PLASTICIZATION OF BLOODMEAL-BASED THERMOPLASTICS

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***Abstract*— Water is the most common plasticizer for protein-based thermoplastics, lowering the softening point to a allow processing without excessive degradation. The biggest drawback of using water a plasticizer is that water easily evaporates from the material during use or storage. This leads to embrittlement and loss of functionality over time. In this study a series of high molecular mass plasticizers were evaluated for their efficiency in plasticizing bloodmeal-based thermoplastics. It was found that propylene glycol, di and tri-ethylene glycol were most efficient in increasing the material's ductility, as measured by elongation at break. Using 10 parts plasticizer per hundred bloodmeal (pphBM) in combination with 10 pph_{BM} urea gave optimal results in terms of Young's modulus, tensile strength and processability. The mechanical properties of plasticized samples showed a stronger dependency on moisture content, compared to un-plasticized samples and reached higher equilibrium moisture content in a shorter time. Using 10 pph_{BM} TEG as plasticizer in resulted in a plastic material with a Young's modulus of 869 MPa, tensile strength of 14.7 MPa and an elongation at break of 46%.**

Keywords-Plasticization; protein; thermoplastic

I. INTRODUCTION

Bloodmeal can be converted to a thermoplastic material by adding appropriate additives and plasticizers to enable sufficient chain movement [1, 2]. Chain movement is required for processing at a temperature lower than its thermal degradation temperature [3].

The glass transition of polymer is a function of molecular motion and not polymer structural change. However, the temperature (glass transition temperature, T_g) at which this occurs is dependent on the structure of the polymer. Chain flexibility is a result of bond rotation; large bulky substituents hinder bond rotation, thereby increasing the T_g. Inter and intra-molecular forces restrict chain segments and higher molecular mass implies less chain ends per unit mass, resulting in less free volume. A decrease in free volume implies an increase in T_g. Cross-linking effectively restricts relative chain movement, thereby increasing the T_g as well [4, 5].

Judging from the above, it can easily be seen why proteins typically have a very high T_g. Most amino acids have large side chains, hindering bond rotation thereby decreasing chain flexibility. It has also been pointed out that the various amino acids lead to a number of possible intermolecular forces, further increasing the T_g.

It is possible to manipulate the T_g of proteins by the use of plasticizers. By lowering the T_g of a polymer, the onset of rubbery-flow is also reduced. If the T_g is sufficiently lowered, the protein can be processed without excessive degradation with reasonable processing conditions.

Water is the most common plasticizer for proteins, but has the distinct drawback of evaporating from the material over time. The result is a loss of processability and a reduction in mechanical properties. In the development of a successful bioplastic it is important to control the material's moisture content in order to ensure consistent material properties [6]. Moisture content directly influences mechanical properties, typically increasing elongation and reducing strength by effectively plasticising the material [5, 6]. Water diffusion increases in the rubbery state as water and plasticizers reduce the amount of protein-protein interactions, creating more free volume between chains [7-9].

The mechanical properties of polymers are largely associated with the distribution and concentration of inter- and intra-molecular forces. Plasticizers can reduce intermolecular interactions between polymer chains and increase the flexibility of the product. The desired effect is to decrease T_g with a minimal decrease in modulus or tensile strength [10]. Hydrogen bonding, van der Waals forces, hydrophobic interactions and ionic bonding are altered upon addition of plasticizers, leading to altered thermal and mechanical properties [9, 11, 12]. Hydrophilic hydroxyl groups are thought to be the active sites for plasticizers of proteins, creating hydrogen bonding between the polymer-plasticizer-water or plasticizer-polymer, interfering with protein-protein interactions and allowing chain mobility [13, 14].

The objective of this study was to evaluate the plasticizing efficiency of various plasticizers that can partially replace water in bloodmeal-based bioplastics by evaluating the material's mechanical properties.

