

# Properties of the Crosslinked Plasticized Biodegradable Poly(vinyl alcohol)/Rambutan Skin Waste Flour Blends

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**ABSTRACT:** Poly(vinyl alcohol) (PVOH)/rambutan skin waste flour (RWF) crosslinked films were successfully prepared by solution casting with glutaraldehyde (GLU) and hexamethylenetetramine (HMTA) and without crosslinker in the presence of glycerol as a plasticizer. The properties of cast films were evaluated by tensile testing, water absorption, and degradation behavior at different weight ratios of PVOH and RWF. The tensile results show that the PVOH/RWF films crosslinked with HMTA exhibited a slight improvement in the tensile strength and Young's modulus but a lower elongation at break than that of GLU-crosslinked films; this was attributed to the better crosslinking effect of HMTA, as shown by the Fourier

transform infrared results. The HMTA-crosslinked film showed a lower water absorption and water vapor transmission rate as compared to the GLU-crosslinked and non-crosslinked films. A natural weathering test revealed that the addition of 1.5 wt % GLU and HMTA did not significantly affect the reduction in tensile properties, but the biodegradability test showed that the weight loss of non-crosslinked films was higher than those of the GLU- and HMTA-crosslinked films. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1127–1135, 2012

**Key words:** additives; biodegradable; blends; crosslinking; water-soluble polymers

## INTRODUCTION

A green environment is considered to be a basic requirement for preserving wildlife and human health. Thus, biodegradable polymers have received much attention as disposable packaging materials for reducing the environmental pollution caused by nondegradable plastic waste, such as polyolefins, polystyrene, and poly(ethylene terephthalate). Among the several kinds of biodegradable polymers, poly(vinyl alcohol) (PVOH) is the most promising polymer because of its good mechanical properties<sup>1,2</sup> and its hydrophilic semicrystalline nature,<sup>3</sup> with technological potential as a water-processable polymer. In addition, Matsumura et al.<sup>4</sup> reported that PVOH has been confirmed to be biodegradable under aerobic conditions. However, cost is a limiting factor for the introduction of PVOH into the market. In this case, PVOH is well suited to be blended with low-cost natural polymers. The conjunction of eco-

nomical and environmental sense has led to the idea of waste utilization.

A number of studies that have used starch as a filler in PVOH blends have been reported. As an example, various starches, such as corn starch, potato starch, tapioca starch, and cassava starch, have been studied in blends with PVOH plastics with the solution-casting method.<sup>1,5,6</sup> However, the use of starch will impact tariff escalation on agricultural products. To the best of our knowledge, there is no study involving tropical fruit waste flours blended with PVOH for the production of biodegradable polymeric materials. Among tropical fruit waste flours, rambutan skin waste flour (RWF) is selected because it possesses similar properties and structure as starch, so that is able to be consumed by microorganisms and contains plenty of hydroxyl groups to form hydrogen bonding with PVOH. However, the weak tensile properties and poor water resistance of the blend films are still an unresolved problem. A plasticizer, such as glycerol, is normally used to increase the flexibility, and it subsequently improves the elongation at break. However, the plasticizing effect causes a reduction in the tensile strength.

A crosslinker is used to create linkages between the hydroxyl group of the PVOH and starch to improve the mechanical properties. Crosslinkers, such as boric acid,<sup>7</sup> epichlorohydrin,<sup>8</sup> and glutaraldehyde (GLU),<sup>3</sup>

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have been used to react with the starch and PVOH to form a macromolecular network, and it was observed that 1.5 wt % crosslinker is the optimum content for the improvement of the tensile strength.<sup>7</sup> Therefore, in the preparation of plasticized biodegradable PVOH/tropical fruit waste flour blends, the weak tensile properties will be improved through the crosslinking reaction. Zhou et al.<sup>9</sup> mentioned that the crosslinkers are usually added to the aqueous solution of the PVOH/starch mixture followed by the casting method to improve their physical and mechanical properties.

In this study, our effort in the preparation of biodegradable polymer films were focused on the effects of chemical crosslinkers on the blending solution based on RWF and PVOH by two kinds of crosslinkers [GLU and hexamethylenetetramine (HMTA)]. This article presents the properties of the crosslinked films with respect to the tensile properties, water absorption, and degradation behavior. Also, the characterization of the crosslinked PVOH/RWF films was studied by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

The selected tropical fruit waste flour in this study was RWF, which obtained from Zarm Scientific & Supplies, Penang, Malaysia. The RWF was analyzed and contained for moisture ( $5.78 \pm 0.14\%$ ), protein ( $5.97 \pm 0.04\%$ ), fat ( $0.42 \pm 0.01\%$ ), crude fiber ( $14.17 \pm 0.22\%$ ), ash ( $3.33 \pm 0.36\%$ ), and carbohydrates ( $70.33 \pm 0.16\%$ ). PVOH was purchased from Sigma-Aldrich. PVOH was fully hydrolyzed with an average molecular weight of 89,000–98,000 g/mol and a density of  $1.269 \text{ g/cm}^3$ . Glycerol and Tween-80 were supplied by Merck, whereas GLU and HMTA were purchased from Sigma-Aldrich. All chemicals were analytical-grade reagents.

### Film preparation

Calculated amounts of PVOH and RWF were dissolved in 200 mL of deionized water, followed by the addition of 15 wt % glycerol, 1.5 wt % GLU or HMTA, and 0.6 wt % Tween-80 into an aqueous solution of the PVOH/RWF blends, homogeneous mixing with constant stirring in a reaction flask, and heating in a water bath for 2 h at  $95 \pm 2^\circ\text{C}$ . Yin et al.<sup>7</sup> reported that 1.5 wt % crosslinker was the optimum dosage for increasing the tensile strength of the film. The mixing composition is shown in Table I. At the end of this incubation, the mixture was cooled to room temperature, and films were cast onto clean glass plates. The dried films were kept in

**TABLE I**  
Formulation for the Preparation of the Crosslinked PVOH/RWF Films

Sample code	PVOH (g)	RWF (g)
PVOH	10	0
PVOH/RWF10	9	1
PVOH/RWF20	8	2
PVOH/RWF30	7	3
PVOH/RWF40	6	4

A similar series of PVOH/RWF blends were prepared with the fixed amounts of GLU and HMTA as crosslinking agents (1.5 wt % GLU or HMTA on the basis of the total weight of the PVOH and RWF).

sealed polyethylene bags and stored in desiccators at room temperature for 3 days before further testing.

