NON-FOOD USE OF CEREAL BY-PRODUCTS

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INTRODUCTION

Because of numerous reasons there is an increasing interest in renewable and biodegradable materials. The growing refuse dumps and the threat of oil depletion are two of these reasons.

Consumption of oil leads to increasing rates of greenhouse gases in the atmosphere. Of all the crude oil that is produced every year 4% goes to plastic products. During 2003 the plastic consumption in Western Europe was 100 kg per capita; 40% of the plastics were used for packaging (Plastics Europe, 2007). In the US, packages constitute over 30% (w/w) of the municipal solid waste (U.S. Environmental Protection Agency, 2006). Approximately one third of the containers and packages are made of plastics (U.S. Environmental Protection Agency, 1999). Biodegradable packages and edible coatings could enhance the waste management significantly. The figure of 4%, which stands for the percentage of crude oil that goes to plastics manufacturing every year, may seem like a small figure, but considering that the prices for crude oil are on the rise, the need for an alternative material source is increasing.

The obvious thing to do is to turn the eyes towards the vegetable kingdom. Here we can find materials that fulfil the requirements of renewability and biodegradability. Trials to develop materials from prolamins (storage proteins of cereals) have given some promising results (Gennadios et al., 1993a; Gennadios et al., 1993b; Gennadios et al., 1993c; Park et al., 1994; Park and Chinnan, 1990). Prolamins constitute a group of globular proteins found mainly in cereals. These proteins are maximally soluble in 50–90% (w/w) ethanol (Martin, 1931; Shukla and Cheryan, 2001). Examples of prolamins are gliadin (wheat), zein (maize), kafirin (sorghum), avenin (oat) and hordein (barley). Since prolamins are edible, they are suitable for coatings, packages applied directly onto the food. Coatings may be used for the release of preservatives, which prolongs the shelf life of the food (Cagri et al., 2004; Guilbert et al., 1996; Petersson et al., 2007). Prolamins are generally excellent oxygen barriers, which makes them suitable as food packaging materials, since food degradation often is oxygen dependent. Today there is a great asset of prolamins that remain unutilised. It exists in the form of low value by-products from agricultural production, such as bran and spent grain from biofuel and brewing, which can be upgraded and used in material applications. For further information on non-food utilisation of cereals components, see the conference proceedings by M. Stading.

Zein (maize prolamin) and kafirin (sorghum prolamin) are both capsulated in protein bodies in the endosperm. The structure and amino acid composition of kafirin is very much alike the ones of zein (DeRose et al., 1989). There are four groups of zein fractions, called α-, β-, γ-, and δ-zein (Lawton, 2002), and three groups of kafirin, called α-, β-, and γ-kafirin (El Nour et al., 1998). Significant amounts of disulphide bonds exist in β-, γ-, and δ-zein (Lawton, 2002), respectively β- and γ-kafirin (El Nour et al., 1998). These need the presence of a reducing agent for extraction. Kafirin is even more hydrophobic than zein (Duodu et al., 2003). Just like zein, kafirin is considered to be safe for those with celiac disease. Further information about kafirin can be found in the proceedings by D. Johansson.

In this study films from kafirin and zein have been manufactured and analyzed with respect to some material properties of interest from a food packaging point of view. The films were plasticized by a mixture of polyethylene glycol, glycerol and lactic acid to reduce brittleness. Glass transition temperature (T_g), stress at break (σ_b), strain at break (ε_b), dry solid content, oxygen permeability (OP) and water vapour permeability (WVP) were measured at three different levels of plasticizer content.

MATERIALS AND METHODS

Protein Preparations

Kafirin, which was kindly provided by Ms S. Buchner of the Council for Scientific and Industrial Research, South Africa, was extracted from decorticated, condensed tannin-free red sorghum grain by means of a procedure similar to the industrial process described for zein by Shukla and Cheryan (2001), and defatted as described by Oom et al. (2006). Commercial zein (Z3625; Sigma-Aldrich, Schnelldorf, Germany) was also defatted as described by Oom et al. (2006).

Film Casting

Kafirin and zein films were cast by mixing protein with 70% (w/w) ethanol and plasticizer (1:1:1 w/w/w PEG:glycerol:LA mixture). Total plasticizer levels were 20%, 30%, and 40% (w/w). The protein mixtures were stirred and heated at 70°C for 10 min. Two aliquots of each protein solution were put into preheated 9-cm-diameter polystyrene Petri dishes. The dishes were placed, level, in a 50°C oven (no forced draft) overnight. The typical film thickness for both materials was 100 µm and was determined individually using a Mitutoyo IDC-112CD micrometer (Mitutoyo Corporation, Kawasaki, Japan). The cast films were stored in a climate chamber under constant 23°C and 50% RH conditions, for at least 48 h prior to testing.

