Xylan/Polyvinyl Alcohol Blend and Its Performance as Hydrogel

Siriporn Tanodekaew, Somruethai Channasanon, Paweena Uppanan

National Metal and Materials Technology Center, 114 Thailand Science Park, Klong Luang, Pathumthani 12120, Thailand

ABSTRACT: Xylan was first modified with maleic anhydride (MA) to obtain xylan-MA. The derivative was then blended with polyvinyl alcohol (PVA) to generate xylan-MA/PVA hydrogel. Xylan-MA was prepared by reacting xylan with MA under an acidic condition. A ring opening of MA occurred, yielding ester linkages between xylan and MA, as verified by ^{13}C-NMR and FTIR. The effects of reaction temperature and weight ratio of xylan to MA on esterification were examined. Thermal stability of modified xylan derivatives was compared with that of pure xylan using TGA. The blends of xylan-MA with PVA became crosslinked gel after being heated at high temperature. The influences of MA and PVA contents on strength and swelling behaviors of the gels were investigated. The cytotoxicity of the gels was also evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1914–1918, 2006

Key words: esterification; hydrogels; biocompatibility; blends; biomaterials

INTRODUCTION

The current trend of using environmentally friendly products has resulted in an extensive exploitation of new materials derived from natural resources. Among those renewable sources, hemicelluloses, which account for 25–35% variously in plants,[1] have shown a great interest in finding new applications both in food and nonfood areas. Hemicelluloses are branched, low-molecular weight polysaccharides with a degree of polymerization of 80–200. They are composed of different types of sugar, with xylan as a major constituent.[2,3] The industrial applications of hemicelluloses were, however, considered a few, compared with those of others extracted from plants, such as cellulose and lignin. Hemicelluloses have been reported to be used as a beater additive in papermaking[4] and as a source of xylitol.[5] They have also found potential use as food additives, thickeners, emulsifiers, and a cancer protective agents.[6,7] Xylose, a pentose sugar repeating unit of xylan, contains two easily accessible hydroxyl groups, offering various possibilities for chemical modifications, for example, benzylation,[8] methacrylation,[9] acetylation,[2,10] long-chain acylation,[11] and succinoylation.[12,13] The appropriate modifications of xylan would lead to functionalized xylan having special properties and suitable utilization, particularly in a biomedical field, which requires naturally friendly materials.

It is, therefore, of our interest to build up a new material derived from xylan and to explore its use as a hydrogel. Hydrogels have been extensively used in biomedical and pharmaceutical applications because of their high water content and rubbery character. The preparations of hydrogels based on hemicelluloses have been reported.[9,14–16] It was evident that film formation was not possible for pure xylan. To promote its film-forming ability, an introduction of other polymers, e.g., by blending with chitosan,[14,15] or by copolymerization with 2-hydroxyethyl methacrylate (HEMA)[9,16], was demonstrated. In this study, the possibility to prepare hydrogel by blending xylan with polyvinyl alcohol (PVA) was investigated. Xylan was first modified with maleic anhydride (MA) and further blended with PVA. The products were characterized using several analytical techniques such as ^{13}C-NMR, FTIR, and TGA. The effects of reaction temperature and weight contents of MA and PVA on the properties of resulting products were examined. The biocompatible ability and other properties affecting gel performances, such as water retention and strength, were investigated.

EXPERIMENTAL

Materials

Xylan, separated from beechwood with over 90% xylose residues, was purchased from Sigma (Steinheim,

Germany). Maleic anhydride (MA) and dimethyl sulfoxide (DMSO) were purchased from Fluka (Buchs, Switzerland). Polyvinyl alcohol (PVA, molecular weight ~30,000–70,000) was purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were used without further purification.

Preparation of xylan-MA/PVA hydrogels

Xylan was made to react with MA with the weight ratios of xylan to MA at 2:1 and 1:1, using DMSO as a solvent. The reactions were performed at 50 and 70°C under acid catalysis for 2 h. The resulting derivative, xylan-MA, was precipitated in isopropanol and dried in an oven. Its chemical structure was investigated by ^{13}C-NMR (Bruker DPX-300 spectrometer) and FTIR (PerkinElmer system 2000). Thermal stability of xylan-MA was also examined using TGA (Netzsch, STA449C). The scans were run from room temperature to 600°C at a rate of 20°C/min under nitrogen atmosphere.