### Tensile properties

The tensile test was carried out with an Instron testing machine (model Instron 3366). The crosshead speed was set at 20 mm/min. The average thickness of the specimen was about 0.10 mm. Other parameters of the tensile machine and conditioning of the tensile specimens followed ASTM D 882. All of these tests were conducted at room temperature, and the average value of five repeated tests was recorded for each composition.

### Water absorption and water vapor transmission

Dried PVOH/RWF films were immersed in distilled water at room temperature ( $25^\circ\text{C}$ ). Once equilibrium was reached (24 h), the moisture on the surface of the films was removed, and the weight of the films was measured. The percentage water absorption ( $W_a$ ) of the film was calculated with the following equation:

$$W_a = [(W_e - W_i)/W_i] \times 100 \quad (1)$$

where  $W_e$  is the weight of the film at the adsorbing equilibrium and  $W_i$  is the initial weight of the dried film.

The water vapor transmission (WVT) was determined according to ASTM E 96. An impermeable cup with desiccant silica gel was closed with a sample of PVOH/RWF film firmly fixed on top. The cups were then weighed with their contents and placed in a desiccator containing distilled water at ambient temperature. The films were weighed every 24 h until a steady increase in weight was achieved. The water vapor transferred through the films and absorbed by the silica gel was determined from the weight gain of the cup. The water vapor transmission rate (WVTR;  $\text{g mm h}^{-1} \text{ m}^{-2}$ ) was calculated according to eq. (2):

**TABLE II**  
**Effect of the Crosslinker Types on the Tensile Properties of the PVOH/RWF Films at Different Weight Ratios**

Blend	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Noncrosslinked PVOH	23.2 ± 1.19	238.6 ± 3.99	106.1 ± 7.19
Noncrosslinked PVOH/RWF10	5.8 ± 0.56	45.0 ± 4.93	131.6 ± 4.99
Noncrosslinked PVOH/RWF20	3.7 ± 0.65	25.5 ± 2.90	159.6 ± 3.17
Noncrosslinked PVOH/RWF30	3.1 ± 0.61	20.2 ± 1.44	173.0 ± 5.88
Noncrosslinked PVOH/RWF40	2.9 ± 0.37	8.2 ± 1.46	181.8 ± 2.129
GLU-crosslinked PVOH	26.0 ± 1.28	252.2 ± 9.25	129.6 ± 3.69
GLU-crosslinked PVOH/RWF10	7.7 ± 0.63	58.4 ± 5.02	142.0 ± 4.57
GLU-crosslinked PVOH/RWF20	5.7 ± 0.49	30.3 ± 4.40	165.9 ± 7.54
GLU-crosslinked PVOH/RWF30	4.6 ± 0.58	25.6 ± 4.89	182.9 ± 5.12
GLU-crosslinked PVOH/RWF40	3.2 ± 0.25	11.5 ± 2.14	188.8 ± 3.88
HMTA-crosslinked PVOH	26.3 ± 2.19	238.2 ± 3.78	136.4 ± 2.46
HMTA-crosslinked PVOH/RWF10	8.9 ± 0.53	52.2 ± 7.36	156.5 ± 3.28
HMTA-crosslinked PVOH/RWF20	6.4 ± 0.85	27.2 ± 4.18	167.9 ± 1.83
HMTA-crosslinked PVOH/RWF30	5.1 ± 0.68	23.5 ± 2.73	197.3 ± 2.68
HMTA-crosslinked PVOH/RWF40	3.7 ± 0.60	10.8 ± 1.73	226.6 ± 2.34

$$WVTR = (\Delta W \times D)/(\Delta t \times A) \quad (2)$$

where  $W$  is the weight of film specimens,  $t$  is time for water vapor transfer,  $A$  is the area exposed to water transfer ( $m^2$ ),  $D$  is the thickness of the film, and  $\Delta W/\Delta t$  is calculated by the linear regression from the points of weight gain ( $\Delta W$ ) and time of transfer ( $\Delta t$ ).

### FTIR spectroscopy

FTIR spectroscopy was used to obtain some qualitative information about the functional groups and the chemical characteristics of the PVOH/RWF films. FTIR spectra were obtained and recorded with a PerkinElmer spectrometer (Massachusetts, USA) in the range 550–4000  $cm^{-1}$  at 4  $cm^{-1}$ . For each spectrum, four scans were co-added.

### Natural weathering exposure

The natural weathering test was conducted at School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Seberang Perai Selatan, Penang, for a period of 3 months, from June 2010 to August 2010, to determine the durability of the biodegradable polymer films in natural conditions. The natural weathering test was performed according to ASTM D 1435. All dumbbell-shaped specimens were attached to a rack with a specimen holder. The rack was adjusted to face the equator at an angle of 45° and situated in an open area, whereby it was free from overshadowed by other objects so that the specimens were exposed to all environmental effects, such as rainfall, sunlight, dew, wind, and so on. The specimens were collected after 1 and 3 months of exposure to environmental effects to determine the degree of degradation. The surface of the specimens was wiped with a clean

towel and left in air for 24 h at room temperature before the required test.

### Natural soil burial

The film specimens were cut into dumbbell shapes and buried in natural soil for a period of 3 months, from June 2010 to August 2010. The buried specimens were collected at regular times intervals (every 7 days) from the soil and washed gently with distilled water. The specimens were dried at 50°C until a constant weight was obtained. The weight loss of the specimen with time was used to determine the degradation rate of the specimen with eq. (3). Tensile testing and surface characterization were also done on the buried specimens:

$$\text{Degradation (\%)} = [(W_i - W_d)/W_i] \times 100 \quad (3)$$

where  $W_i$  is the initial dry weight of the specimen and  $W_d$  is the dry weight of the specimen after the soil burial test.