II. EXPERIMENTAL

A. Materials

Bloodmeal was obtained in powder form from Wallace Corporation, Hamilton New Zealand and sieved to 700 μm. Technical grade sodium dodecyl sulphate (SDS) was obtained from Biolab NZ, analytical grade sodium sulphite from BDH Lab supplies and agricultural grade urea from Balance Agri-nutrients (NZ).

B. Method

Bloodmeal based thermoplastic (BMT) has been developed earlier and has been patented by Novatein Ltd, New Zealand [17]. Thermoplastic protein was prepared by blending 100 parts by mass bloodmeal (pph_{BM}) with 3 parts SDS, 3 parts sodium sulphite and 10 parts urea dissolved in water. Samples were prepared by dissolving all additives in the appropriate amount of water, followed by blending with bloodmeal powder in a high-speed mixer, after which the required amount of additional plasticizer was added. The mixtures were stored over night prior to extrusion.

Four kinds of experiments were performed; firstly, the additional plasticizer type was changed (10 pph_{BM}), based on their degree of hydrophilicity (percentage hydrophilic groups, %HG) and hydrogen bonding ability (Table 1). Secondly, the total amount of plasticizer (water plus triethylene glycol) was kept constant at 60 pph_{BM}, but the amount of TEG was varied from 0 to 30 pph_{BM}. Thirdly, the ratio of urea to TEG was varied at a constant total amount of urea plus TEG (20 pph_{BM}). Lastly, samples at constant plasticizer amount and type, were conditioned (50 % relative humidity, 23 °C) to different equilibrium moisture contents before measuring its mechanical properties.

Extrusion trials were performed using a ThermoPrism TSE-16-TC twin-screw extruder at a screw speed of 150 rpm using a temperature profile and screw configuration shown in Figure 1. Actual melt temperatures were within 2 to 5 □C of the set temperatures. The extruder had a screw diameter of 16 mm, an L/D ratio of 25 and was fitted with a single 10 mm circular die. A relative torque of 50-60% of the maximum allowed in the extruder was maintained (12 Nm per screw maximum), by adjusting the mass flow rate of the feed. The extruder was fed by an oscillating trough and the extruded material was granulated using a tri-blade granulator from Castin Machinery Manufacturer Ltd., China. Samples were injection moulded directly after extrusion and granulation, without further conditioning.

TABLE I. PLASTICIZERS USED

Plasticizer	Molecular mass (g/mol)	H-Bonds	%HG
Water	18	4	100
PD Propylene glycol	76	6	44.7
TEG Tri-ethylene glycol	150	10	44
EG Ethylene glycol	62	6	54.8
DEG Di-ethylene glycol	106	8	47.2
GLY Glycerol	92	9	55.4

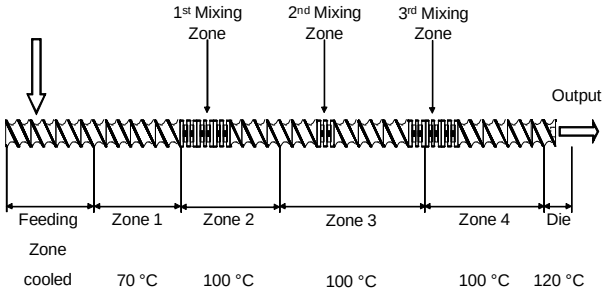

Figure 1. Extruder configuration

Specimens for tensile test were produced using a 22 mm screw diameter BOY 15 S Injection Moulding Machine. Specimens were injected through a cold runner into a water-heated mould. The shape of the tensile test specimens was in accordance with ASTM D638. A temperature profile of 70 (feed zone), 115 and 120 °C (die zone) was used employing 1200 bar injection pressure and 400 bar back pressure at screw speed of 150 min^{-1}. A 20 second cooling time was allowed in a mould locked with 30 kN locking force.

Tensile strength (TS), elongation (E) and modulus of elasticity (EM) of each specimen have been determined according to ASTM standard D638-03. Samples were injection moulded into a standard dog bone shape, 12 mm wide, 3 mm thick with a 50 mm gauge length. After conditioning, tensile properties were determined using an Instron model 33R4204. An extension rate of 5 mm/min and a extensometer gauge length of 50 mm was used for testing. Samples were tested in replicas of six directly after removal from the humidity chambers. Samples were conditioned for up to 15 days at 23 ^{o}C and 50% relative humidity before tensile testing.