To prepare xylan-MA/PVA hydrogel, the dried xylan-MA was blended with PVA at various PVA weight contents under acidic condition. The blends were heated at 70°C for 4 h. The obtained crosslinked xylan-MA/PVA blends were washed with deionized water to remove any soluble materials and then dried.

Swelling test

The preweighed crosslinked xylan-MA/PVA blends were immersed in deionized water at room temperature. At certain time, the swollen gels were removed from the water, quickly wiped to remove excess water on the surface, and weighed. The degree of swelling was calculated as follows:

$$DS = (W_w - W_d)/W_d$$

where W_w and W_d are weights of wet and dry blends, respectively.

Compressive strength test

The disc specimens of crosslinked xylan-MA/PVA blends (6 mm in diameter and 3 mm in thickness) were prepared and stored in deionized water for 3 days at room temperature prior to testing. The measurement of relative gel strength of the blends was conducted using a rheometer (Advanced Rheometrics Expansion System). The specimens were placed between parallel plates (25 mm in diameter). The compressive load was then applied at a uniform crosshead speed of 0.02 mm/s until specimen failure occurred. The maximum stress developed in specimen before failure was recorded.
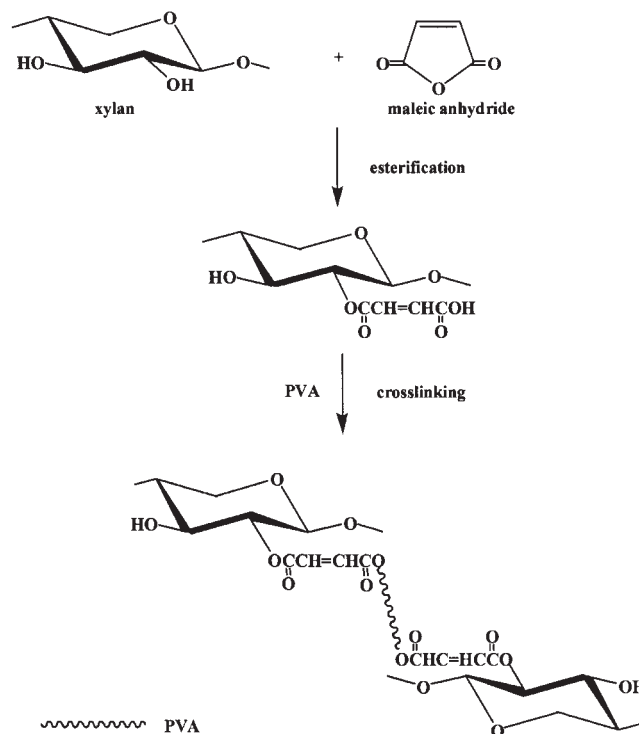

Figure 1 Scheme of preparation of xylan-MA/PVA hydrogel. 55×63 mm^2 (600×600 DPI).

Cytotoxicity test

Direct contact test was used for the cytotoxicity study. The xylan-MA/PVA samples were cut into small pieces and allowed to absorb the growth medium before test. Each hydrated sample was then placed in a 35-mm dish seeded with L929 cells at a density of 6×10^4 cells/dish. After 48 h incubation, cell morphology and the toxic zone were evaluated. The cells were stained with 0.01% neutral red in phosphate-buffered saline for membrane integrity. High-density polyethylene (HDPE) and natural rubber containing carbon black were used as a negative and a positive control, respectively.