### SEM

The surface morphology of the PVOH/RWF films before and after degradation was observed with a scanning electron microscope (model Zeiss Supra 35VP). The specimen was mounted on aluminum stubs and sputter-coated with a thin gold layer to prevent electrostatic charging and poor resolution during examination.

## RESULTS AND DISCUSSION

### Tensile properties

Table II shows the comparison of GLU against HMTA as a crosslinker in the PVOH/RWF films. For the PVOH/RWF without the addition of the

**TABLE III**  
**Water Absorption and WVTR of the PVOH/RWF Films with and without Various Types of Crosslinkers**

Blend	Water absorption (%)	WVTR (g mm h <sup>-1</sup> m <sup>-2</sup> )
Noncrosslinked PVOH	151.2 ± 1.79	6.48 ± 0.35
Noncrosslinked PVOH/RWF10	157.2 ± 1.12	6.59 ± 0.11
Noncrosslinked PVOH/RWF20	158.7 ± 2.19	6.91 ± 0.08
Noncrosslinked PVOH/RWF30	161.1 ± 1.23	6.96 ± 0.05
Noncrosslinked PVOH/RWF40	168.1 ± 1.14	7.7 ± 0.35
GLU-crosslinked PVOH	135.4 ± 2.14	5.6 ± 0.09
GLU-crosslinked PVOH/RWF10	138.3 ± 0.14	6.0 ± 0.13
GLU-crosslinked PVOH/RWF20	139.7 ± 1.59	6.5 ± 0.03
GLU-crosslinked PVOH/RWF30	142.5 ± 0.77	6.5 ± 0.15
GLU-crosslinked PVOH/RWF40	145.6 ± 0.78	7.2 ± 0.18
HMTA-crosslinked PVOH	131.4 ± 1.16	4.9 ± 0.05
HMTA-crosslinked PVOH/RWF10	137.1 ± 2.02	5.6 ± 0.03
HMTA-crosslinked PVOH/RWF20	138.6 ± 1.01	6.0 ± 0.11
HMTA-crosslinked PVOH/RWF30	139.8 ± 0.78	6.4 ± 0.01
HMTA-crosslinked PVOH/RWF40	140.5 ± 0.17	6.5 ± 0.07

crosslinker, the tensile strength of the films decreased from 23 to 3 MPa with increasing RWF content. Similar trends were observed in the PVOH/RWF films crosslinked with GLU and HMTA. The reduction of the tensile strength was mainly due to the weak intermolecular hydrogen bonding between RWF and PVOH. It is believed that the RWF tended to agglomerate because of the intramolecular hydrogen bonds, which caused poor dispersion in the PVOH matrix, particularly at higher RWF contents. These results are similar with earlier findings by Elizondo et al.<sup>10</sup> on blends of *Amaranthus cruentus* flour and PVOH. However, when 1.5 wt % GLU and HMTA were added to the PVOH/RWF10 blend, the tensile strength of the crosslinked film was slightly improved, from 5.8 to 7.7 and 8.9 MPa, respectively; the same trend was followed in other weight ratio PVOH/RWF blends. This was due to the effectiveness of the crosslinker in enhancing the interaction and, hence, the increased strength of the bonding of PVOH and RWF.

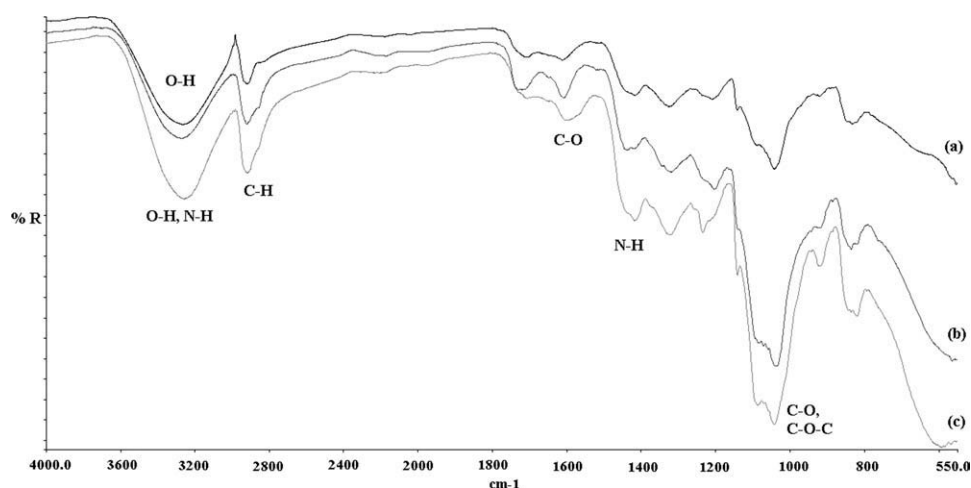
As expected, for the PVOH/RWF films with and without crosslinker, the elongation at break of the films decreased with increasing RWF content, whereas the Young's modulus increased (Table II). The increment of Young's modulus after the addition of RWF was attributed to the stiffening effect of RWF. Table II shows that the elongation at break and Young's modulus of the crosslinked PVOH/RWF films were higher than those of the noncrosslinked PVOH/RWF films. The improvement in the tensile properties, including the tensile strength, elongation at break, and Young's modulus, resulted from the crosslinking reaction. In a comparison between GLU and HMTA, the HMTA-crosslinked films exhibited higher tensile strength and Young's modulus values, but their elongation at break was lower than that of the GLU-crosslinked films. As stated by Kiernan,<sup>11</sup>

GLU has fairly small molecules, with two aldehyde groups separated by a flexible chain of three methylene bridges, whereas HMTA is a heterocyclic organic compound with a symmetric tetrahedral structure. Therefore, the crosslinking appeared to be extensive for the crosslinked films containing the flexible crosslinker (GLU) compared to those containing the rigid crosslinker (HMTA). Further evidence of the interaction between PVOH and RWF in the presence of GLU and HMTA crosslinker is discussed with the FTIR spectroscopy results.