III. RESULTS AND DISCUSSIONS

A. Effect of plasticizer type

The mechanical properties of bioplastics produced using different plasticizers (Table 1) are shown in Fig. 2. All samples were conditioned for 15 days prior to mechanical testing. At this point, equilibrium moisture content has been reached, at approximately 10 wt% water.

It can be seen from these figures that un-plasticized samples had the highest tensile strength and Young's modulus. Plasticization typically led to a reduction in Young's modulus and tensile strength. Increased flexibility due to chain movement also led to an increase in extensibility, or a more ductile material.

Plasticizers with the lowest %HG were most effective at leading to a bioplastic with high extensibility (PD and TEG). Ethylene glycol was the only exception to this, which displayed similar results to DEG and TEG, although having a %HG similar to glycerol. Comparing EG with GLY, one can see that glycerol has more hydrogen bonding capability. A plasticizer with a high %HG and a high H-bond capability would therefore preferentially interact with water, leading to a reduction in plasticization. Choosing an efficient plasticizer is therefore made firstly on it %HG and then secondly on it hydrogen bonding capability.

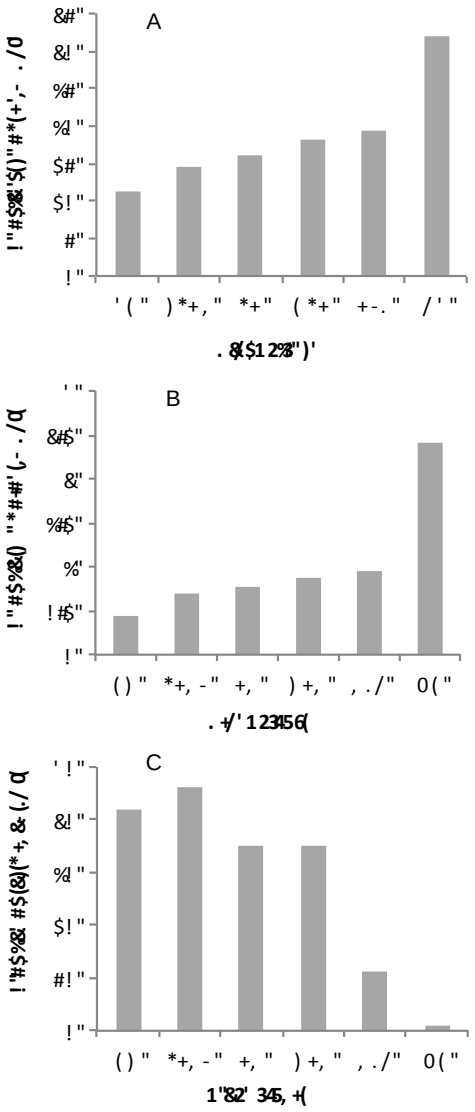

Figure 2. A. Tensile strength, B. Young's modulus and C. Elongation at break for samples containing different plasticizers at 10 pph_{BM}

From Fig. 3 it is evident that Young's modulus varies almost linearly with tensile strength, i.e. stronger bioplastics were generally also stiffer. The same was not true for elongation at break; the high strength materials were generally very brittle. Selecting an appropriate plasticizer is therefore based on a trade-off between high strength and sufficient ductility.

In order to further clarify the ductility of samples tested, light microscope images were taken and evaluated of fracture surfaces of relevant samples (Fig. 4). Without plasticizer, fracture surfaces indicated a brittle fracture mechanism evident from sharp ridges along the fracture surface. Using TEG or DEG, the fracture surface was indicative of some ductile behaviour, while glycerol plasticized samples also showed brittle fractures, although not as sever as without plasticizer.

