibit crystallization may be explained by molecular hindrance, or penetration of polyols into the amorphous regions of the polymer network. Thus, local mobility of polymer chain was lowered and reorientation into a crystalline structure was inhibited (Baik & Chinachoti, 2001). Both or the combined effects of the two may be responsible for the decrease in melting enthalpy with increasing plasticizer content at low moisture content. On the other hand, successive addition of plasticizer at a particular high moisture content (>20%) enhanced the melting enthalpy of polyol-plasticized KGM films. This was attributed to the plasticizing effect of polyol molecules that enhanced molecular mobility and formation of a stable crystalline structure.

Studying melting enthalpy of the polyol-plasticized KGM films, it was clearly shown that melting enthalpy of glycerol-plasticized KGM films were relatively more moisture sensitive than sorbitol-plasticized ones. This suggests that sorbitol-plasticized KGM films were stiffer than glycerol-plasticized films. This is shown in the coming discussion on the tensile properties of polyol-plasticized KGM films.

3.3. *Tensile properties*

Moisture and plasticizer contents over the respective range studied had no significant (P>0.05) effects on tensile strength, which fell within a range of $3.5 \times 10^7 - 5.5 \times 10^7$ Pa. Changes in elastic modulus (*EM*) and tensile elongation (*TE*) of polyol-plasticized KGM films as a function of moisture or plasticizer contents are shown in Figs. 7 – 10.

Overall, a sharp decrease in *EM* (Fig. 7 and Fig. 8) and increase in *TE* (Fig. 9 and Fig. 10) was observed with increase in humidification An exception was observed for *TM* of glycerol- and sorbitol-plasticized films, in which *TM* increased over the lower range of humidification. This is a common phenomenon associated with antiplasticization by water in biopolymer films previously reported by many other researchers (Kumar et al., 1991; Gontard et al., 1993; Chang et al., 2000).

According to Coupland et al. (2000), a polyol, such as glycerol, has two plasticizing effects; first as a result of its presence in the film and second because its intensively hygroscopic character tends to draw additional water into the matrix. Coupland et al. (2000) suggested that the latter effect is uniquely responsible for the plasticizing properties of glycerol. However, the water sorption and tensile data obtained in this study goes against their suggestion. At low a_w range (0-0.6) the amount of water sorbed (ranged from 0 – 15%) was reduced with increasing plasticizer content (Fig. 1 and Fig. 2). However, within the same moisture content, the plasticizing effect of polyol on *EM* and *TE* was not counteracted (Figs. 7 – 10), even though smaller amount of water sorbed. On the other hand, at higher a_w, WSC of polyol-plasticized KGM films increased drastically when the plasticizer concentration was progressively increased. At this high moisture level, *EM* and *TE* were drastically reduced and increased, respectively., This was due probably to the cumulative and/or synergistic effect caused by glycerol and water. However, according to Mueller-Plathe (1991a,b; 1992), such a cumulative effect is too complicated to be elucidated because the system involves too many set of relative strength imparted by the interactions occur between polymer, polyol and/or water molecule.

At a particular moisture content, *EM* decreased with increasing plasticizer contents and the reverse was true for *TE*. Such effects are an indirect indication of the degree of plasticization exerted by glycerol and sorbitol. When plasticized KGM films were under stress, water as well as plasticizers can act as a lubricant and improve flow between polymer chains.

Furthermore, at a given moisture content, a higher sorbitol than glycerol concentration was required to achieve a similar *EM* and *TE*. In other words, at any moisture and plasticizer content, glycerol imparted a greater plasticizing effect (relatively lower *EM* and higher *TE*) on KGM films when compared with sorbitol. This is because glycerol has greater molar content per mass unit, as well as a smaller molecular size that would facilitate its penetration into the film matrix (Donhowe & Fennema, 1993; McHugh & Krochta, 1994). In conclusion, sorbitol-plasticized KGM films were stiffer and stronger than glycerol-plasticized ones, thus more stress will be required to produce a given amount of deformation (Banker, 1966).

