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Maillard reaction products from chitosan–xylan ionic liquid solution

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ABSTRACT

A facile method is reported to prepare Maillard reaction products (MRPs) from chitosan and xylan in co-solvent ionic liquid. UV absorbance and fluorescence changes were regarded as indicators of the occurrence of Maillard reaction. FT-IR, NMR, XRD and TG were used to investigate the structure of chitosan–xylan conjugate. The results revealed that when chitosan reacted with xylan in ionic liquid, the hydrogen bonds in chitosan were destroyed, the facts resulted in the formation of chitosan–xylan MRPs. Moreover, when the mass ratio of chitosan to xylan was 1:1, the Maillard reaction proceeded easily. In addition, relatively high antioxidant property was also noted for the chitosan–xylan conjugate with mass ratio 1:1. So the obtained chitosan–xylan MRP is a promising antioxidant agent for food industry.

1. Introduction

Chitosan, one linear copolymer of β→(1–4) linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glycopyranose, is the deacetylated derivative of chitin extract from shrimp shell, fungi and exoskeleton of insects (Chung, Yeh, & Tsai, 2011). As the only abundant basic polysaccharide in nature, it has drawn much attention for its multi-functional reaction activity, nontoxic and excellent biodegradability properties. Substantial works have been done on the application of chitosan, but some reports indicated that chitosan alone was ineffective for preventing oxidative rancidity (Dash, Chiellini, Ottenbrite, & Chiellini, 2011; Sinha et al., 2004).

Some Maillard reaction products (MRPs) like chitosan–glucose complex exhibited high antioxidative properties without changing the antimicrobial activity of chitosan (Kanatt, Chander, & Sharma, 2008). It has also been reported the quercetin-modified chitosan showed an enhancement of plastic, antioxidant and antimicrobial properties (Torres et al., 2012). There were also some reports about Maillard reaction products between chitosan and hemicelluloses, such as Maillard reacted chitosan–hemicellulose films (Umemura & Kawai, 2008) and xylan–chitosan conjugate as food preservative (Li, Shi, Wang, & Du, 2011). However, chitosan can be only soluble in some specific organic acid, while most hemicelluloses can be only soluble in alkaline solution, when they were mixed together; it is hard to control the reaction. Therefore, it is necessary to find a common solvent for the Maillard reaction between chitosan and hemicelluloses.

Ionic liquids, which are composed of cations and anions, possess negligible vapor pressure, non-flammability, low melting point and good thermal stability (El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007), as a green solvent, it has shown great potential to replace conventional organic solvents for sample preparation. At present, there is no related report about the Maillard reaction between chitosan and hemicelluloses in ionic liquid, which will provide reference technology for deeply industrialization of chitosan and hemicelluloses.

In this study, xylan, a hemicelluloses model, was used to react with chitosan by dissolving in the co-solvent (ionic liquid). FT-IR, NMR, XRD and TG were used to investigate the structure of chitosan–xylan conjugate. At last, the antioxidant activity of chitosan–xylan MRPs was evaluated.

2. Materials and methods

2.1. Materials

Chitosan was purchased from Jinan Haidebei marine bio-engineering Co., Ltd. (Jinan, China). Its degree of deacetylation was 85%, and its weight average molecular weight (M_w) was

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2.0×10^5 g/mol. Xylan isolated from bagasse was purchased from Shanghai Yuanye Biotechnology Co., Ltd. (Shanghai, China). Its M_w was 4.9×10^4 g/mol. Ionic liquid (1-butyl-3-methylimidazolium chloride) was provided by Shanghai Chengjie chemistry Co., Ltd. (Shanghhai, China). All other chemicals were of analytical grade.

2.2. Sugar composition of xylan

The xylan sample was hydrolysed in 4% sulfuric acid for 4 h at 121 °C, the liberated neutral sugars were analyzed by high performance anion exchange chromatography (Dionex ICS-3000, USA) using a Dionex GP50 gradient pump, ED50 electrochemical detector, and a CarbopacTM PA1column. Total sugar and uronic acids were determined colorimetrically by the method of Blumenkrantz and Asboe-Hansen (1973).