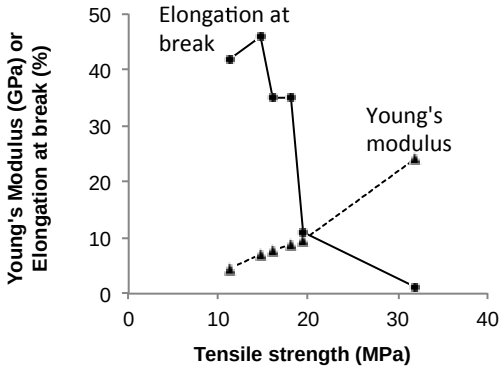

Figure 3. The relationship between Young's modulus and tensile strength

B. Effect of plasticizer content

Fig. 5A shows the variation of mechanical properties as a function of plasticizer content, at constant urea content. In these experiments, TEG was selected as the plasticizer of choice. If it is recognized that urea also acts as a plasticizer, the effect of varying the amount of TEG thereby changes both the ratio of TEG to urea and the total plasticizer content. In Fig. 5B, the ratio TEG: urea was varied at a constant total plasticizer (TEG+urea) content. The result of both these experiment can therefore be used to assess the effect of plasticizer content.

As expected, Young's modulus and tensile strength decreased with increasing plasticizer content, while elongation at break increased significantly. A 1:1 ratio of TEG to urea was optimal, highlighting the importance of urea as a denaturant. The final choice of plasticizer content may therefore also require an assessment of processability, rather that mechanical properties alone. Using excessive urea may have increased the tensile strength and modulus somewhat (by displacing plasticiser), but compromised elongation at break severely. The reduction in elongation is most likely due to the reduction in hydrogen bonding between protein chains.

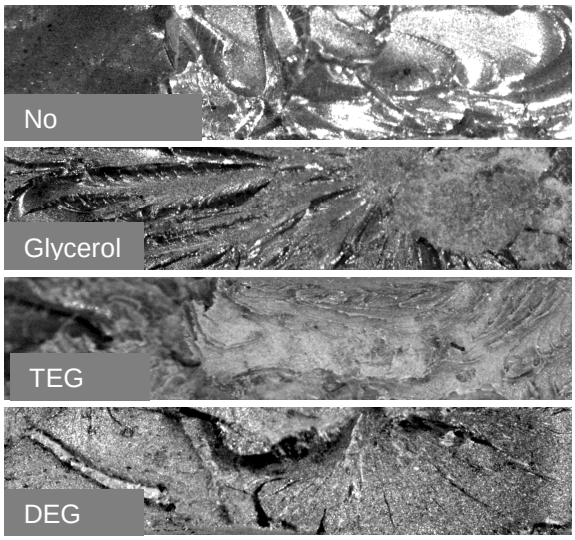

Figure 4. Fracture surfaces of selected bioplastics

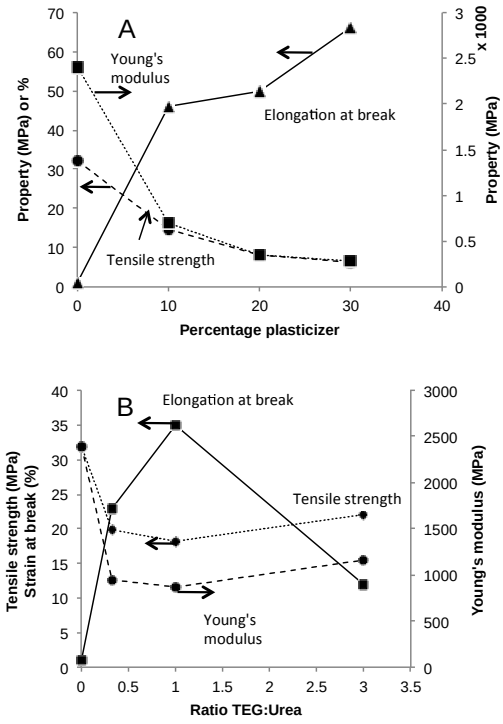

Figure 5. A. Variation of mechanical properties as a function of plasticizer content. B Variation of mechanical properties as a function of the ratio TEG:urea.