#### Water absorption and WVTR

Besides tensile properties, water absorption capability is important and widely studied for biodegradable films. Table III illustrates the water absorption of the PVOH/RWF films with and without crosslinker. The water absorption of the crosslinked and noncrosslinked PVOH/RWF films increased with increasing RWF content because the water absorption capacity of RWF was higher than that of PVOH. Both GLU and HMTA were added to the PVOH/RWF films to improve their strength and compatibility. It could be observed that the water absorption of the crosslinked PVOH/RWF film was lower than that of the noncrosslinked PVOH/RWF films. This was attributed to the crosslinking reaction by HMTA and GLU, which could decrease the interchain distance and improve the water barrier properties. According to Elizondo et al.,<sup>10</sup> the capacity of the polymer film to absorb water was reduced because of the strong interaction between the two polymers and the homogenization of the blends. As shown in Table III, the HMTA-crosslinked PVOH/RWF films showed lower water absorption values than the GLU-crosslinked films. This indicated that the incorporation of HMTA, as a crosslinker, was effective in





**Figure 1** Spectra of the PVOH/RWF40 films (a) without crosslinker, (b) with GLU, and (c) with HMTA. %R = %Reflectance.

decreasing the interchain distance; this resulted in a low water absorption value for the PVOH/RWF films.

WVTR was used to measure the capability of water vapor to pass through the PVOH/RWF film with different crosslinker types, as shown in Table III. As shown by these results, WVTR of the non-crosslinked PVOH/RWF films increased slightly with increasing RWF content. However, with the addition of crosslinker, WVTR of the crosslinked PVOH/RWF films decreased significantly. Zhou et al.<sup>9</sup> mentioned that the crosslinking points restricted the molecular mobility of the polymer chains. Between the crosslinker types, HMTA was more effective in reducing WVTR than GLU because HMTA could strengthen the bonding and reduce the interchain spacing of PVOH and RWF than the latter. Thus, the water vapor molecules had difficulty diffusing via the films; this caused an increase in the water vapor barrier properties.

### FTIR spectroscopy

The IR spectra of the noncrosslinked PVOH/RWF40 film was studied and compared with those of the PVOH/RWF40 films in the presence of GLU and HMTA as crosslinkers. All of the IR spectra are shown in Figure 1. The strong and wide absorption band of the noncrosslinked PVOH/RWF40 films [Fig. 1(a)] appearing at  $3275\text{ cm}^{-1}$  indicated the stretching vibration of hydroxyl groups and the association of hydrogen bonds in hydroxyl groups, whereas the stretching peak of C–H and the vibration peak of C–O in the associating hydroxyl group appeared at  $2919$  and  $1612\text{ cm}^{-1}$ , respectively. Meanwhile, the bands in the  $1000\text{--}1150\text{-cm}^{-1}$  region were attributed to the stretching vibration of C–O in the C–O–C groups, which correspond to the previous study reported by Yin et al.<sup>7</sup>

In a comparison of the spectra of the crosslinked PVOH/RWF40 films in the presence of GLU and HMTA, there was no occurrence of new peaks that arose because of the changing nature of the functional groups on the surface of specimens. However, with the addition of crosslinker, the intensities and characteristic peaks tended to be stronger and sharper because of the new structure of hydrogen bonding resulting from the crosslinking effect. For the PVOH/RWF40 films with the addition of GLU [Fig. 1(b)], it was found that the intensities of the broad bands around  $3267$ ,  $1610$ ,  $1143$ , and  $1035\text{ cm}^{-1}$  were stronger than those of the PVOH/RWF40 film without crosslinker. The high absorption peak at  $3367\text{ cm}^{-1}$  was assumed to arise from the stretching of the hydroxyl groups of PVOH and GLU itself. Other strong band intensities could be attributed to the overlapping of carbonyl groups and the association of hydrogen bonds in hydroxyl groups. In the spectra of the PVOH/RWF40 films crosslinked with HMTA [Fig. 1(c)], the stronger intensities of the broad band around  $3263\text{ cm}^{-1}$  were due to hydrogen bonds in association with the N–H stretching vibrations. Meanwhile, the stronger peak at  $1603\text{ cm}^{-1}$  could be assigned to the overlapping C–O stretching and hydrogen bonding coupled with COO stretching, whereas the sharper peak around  $1000\text{--}1150\text{ cm}^{-1}$  indicated an increase in intermolecular bonding within the C–O in the C–O–C groups. Besides, Tang et al.<sup>12</sup> also reported a stronger peak of the absorption band shifted to a lower wave number and indicated an increase in intermolecular hydrogen bonding.