4. Conclusions

The present study underlines the significant influence of "equilibrium" moisture content in altering the plasticizing effect of polyols on KGM films. Incorporation of glycerol or sorbitol to KGM films did not significantly reduce film tensile strength but enhanced their flexibility and extensibility. This resulted in stretchable films suitable for use at moderately high relative humidity.

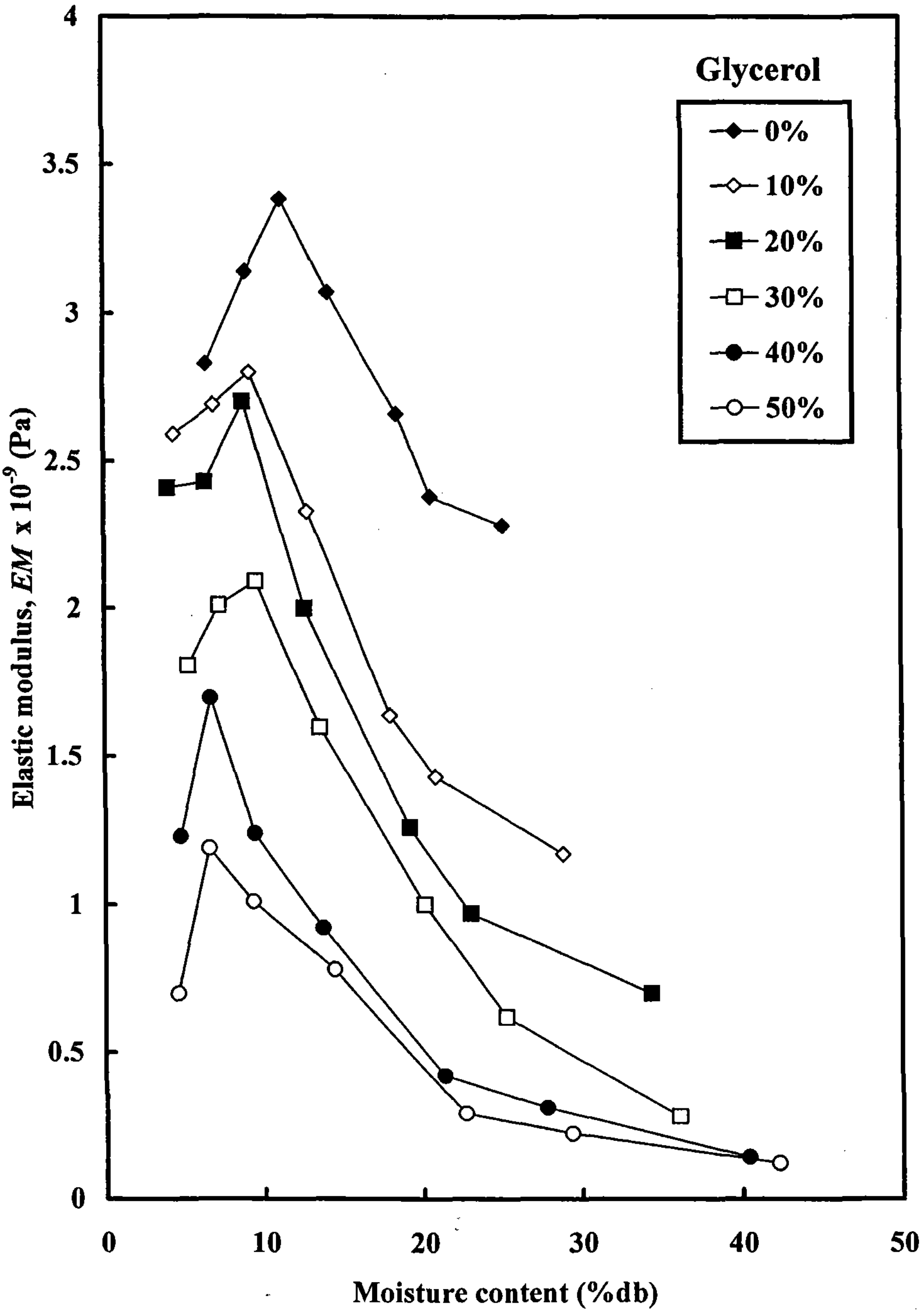

Fig.7. Elastic modulus of konjac glucomannan films containing different concentrations of glycerol as a function of moisture content.