Material Analysis

Dry solid content was measured by placing samples in glass Petri dishes and weighing them before and after 24 h storage at 105°C. T_g was determined as the temperature of the intersection of the E’ linear fits, which indicated the drop of E’, and was measured using DMA analysis using a Rheometrics RSAII rheometer (Rheometrics Scientific, Piscataway, NJ, USA). Mechanical properties were measured using an Instron 5542 single-column universal materials testing machine (Instron, Norwood, MA, USA) in accordance with the ASTM D882-91 standard. OP was measured using a MOCON OX-TRAN 2/20 oxygen permeation instrument (MOCON, Minneapolis, MN, USA) according to the ASTM F1307-90 standard. The tests were run at 23°C and 50% RH. WVP was measured at 23°C and 50% RH in accordance with the ASTM E96-90 standard. The results were corrected for the stagnant air layer between the film underside and the water surface according to McHugh et al. (1993).

RESULTS AND DISCUSSION

Dry Solid Content

Figure 1 shows that increased plasticizer content led to decreased dry solid content in zein films. The variations among the kafirin results were within the margin of error, so no conclusions could be drawn. From the zein results, it seems like addition of plasticizer makes the films more hydrophilic.

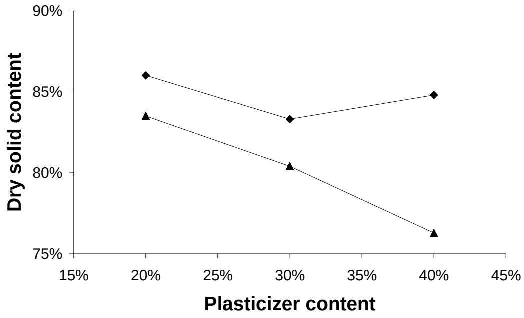

Figure 1. Dry solid content (w/w) of prolamin films with different plasticizer contents.
kafirin, zein

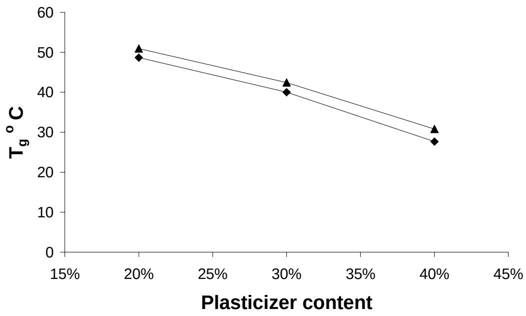

Figure 2. T_g of prolamin films with different plasticizer contents.
kafirin, zein

Thermomechanical Analysis

The T_g values of both kafirin and zein decreased with increased plasticizer content. Results, presented in figure 2, show that zein and kafirin are similar regarding this factor.

Mechanical Properties Analysis

The mechanical properties σ_b and ε_b are shown in figure 3. Increased plasticizer levels decreased σ_b but increased ε_b. The change was greater between 30% and 40% plasticizer content than between 20% and 30%. This was in line with the measured T_g values. Compared to synthetic polymers, zein and kafirin had similar strength, but were rather non-extensible. Low density polyethylene (LDPE, a common packaging material) has σ_b = 8.6–17.3 MPa and ε_b = 500% for example (Briston, 1989).

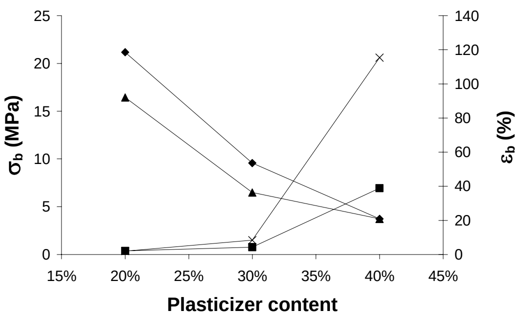

Figure 3. Stress at break and strain at break of prolamin films with different plasticizer contents.
kafirin σ_b, zein σ_b, kafirin ε_b, zein ε_b

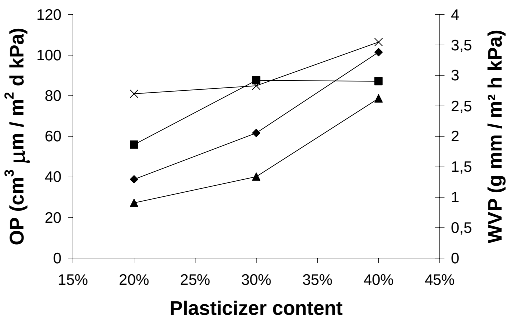

Figure 4. Barrier properties of films with different plasticizer contents.
kafirin OP, zein OP, kafirin WVP, zein WVP