2.3. Preparation of chitosan–xylan MRPs

Chitosan and xylan were dissolved in ionic liquid to obtain 1% (w/v) and 2% (w/v) solution, respectively. The above solutions were mixed and co-heated at 110 °C in oil bath. After 0 min, 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 10 h and 24 h, the reaction mixture were withdrawn and cooled in an ice bath. The mass ratios of chitosan to xylan were adjusted to 3:1, 1:1 and 1:3, the obtained MRPs were regarded as CS3–XY1, CS1–XY1 and CS1–XY3, respectively. Chitosan alone with the concentration of 1% (w/v) and xylan alone with the concentration of 2% (w/v) in ionic liquid were heated according to the above method. The samples were taken out after 10 h and they were designated as chitosan-10 h and xylan-10 h, respectively.

2.4. Spectrophotometric analysis

The reaction mixtures were appropriately diluted and measured using a UV-vis spectrophotometer (TU-1810, Beijing, China) with the absorbance at 284 nm and 420 nm. The fluorescence intensity was measured at an excitation wavelength of 343 nm and emission wavelength of 350–600 nm using a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The excitation voltage was 600 V.

2.5. Structure characterization

Fourier transform infrared (FT-IR) spectra were conducted on Vector 33 spectrophotometer (Bruker, Germany) under a dry air at room temperature by the KBr pellets method. The spectra were collected over the range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The crystallinity was investigated by using X-ray diffraction (XRD) analysis on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 50 mA. The relative intensity was recorded in the scattering range of 5–45° (2θ) at a scanning rate of 2°/min.

Solid-state cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra of samples were obtained at 100 MHz using a Bruker AV-III 400 M spectrometer (Germany). Sample was packed in 4 mm zirconia (ZrO_2) rotors and the measurement was performed using a CP pulse program with 1 ms match time and a 2 s delay between transients. Spinning rate was 5 kHz.

2.6. Thermal behavior

Thermogravimetric analysis (TGA) was carried out on a SDT-Q500 simultaneous thermal analyzer (TA, USA) under a nitrogen atmosphere from room temperature to 700 °C and at a heating rate of 20 °C/min.

2.7. Antioxidant activity

2.7.1. Scavenging activity of hydrogen peroxide

5 mg/mL samples solution (3.4 mL) was added to a solution of 43 mmol/L H_2O_2 (0.6 mL), the mixture reacted at 37 °C for 30 min, the absorbance of the solutions was measured at 230 nm. The reaction mixture without test sample was used as control, the samples without reaction agent were used as background. All the analyses were done in triplicates and average values were taken. H_2O_2 scavenging ability was expressed as follows:

$$H_2O_2 \text{ scavenging activity}\,(\%) = \left[1 - \frac{A_1 - A_0}{A_2 - A_0}\right] \times 100,$$

where A_0 was the absorbance of the background, A_1 was the absorbance of the sample and A_2 was the absorbance of the control.

2.7.2. Scavenging activity of superoxide radical

The assay was based on the capacity of the samples to inhibit the photochemical reduction of nitroblue tetrazolium (NBT) in the riboflavin–light–NBT system (Robak & Gryglewski, 1988). Reagent (3 mL), containing 50 mM sodium phosphate buffer of pH 7.8, 13 mM methionine, 2 μM riboflavin, 100 μM EDTA, 75 μM NBT, was mixed with 5 mg/mL sample solution (1 mL). The production of blue formazan was followed by monitoring the increase in absorbance at 560 nm after 10 min illumination from a fluorescent lamp. The entire reaction assembly was enclosed in a box lined with aluminum foil. Identical tubes containing the reaction mixture and water (1 mL) were kept in the dark and served as blanks. Calculations were based on the following equation:

$$O_2^- \text{ scavenging activity}\,(\%) = \left[\frac{A_0 - A_1}{A_0}\right] \times 100;$$

where A_0 was the absorbance of the control and A_1 was the absorbance of the samples.