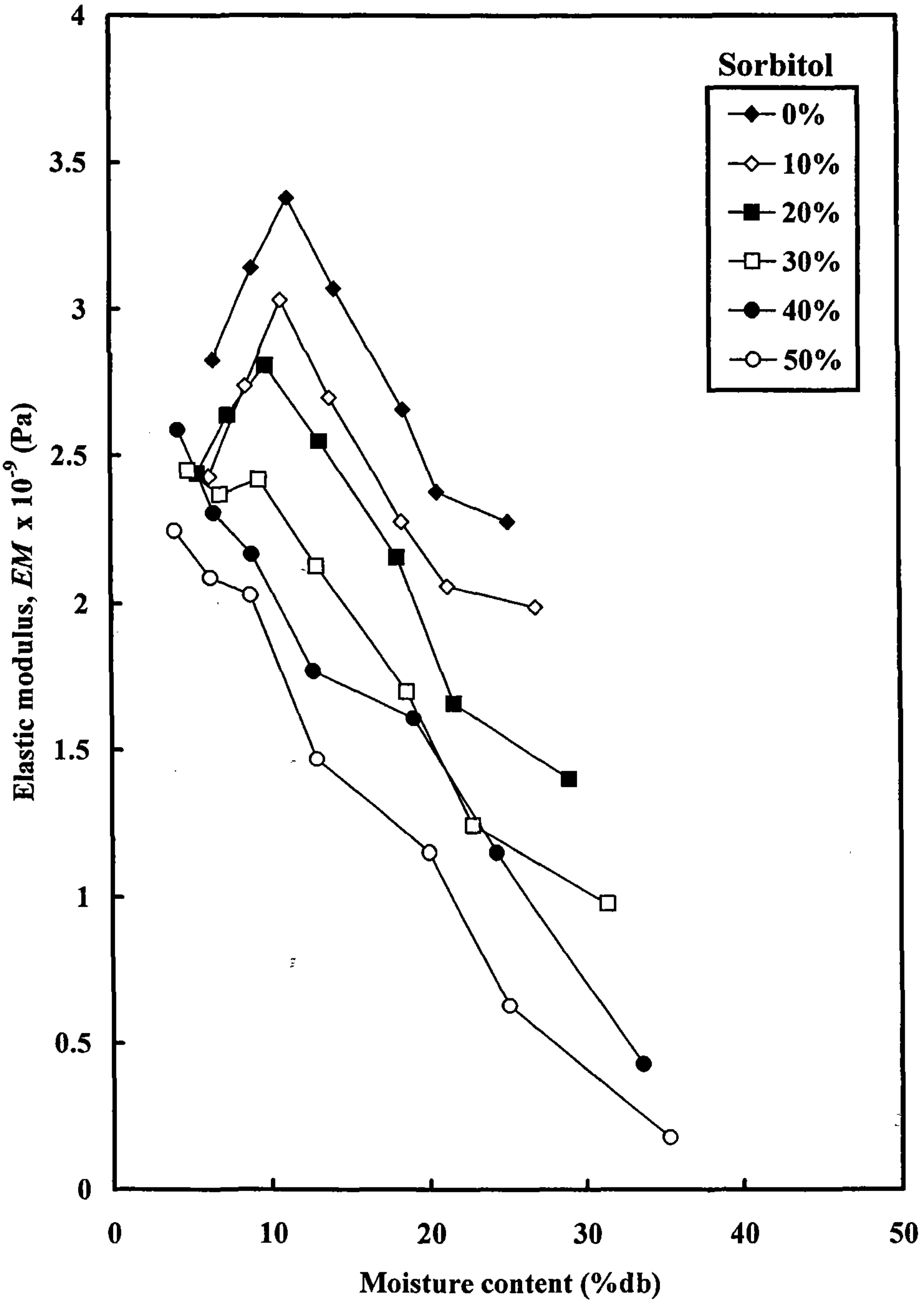

Fig.8. Elastic modulus of konjac glucomannan films containing different concentrations of sorbitol as a function of moisture content.