RESULTS AND DISCUSSION

Preparation of xylan-MA/PVA hydrogels

The preparation of xylan-MA/PVA hydrogels is illustrated in Figure 1. A hydroxyl group of xylan reacted with a carbonyl carbon of MA to form an ester linkage. A ring opening of MA occurred, yielding maleic-modified xylan containing carboxylic acid groups. The evidence of ester linkages was clearly revealed by ^{13}C-NMR. As seen in Figure 2, two additional peaks at 166.8 and 130.2 ppm, designated to signals of carbonyl and unsaturated carbons of maleic acid, respectively, were observed apart from those at 104.8, 78.8, 77.2, 75.8, and 66.0 ppm, originating from the main five
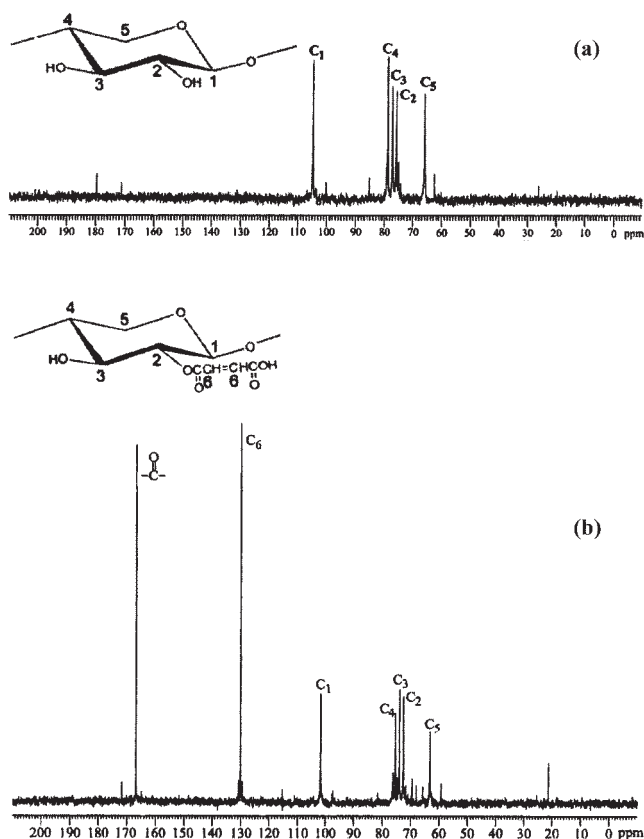
Figure 2 ^{13}C-NMR spectra of (a) xylan and (b) xylan-MA derivative. 66×88 mm^2 (600×600 DPI).

carbon atoms in the xylose repeating unit.[12,17,18] The modified xylan was also verified by FTIR to support the existence of the ester linkages. As illustrated in Figure 3, the esterification of xylan resulted in the
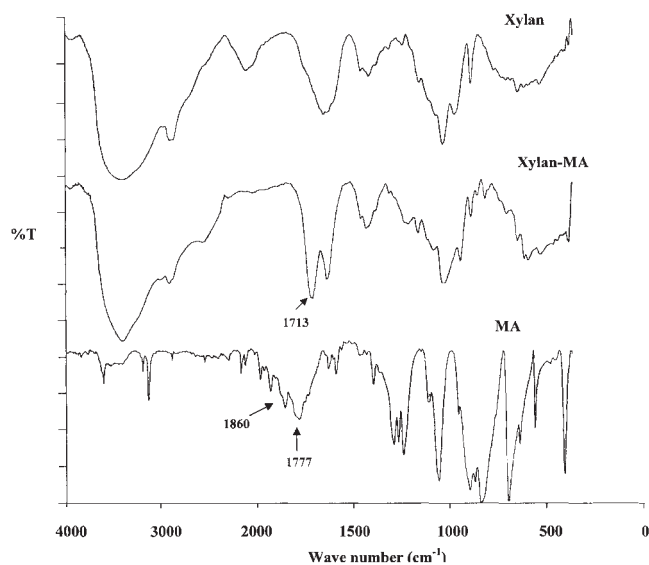

Figure 3 FTIR spectra of xylan, xylan-MA, and MA. 45×45 mm^2 (600×600 DPI).