C. Effect of moisture content on mechanical properties

Plasticized samples were prepared using 10 pph_{BM} urea and 10 pph_{BM} TEG. Following injection moulding, samples were conditioned at 50% relative humidity and analysed for moisture content at regular intervals.

Un-plasticized samples approached a very low moisture content after 15 days (Fig. 6), while plasticized samples equilibrated to approximately 10 wt% water. In addition, Fig. 7 indicated that Young's modulus and tensile strength values also reached a plateau after about 15 days conditioning. Elongation at break, however, equilibrated after 7 days.

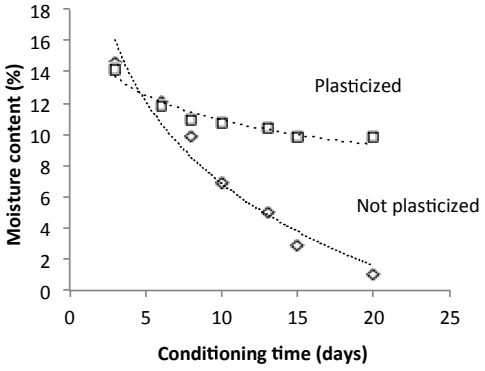

Figure 6. Effect of conditioning time on the equilibrium moisture content

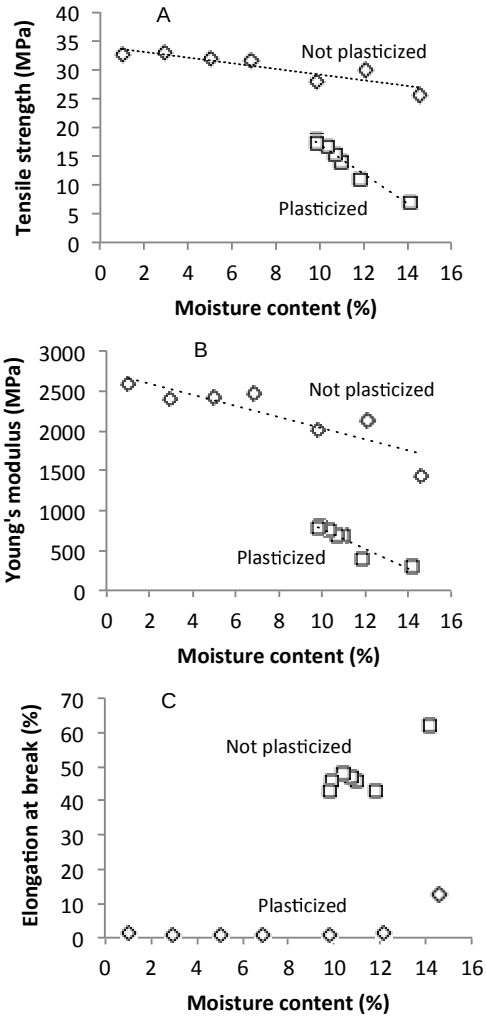

Figure 7. Effect of moisture content on the mechanical properties of samples with and without TEG as plasticizer

From these figures it is also evident that Young's modulus and tensile strength varied linearly with moisture content. Plasticized samples showed a stronger dependency on moisture content, decreasing more steeply with increasing moisture content. The results highlight the importance of ensuring constant moisture content in the material. Material use and storage could both potentially influence moisture content and should be controlled.

CONCLUSIONS

Propylene glycol, tri and di-ethylene glycol were the most efficient plasticizers for bloodmeal. Including these plasticizers at 10 pph_{BM} in conjunction with 10 pph_{BM} urea led to a material with acceptable mechanical properties and good processability. TEG was selected as most appropriate only because it is least volatile from the one trialled (T_{BP} = 285□C) and would therefore lead to the slowest rate of evaporation.