### Effect of natural weathering on the tensile properties

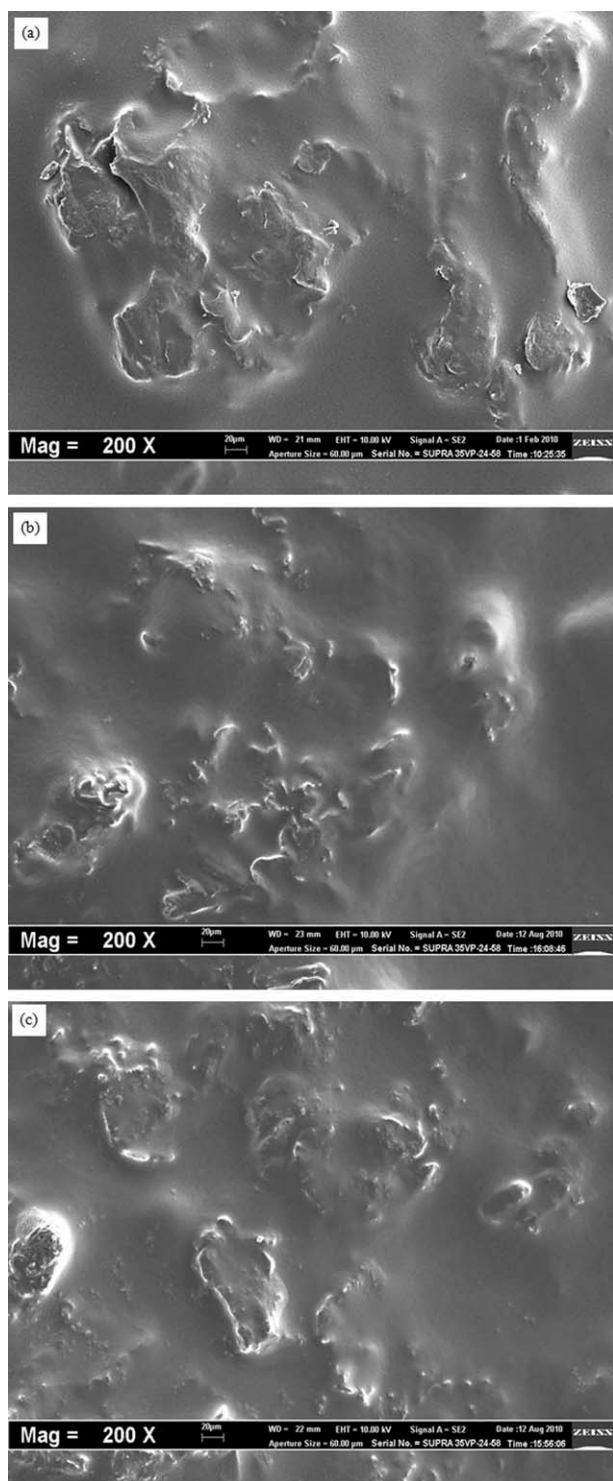
The PVOH/RWF films at different weight ratios with and without crosslinker were exposed to natural weathering, and their abilities to withstand all

environment effects, such as rainfall, sunlight, dew, wind, and so on, were determined by an evaluation of the tensile properties, including tensile strength, elongation at break, and Young's modulus. As shown by the experimental results in Table IV, the tensile strength and elongation at break of all of the crosslinked and noncrosslinked PVOH/RWF films subjected to natural weathering tended to decrease significantly and further deteriorate with longer times of exposure. As reported by Yew et al.,<sup>13</sup> natural weathering usually involves a combined effect of two or more degradation phenomenon and, thus, results in the deterioration of a polymer's mechanical properties and leads to embrittlement and catastrophic failure of the polymer's product. This could explain the increment of Young's modulus of the crosslinked and noncrosslinked PVOH/RWF films with different weight ratios after 1 month of exposure to natural weathering, as shown in Table IV. However, the Young's modulus tended to decline upon 3 months of exposure to natural weathering. The reduced Young's modulus may have been due to surface cracking and degradation as a result of chain scission. This was in agreement with the morphological observation on the exposed surface, which showed the formation of cracks and pores (Fig. 3, shown later). Recall that PVOH and RWF contained plenty of hydroxyl groups, whereas both GLU and HMTA crosslinker were also very water-soluble. Thus, rain caused the crosslinked and noncrosslinked PVOH/RWF films to absorb water and, thus, resulted in a hydrolysis depolymerization process. The crosslinked and noncrosslinked PVOH/RWF films were moistened by rains (swelling effect), and water was released by sunlight (shrinkage effect); this was a so-called the annealing effect and resulted in surface cracking and led to a reduction in the tensile properties of both the crosslinked and noncrosslinked PVOH/RWF films. In short, the addition of GLU and HMTA crosslinker did not significantly affect the weatherability of the PVOH/RWF films when they were exposed to natural weathering as compared to the noncrosslinked PVOH/RWF films.

To examine the surface degradation on the PVOH/RWF films in the presence of GLU and HMTA crosslinker, SEM micrographs were taken from the specimen surface of noncrosslinked, GLU-crosslinked, and HMTA-crosslinked PVOH/RWF films at 40 wt % RWF before and after exposure to natural weathering and are shown in Figures 2 and 3, respectively. Severe surface deterioration occurred in all of the weathered PVOH/RWF films. Interestingly, the microorganisms, surface cracks, and holes were observed by SEM. This was in agreement with the dramatic reduction in the tensile properties of the PVOH/RWF films with and without crosslinker.

**TABLE IV**  
**Tensile Properties of the Noncrosslinked PVOH/RWF Films, GLU-Crosslinked PVOH/RWF Films, and HMTA-Crosslinked PVOH/RWF Films after Exposure to Natural Weathering for up to 3 Months**