TABLE I
Compositions of Xylan-MA Derivatives Characterized by ^{13}C-NMR

	Reaction condition		Determined by ^{13}C NMR	
Temperature (°C)	Xylan : MA (weight ratio)	Xylan : MA (mol ratio)	Xylan : MA (mol ratio)	MA content (wt %)
50	1 : 1	1 : 1.35	1 : 1.11	45
50	2 : 1	1 : 0.67	1 : 0.37	21
70	1 : 1	1 : 1.35	1 : 0.89	40
70	2 : 1	1 : 0.67	1 : 0.15	10

formation of a new peak at 1713 cm^{-1}, due to the carbonyl groups linked to xylan. The absence of bands at 1860 and 1777 cm^{-1}, corresponding to asymmetric and symmetric C=O stretch of MA, proved that there was no unreacted anhydride remaining in the resulting product. The incorporation of MA into xylan resulted in the xylan-MA derivative having carboxylic acid groups. These groups acted as crosslinking sites and also promoted the hydrophilicity of the derivative. As a result, the xylan-MA derivative was found easier to be dissolved in water than original xylan. The blend of xylan-MA with PVA in acidic condition underwent an interchain crosslinking, via a typical esterification under a thermal treatment. The carboxylic acid groups of xylan-MA were esterified with the hydroxyl groups of PVA, providing the crosslinked gels with an ability to absorb and hold certain amount of water in their structures.

The effects of reaction temperature and weight ratio of xylan to MA on the esterification are exhibited in Table I. It was evident that the esterification increased by increasing the amount of MA. At the higher reaction temperature (70°C), the amount of incorporated MA was lower than that of the 50°C product. The 70°C product was also found brownish in color, which indicated possible involvement of various side reactions, such as decomposition or acid-catalyzed hydrolysis of xylan. These side reactions were found less favorable at low temperature. Consequently, the esterification was efficiently performed at 50°C with weight ratio of xylan to MA at 1 : 1.

The thermogravimetric curves of xylan and xylan-MA are compared in Figure 4. The weight loss in the temperature range of 70–140°C was assigned to the evaporation of water from the samples. The decomposition temperature of xylan began at 220°C with two maximum at 260 and 420°C. These decomposition stages could be ascribed to backbone scission and following fragmentation of xylan. The thermogram of xylan-MA exhibited a similar pattern to that of xylan, but its degradation occurred at a lower temperature. The shift of the two decomposition peaks of xylan-MA to 190 and 320°C indicated a slight decrease of the
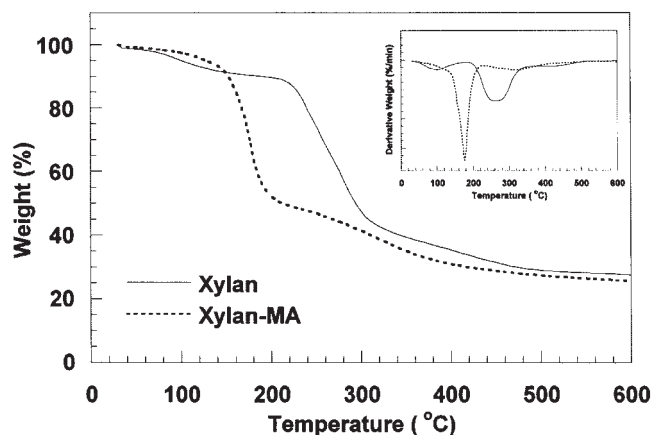
Figure 4 Thermograms of xylan and xylan-MA. 36×26 mm^2 (600 × 600 DPI).

thermal stability resulted from the alteration in chemical structure of xylan.

Swelling test

The xylan-MA/PVA gels were immersed in deionized water and their swelling behaviors were examined. The gels reached their equilibrium swelling within 1 day and showed no sign of structural disintegration thereafter for a few weeks. At equilibrium swelling, the gels exhibited very high water sorption ability in the range of 10–30 times of their original weights, depending upon the contents of MA and PVA in the gels. This finding was clearly demonstrated in Figure 5 where equilibrium swelling of each gel was plotted against weight fraction of PVA. It was expected that the swelling behavior of the gels was directly related to their crosslinking density and hydrophilicity. An
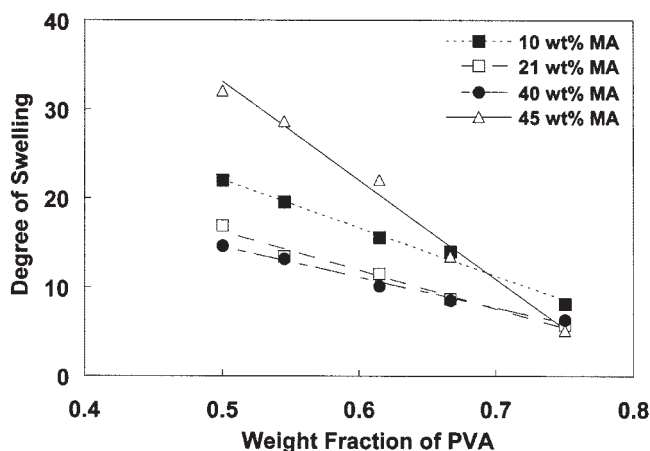