Increasing plasticizer content from 10 to 30 pph_{BM} resulted in an increase in ductility and a reduction in Young's modulus and tensile strength, as expected for a polymer. It was concluded that, within these limits, processability would be the

determining factor in selecting the required amount of plasticizer. In addition, it was found that using a 1:1 ratio of plasticizer to urea was required to optimize mechanical properties.

Plasticized and un-plasticized samples showed a significant difference in their equilibrium moisture content. Plasticized sample equilibrated after about 15 days to a 10% moisture content, whereas un-plasticized samples continued to lose water up to about 20 days. It was concluded that the hydrogen bonding ability of the plasticizer led to a stronger interaction with water, therefore resulting in less water loss when conditioned. A good plasticizer for bloodmeal is therefore a substance with a high boiling point and relatively low percentage hydrophilic groups.

Based on this study it is clear that water can be partially replaced in the formulation, but will always be required for processing. It is recommended that a master batch should be sold in sealed bags, preventing water loss before injection moulding. After moulding, articles should be equilibrated at atmospheric conditions before use.

REFERENCES

[1] Verbeek, C.J.R. and L.E. van den Berg, *Development of Proteinous Bioplastics Using Bloodmeal.* Journal of Polymers and the Environment, 2011. **19**(1): p. 1-10.

[2] Verbeek, C.J.R. and L.E. van den Berg, *Mechanical Properties and Water Absorption of Thermoplastic Bloodmeal.* Macromolecular Materials and Engineering, 2011. **296**(6): p. 524-534.

[3] Bier, J.M., C.J.R. Verbeek, and M.C. Lay, *Identifying transition temperatures in bloodmeal-based thermoplastics using material pocket DMTA.* Journal of Thermal Analysis and Calorimetry, 2012: p. 1-13.

[4] Verbeek, C.J. and L.E. Van Den Berg, *Recent Developments in Thermo-Mechanical Processing of Protenous Bioplastics.* Recent Patenets on Materials Science, 2009. **2**(3).

[5] Verbeek, C.J.R. and L.E. van den Berg, *Extrusion Processing and Properties of Protein-Based Thermoplastics.* Macromolecular Materials and Engineering. **295**(1): p. 10-21.

[6] Verbeek, C. and N. Koppel, *Moisture sorption and plasticization of bloodmeal-based thermoplastics.* Journal of Materials Science, 2011: p. 1-9.

[7] Kristo, E. and C.G. Biliaderis, *Water sorption and thermo-mechanical properties of water/sorbitol-plasticized composite biopolymer films: Caseinate-pullulan bilayers and blends.* Food Hydrocolloids, 2006. **20**(7): p. 1057-1071.

[8] Mali, S., et al., *Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect.* Carbohydrate Polymers, 2005. **60**(3): p. 283-289.

[9] Zhang, Y. and J. Han, *Sorption Isotherm and Plasticization Effect of Moisture and Plasticizers in Pea Starch Film.* Journal of Food Science, 2008. **73**(7): p. E313-E324.

[10] Vanin, F.M., et al., *Effects of plasticizers and their concentrations on thermal and functional properties of gelatin-based films.* Food Hydrocolloids, 2005. **19**(5): p. 899-907.

[11] Hernandez-Izquierdo, V.M. and M.J. Krochta, *Thermoplastic Processing of Proteins for Film Formation- A Review.* Journal of Food Science, 2008. **73**(2).

[12] Su, J.-F., et al., *Moisture sorption and water vapor permeability of soy protein isolate/poly(vinyl alcohol)/glycerol blend films.* Industrial Crops and Products, 2009. **31**(2): p. 266-276.

[13] Cho, S.Y. and C. Rhee, *Sorption Characteristics of Soy Protein Films and their Relation to Mechanical Properties.* Lebensmittel-Wissenschaft und-Technologie, 2002. **35**(2): p. 151-157.

[14] Maria Martelli, S., et al., *Influence of plasticizers on the water sorption isotherms and water vapor permeability of chicken feather keratin films.* LWT - Food Science and Technology, 2006. **39**(3): p. 292-301.