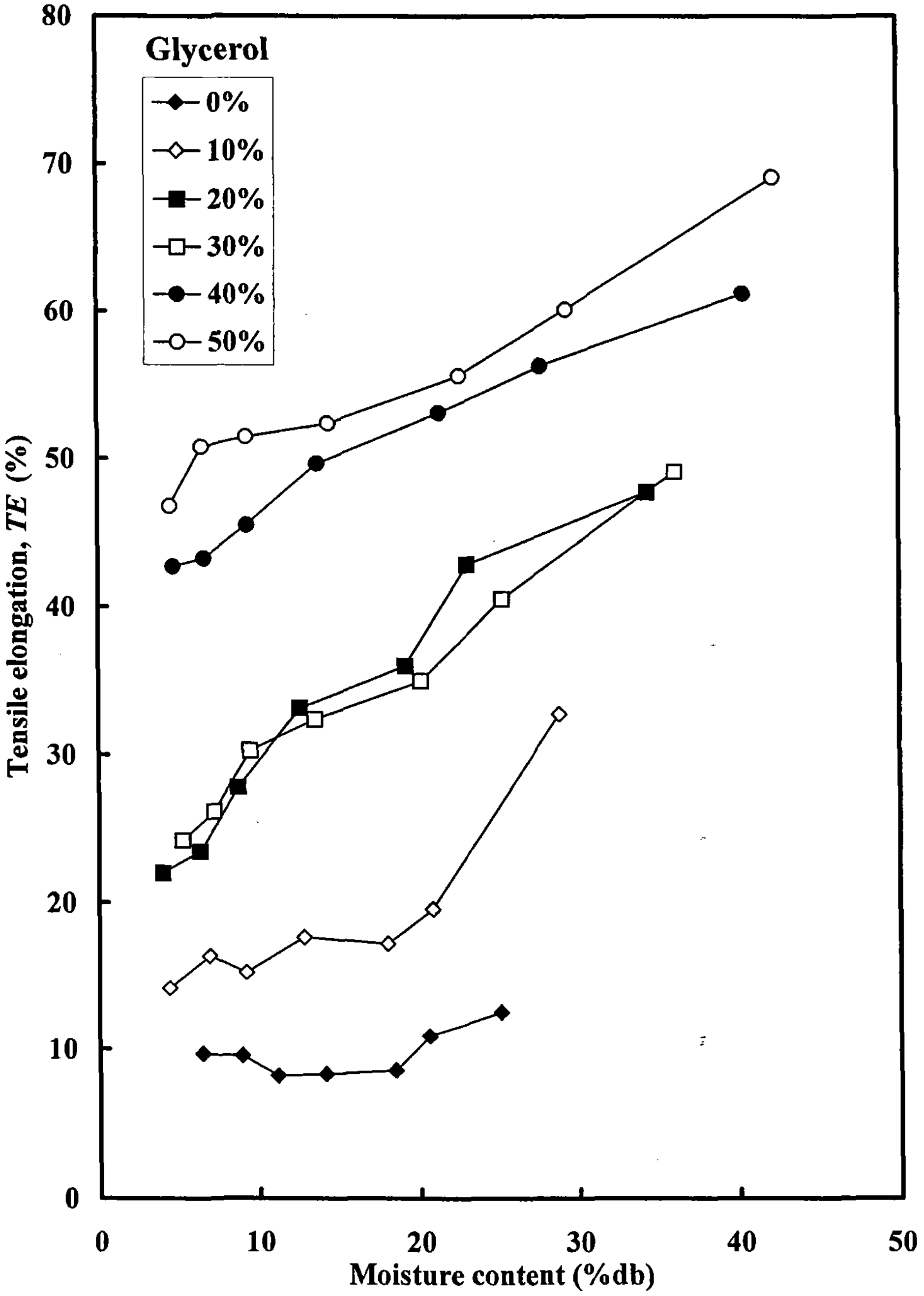

Fig.9. Tensile elongation of konjac glucomannan films containing different concentrations of glycerol as a function of moisture content.

