Crosslinked Glutinous Rice Starch Filled Polyvinyl Alcohol Films

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The influence of glutinous rice starch (GRS) content and sodium hexametaphosphate (SHMP) in polyvinyl alcohol (PVOH) films were studied. The increase of GRS content (0–40 wt%) reduced the tensile strength (from 14.3 to 4.3 MPa) and elongation at break (from 183 to 52.5) of PVOH/GRS films. Nevertheless, the modulus of elasticity of PVOH/GRS films increased with GRS content, from 20.3 to 132.83 MPa. SHMP was used as a crosslinking agent, which improved more than 30% of tensile strength and modulus of elasticity of PVOH/GRS films. However, the elongation at break reduced after crosslinking process of the films. The crosslinked film showed better interaction between GRS and PVOH, as demonstrated by scanning electron microscopy. Conversely, the crosslinked films exhibited a lower swelling degree, but a higher gel content compared to uncrosslinked films. J. VINYL ADDIT. TECHNOL., 2019. © 2019 Society of Plastics Engineers

INTRODUCTION

In recent years, the development of biodegradable polymers from renewable resources keep increasing, especially for packaging and disposable applications [1]. This can be maintained by the sustainable development of economical and ecological technology, as well as toward a greener environment [2,3]. Among of these biopolymer, starch is one of the promising biodegradable polymers [4]. Starch is an abundant and renewable polymer. Usually, the sources of starch are from corn, tapioca, potato, wheat, and rice. The starch is the major polysaccharide reserve of plants that contains amylose and amylopectin [5,6]. Glutinous rice (Oryza sativa L.), which is also known as sticky rice, is commonly cultivated in the northeast area of Thailand [7]. Glutinous rice starch (GRS) is a biopolymer which is widely used in the food industry [7,8], which contains nearly 100% of amylopectin. However, the GRS presents a branch chain structure and high hydrophilic nature [7], which is not feasible to produce film alone. Therefore, blending GRS with polyvinyl alcohol (PVOH) can be a potential to produce thermoplastic starch (TPS) films.

PVOH is a material suitable for blending with starch to produce film. This is due to its good film forming ability, biocompatibility, and nontoxicity. Hence, it has been widely used in industrial application, adhesives, packaging application, paper coating agents, and drug delivery carriers [9]. Moreover, PVOH is compatible with starch because it consists of hydroxyl groups that may form hydrogen bonding with starch and water [10]. However, GRS’s hydrophilic nature leads to the moisture content in TPS film, which results in poor mechanical properties of TPS film. A similar observation was reported by Liu et al. [5]. The hydrophobicity properties of PVOH/GRS films can be improved by chemical modification in order to reduce the moisture content in PVOH/GRS films. Das et al. claimed that the crosslinking of starch/PVOH blends carried out with epichlorohydrin (crosslinker). The results showed decrease in -OH groups, due to the crosslinking process [10].

Generally, chemical modifications such as esterification [11], crosslinking [12], and grafting [13] are able to enhance the tensile properties of films, reducing water swelling and water uptake of the film. Sodium hexametaphosphate (SHMP) is a crosslinking agent used in this present work. SHMP can form intra- and inter-ester linkages with starch and PVOH to improve the properties of films. Conversely, the formation of intra- or intermolecular linkages would reduce the chain mobility of GRS and PVOH in PVOH/GRS films. Therefore, sodium carbonate (Na2CO3) was used to promote the crosslinking reaction in PVOH/GRS films when using SHMP as a crosslinking agent [5].

This article presents the preparation of uncrosslinked and crosslinked PVOH/GRS films with SHMP. The effect of GRS content on tensile properties, swelling degree (SD) and gel content, as well as the morphology study of PVOH/GRS films were investigated. In addition, the effect of SHMP as a crosslinking agent in PVOH/GRS films was also studied. The work on PVOH/GRS film has not been reported. Therefore, authors were focused on the preparation of PVOH/GRS film...
and proposed this research project to apply in packaging application.

**METHODOLOGY**

**Materials**

PVOH was supplied by Acros Organics, Malaysia. The PVOH was 95.5–96.5% hydrolyzed with a molecular weight average of 85,000–126,000. GRS was obtained from a Market, in Perlis, Malaysia. The average particle size of GRS was 93.81 μm. Glycerol and Na₂CO₃ were purchased from HmbG Reagent Chemical, Selangor, Malaysia. Meanwhile, SHMP was obtained from Fisher Scientific, Penang, Malaysia.

