PII: S0032-3861(97)00082-7

Polymer Vol. 38 No. 21, pp. 5401–5406, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials

D. Lourdin*, L. Coignard, H. Bizot and P. Colonna
Institut National de la Recherche Agronomique, 44316 Nantes cedex, France
(Revised 9 January 1997)

Sorption behaviour and calorimetric glass transition were measured on cast starch films plasticized with varying concentrations of different components (glycerol, sorbitol, lactic acid sodium, urea, ethylene glycol, diethylene glycol, PEG 200, glycerol diacetate). Precision analysis showed that the water level in samples conditioned at 57% relative humidity reached a minimum for a plasticizer content of 10–20% (dry basis). Starting from 14.8% of water (dry basis) as measured in the amorphous starch–water system, a minimum of 12.7 to 14.4% can be attained according to the type of plasticizer added. Glass transition, as determined on samples conditioned at a constant relative humidity (57%), depended on the type of plasticizer used, although general behaviour was broadly similar for all components except glycerol diacetate. Casting trials performed with this substance revealed an evident phase separation and T_g of starch did not appear really modified by its presence. For glycerol, sorbitol and lactic acid sodium, glass transition was measured with respect to plasticizer and water content. Couchman's relation was applied, which describes the T_g variation of the monophasic polymer–diluant system. The likelihood of phase separation for a high plasticizer level is considered. © 1997 Elsevier Science Ltd.

(Keywords: starch; amylose; sorption)

INTRODUCTION

The elaboration of biodegradable packaging materials containing renewable raw materials is a current research concern. Studies[1–4] have shown that starch is a particularly interesting substrate because it is inexpensive and has a thermoplastic behaviour for the performance of classical technical processes (extrusion, injection-moulding, thermal moulding). The mechanical properties of starch in mean ambient humidity, particularly poor elongation (6%) and a rather high maximal strength (40–50 MPA), are indicative of a vitreous material with a glass transition temperature (T_g) above ambient temperature. It was demonstrated[5] that T_g of amylopectin (branched macromolecule of starch) was lower than T_g of amylose (linear macromolecule) but other studies[6–8] relate the particular interest to use amylose for its beneficial effect on the mechanical behaviour of starch materials. These materials could be used more extensively if the temperature range corresponding to the rubbery plateau were enlarged to include ambient temperature. As with classically produced synthetic polymers, the glass transition temperature of amorphous starch is controlled by adding a plasticizer. Various studies (most of which relate to patents)[9–11] include lists of starch plasticizers which are too exhaustive to allow any understanding of optimization criteria. The purpose of the present work was to investigate the relationship between the glass transition temperature of films produced by the casting method and their residual water content, as well as the nature and concentration of the plasticizer added to the solution. The study of this ternary system is complex because water content at a given relative humidity results from the combined affinities of the macromolecular network and the characteristics of more or less absorbent plasticizers.

EXPERIMENTAL

Materials

Potato starch was generously provided by the Roquette Company (Lestrem, France).

The purities and commercial sources of the different plasticizers used are indicated in the following table.

Plasticizer	Source	Purity
Glycerol	Merck	>98%
Sorbitol	Prolabo	-
Lactic acid sodium	Aldrich	99%
Urea	Panreac	99%
Ethylene glycol	Merck	>99.5%
Diethylene glycol	Fluka	>99%
PEG 200	Sigma	—
Glycerol diacetate + triacetate (1/1)	Fluka	—

---

* To whom correspondence should be addressed

Sample preparation

Films were obtained by the casting method. Native starch was solubilized in a high-pressure reactor at 130°C for 20 min using a 4% suspension in ultrapure water with a precise quantity of glycerol. The procedure was performed under a nitrogen atmosphere to avoid any risk of degradation. The solution was evenly spread on a Teflon®-coated hotplate maintained at 70°C until film no longer adhered to the plate and edge curling occurred. The transparent film obtained had a mean thickness of about 100 μm and contained about 10% water (dry basis). Before testing, all films were stored for 48 h in an atmosphere controlled by a saturated sodium bromide solution (r.h. 57% at 25°C). Films were reduced to powder by a cryogrinder and stored at constant relative humidity.