2.7.3. Metal ion-chelating capacity

The ferrous ion-chelating potency of the samples was investigated according to the method of (Yen & Chung, 1999). Briefly, 5 mg/mL of the samples (1 mL) were added to a solution of 2 mM $FeCl_2$ (50 μL). The reaction was initiated by the addition of 5 mM ferrozine (0.2 mL). After the mixture had reached equilibrium, the absorbance of the solution was measured spectrophotometrically at 562 nm. The ability of the chitosan, xylan and chitosan–xylan MRPs to chelate ferrous ion was calculated using the following equation:

$$\text{Chelating ability}\,(\%) = \left[\frac{A_0 - A_1}{A_0}\right] \times 100;$$

where A_0 was the absorbance of the control and A_1 was the absorbance of the samples.

2.7.4. Measurement of reducing power

The reducing power of the samples was assessed by the method described by (Jayanthi & Lalitha, 2011) with slight modification. 1 mL of reaction mixture, containing 5 mg/mL sample in phosphate buffer (0.2 M, pH 6.6), was incubated with potassium ferricyanide (1%, w/v) at 50 °C for 20 min. 10% (w/v) trichloroacetic acid (2.5 mL) was added and centrifuged at 3000 rpm for 10 min. The upper layer of solution (2.5 mL) was mixed with distilled water (2.5 mL) and 0.1% (w/v) ferric chloride (0.5 mL), then reacted for 10 min. The absorbance values of the reaction mixtures were determined at 700 nm. The absorption indicated the intensity of reducing ability, and an increased absorbance of the reaction mixture indicated an

Table 1
Sugar composition of xylan.

Sugar composition (wt%)			
Xylose	Arabinose	Glucose	Glucuronic acid
87.79	9.33	0.81	2.07

increased reducing power. To 100 μmol/L L-cysteine hydrochloride as a control, reducing power (RP) was calculated as:

$$RP = A_1 - A_{10} - A_0;$$

where A_1 and A_0 are the absorbance for the sample and the blank at 700 nm after being reduced; A_{10} for the sample absorbance at 700 nm by itself.

2.8. Statistical analyses

Data were expressed as the mean standard deviation of the means (S.D.). Analysis of variance was performed by *t*-test using SPSS 19.0 for comparison of H_2O_2 scavenging activity, chelating activity, O_2^--scavenging activity and reducing power between the chitosan–xylan MRPs and chitosan. The data were considered to be significant differences at $p < 0.05$.

3. Results and discussion

3.1. Properties of xylan

Composition of xylan is given in Table 1. This kind of xylan mainly contains arabinose and xylose as neutral sugars, this xylan has less arabinose compared with the water-soluble xylan, in which more than 15% of the backbone should be substituted (Ebringerova, Alfodi, & Hribalova, 1998). Therefore, in this study, the fewer branches resulted in xylan insolubility in water, the xylan can only be solved in alkali, while chitosan can only be solved in acid, and thus ionic liquid (1-butyl-3-methylimidazolium chloride) was used as the co-solvent to solve xylan and chitosan.

3.2. UV absorbance and fluorescence of chitosan–xylan MRPs

Fig. 1 depicts UV absorbance at 284 nm and 420 nm of the MRPs depending on different times. The absorbance at 284 nm and 420 nm were the indicator of Maillard reaction products (Liu & Kitts, 2011). The UV absorbance of all the MRPs showed a sharp increase at the first 6 h of heating, small changes were found with increasing heating time up to 24 h. Moreover, we can find that the absorbance of both pure xylan and chitosan also increased, implying that caramel reaction occurred when pure xylan or chitosan solution were heated alone. Among all the chitosan–xylan mixture, CS1–XY1 and CS1–XY3 have much stronger UV absorbance than xylan or chitosan. Although the xylan content of CS1–XY3 was larger than that of CS1–XY1, the absorbance intensity was similar, suggesting that the content of CS1–XY1 MRP may be more than that of CS1–XY3 MRP. Interestingly, when the mass ratio of chitosan to xylan was 3:1, the UV absorbance increased compared with chitosan but decreased greatly compared with xylan, it suggests that the Maillard reaction was weaker in this case.