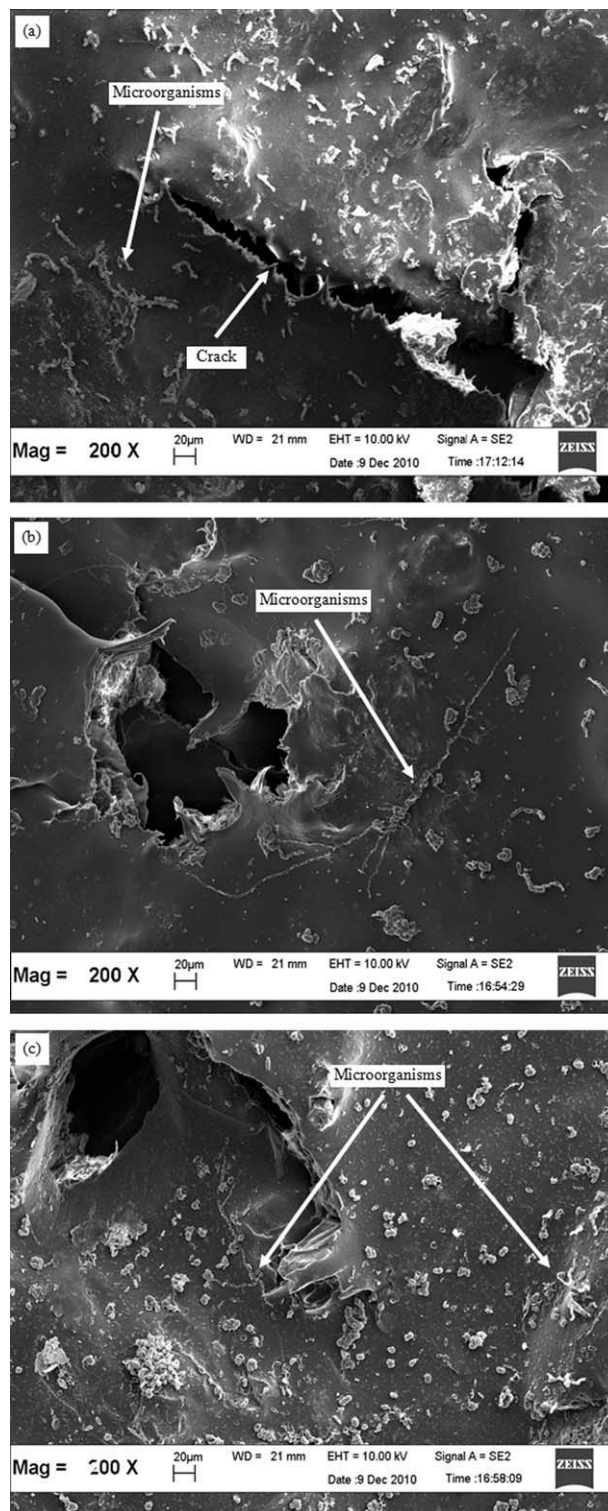
Blend	Initial state			After 1 month of weathering			After 3 months of weathering		
	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Noncrosslinked PVOH	23.2 ± 1.19	238.6 ± 3.99	106.1 ± 7.19	10.1 ± 2.55	16.7 ± 3.91	136.4 ± 2.35	5.6 ± 1.36	8.1 ± 1.84	137.4 ± 4.51
Noncrosslinked PVOH/RWF10	5.8 ± 0.56	45.0 ± 4.93	131.6 ± 4.99	3.9 ± 1.99	11.9 ± 1.73	141.1 ± 3.98	1.4 ± 0.39	3.8 ± 1.84	124.2 ± 3.87
Noncrosslinked PVOH/RWF20	3.7 ± 0.65	25.5 ± 2.90	159.6 ± 3.17	2.4 ± 0.33	5.2 ± 0.32	161.8 ± 6.76	1.1 ± 0.19	3.7 ± 0.14	117.4 ± 2.88
Noncrosslinked PVOH/RWF30	3.1 ± 0.61	20.2 ± 1.44	173.0 ± 5.88	2.0 ± 0.73	2.4 ± 0.82	176.0 ± 2.19	1.1 ± 0.33	1.5 ± 0.03	118.4 ± 1.72
Noncrosslinked PVOH/RWF40	2.9 ± 0.37	8.2 ± 1.46	181.8 ± 2.13	1.1 ± 0.99	1.6 ± 0.73	188.3 ± 2.68	0.2 ± 0.11	1.2 ± 0.06	113.7 ± 5.62
GLU-crosslinked PVOH	26.0 ± 1.28	252.2 ± 9.25	129.6 ± 3.69	11.2 ± 2.55	52.3 ± 2.19	143.0 ± 4.35	8.5 ± 1.96	17.9 ± 1.38	137.8 ± 4.52
GLU-crosslinked PVOH/RWF10	7.7 ± 0.63	58.4 ± 5.02	142.0 ± 4.57	5.4 ± 0.07	13.3 ± 0.87	150.8 ± 3.40	3.1 ± 0.34	4.2 ± 1.29	129.4 ± 2.37
GLU-crosslinked PVOH/RWF20	5.7 ± 0.49	30.3 ± 4.40	165.9 ± 7.54	3.8 ± 0.35	5.1 ± 2.73	173.1 ± 5.39	1.4 ± 0.26	3.4 ± 1.25	151.4 ± 5.29
GLU-crosslinked PVOH/RWF30	4.6 ± 0.58	25.6 ± 4.89	182.9 ± 5.12	3.4 ± 0.49	2.6 ± 1.32	185.0 ± 1.45	1.1 ± 0.25	2.1 ± 0.25	123.5 ± 2.44
GLU-crosslinked PVOH/RWF40	3.2 ± 0.25	11.5 ± 2.14	188.8 ± 3.88	1.3 ± 0.11	2.2 ± 0.1	187.4 ± 2.12	0.6 ± 0.14	1.5 ± 0.02	119.6 ± 1.19
HMTA-crosslinked PVOH	26.3 ± 2.19	238.2 ± 3.78	136.4 ± 2.46	13.2 ± 1.38	51.0 ± 2.03	154.7 ± 3.45	9.1 ± 0.98	10.1 ± 1.73	126.2 ± 3.68
HMTA-crosslinked PVOH/RWF10	8.9 ± 0.53	52.2 ± 7.36	156.5 ± 3.28	6.0 ± 2.99	14.2 ± 1.73	162.1 ± 4.98	3.0 ± 1.60	3.9 ± 1.43	145.8 ± 3.87
HMTA-crosslinked PVOH/RWF20	6.4 ± 0.85	27.2 ± 4.18	167.9 ± 1.83	4.9 ± 2.33	10.8 ± 0.32	174.0 ± 6.76	1.5 ± 0.09	1.8 ± 0.14	137.2 ± 2.88
HMTA-crosslinked PVOH/RWF30	5.1 ± 0.68	23.5 ± 2.73	197.3 ± 2.68	3.4 ± 1.43	6.7 ± 0.82	209.7 ± 4.18	1.2 ± 0.53	1.7 ± 0.04	133.8 ± 1.72
HMTA-crosslinked PVOH/RWF40	3.7 ± 0.60	10.8 ± 1.73	226.6 ± 2.34	1.5 ± 0.99	2.7 ± 0.73	244.3 ± 3.68	0.7 ± 0.21	1.3 ± 0.07	91.2 ± 3.62



**Figure 2** SEM micrographs (200 $\times$  magnification) taken from the surface of the (a) uncrosslinked PVOH/RWF40 film, (b) GLU-crosslinked PVOH/RWF40 film, and (c) HMTA-crosslinked PVOH/RWF40 film before degradability testing.