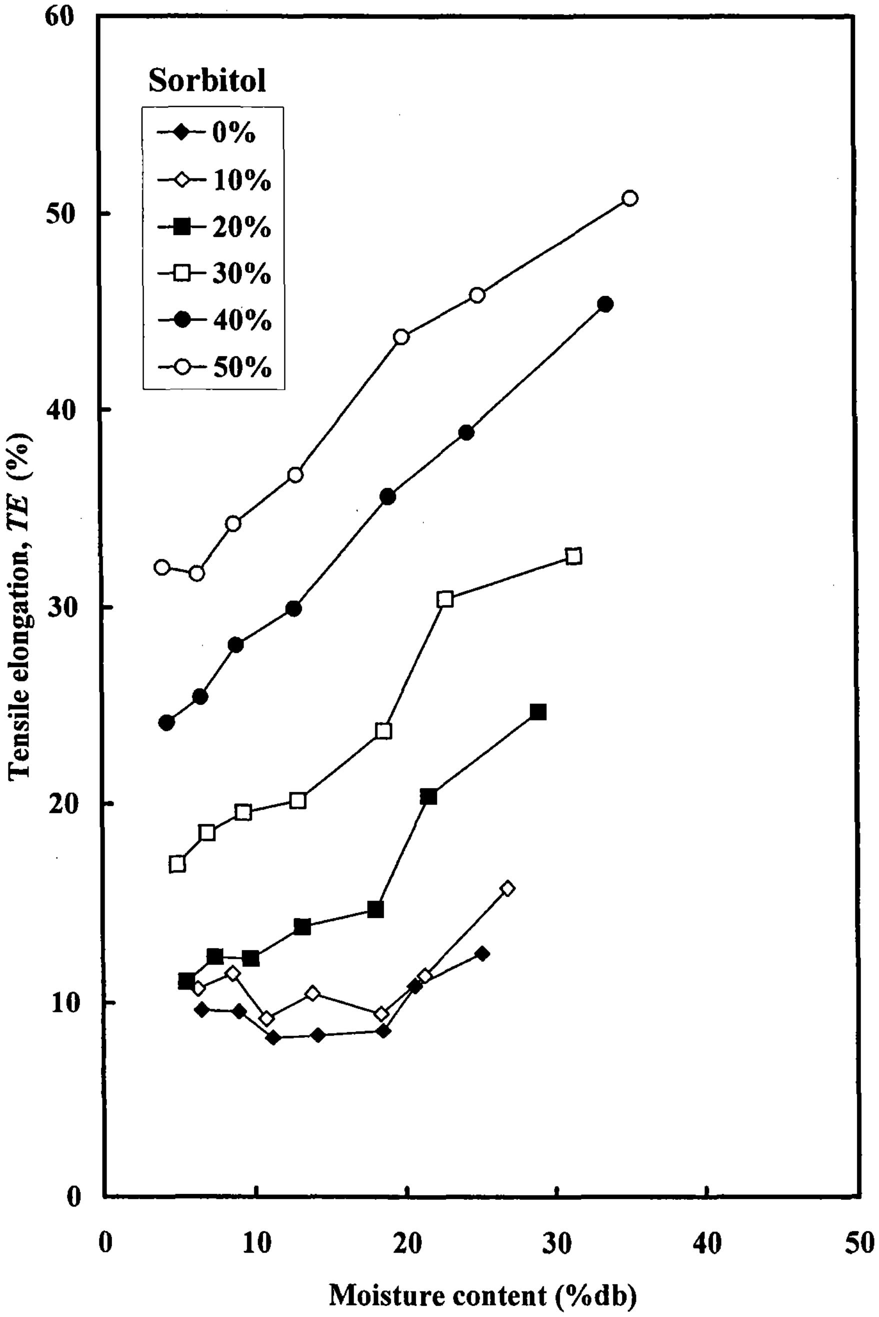

Fig.10. Tensile elongation of konjac glucomannan films containing different concentrations of sorbitol as a function of moisture content.

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