Sample conditioning

A study of the effect of water content requires well-controlled film preparation. After drying and grinding, the hydration of samples containing various amounts of plasticizer was controlled by isopiestic equilibration at different water activities but without taking the negligible plasticizer volatility into account. Samples in jars containing saturated salt solutions were maintained at 25 ± 0.1°C for 7 days. Although samples may not be in a true equilibrium state after 7 days of conditioning, this period seemed optimal to avoid any possible changes within the sample (retrogradation, recrystallization, etc.).

The salts used (with their corresponding relative humidities at 25°C) were $MgCl_2$ (33%), K_2CO_3 (43%), $Mg(NO_3)_2$ (52%), NaBr (57%) and $SrCl_2$ (70%). These choices were made in accordance with the recommendations of the BCR[12].

For films plasticized by glycerol, sorbitol and lactic acid sodium, the study concerned all five equilibrium relative humidities (ERH) chosen. For the other plasticizers, conditioning was performed only at 57% ERH.

Water and plasticizer analysis in samples

Water and plasticizer concentrations are expressed in relation to dry basis (d.b.).

Water content was determined by the Karl–Fisher method, and all analyses were tested in triplicate. Plasticizer concentration was measured by high-performance liquid chromatography (h.p.l.c.). After heating, the sample (about 15 mg) was washed in pure water (100 ml) under vigorous stirring to achieve complete diffusion of the plasticizer in the solution. Plasticizer was then determined by h.p.l.c. on an Acidex H^+ column using water elution at 0.6 ml min^{-1} and differential refractometry detection at ambient temperature.

Differential scanning calorimetry (d.s.c.)

Measurements of the glass transition temperature of the plasticized films were performed by d.s.c. on automated DSC 121 equipment (SETARAM, France). Powders were placed in pressure-tight d.s.c. cells (about 80 mg of matter per cell). The calorimetric measurement procedure was similar for all samples regardless of composition. A first scanning was performed from −30 to +150°C to avoid the influence of any thermal events which may have occurred during the conditioning and storage of the samples. Rapid cooling (60°C min^{-1}) to −30°C allowed the thermoplastic starch to be frozen in an amorphous state. The actual measurement was performed during a second scanning at 3°C min^{-1}. Graphic determination of glass transition temperature was done according to the procedure recommended by Wunderlich[13]. For a polymer, T_g was taken at the half-variation in heat capacity occurring at the transition (T_g 1/2). Tests performed in triplicate showed that variations were of the order of ±3°C.

RESULTS

Most samples were homogeneous and showed good mechanical cohesion. However, after casting, PEG and glycerol diacetate samples became brittle, opaque, nonhomogeneous dry products which could not be considered as suitable materials. All samples were ground for further characterization. For glycerol diacetate, phase separation from starch was clearly apparent.

Water content vs. equilibrium relative humidity

Figure 1 shows the hydration rates for the different plasticized films after conditioning at 57% ERH. To facilitate comparison of the different plasticizers, water levels are superposed on the Y-axis. Plasticizer concentrations in water are expressed in g/100 g of dry starch. For films without additives other than water, the hydration rate became stable at 14.8% (d.b.), which is close to values measured on extruded starches. For plasticized materials, the different curves had broadly similar features regardless of the additive employed. An increase in low plasticizer concentrations induced a drop in sample hydration. With higher plasticizer levels (>15%) the hydration rate increased. The concentration corresponding to minimum hydration was between 10%