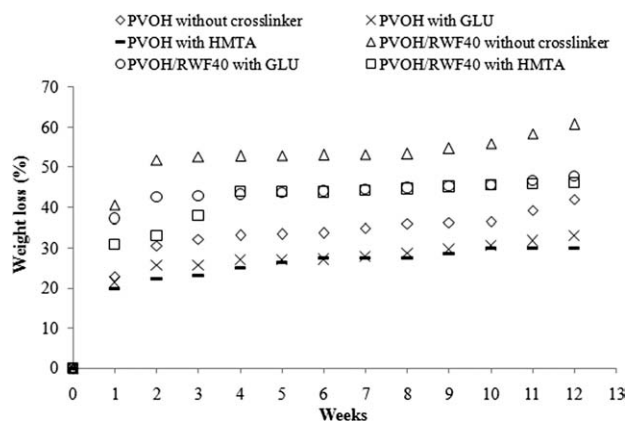
A variety of microorganisms tended to attack and grow on the PVOH/RWF films, especially in the warm humid climate, causing the degradation of the tensile properties and, subsequently, product failure.

Besides, because of the annealing effect, large cracks appeared on the surface of all of the PVOH/RWF film, which apparently resulted in collapse; a similar observation was reported by Danjaji et al.<sup>14</sup> for the



**Figure 3** SEM micrograph (200 $\times$  magnification) taken from the surface of the weathered (a) uncrosslinked PVOH/RWF40 film, (b) GLU-crosslinked PVOH/RWF40 film, and (c) HMTA-crosslinked PVOH/RWF40 film.





**Figure 4** Weight loss of PVOH and the PVOH/RWF film with and without GLU and HMTA crosslinker during biodegradation in natural soil burial testing.

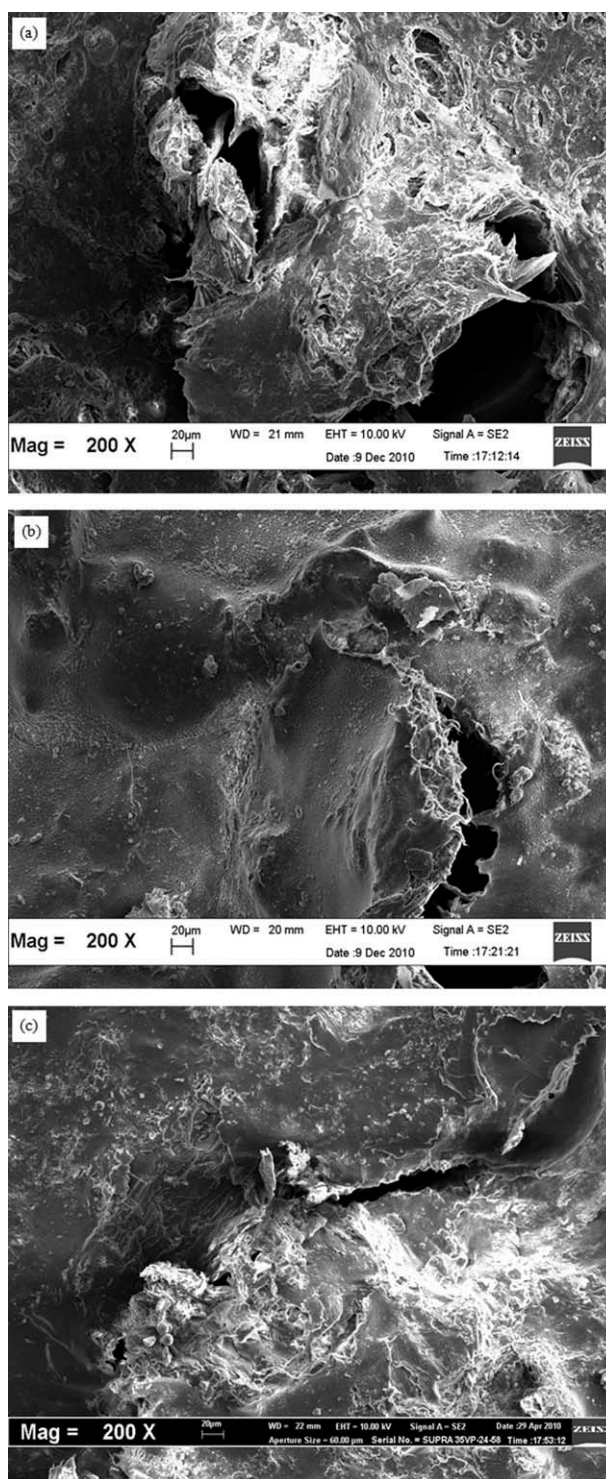
surface of linear low-density polyethylene/sago starch films.

#### Biodegradability of the crosslinked PVOH/RWF films

The results of the weight loss of the PVOH/RWF films in the presence of GLU and HMTA crosslinker during the experiment are shown in Figure 4. The weight loss of the unfilled PVOH film, used as a control sample, was also determined. As expected, RWF was more rapidly biodegraded compared to PVOH. As shown in Figure 4, decreases in the weights of all of the buried films, especially the PVOH/RWF films with 40 wt % RWF content and without crosslinker, were observed during the degradation time in natural soil conditions. The weight loss was rapid during the first week; thereafter, it proceeded slowly. This finding was consistent with the degradation studies by Goheen and Wool<sup>15</sup> on polyethylene/starch composites.

