Effect of Adipic Acid Content on Properties of Soy Protein Isolate/ Kapok Husk Biocomposite films

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Abstract

The adipic acid (AA) was used as a crosslinking agent to improve the properties of kapok husk (KH) filled soy protein isolate (SPI) biocomposite films. The effects of AA content on tensile properties and morphology of SPI/KH biocomposite films were investigated. The increasing of AA content from 0% to 1.0% has increased the tensile strength and modulus of elasticity of biocomposite films, whereas the elongation at break decreased. Incorporation of 1.0% of AA showed the highest tensile strength and modulus of elasticity of crosslinked biocomposite films. In addition, at 1.5% of AA the tensile strength and modulus of elasticity decreased but elongation at break increased. Thus, at higher AA content it performs plasticity effect to the SPI/KH biocomposite films. The morphology study indicates the crosslinking with AA improved the interfacial interaction between KH filler and SPI matrix.

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1. Introduction

Currently plastics are low cost and diverse material. It can be easily extruded or moulded into mass products. Biopolymer based packaging materials originated from natural renewable resources such as proteins, lipids and polysaccharides have become the focus of worldwide attention in recent years since such biopolymers offer favourable environmental advantages of recyclability and reutilization compared to conventional petroleum based synthetic polymers.1

Proteins from numerous plant sources such as corn, soy and wheat have been researched due to their film forming abilities. Soy protein films have poor vapour and moisture barrier properties due to their hydrophilicity and the significant amounts of hydrophilic plasticizer used in film preparation. Recent reports have described the use of soy protein isolate to develop edible and biodegradable films.2,3 Soy protein isolate is a complex mixture of proteins with widely different molecular properties. The major soybean proteins have molecular weights ranging from 200 to 600 kDa. Most soy proteins (~90 %) are globulins, which can be fractionated in 2S, 7S, 11S and 15S according to their sedimentation coefficients. The 7S and 11S fractions, the main fractions making up about 37 % and 31 % of the total extractable protein, have the capability of polymerization.4 Plasticizers are commonly used to develop SPI films products and also improve the flexibility. A variety of common plasticizers used in edible films include glycerol, polyethylene glycol (PEG), sorbitol, propylene glycol (PG) and ethylene glycol (EG), monosaccharide, disaccharide or oligosaccharide, lipids and their derivatives.5

Natural fillers are typically derived from fast-growing renewable plants and therefore are not only low cost and much less subject to economic fluctuations, but also reduce environmental concerns associated with the depletion of natural resources. Kapok husk is obtained from the seed pods of the kapok tree (Ceiba pentandra) from the Bombacaceae family. The seeds are enclosed in capsules or pods that are picked and broken open with mallets. The husk is exceedingly light with a circular cross-section thin walls and a spacious lumen. Some researchers reported the utilization of natural fillers in soy protein isolate films such as SPI/flax, SPI/ramie, SPI/starch, SPI/gelatin, SPI/wheat gluten, SPI/cellulose, SPI/chitosan.6

Chemical modification of soy protein isolates allows formed biopolymers to approach the properties of synthetic polymers. In general, crosslinking reaction is an example of chemical modification to improve the properties of SPI biocomposite films.7 Crosslinking can also increase strength and rigidity, but may also have detrimental effects on the biodegradability of protein plastics. Adipic acid (AA) is distinguished with the ability to react with protein to produce crosslinked polymer. In our previous study reported the effect of KH and SPI biofilms on tensile properties and morphology of Soy Protein Isolate/ Kapok husk biofilms.8,9 The aim of this research was to study the influenced of AA as crosslinking agent on tensile properties and morphology of uncrosslinked and crosslinked SPI/KH biocomposite films.

2. Materials and method

2.1. Materials

Soy protein isolate (SPI) with 90% protein was provided by supplied by Shandong Wonderful Industrial Group Co., Ltd., Dongying with an average particle size of 63 μm, China. Kapok husk was obtained from rural area, Perlis, Malaysia. Kapok fiber removed from kapok pod. Cleaned kapok pod was crushed and ground into powder. The average particle size of kapok husk was 16 μm. Glycerol was supplied by HmbG® Reagent Chemical, Selangor, Malaysia. Adipic acid was supplied by Sigma-Aldrich, Penang, Malaysia.

2.2. Preparation of Biocomposite Film

SPI/KH biocomposite films were prepared by casting technique. The ratio of SPI and glycerol used 2:1 for each blend biocomposite films. The SPI was dissolved in distilled water and stirred in a water bath at 90°C for 15 minutes. Then, KH added to SPI, followed by sequential addition of glycerol with constant stirring for another 15 minutes. The total mixing time was 30 minutes. For crosslinked SPI/KH biocomposite films, AA was first dissolved in distilled water to produce 0.5, 1.0 and 1.5% (v/v) solution. Then, AA solution was added to the SPI/KH solution at 28 minutes and stirred until 30 minutes. Finally, uncrosslinked and crosslinked SPI/ KH solutions were
poured into plastic mold and dried in the oven at 50 °C for 24 h. The films were carefully peeled off from the plastic surface. Table 1 shows the formulations of uncrosslinked and crosslinked SPI/KH biocomposite films.