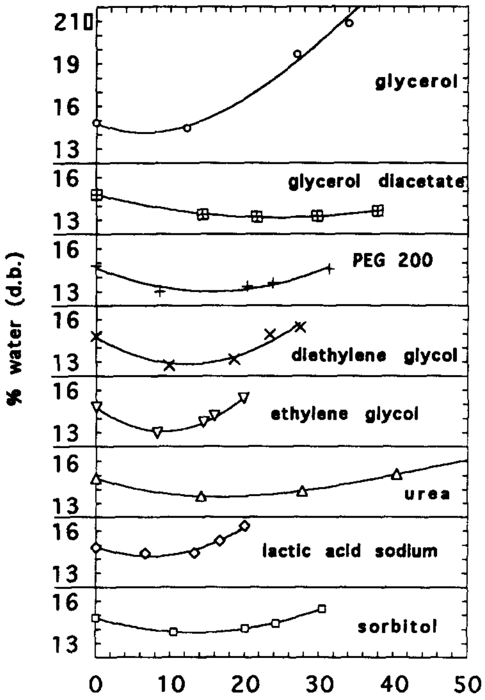

Figure 1 Water uptake of plasticized potato starch films conditioned at 57% ERH vs. plasticizer content. Each curve is shifted vertically for easier reading and smoothed by a third-order polynomial

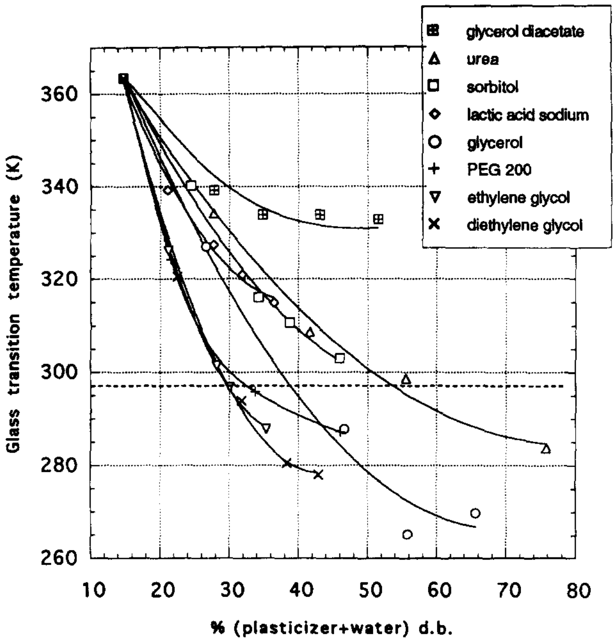

Figure 2 Variations in calorimetric glass transition temperature (at 3° min^{-1}) vs. total water and plasticizer content (dry basis) for samples equilibrated at 57% RH

and 15% plasticizer content except for urea and glycerol diacetate (about 20%). However, minimum hydration was highly dependent on the nature of the additive employed. For films plasticized by ethylene glycol or diethylene glycol, the minimum was respectively 12.9 and 12.7%, whereas water content for lactic acid sodium and glycerol was only 14.4% d.b.

Glass transition temperature vs. equilibrium relative humidity

Glass transition temperatures determined on films conditioned at a constant relative humidity of 57% are shown in *Figure 2*. Variations were due to the combined effect of plasticizer and water on the polymer. The X-axis corresponds to the sum of plasticizer + water concentrations compared to the percentage of dry starch (d.b.). Experimental points were adjusted according to a second-order polynomial law. The conditioning temperature is indicated by a horizontal line at 298 K.

On starch films containing no plasticizer except 14.8% of water after storage at 57% ERH, the glass transition temperature was determined at 363 K. These results are in agreement with data published by Bizot *et al.*[14] showing a T_g at 373 K and 357 K respectively for amorphous potato starch containing 12.6% and 14.6% water (d.b.).

As might be expected, an increase in the concentration of the additive caused a decrease in glass transition temperature. However, the intensity of this variation was highly dependent on the nature and quantity of the plasticizer added. Ethylene, diethylene and polyethylene glycol proved to be the most efficient plasticizers since the addition of about 16% of one of these additives (relative to starch mass) was sufficient to lower T_g to the level of ambient temperature. Conversely, about 40% of urea had to be added to obtain a T_g of 298 K. For materials containing glycerol diacetate, the decrease in T_g was slight and rapidly independent of the quantity introduced.