**Preparation of PVOH/GRS Films**

PVOH/GRS films were prepared via a simple solvent casting method. First, PVOH powder was dispersed in distilled water and stirred at 95°C for 1 h until a homogeneous solution was obtained. Next, the GRS and glycerol were mixed together and added to distilled water and then heated with stirring at 95°C for 30 min to produce gelatinized of GRS solution. Then, the prepared PVOH solution was added to GRS solution. The mixture was kept stirring at 95°C for 30 min to obtain a homogeneous gel solution. After that, PVOH/GRS solution was poured into a plastic mold with the size of 250 × 160 mm and dried at 50°C for 24 h to produce PVOH/GRS films. The formulations of uncrosslinked and crosslinked PVOH/GRS films are listed in Table 1.

**Crosslinking Modification of PVOH/GRS Films**

PVOH/GRS films were cut into rectangular shapes with the dimensions of 10 × 100 mm. These specimens were soaked in 3% of Na₂CO₃ aqueous solution for 10 s, and then soaked again in 1% of SHMP aqueous solution for 30 s. After that, PVOH/GRS films were removed from the solutions. A filter paper was used to absorb excess solution from the surface of PVOH/GRS films. Finally, the crosslinked PVOH/GRS films were transferred into an oven at the temperature of 50°C for 2 h to complete the crosslinking reaction.

**Tensile Test**

Tensile test was carried out using an Instron universal testing machine, Model 5569 according to ASTM D-882. The dimensions of the specimens were 10 × 100 mm. Tensile strength, modulus of elasticity and elongation at break results were obtained from the tensile testing machine. The cross-head speed of testing was 10 mm/min at 25 ± 3°C. At least 15 specimens of each sample were tested to obtain an accurate average values.

**Morphology Study**

The fracture surface of PVOH/GRS films was analyzed using a scanning electron microscope (SEM), JEOL JSM-6460LA, at a voltage of 15 kV. The PVOH/GRS films were mounted on aluminum steels and allowed to coat with a thin palladium layer to avoid electrostatic charged during the examination.

**Fourier-Transform Infrared Spectroscopy**

Fourier-transform infrared spectroscopy (FTIR) analysis was performed using a Perkin Elmer, Model L1280044 instrument. The attenuated total reflectance method was used. Sixteen scans in the wavenumber (cm⁻¹) range of 600–4,000 cm⁻¹ with a resolution of 4 cm⁻¹ were recorded for each specimens.

**SD and Gel Content**

The SD and gel content of PVOH/GRS films were determined according to the procedure reported by Delville et al. [2]. First, the crosslinked PVOH/GRS films were immersed in 10 mL of dimethylsulfoxide (DMSO) for 48 h. After that, the insoluble part from PVOH/GRS films was rinsed in water and then in ethanol to remove DMSO. After that, the insoluble part of film was dried in an oven at 50°C for 24 h. The SD and gel content can be calculated using Eqs. 1 and 2, respectively [2,5]:

\[
SD = \frac{m_s - m_d}{m_d \times A}
\]

\[
\text{Gel content} = \frac{m_d}{m_o} \times 100\%
\]

where, \(m_o = \) original weight of the films before immersed in DMSO; \(m_s = \) weight of swollen film after filtered out from DMSO; \(m_d = \) weight of dried film; \(A = \) surface area of specimen before immersed in DMSO.

**Statistical Analysis**

Statistical analyses of the tensile properties were performed using analysis of variance (ANOVA). The ANOVA was carried out using Microsoft Excel 2013 to check the significance of the collected data. The collected data was considered significant, when \(P \leq 0.05\).

**RESULTS AND DISCUSSION**

**Tensile Properties**

Figure 1a shows the tensile strength of uncrosslinked and crosslinked PVOH/GRS films with SHMP. From Fig. 1a, it
can be clearly seen that the tensile strength decreased with the increase of GRS content. This is due to poor interfacial interaction between PVOH and GRS, although hydrogen bonding is present between PVOH and GRS. A similar observation was noted by other researchers [11,12]. However, the crosslinked PVOH/GRS films showed higher tensile strength compared to uncrosslinked films. This might be due to the presence of SHMP as a crosslinking agent improved the tensile strength \( (P = 0.1) \) of PVOH/GRS films. SHMP reacted with the hydroxyl groups of GRS and PVOH molecules, forming intra- and inter-ester linkages. The hydroxyl groups in PVOH/GRS films were reduced, which resulted in reduced moisture content in the films. Therefore, the hydrophobicity of the films improved after crosslinking reaction with SHMP. Besides, the interfacial interaction between PVOH and GRS improved and consequently enhanced tensile strength. The proposed schematic crosslinking reaction of SHMP and PVOH/GRS is shown in Fig. 1b.