According to Guohua et al.,<sup>16</sup> the soil burial test can provide a realistic environment where temperature, pH, and humidity are less in control and change with the season. Also, Rutkowska et al.<sup>17</sup> demonstrated that different conditions should have an effect on the process of biological degradation of polymer samples because all of the parameters, including temperature, pH, and humidity, have significant effects on development of living microorganisms that cause the biodegradation process to occur. During the period of experiment, the HMTA- and GLU-crosslinked PVOH/RWF films showed comparable weight losses that were lower than those of the noncrosslinked PVOH/RWF films. This result was in agreement with the studies on PVOH/waste gelatin films crosslinked with GLU reported by Chiellini et al.<sup>18</sup> The lower weight losses for the GLU- and HMTA-crosslinked PVOH/RWF films

was due to the crosslinking effect and water absorption capacity, which were further proven by SEM observations. Recall that the average rainfall and mean relative humidity during the experiment were



**Figure 5** SEM micrograph (200 $\times$  magnification) taken from the surface of the buried specimen: (a) uncrosslinked PVOH/RWF40 film, (b) GLU-crosslinked PVOH/RWF40 film, and (c) HMTA-crosslinked PVOH/RWF40 film in natural soil conditions.



201.6 mm and 80.9%, respectively. In addition, the PVOH and RWF had overall hydrophilic properties and tended to absorb rainwater. Thus, the moist environment enabled more microorganisms to survive, grow, and be able to break down the biopolymers by hydrolytic enzymes.<sup>19</sup>

The SEM micrographs of the surface degradation of the PVOH/RWF films with and without crosslinker are shown in Figure 5. It is interesting to note that traces of soil could be observed on the buried PVOH/RWF films because of the tendency of the humid soil to diffuse into the water-sensitive PVOH/RWF40 films, and additionally, the microorganisms might have been removed during the sanitizing process. Thus, the microorganisms were observed less in the SEM micrograph of the buried PVOH/RWF films compared to that of the weathered specimen. Surface cracks and holes could be observed on the surface of all buried PVOH/RWF40 films. These were due to natural soil environmental effects, which caused the buried PVOH/RWF40 films to swell and shrink. However, the surface degradation occurring on the uncrosslinked PVOH/RWF40 films was greater than those of the GLU- and HMTA-crosslinked PVOH/RWF40 films. As shown in Figure 5(a), the cracks and holes were bigger than in the crosslinked PVOH/RWF films. This was mainly due to the lower strength of the uncrosslinked PVOH/RWF films to withstand natural soil environmental effects. Therefore, the weight loss of the uncrosslinked PVOH/RWF40 films was highest.

### CONCLUSIONS

PVOH and RWF was successfully prepared by solution casting in the presence of a crosslinker, HMTA or GLU. The HMTA-crosslinked films exhibited good water resistance and low WVTR with improved tensile strength and Young's modulus. However, the GLU-crosslinked films could be elongated at a higher elongation at break with the

intrinsic flexibility characteristic of GLU. Natural weathering tests revealed that the addition of crosslinker did not significantly affect the reduction of tensile properties, but the soil burial test showed that the noncrosslinked PVOH/RWF films showed substantially more weight loss than the crosslinked films. More interestingly, severe cracks and hollows were evident on the surface of the degraded PVOH/RWF film under SEM observation.

### References

1. Ramaraj, B. *J Appl Polym Sci* 2007, 103, 1127.
2. Sedlarik, V.; Saha, N.; Kuritka, I.; Saha, P. *J Appl Polym Sci* 2007, 106, 1869.
3. Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. A. P. *Mater Sci Eng C* 2008, 28, 539.
4. Matsumura, S.; Kurita, H.; Shimokobe, H. *Biotechnol Lett* 1993, 15, 749.
5. Chen, L.; Imam, S. H.; Gordon, S. H.; Greene, R. V. *J Environ Polym Degrad* 1997, 5, 111.
6. Yun, Y. H.; Yoon, S. D. *Polym Bull* 2009, 64, 553.
7. Yin, Y.; Li, J.; Liu, Y.; Li, Z. *J Appl Polym Sci* 2005, 96, 1394.
8. Sreedhar, B.; Chattopadhyay, D. K.; Karunakar, M. S. H.; Sasstry, A. R. K. *J Appl Polym Sci* 2006, 101, 25.
9. Zhou, J.; Ma, Y.; Ren, L.; Tong, J.; Liu, Z.; Xie, L. *Carbohydr Polym* 2008, 76, 632.
10. Elizondo, N. J.; Sobral, P. J. A.; Menegalli, F. C. *Carbohydr Polym* 2009, 75, 592.
11. Kiernan, J. A. *Microscopy Today* 2000, 1, 8.
12. Tang, S.; Zou, P.; Xiong, H.; Tang, H. *Carbohydr Polym* 2008, 72, 521.
13. Yew, G. H.; Chow, W. S.; Mohd Ishak, Z. A. *J Elastom Plast* 2009, 41, 369.
14. Danjaji, I. D.; Nawang, R.; Ishiaku, U. S.; Ismail, H.; Mohd Ishak, Z. A. *Polym Test* 2002, 21, 75.
15. Goheen, S. M.; Wool, R. P. *J Appl Polym Sci* 1991, 42, 2691.
16. Guohua, Z.; Ya, L.; Cuilan, F.; Min, Z.; Caiqiong, Z.; Zongdao, C. *Polym Degrad Stab* 2006, 91, 703.
17. Rutkowska, M.; Krasowska, K.; Heimowska, A. *Iran Polym J* 2000, 9, 221.
18. Chiellini, E.; Cinelli, P.; Corti, A.; Kenawy, E. R. *Polym Degrad Stab* 2001, 73, 549.
19. Khachatourians, G. G.; Qazi, S. S. In *The Mycota, Human and Animal Relationships*, 2nd ed.; Brakhage, A. A.; Zipfel, P. F., Eds.; Springer-Verlag: Berlin, 2008; p 33.