Water content vs. plasticizer content and equilibrium relative humidity

Tables 1, 2 and *3* indicate the water contents of starch plasticized respectively by glycerol, sorbitol and lactic acid sodium as a function of water activity during storage and platicizer concentration. Regardless of the plasticizer used, two opposite types of behaviour were observed after ERH was obtained.

For low relative humidities, water content decreased when plasticizer content increased. For example, in the case of starch plasticized by glycerol and conditioned at 33% ERH, water content was 11.1% without any plasticizer and no more than 9.2% with 40% glycerol (*Table 1*, column 1).

For high activities, water content increased markedly when plasticizer concentration increased. With 40% glycerol, water content in the sample conditioned at 70% ERH increased from 17.8 to 29.5% (*Table 1*, column 4).

Thus, the water content of materials was far more dependent on ERH when a plasticizer was included. The increase in sensitivity to water activity was not linear but became more marked for high plasticizer contents. This effect occurred above concentrations of 12, 10.6 and 13.3% respectively for films containing glycerol, sorbitol and lactic acid sodium.

Glass transition temperature vs. plasticizer and water content

Figures 3, 4 and *5* indicate glass transition temperatures as a function of water and plasticizer content for

Table 1 Water content in g H_2O/100 g dry starch for ternary mixtures of glycerol/starch/water systems equilibrated at various ERH

	Water activity				
% Plasticizer	0.33	0.43	0.52	0.57	0.70
0	11.1	13.5	13.9	14.8	17.8
12.3	10.9	12.1	13.4	14.4	18.9
27.0	9.3	12.6	15.7	19.7	28.6
34.0	11.3	14.2	20.9	21.8	30.4
40.0	9.2	15.7	18.5	25.5	29.5

Table 2 Water content in g H_2O/100 g dry starch for ternary mixtures of sorbitol/starch/water systems equilibrated at various ERH

	Water activity				
% Plasticizer	0.33	0.43	0.52	0.57	0.70
0	11.1	13.5	13.9	14.8	17.8
10.6	9.5	11.2	12.3	13.8	16.5
20.1	8.8	12.5	11.7	14.1	17.9
24.3	8.4	10.5	11.5	14.4	19.1
30.5	8.0	10.6	12.7	15.5	20.7

Table 3 Water content in g H_2O/100 g dry starch for ternary mixtures of lactic acid sodium/starch/water systems equilibrated at various ERH

	Water activity				
% Plasticizer	0.33	0.43	0.52	0.57	0.70
0	11.1	13.5	13.9	14.8	17.8
6.6	10.3	12.1	13.3	14.4	18.4
13.3	10.1	11.9	13.2	14.4	19.4
16.6	10.6	12.7	14.1	15.3	21.7
20.1	11.2	12.6	14.2	16.4	23.2

films containing glycerol, sorbitol and lactic acid sodium.

A smoothing of experimental points performed with the Couchman relation[15,16] enabled us to calculate the glass transition temperature of a compatible blend from pure constituent properties

$$T_{g_{mix}} = \sum X_i \Delta C_{p_i} T_{g_i} / \sum X_i \Delta C_{p_i}$$

where X_i is the molar fraction of constituent i, T_{g_i} is the glass transition temperature of the pure constituent i, and ΔC_{p_i} is the variation of the heat capacity at T_g of the pure constituent i.