As shown in Fig. 2, when pure xylan and chitosan solution were heated alone, xylan did not show great change in fluorescence intensity, while fluorescence intensity of chitosan reached the maximum after 10 h. In contrast, the fluorescence intensity of chitosan–xylan conjugate increased to a maximum within the first several hours, indicating the formation of fluorophores, that is to say, the Maillard reaction between xylan and chitosan happened. But the fluorescence intensity decreased with the increase of the

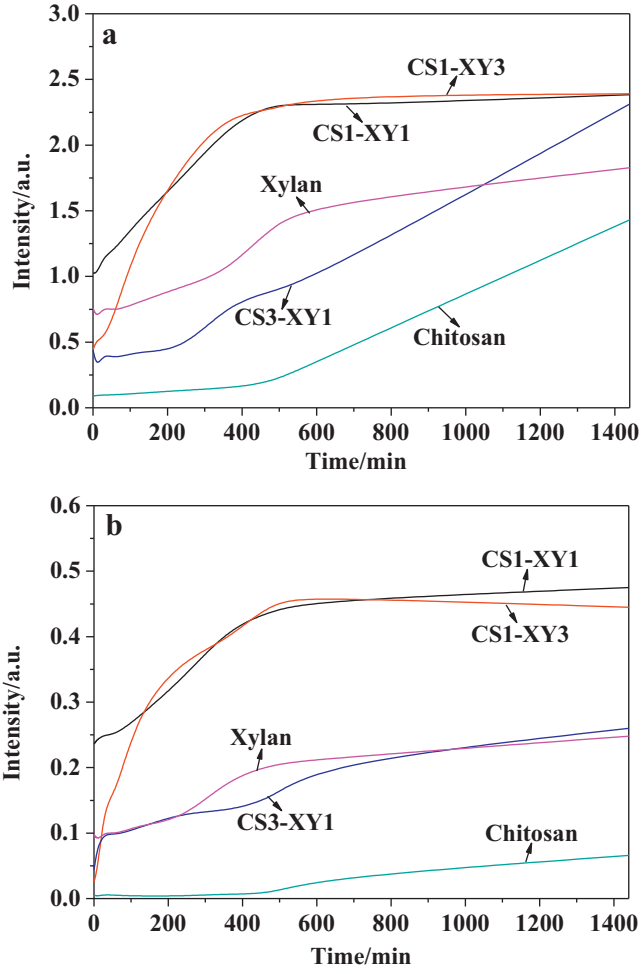

Fig. 1. UV absorbance at 284 nm (a) and 420 nm (b) of chitosan, xylan and chitosan–xylan MRPs.

heating time, it can be explained that during the later stage of Maillard reaction, some of the fluorescence compounds may take part in the formation of melanoidins. Moreover, the fluorescence intensity of CS1–XY1 was the strongest, further confirming that the Maillard reaction happened easily between xylan and chitosan when their mass ratio was 1:1. In addition, CS3–XY1 also showed the

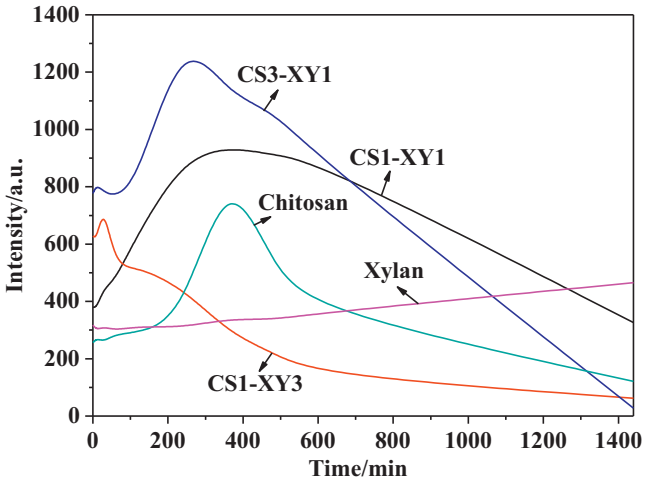

Fig. 2. Fluorescence intensity of chitosan, xylan and chitosan–xylan MRPs.

