PROPERTIES OF GLYCEROL PLASTICIZED WHEY FILMS MODIFIED BY GLUINIODINE THIOCYNATE

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Introduction

Non-biodegradable polymers based packaging materials are in large extent responsible for environmental pollution and accumulation of non-biodegradable waste in nature. This situation was unclear in the past decades but now it is realized that the amount of non-biodegradable waste is growing at an enormous rate, and a need for packaging materials based on biodegradable polymers is urgent [1].

Whey is a globular protein that is a byproduct of diary industry; it possesses good film forming and gas barrier properties. Whey films have been extensively studied as a raw material for bio-based food packaging applications. In the past packaging films are formed from whey protein concentrate and isolate by solvent casting and compression molding [2]. Whey protein concentrate / isolate when dissolved in water and cast onto petri dish do not form film as the globular structure of the protein does not allow the solution to acquire desired viscosity for film formation. To overcome this it becomes necessary to heat the solution up to its denaturing temperature to denature the protein structure, enabling the protein chains to straiten and form intermolecular disulfide bonds resulting increase in the viscosity of the solution to form film. These unmodified films formed are brittle in nature and can't be used in any application as it is, so a plasticizer/chaotropic agent of some sort is required to add flexibility to the films. Glycerol, sorbitol, propylene glycol are few examples of plasticizers that are used to form flexible films with moderate elongation. guanidine thiocyanate is a very effective chaotropic agent that can act as a super-plasticizer and lowers the glass transition temperature by disrupting the molecular structure at lower concentrations of plasticizer. These plasticizers are added in relatively small amount to compete with the hydrogen bonding and other hydrophobic interactions present within the protein.

The aim of this research was to form packaging films from whey protein concentrate by solvent casting using water as a solvent, glycerol as the plasticizer and guanidine thiocyanate as chaotropic agent. Various properties of the films like mechanical, surface morphology and glass transition temperature are measured for different compositions to analyze the effect of each component.

Experimental

Materials

Whey protein concentrate (72-75% protein) supplied by NZMP, Glycerol and all other chemicals were supplied by Sigma-Aldrich Chemicals Ltd.

Preparation of films Whey protein concentrate was added to deionized water and stirred for 2hrs to give a final protein concentration of 10%. This solution was thereafter kept in a water bath for 30 min at 78^{o}C with a ramp rate of 2^{o}C/min. This solution was then kept at room temperature to cool down to ambient temperature and then subsequently adjusted to a pH of 7.0. Glycerol and thereafter guanidine thiocyanate are added in proportion 0-7.5% (w/v) and 0.1M to 0.3M respectively. The solution was thereafter stirred for 20 min. 20ml of this was cast onto 7in ID Petri dishes. These films were then kept in 50% ± 5% relative humidity in a glass desecrator for 2 days.

Apparatus and Procedures

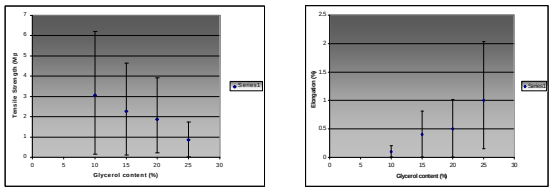
Tensile tests were performed using Instron Universal Testing Instrument (Model 5567, Instron Ltd., U.K). Film samples were tested according to universal testing method ASTM D882-02.

DSC experiments were performed by DSC Q 2000 instrument. Aluminum pans were filled with 8-10 mg of sample. These pans were then kept into the DSC chamber for analysis.

Scanning electron microscopy were examined by Philips XL30 FEG, Holland. Samples were attached to stainless steel and examined using an accelerating voltage of 15kV.

Results and Discussion

There are various formulations being formed with 10% protein concentration by varying the proportion of glycerol and guanidine thiocyanate. Glycerol is used in the range 0-7.5% (w/v) and guinodine thiocynate from 0.1M – 0.3M. It was observed in mechanical test results (Fig.1), formulations containing lower concentration of glycerol had more strength and lesser elongation. The reason for this being that intra and inter molecular hydrogen bonding in the protein chains is ruptured enabling them to straighten the polypeptide chains by opening of globular structure.



(a) (b)

Fig.1 Effect of increasing Glycerol content on (a) Tensile Strength (b) Elongation

The glass transition temperature as discussed earlier is a very important property for determining the behavior of protein at different thermal conditions. Increasing amount of glycerol lowered the glass transition temperature due to increased mobility in protein chains. This increased the flexibility and elongation as supported by the tensile test results.

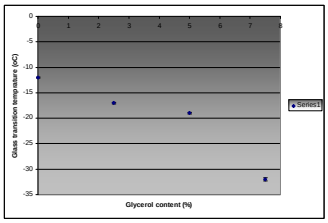
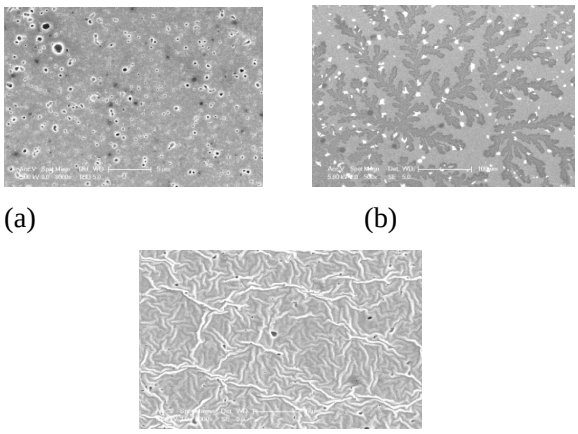


Fig. 2 Effect of increasing glycerol content on glass transition temperature

Scanning electron microscope was used to examine surface morphology of whey films. Figure 2 show scanning electron micrograph of the surface. The surface of films was porous with pores of variable sizes on the surface typically ranging from 500nm to 50 nm. The size of pores was found to be decreasing with increasing concentration of guanidine thiocyanate and glycerol. Film with highest glycerol (2.5% w/w) and 0.1M guanidine thiocyanate had smooth surface with pores of relatively small size. The pores are assumed to be formed by disruption of inter and intramolecular hydrogen bonds of whey protein and dissociation of aggregates resulting in residual void space in the films with higher concentration of guanidine thiocyanate compared to glycerol. Film with intermediate glycerol concentration (5%w/v) and high concentration of guanidine thiocyanate (>0.2M) formed new crystal phases. A shinkage pattern was seen in film containg 7.5% glycerol and 0.2M guanidine thiocyanate, which may be due relatively high amount of both glycerol and guanidine thiocyanate increasing the hygroscopic nature of films.



(a) (b)

(c)

Fig. 3 SEM images for films with (a) Whey Protein / 2.5 % Glycerol / 0.1M GTC (b) 10% Whey Protein / 5.0% Glycerol / 0.3M GTC (c) 10% Whey Protein / 7.5 % Glycerol / 0.2M GTC

Addition of guanidine thiocyanate enabled the formation of films even with no external plasticizer although the tensile properties of the films were compromised with higher concentration of. All the films were translucent and light yellow in color, the appearance could be improved by addition of another protein like gelatin for enhancement of appearance and mechanical properties.

References

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[2] Sothornvit, R.; Olsen, C. W.; McHugh, T.H.; Krochta, J.M. 2007. "Tensile properties of compression-molded whey protein sheets: Determination of molding condition and glycerol-content effects and comparison with solution-cast films", *J. of Food Engineering*, 78, pp855-860.