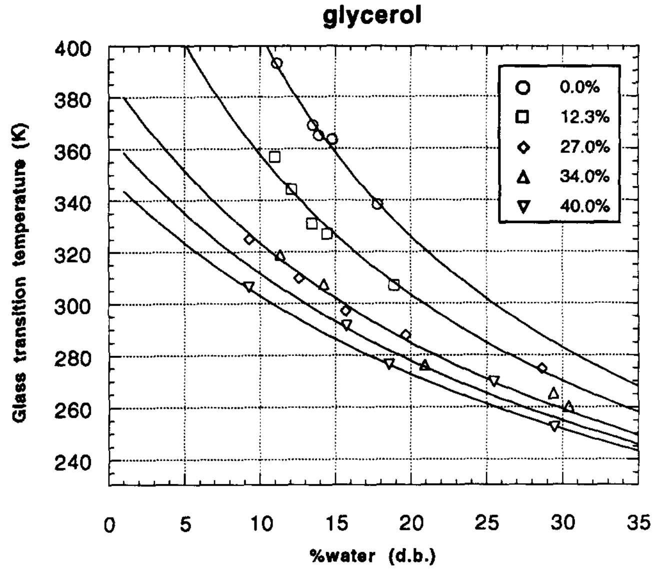

Figure 3 Variations in calorimetric glass transition temperature (at 3° min^{-1}) vs. water content for samples plasticized with different glycerol concentrations

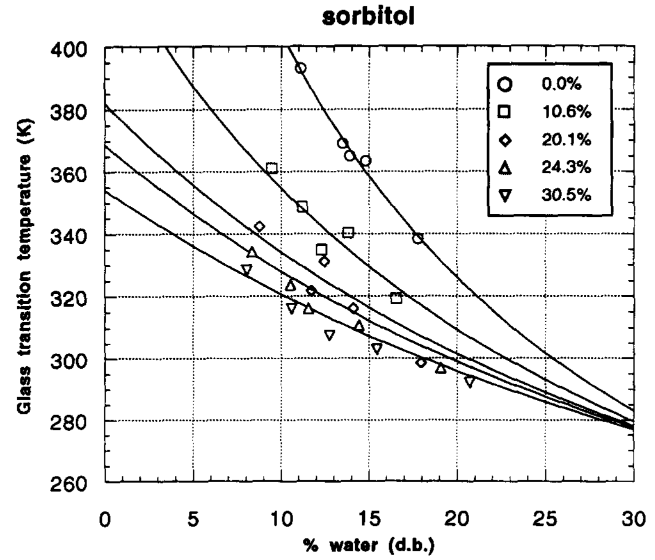

Figure 4 Variations in calorimetric glass transition temperature (at 3° min^{-1}) vs. water content for samples plasticized with different sorbitol concentrations

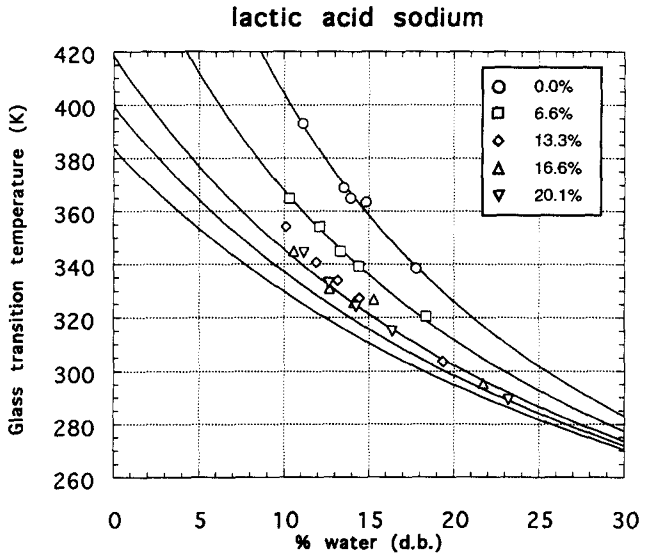

Figure 5 Variations in calorimetric glass transition temperature (at 3° min^{-1}) vs. water content for samples plasticized with different lactic acid sodium concentrations

Table 4 Glass transition temperature used and coefficient $\Delta C_{p_y}/\Delta C_{p_w}$ calculated with Couchman relation