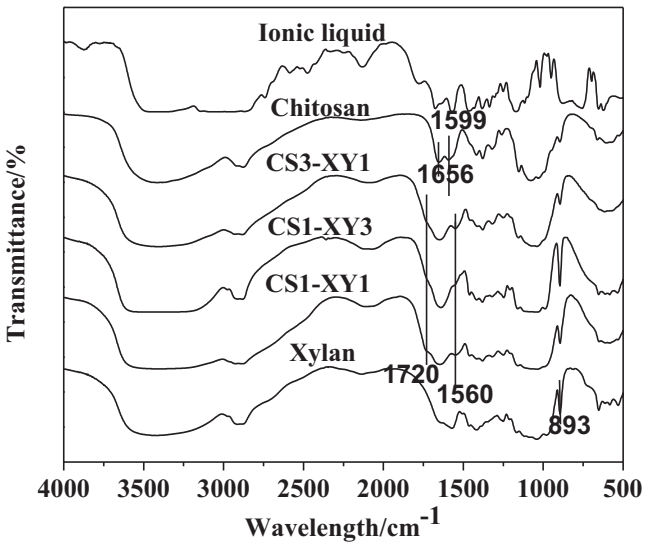

Fig. 3. FT-IR spectra of ionic liquid, chitosan, xylan and chitosan–xylan MRPs.

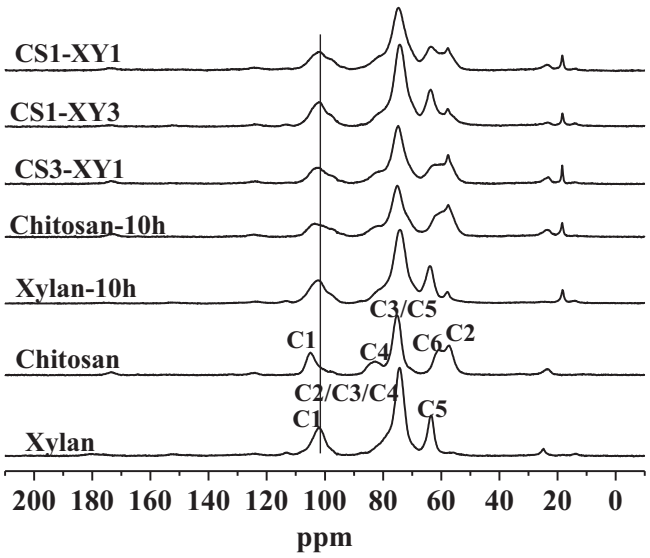

Fig. 4. Solid-state ^{13}C NMR spectra of chitosan, xylan and chitosan–xylan MRPs.

strong fluorescence intensity, which may contribute to the relatively high fluorescence intensity of chitosan, since a few MRPs formed according to the result of UV absorbance. But CS1–XY3 showed weaker fluorescence intensity compared with other samples, it may be induced by the relatively low fluorescence intensity of xylan. What is more, we can see clearly that the absorbance of CS1–XY3, CS3–XY1 and CS1–XY1 reached maximum at 30 min, 240 min and 360 min, respectively. The fact implies that the higher xylan content may accelerate the reaction rate.

3.3. FT-IR analysis

Fig. 3 shows the FT-IR spectra of CS1–XY1, CS1–XY3, CS3–XY1, chitosan, xylan and ionic liquid. It is obvious that the spectra of chitosan–xylan MRPs showed the combined characteristic peak of chitosan and xylan, they did not include the adsorption peak of ionic liquid, indicating that chitosan–xylan MRPs can be separated from ionic liquid totally. In the spectrum of chitosan, the absorption peak at 3480 cm^{-1} was described to O—H stretching combined with N—H stretching vibration, the characteristic absorption band at 1599 cm^{-1} was assigned to the vibration of $-NH_2$ (Umemura & Kawai, 2008). For xylan, a series of bands in the region of 1176–916 cm^{-1} were attributed to the C—O, C—C stretching or C—H bending vibration. The absorption peak at 893 cm^{-1} belonged to the characteristic peak of β-D-glycosidic linkage between the sugar units (Kacurakova, Belton, Wilson, Hirsch, & Ebringerova, 1998).