Figure 5 The effect of MA and PVA contents on swelling degree of xylan-MA/PVA hydrogels. (△) 45 wt % MA content; (●) 40 wt % MA content; (□) 21 wt % MA content; (■) 10 wt % MA content. 36×26 mm^2 (600 × 600 DPI).

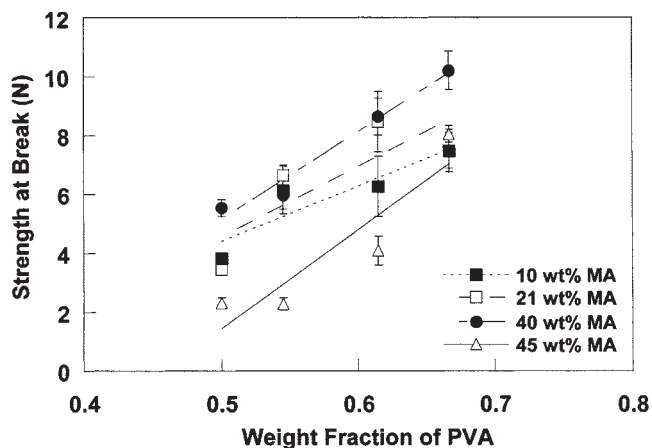**Figure 6** The effect of MA and PVA contents on strength of xylan-MA/PVA hydrogels. (△) 45 wt % MA content; (●) 40 wt % MA content; (□) 21 wt % MA content; (■) 10 wt % MA content. 36×28 mm^2 (600 × 600 DPI).

increasing amount of MA incorporated into xylan yielded more crosslinkable sites to react with PVA, which resulted in a lower swelling degree. Accordingly, at a certain amount of incorporated PVA, the gel having a higher MA content should have a lower swelling degree, as evidently observed for those gels with 10–40 wt % MA content. It was, on the contrary, apparent that when the amount of incorporated MA was very high, i.e., 45 wt %, the gel showed very high water uptake. This was attributed to the fact that carboxylic groups of xylan-MA were not all consumed by the introduction of PVA. The presence of free carboxylic groups, therefore, enhanced the hydrophilicity of the gels and increased their swelling degree. This effect was found more pronounced at low weight fraction of PVA. The effect of PVA content on swelling was straightforward. As observed in Figure 5, a higher PVA content resulted in a greater crosslinking density and, hence, a lower swelling degree.

Compressive strength test

As seen in Figure 6, the strength of the xylan-MA/PVA hydrogels were found dependent on the MA and PVA contents that, in turn, depended on crosslinking density and hydrophilicity of the gels. The results were in good agreement with the swelling results, but in an inverse relation. The greater the amount of MA or PVA incorporated in the gel, the lower swelling degree, but the higher strength of the gel was achieved. The significant reduction of strength found in the high MA content gel (45 wt % MA content) was due to the presence of unreacted carboxylic groups, as previously described.