Y	T_g (K)	T_g reference	$\Delta C_{p_y}/\Delta C_{p_w}$ calculated
Starch	589	14	0.14
Water	134	17	1
Glycerol	187	18	0.53
Sorbitol	271	19	1.34
Sodium lactate	246	Our d.s.c. measurements	1.07

This equation, when rearranged for a three-component system, can be written as (example for the water–plasticizer–starch system)

$$T_{g_{mix}} = \frac{X_w T_{g_w} + X_p T_{g_p}(\Delta C_{p_p}/\Delta C_{p_w}) + (1 - X_w - X_p) T_{g_s}(\Delta C_{p_s}/\Delta C_{p_w})}{X_w + X_p(\Delta C_{p_p}/\Delta C_{p_w}) + (1 - X_w - X_p)(\Delta C_{p_s}/\Delta C_{p_w})} \qquad (1)$$

where the indices w, p and s correspond respectively to water, plasticizer and starch.

Table 4 shows the glass transition temperature values for pure constituents and the corresponding reference values. For anhydrous potato starch, the selected T_g (589 K) was that calculated by Bizot *et al.* on the basis of a large number of experimental T_g values for the same substrate determined with respect to the hydration rate[14]. Since it is difficult to study the heat capacity variations of pure constituents, considerable variation is found in published values. The $\Delta C_{p_s}/\Delta C_{p_w}$ and $\Delta C_{p_p}/\Delta C_{p_w}$ coefficients were obtained by fitting equation (1) to the experimental data; the former ratio resulted from the fit of the binary mixture starch–water and the second was deduced from the data of the samples containing the lowest plasticizer level and the value previously determined. For more concentrated plasticizer contents, no parameters were adjusted and the curve corresponded to the Couchman model based on previously identified coefficients.

For glycerol and sorbitol (*Figures 3* and *4*), the curves calculated according to the model corresponding to a plasticizer isoconcentration did not differ greatly from experimental values in the concentration range studied. However, there was a relative scattering of values for high hydration rates. The general tendency propagated by the model corresponded to a decrease in curve slopes when plasticizer concentration increased. For example, for an increase in water content from 12 to 15%, starch film T_g decreased by 24 K, whereas this decrease amounted to only 10 K for films containing 24% sorbitol. These results indicate that the plasticizing action of water, a factor often considered important in the literature[19], is decreased by the presence of a second plasticizer, probably due to reduction of the quantity of water available for efficient plasticization.

The T_g measured on films containing high quantities of lactic acid sodium (*Figure 5*) show an important discrepancy with the values predicted by the Couchman model under form (1). In fact, a juxtaposition of temperatures was noted in formulations with a plasticizer content above about 13%. In other terms, if water content is constant, lactic acid sodium has only a very slight effect on glass transition temperature above this limit. For example, for a water content of 14%, the minimum T_g was around 328 K. This value, obtained by adding 13% of lactic acid sodium, remained nearly constant for higher additive concentrations.

DISCUSSION

The sorption results obtained here for plasticized starch films are in complete agreement with those of Guo[20] for cellulose acetate plasticized by different polyethylene glycols. This author found a minimum of permeability when about 10% of plasticizer was added to these materials and suggested that strong interactions between the plasticizer and the polymer (probably by means of a hydrogen bond) induce a loss of macromolecular mobility. This assumption is similar to that of Scandola *et al.*[21] who considered that amylose was plasticized by residual water. These authors supposed that there are at least two types of interaction between the polymer and water. For quantities with less than 10% water content, the polymer–water system formed by hydrogen bonds is more compact than the polymer–polymer system. Above 10% water content, a looser network is formed due to the occurrence of water–water interactions.