A simple model such as Nicolais–Narkis equation [3,14] was used to determine the adhesion interaction between polymer matrix and filler. This equation has been reported by other researchers [3,14–16]. The equation assumes that the composites have uniformly distributed spherical filler particles of equal radius. The relative tensile strength was estimated using Eq. 3 and the experimental results are plotted in Fig. 1c. From the figure, if the slope plotted is less negative than the value of \(-1.21\) (the slope from Nicolais–Narkis equation), this indicates that there is no adhesion between the matrix and particles [3,14]. Based on Fig. 1c, the uncrosslinked and crosslinked PVOH/GRS films showed higher negative value than \(-1.21\). This is due to some adhesion interaction between PVOH and GRS in both uncrosslinked and crosslinked films. However, the slope of the crosslinked film was more negative than the slope of the uncrosslinked film. Hence, the crosslinked films showed a higher interfacial interaction than the uncrosslinked film with the presence of ester linkages. The enhancement of the interaction between PVOH and GRS was due to the presence of both hydrogen bonds and ester linkages. Furthermore, this proves that the addition of SHMP enhances interfacial interaction, which improves the tensile properties of films.

\[
\sigma_c = \sigma_o \left(1 - 1.210^{2/3}\right) \tag{3}
\]

where, \(\sigma_c\) = tensile strength of PVOH/GRS; \(\sigma_o\) = tensile strength of PVOH; \(\varnothing\) = volume fraction of GRS.
The modulus of elasticity of PVOH/GRS films with and without SHMP crosslinking agent is displayed in Fig. 2. As observed, the modulus of elasticity of both uncrosslinked and crosslinked PVOH/GRS films increased as GRS content increased from 10 to 40 wt%. The increase in modulus of elasticity is related to the chain mobility and stiffness of PVOH chain. The molecular mobility of PVOH was restricted by GRS granules, which resulted in high stiffness when GRS was added to PVOH film. Nevertheless, the modulus of elasticity of crosslinked PVOH/GRS films was 47.7% higher ($P = 0.05$) compared to uncrosslinked PVOH/GRS films at 20 wt% of GRS content. The formation of ester cross-linkages increased the stiffness of PVOH/GRS films. PVOH/GRS films were resistant to stretch after crosslinked with SHMP. Other researchers have reported similar results in their study [5].

The effect of GRS content on elongation at break of both uncrosslinked and crosslinked PVOH/GRS films is illustrated in Fig. 3a. Obviously, the elongation at break of both uncrosslinked and crosslinked PVOH/GRS films decreased with increasing GRS content. These results revealed that the incorporation of GRS restrained the chain mobility and increased the rigidity of PVOH/GRS films. Besides, the crosslinked PVOH/GRS films exhibited a lower elongation at break compared to uncrosslinked films. As expected, the presence of GRS and also SHMP in the PVOH matrix enhanced the rigidity of PVOH/GRS films, resulting in a lower elongation at break. The elongation at break of crosslinked PVOH/GRS film decreased ($P = 0.2$) around 16.15% compared to uncrosslinked PVOH/GRS film at 20 wt% of GRS content.

Based on Nielsen equation (Eq. 4), it is noted that there is a relationship between elongation at break and volume fraction of GRS particles [3,14]. From this equation, it can be determined whether any interaction occurred between PVOH and GRS and affected the elongation properties of the films.

$$\varepsilon_c = \varepsilon_o \left(1 - \theta^{1/3}\right)$$

where, $\varepsilon_c = \text{elongation at break of PVOH/GRS}; \varepsilon_o = \text{elongation at break of PVOH}$.

Ramaraj [3,14] reported that a more negative slope means there is more adhesion interaction between particles and matrix than that predicted using Eq. 4. The elongation at break was estimated using Eq. 4 (theoretical values) and the experimental results are plotted in Fig. 3b. Apparently, the slope of uncrosslinked PVOH/GRS film was slightly more negative than the theoretical values. This may be due to the presence of hydrogen bonding between PVOH and GRS, which results in some adhesion between PVOH and GRS. On the contrary, the crosslinked PVOH/GRS film with SHMP showed a more negative slope than the uncrosslinked PVOH/GRS film and the theoretical results. This indicates that the formation of ester linkages and hydrogen bonds in PVOH/GRS enhanced the interfacial interaction between PVOH and GRS.