Compared with chitosan, the characteristic peak at 3480 cm^{-1} shifted to higher wavenumber in the spectra of chitosan–xylan MRPs, revealing that the intermolecular and intramolecular hydrogen bonds in chitosan were weakened (Fan, Hu, & Shen, 2009). Moreover, the absorption peak at 1599 cm^{-1} disappeared while two new peaks at 1560 cm^{-1} and 1720 cm^{-1} appeared in the spectra of chitosan–xylan MRPs. The band at 1560 cm^{-1} and 1720 cm^{-1} were ascribed to the characteristic peaks of stretching C—N group and C=N double group, respectively, indicating the formation of Schiff base (C=N double bond) between the reducing end of xylan and the amino groups of chitosan (Dash et al., 2011). In contrast to the spectra of CS1–XY3 and CS3–XY1 MRPs, the spectrum of CS1–XY1 MRP showed more obvious absorbance at 1720 cm^{-1} and 1560 cm^{-1}, confirming that the content of CS1–XY1 MRP was the most, which coincides with the UV and fluorescence absorbance results.

Compared with xylan, the absorption peaks of CS1–XY1 and CS3–XY1 at 893 cm^{-1} became weaker, indicating the cleavage of the sugar unit of xylan. While this peak of CS1–XY3 became stronger, this may be induced by the unreacted xylan in the sample.

3.4. Solid-state ^{13}C NMR analysis

The results of solid-state ^{13}C NMR are illustrated in Fig. 4. In ^{13}C NMR spectrum of chitosan, the signals at 20.3, 57.5, 61.3, 75.2, 82.4, and 103.5 ppm were attributed to GlcNAc residues, C2, C6, C3/C5, C4 and C1 of chitosan chain, respectively. Chitosan-10 h did not show much difference compared with chitosan, so we can infer that the pyrrole ring structure of chitosan was saved after the reaction, and only hydrogen bonds were broken *via* the Maillard reaction on the amino groups, which coincides with the FT-IR result.

For xylan, the signals at 23.2, 63.2, 75.1 and 102.2 ppm were attributed to acetyl groups, C5, C2/C3/C4 and C1 of xylan chain, respectively. While xylan-10 h had a new signal at 57.0 ppm, this may be induced by the break of β→(1–4) glycosidic bond and the ring-cleavage reaction in xylan, and provided the carbonyl group for the Maillard reaction.

When the polymers heated together, the C1 signal in the MRPs became wider compared with that of xylan, suggesting the formation of Schiff bases at C1 in xylan. Compared to chitosan, C1 signal of the MRPs shifted to higher field, it further demonstrates that there were interaction between chitosan and xylan. Compared with the dominant signal at 57.5 ppm from non-transformed $C—NH_2$ in chitosan, the C2 signals of CS1–XY1 and CS1–XY3 decreased, which may be caused by the reaction between amino group in chitosan and carbonyl group in xylan. It is noted that there was a new peak at 98 ppm in the spectra of MRPs, which was ascribed to the absorption of C=, further confirming the formation of MRPs. In addition, the peak was the strongest in the spectrum of CS1–XY1, so it is further proof that the Maillard reaction proceeded most easily when the mass ratio of chitosan to xylan was 1:1.