Glass transitions occur below or above ambient temperature as a function of plasticizer or water content. Previous studies[22,23] of the starch–glycerol system indicated that calorimetric glass transition temperature is in accordance with the main mechanical relaxation known as α. However, these results are in marked conflict with published data[24] indicating that calorimetric T_g for the same materials ranged between −50 and −100°C for samples containing 2–30 wt% of water and at least 14 wt% of glycerol. The fact that the temperature of this transition remains close to pure glycerol T_g, regardless of the concentration used, suggests that phase separation occurs. This hypothesis has already been advanced by Kalichevsky *et al.*[25] for results above a certain sugar concentration in amylopectin–sugar mixtures.

Although this hypothesis was clearly demonstrated for glycerol diacetate in the present work, it was less evident for most of the other systems. If this mechanism is involved, two glass transitions should occur: a high-temperature T_g intrinsic to a polymer-rich phase and a low-temperature T_g intrinsic to a plasticizer-rich phase. In this situation, Couchman's relation should be rearranged to take into account the respective compositions of the two phases involved[26]

$$T_{g_{\mathrm{mix},a}} = \sum X_{i,a}\Delta C_{p_i} T_{g_i} \Big/ \sum X_{i,a}\Delta C_{p_i} \qquad (2)$$

where $T_{g_{\mathrm{mix},a}}$ is the glass transition temperature of phase a, X_i is the molar fraction of the constituent i within phase a, T_{g_i} is the glass transition temperature of the pure constituent i, and ΔC_{p_i} is the variation of the heat capacity at T_g of the pure constituent i; and in which the T_g of phase b would be written in the same manner.

This relationship allows access to the composition of the two phases on the basis of their respective glass transition temperatures.

For glycerol and sorbitol, the differences between experimental points and those predicted by Couchman's model under form (1) were relatively slight, neither confirming nor invalidating the presence of two phases with the concentrations studied. With high plasticizer contents, the results obtained by Forssell *et al.*[24] may correspond to this second glass transition. However, in the case of a low glycerol concentration (<27% d.b.) recent study[22] has indicated that phase separation is improbable and that a relaxation intrinsic to starch must be taken into account when interpreting low temperature relaxation.

For lactic acid sodium, the large differences found at high plasticizer contents between experimental points and Couchman's model under form (1) suggest a phase separation although no transition for such a phase could be detected by d.s.c. down to −70°C.

In molecular terms, the different observations in this study concerning at least the starch–lactic acid sodium–water system can be interpreted by using the hypotheses developed above and analysing the mechanisms according to two states.

The first plasticizer molecules added form relatively strong interactions (hydrogen type bonds) with monomeric units. As a result, some sites initially occupied by water molecules are then occupied by the plasticizer. There is a decrease of the number of water molecules surrounding the monomeric units to the extent that plasticizer molecules increase. In steric terms, all the small molecules (water and plasticizer) can then interact with starch. A certain stoichiometry obtained at the dynamic saturation of the potential bonds could correspond when measurements indicate water adsorption is minimal. In this concentration range, the three components form a monophasic system, and glass transition temperature undergoes variations which can in fact be modelled using Couchman's relation under form (1).

The second molecular state intervenes when plasticizer concentration is above a 'limit' rate described precedently. In this case, all the sites surrounding polymeric units are occupied by plasticizer and water molecules. The interactions that occur when the plasticizer is added in greater quantity are plasticizer–plasticizer type and thus more mobile. Moreover, plasticizer–water interactions may be created or destroyed, accounting for the increased sensitivity at ambient relative humidity.

For lactic acid sodium, minimum adsorption at around 10% of plasticizer corresponded rather well to the content at which calorimetry results are suggestive of phase separation. However, for the other plasticizers, minimum adsorption was apparent at much lower plasticizer rates, although phase separation was not clearly observed.

For glycerol diacetate, the monophasic domain did not exist or occupied only an extremely short range of plasticizer content. Glass transition temperature varied very little even for low concentrations of this plasticizer. This incompatibility was probably due to a low concentration of groups capable of achieving hydrogen bonds.

ACKNOWLEDGEMENT

This work was supported by the European Union in the AIR contract "Thermoplastic Starches".