**SD and Gel Content**

According to Liu et al. [5], they reported that SD corresponds to the crosslink density of the newly formed cross-linkages in
polymer composites. Hence, the lower the SD, the higher the crosslink density of films. Figure 4a shows the SD of uncrosslinked and crosslinked PVOH/GRS films. The SD of both uncrosslinked and crosslinked PVOH/GRS decreased slightly with GRS content. This is attributed to the formation of intra- and inter-hydrogen bonds between the OH groups of PVOH and the OH groups of GRS in uncrosslinked PVOH/GRS films. Nevertheless, the crosslinked PVOH/GRS films exhibited 32.3% lower SD than the uncrosslinked films. This is due to the formation of ester linkages between SHMP crosslinker and GRS or PVOH, which may result in higher crosslink density as compared to uncrosslinked films.

In addition, gel content is the amount of starch and PVOH macromolecules available in the formation of the cross-linkages of films [5]. The gel content results of uncrosslinked and crosslinked PVOH/GRS films are displayed in Fig. 4b. The gel content of uncrosslinked and crosslinked PVOH/GRS films increased with increasing GRS content. From Fig. 4, it can be observed that the gel content of crosslinked PVOH/GRS film increased drastically compared to uncrosslinked films. This could be attributed to the presence of ester cross-linkages in PVOH/GRS films. This finding is in line with the SD results, which are explained earlier in the SD section. As a result, lower SD
might lead to higher gel content, which indicated that PVOH/GRS macromolecules crosslinked with higher crosslink density. Delville et al. [2] and Liu et al. [5] also reported a similar trend in their research of SD and gel content of polymer composites.

**Fourier-Transform Infrared Spectroscopy**

Figure 5 displays the FTIR spectra of PVOH, GRS, and crosslinked PVOH/GRS film. From the FTIR spectrum of PVOH, the peaks at 2,925, 1,087, 1,023, and 841 cm$^{-1}$ are related to methylene (CH$_2$) groups. Additionally, the band at 1,732 cm$^{-1}$ corresponds to carbonyl groups (C=O). The OH groups of PVOH are found at the peaks of 3,298 and 1,240–1,000 cm$^{-1}$. From Fig. 5, it can be seen that the functional groups of PVOH are also found in the FTIR spectrum of crosslinked PVOH/GRS films. However, the carbonyl group (1,732 cm$^{-1}$) is absent in the spectrum of GRS. Besides, the intensity peak at 2,929 cm$^{-1}$ (CH$_2$ groups) of GRS and crosslinked PVOH/GRS films is lower compared to PVOH. Furthermore, the intensity peaks of hydrogen groups (OH) increased as shown in the FTIR spectrum of crosslinked PVOH/GRS film. This could be due to the formation of hydrogen bonding between PVOH and GRS. The characteristic band at 1,732 cm$^{-1}$ in the FTIR spectrum of crosslinked PVOH/GRS film is attributed to the presence of ester linkages (C=O). According to Xiao and Yang [13], they reported that no carbonyl peak is found in the spectrum of uncrosslinked PVOH/starch. A similar observation was also reported by other researcher [13].

**Morphology Study**

Figure 6a presents the SEM micrograph of PVOH film. The tensile fracture surface of neat PVOH film shows smooth and homogenous surface. The SEM micrograph of uncrosslinked and crosslinked PVOH/GRS films were shown in Fig. 6b and c, respectively. The tensile fracture surface of uncrosslinked PVOH/GRS film exhibits a rough surface, some holes, and cavities. These holes and cavities are related to GRS pulled out from PVOH matrix, resulting in poor interfacial interaction between PVOH and GRS. Conversely, the fracture surface of crosslinked PVOH/GRS film shows a smoother failure surface than uncrosslinked film. From SEM micrograph (Fig. 6c), it can be seen that there are fewer holes and cavities, and GRS is embedded on the surface of PVOH. This indicates that the
crosslinking modification has improved the interfacial interaction between PVOH and GRS. The improvement of interfacial adhesion on crosslinked PVOH/GRS film is also proven by Nielsen and Nicolais–Narkis equations.

CONCLUSIONS

As a result, the tensile strength and elongation at break for both uncrosslinked and crosslinked PVOH/GRS films decreased with increasing GRS. However, the modulus of elasticity increased with increasing GRS. The addition of SHMP improved the tensile strength and modulus of elasticity of PVOH/GRS films by enhancing the adhesion interaction between PVOH and GRS, as demonstrated in SEM study. The crosslinked PVOH/GRS films showed higher crosslink density than uncrosslinked films due to the formation of ester linkages between SHMP and PVOH/GRS films. These results correspond to the SD and gel content of the films. The crosslinked PVOH/GRS films showed lower SD and higher gel content as compared to the uncrosslinked PVOH/GRS films. The presence of ester bonds and hydrogen bonding in PVOH/GRS films was proven by FTIR study.

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