Table 1. Formulations of uncrosslinked and crosslinked SPI/KH biocomposite films.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Uncrosslinked SPI/KH</th>
<th>Crosslinked SPI/KH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soy protein isolate (SPI) (wt%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Kapok husk (KH) (wt%)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Glycerol (wt%)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Adipic acid (AA) (%)</td>
<td>-</td>
<td>0.5, 1.0, 1.5</td>
</tr>
</tbody>
</table>

2.3. Tensile Testing

The tensile properties such as tensile strength, elongation at break and modulus of elasticity of unmodified and modified SPI/KH biocomposite films were determined with an Instron Universal Testing Machine (model 5569) according to ASTM D882. Cross head speed was set at 10 mm/min and the initial grip separation was set at 50 mm. For this testing about 10 samples were measured to obtain the average results.

2.4. Morphology Analysis

Uncrosslinked and crosslinked SPI/KH biocomposite films were examined for tensile fracture surface using scanning electron microscope (SEM) (JEOL JSM-6460-LA) operated at 10 kV. The samples were coated with a thin layer of palladium for imaging and allow surface visualization.

3. Results and discussion

3.1. Tensile Testing

Fig. 1. (a) presents the stress-strain curve of uncrosslinked and crosslinked SPI/KH biocomposite films at 40% of KH loading with different AA content. The incorporation of AA reduced the ductility by increasing the strength of biocomposite films until 1% of AA content due to increment of crosslinkages. In contrast, at 1.5% of AA content, the tensile strength of SPI/KH biocomposite films decreased due to plasticity effect. Fig. 1. (b) shows the effect of AA on tensile strength of SPI/KH biocomposite films at different AA content. From the graph shown as the content of AA increases with 0.5 % and 1 %, tensile strength increased. However, at 1.5 % of AA content, tensile strength lowers than 1.0%. This is due to the fact that at higher AA content it reduces the interactions between protein chains, thus increase the chain mobility and association between polypeptide chains of SPI/KH biocomposite films. The addition of KH also has increased the tensile strength of biocomposite films. This indicates that KH acted as reinforcing filler, at higher amount of KH yield the tensile strength of SPI/KH biocomposite films. The strengthening of tensile strength of SPI/KH biocomposite films due to the formation of inter molecular hydrogen bonds between SPI matrix and KH filler. The schematic reaction between SPI and adipic acid was illustrated in Fig. 2. There is a formation of amide linkages between ester groups of AA and amino groups of SPI.
Fig. 1. (a) Stress-strain curve of AA content; (b) Effect of AA content on tensile strength of uncrosslinked and crosslinked SPI/KH biofilms at 40% KH loading.

![Stress-strain curve and tensile strength graph]

Fig. 2. Schematic reaction between SPI and adipic acid.

![Schematic reaction diagram]

The effect of AA content on elongation at break of uncrosslinked and crosslinked SPI/KH biofilms at 40 wt% KH loading is shown in Fig. 3a. It can be seen that the elongation at break decreased with increasing AA content, but increased at 1.5%. This probably because the matrix and filler was fully occupied by the AA molecules and it causes lubricating effect on the crosslinked SPI/KH biocomposite films.

![Elongation at break graph]

Fig. 3. (a) Effect of AA content on elongation at break; (b) modulus of elasticity of uncrosslinked and crosslinked SPI/KH biocomposite films at 40% KH loading.

![Modulus of elasticity graph]
Fig. 3b illustrates the effect of AA content on modulus of elasticity of uncrosslinked and crosslinked SPI/KH biocomposite films at 40 wt% of KH loading. The results indicated the modulus of elasticity of SPI/KH biocomposite films increased with 0.5 % and 1.0% of AA content. The modulus of elasticity is an indication of the relative stiffness of biocomposite films. The increase in modulus of elasticity was expected as the AA content increases, due to more crosslinking reaction occur between SPI matrix and leads to stiffness of the biofilms. However, at 1.5% of AA content the modulus of elasticity decreased caused by high flexibility of the biocomposite films. In addition, the values of modulus of elasticity, also depends on many factors such as the ratio of filler to matrix, adhesion between filler and matrix. The increased of modulus of elasticity of blend films with addition of cellulose derivatives/soy protein isolate also reported by Zhou 12.

3.2. Morphology Analysis

Fig. 4. (a,b) illustrates the SEM micrograph of the tensile fracture surface of uncrosslinked and crosslinked SPI/KH biocomposite films at 40% KH loading. Crosslinked SPI/KH biocomposite film exhibits rough tearing than uncrosslinked biocomposite film. The presence of AA as the crosslink agent had enhanced the adhesion of biocomposite films by crosslinking formation. The formation of a crosslink network has enabled the biocomposite films to be stretched to greater extent before failure.

4. Conclusion

The tensile strength and modulus of elasticity of both uncrosslinked and crosslinked SPI/KH biocomposite films at 40% KH loading increased with increasing adipic acid (AA) content from 0.5% to 1.0 %. However, at 1.5% of AA content both tensile strength and modulus of elasticity decreased. The AA was used as a crosslinking agent in the SPI/KH biocomposite films. AA has improved the tensile strength of the film due to formation of amide linkages between ester groups of AA and amino groups of SPI. The presence of AA enhanced the adhesion between the SPI matrix and the KH filler was proven by SEM study.

Acknowledgements

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