Barrier Properties

The plasticizer content increased the permeability; WVP as well as OP. Dry solid content results showed that increased plasticizer content increased the hydrophilicity of the films, at least of zein. It could therefore be considered expected that increased plasticizer content resulted in increased WVP. The increased OP is more difficult to explain on this basis, whereas oxygen is a non-polar molecule (dielectrical constant 1.00). However, permeability increases with enhanced motion of the polymer segments (Rogers, 1985), which was achieved by increased plasticization. In line with the variations of the T_g values, there was a greater difference between films with 30% respectively 40% plasticizer content, than between films with 20% and 30% plasticizer content. The slightly higher OP and lower WVP of kafirin were seen as effects of the greater hydrophobicity of kafirin. Compared to LDPE, which has 1600–2100 cm^3 µm / m^2 d kPa OP and 0.0026–0.0035 g mm / m^2 h kPa (Briston, 1989), the prolamins had markedly lower OP and considerably higher WVP.

CONCLUSION

Generally, there were greater differences between the properties of the 30% and the 40% plasticizer containing films, than between the properties of the 20% and the 30% plasticizer containing films. The results showed that addition of plasticizer led to hydrophilization of the zein films. As there were no significant differences between the separate points of measuring of kafirin, no conclusion could be drawn, but it is likely that hydrophilisation of kafirin films by addition of the plasticizer could be shown in a more extensive study. Whereas most biopolymeric materials are brittle in unplasticized condition, especially zein films could be made rather extensible when most plasticized. As expected, the films displayed high quality oxygen barrier properties, whereas they did exhibit, compared to synthetic polymers, inferior water vapour barrier properties. Materials from kafirin as well as zein have potential within packaging and wrapping, but do presently not possess the features that would make them serious alternatives to petroleum based plastic materials. More research is needed to achieve sustainability within this area.

REFERENCES

Briston, J.H. (1989) Plastic Films. New York: Longman Scientific & Technical in assosiation with Plastics and Rubber Institute. 407.

Cagri, A., Ustunol, Z., Ryser, E.T. (2004) J. Food Prot. 67: 833-848.

DeRose, R.T., Ma, D.P., Kwon, I.S., Hasnain, S.E., Klassy, R.C., Hall, T.C. (1989) Plant Mol. Biol. 12: 245-256.

Duodu, K.G., Taylor, J.R.N., Belton, P.S., Hamaker, B.R. (2003) J. Cereal Sci. 38: 117-131.

El Nour, I.N.A., Peruffo, A.D.B., Curioni, A. (1998) J. Cereal Sci. 28: 197-207.

Gennadios, A., Weller, C.L., Testin, R.F. (1993b) Transactions of the ASAE 36: 465-470.

Gennadios, A., Weller, C.L., Testin, R.F. (1993c) J. Food Sci. 58: 212-214.

Guilbert, S., Gontard, N., Gorris, G.M. (1996) Lebensm.-Wiss u.-Technol. 29: 10-17.

Lawton, J.W. (2002) Cereal Chem. 79: 1-18.

Martin, W.M. (1931) J. Phys. Chem. 35: 2065-2090.

McHugh, T.H., Avena-Bustillos, R., Krochta, J.M. (1993) J. Food Sci. 58: 899-903.

Oom, A., Pettersson, A., Taylor, J.R.N., Stading, M. (2006) J. Cereal Sci. IN PRESS.

Park, H.J., Bunn, J.M., Weller, C.L., Vergano, P.J., Testin, R.F. (1994) Transactions of the ASAE 37: 1281-1285.

Park, H.J., Chinnan, M.S. (1990) ASAE Paper no. 90-6510.

Petersson, M., Hagström, J., Nilsson, K., Stading, M. (2007) Food Hydrocolloid 21: 1256-1264.

Plastics Europe (2007) http://www.plasticseurope.org/, accessed on April 3, 2007.

Rogers, C.E. (1985) Permeation of Gases and Vapours in Polymers.Comyn, J. (ed.) Polymer Permeability. London: Elsevier Applied Science Publishers. 11-73.

Shukla, R., Cheryan, M. (2001) Industrial Crops and Products 13: 171-192.

U.S. Environmental Protection Agency (1999) Characterization of Municipal Solid Waste in the United States: 1998 Update. Prairie Village, KS: Municipal and Industrial Solid Waste Division

U.S. Environmental Protection Agency (2006) http://www.epa.gov/, accessed on April 12, 2006.