CONCLUSION

This work demonstrates that efficiency plasticizers have to form favourable interactions (probably hydrogen bonds) with starch. The unfavourable case is given by the mix obtained with glycerol diacetate having a very marked phase separation, even with low plasticizer concentrations. This behaviour, which is attributable to a deficit in the polar groups of the compound, suggests that the lists of plasticizers described in many patents must be regarded with due caution.

In general, the starch–plasticizer–water systems studied in this work were more sensitive to ambient humidity when plasticizer content was high, owing to the creation of hydrogen bonds between the plasticizer and water. For measurements of glass transition, an application of Couchman's relation showed that phase separation occurred in samples containing more than about 13% of lactic acid sodium. For glycerol and sorbitol, phase separation was not clearly apparent but could conceivably occur with high plasticizer contents[22] (>27% d.b. for glycerol).

REFERENCES

1. Doane, W. M., *Cereal Food World*, 1994, **39**, 556.
2. Savary, C., Colonna, P. and DellaValle, G., *Industrie des Cereales*, 1993, **10**, 17.
3. Shogren, R. L., Fanta, G. F. and Doane, W. M., *Starch*, 1993, **8**, 276.
4. Fritz, H. G., Aichholzer, W., Seidenstücker, T. and Wiedman, B., *Starch*, 1995, **47**, 475.
5. Cowie, J. M. G. and Henshall, S. A. E., *Eur. Polym. J.*, 1976, **12**, 215.
6. Jane, J.-L., Lim, S.-T., Paetau, I., *Biodegradable Polymers and Packaging*. Technomic Publishing, 1993.
7. Lourdin, D., DellaValle, G. and Colonna, P., *Carbohydr. Polym.*, 1995, **27**, 261.
8. Van Soest, J. J. G. and Esser, P., *Polymer*, 1996, **37**, 543.
9. Bastioli, C., Patent 91/02024, 1991.
10. Stepto, R. F. T., Patent 0282451, 1987.
11. Tomka, I., Patent 118240, 1990.
12. Jowitt, R. and Wagstaffe, P. J., The certification of water content of microcrystalline cellulose (MCC) at 10 water activities, Commission of the European Community, Community Bureau of Reference, BCR Information: Reference materials, CRM 302, EUR 12429 EN, 1989, 1–54.
13. Wunderlich, B., *Thermal Analysis*. Academic Press, Boston, USA, 1993.
14. Bizot, H., LeBail, P., Davy, J., Roger, P. and Buleon, A., Accepted in *Carbohydr. Polym.*, 1997, **32**, 33.
15. Couchman, P. R. and Karasz, F. E., *Macromolecules*, 1978, **11**, 117.
16. Couchman, P. R., *Polym. Eng. and Science*, 1987, **27**, 618.
17. Suzuki, T. and Francks, F., *J. Chem. Soc. Faraday Trans.*, 1993, **89**, 3283.
18. Champeney, D. C. and Ould Kaddour, F., *Molecular Physics*, 1984, **52**, 509.
19. Slade, L. and Levine, H., *J. Food Eng.*, 1994, **22**, 143.
20. Guo, J. H., *Drug Dev. Ind. Pharm.*, 1993, **19**, 1541.
21. Scandola, M., Ceccorulli, G. and Pizzoli, M., *Int. J. Biol. Macromol.*, 1991, **13**, 254.
22. Lourdin, D., Bizot, H. and Colonna, P., *Macromol. Symp.*, in press.
23. Lourdin, D., Bizot, H. and Colonna, P., *J. Appl. Polym. Sci.*, 1997, **63**, 1047.
24. Forssell, P., Mikkilä, J., Suortti, T., Seppälä, J. and Poutanen, K., *Pure Appl. Chem.*, 1996, **5**, 703.
25. Kalichevsky, M. T., Jaroszkiewicz, E. M. and Blanshard, J. M. V., *Polymer*, 1993, **34**, 346.
26. Yang, H., *Macromolecules*, 1991, **24**, 5218.