Cytotoxicity test

Cell morphology and cell membrane integrity were examined after a 48 h exposure to the xylan-MA/PVA
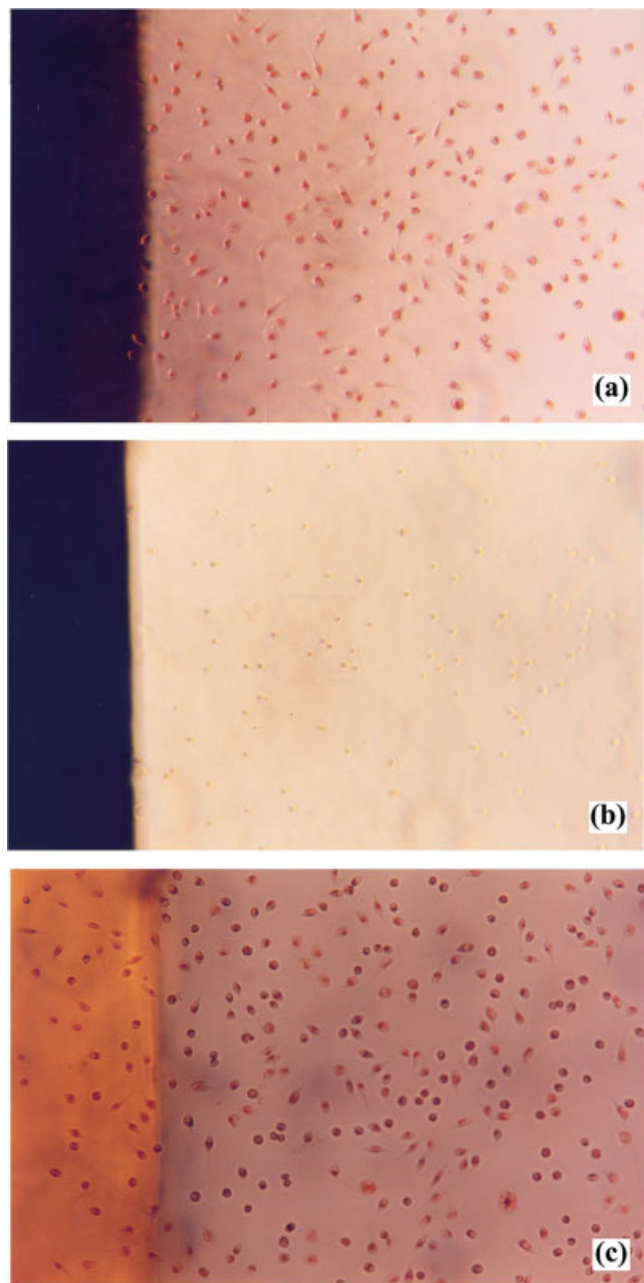
Figure 7 Photographs of the L929 cells cultured for 48 h in contact with: (a) HDPE, negative control; (b) natural rubber, positive control; and (c) xylan-MA/PVA hydrogel. 49 × 98 mm² (600 × 600 DPI). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydrogel. The photographs of L929 cells adjacent to the negative and positive controls as well as the hydrogel are shown in Figure 7. The cells in contact with the hydrogel were found intact, incorporating the neutral red dye, and proliferated without an inhibition zone. The results suggested that this hydrogel was noncytotoxic and there was absence of unreacted monomers or degradation products that may leach into the medium and possibly damage the cells.

CONCLUSIONS

The xylan-MA/PVA hydrogels were developed and could be designed to meet the swelling and strength requirements by variation of the MA and PVA contents in the gels. Modified xylan with MA resulted in functional carboxylic groups attached to xylan via ester bonds, providing reactive sites for further chemical reactions. The differences in the chemical structure of xylan brought about by the esterification were evidenced by ^{13}C-NMR and FTIR. These xylan derivatives exhibited relatively less thermal stability, compared with pure xylan as observed by TGA. The esterification reaction was found efficient with increasing the amount of MA. At high-reaction temperature (70°C), the side reactions were involved, which resulted in a reduction of incorporated MA in xylan. The results indicated that the reaction performed at 50°C with the 1 : 1 weight ratio of xylan to MA was the suitable reaction condition to prepare xylan-MA. The blends of xylan-MA with PVA generated the swellable gels under a thermal treatment. A gel with high-swelling degree possessed a low-compressive strength. The MA and PVA contents, which affected the crosslinking density and hydrophilicity of the gels, were found responsible for swelling and strength behaviors of the gels. The behavior of the L929 cells on the xylan-MA/PVA gel suggested that the gel was noncytotoxic and had a potential for biomedical application.

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