3.5. XRD patterns analysis

Fig. 5 shows the X-ray diffraction patterns of CS1–XY1, CS1–XY3, CS3–XY1, chitosan and xylan powder. It has been reported that the crystallization behavior of the xylan-rich hemicelluloses depends on the substituted regions of their main chains (Grondahl, Eriksson, & Gatenholm, 2004). Xylan is mainly amorphous in nature,

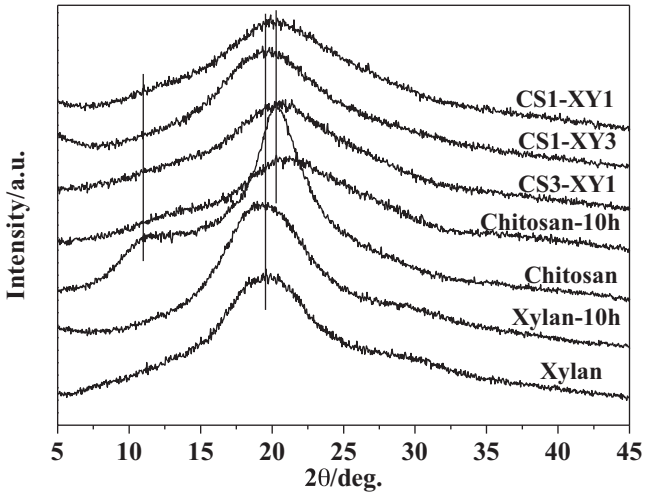

Fig. 5. XRD patterns of chitosan, xylan and chitosan–xylan MRPs.

the substituted sequences may hinder the xylan backbone to approach each other and consequently form crystalline regions (Andrewartha, Phillips, & Stone, 1973). Thus there are only two diffraction peaks at $2\theta = 19.2^\circ$ and $2\theta = 29.5^\circ$. In the XRD pattern of chitosan, the diffraction peaks at $2\theta = 13.7^\circ$ and $2\theta = 21.1^\circ$ were observed, which corresponded to the diffraction peaks of (0 2 0) and (2 0 0) crystal plane. When chitosan and xylan were heated alone in ionic liquid, the diffraction peaks of chitosan at 13.7° and xylan at 29.5° disappeared, revealing the crystallization structures of chitosan and xylan were broken. Moreover, the crystallinity of chitosan–xylan MRPs was lower compared to chitosan and xylan, due to the occurrence of interaction between chitosan and xylan.

According to FT-IR, NMR and XRD results, it can confirm that during the Maillard reaction, the hydrogen bonds in chitosan chain were destroyed to supply more free $-NH_2$, and the ring-cleavage reaction in xylan provided the carbonyl groups, and then the Maillard reaction happened between the amino groups of chitosan and the reducing end of xylan.

3.6. Thermal behavior analysis

The polymer decomposition and the weight fraction of CS1–XY1, CS1–XY3, CS3–XY1, chitosan and xylan were analyzed through thermogravimetric analysis (TG and DTG) and the results are shown in Fig. 6(a). On the TGA curves, the decomposition process can be divided into two stages, the first stage was a weight loss below 100 °C due to loss of water (either adsorbed of bound). At temperature 200–300 °C, the rate of decomposition and weight loss was maximum that mainly corresponds to the degradation of polymers (Sanoop, Mahesh, Nampoothiri, Mangalaraja, & Ananthakumar, 2012).

The amount of remaining polymer at 700 °C for CS1–XY1, CS1–XY3, CS3–XY1, chitosan and xylan were 33.4%, 28.7%, 36.6%, 31.5% and 22.2%, respectively. The residual amount of the MRPs was higher than those of only chitosan and xylan, further proving the occurrence of Maillard reaction between chitosan and xylan. In addition, it can see that the maximum weight loss temperatures (T_{max}) of CS1–XY1, CS1–XY3, CS3–XY1, chitosan and xylan were 229.3 °C, 234.5 °C, 239.6 °C, 303.2 °C and 291.2 °C, respectively. T_{max} of the MRPs were lower than those of only xylan and chitosan, which coincides with the report (Zeng et al., 2007), it further indicates the formation of easily thermal decomposition MRPs. Moreover, CS1–XY1 in all MRPs showed the lowest T_{max}, indicating that the mass ratio of 1:1 was the best Maillard reaction ratio between chitosan and xylan, which coincides with the above analysis.

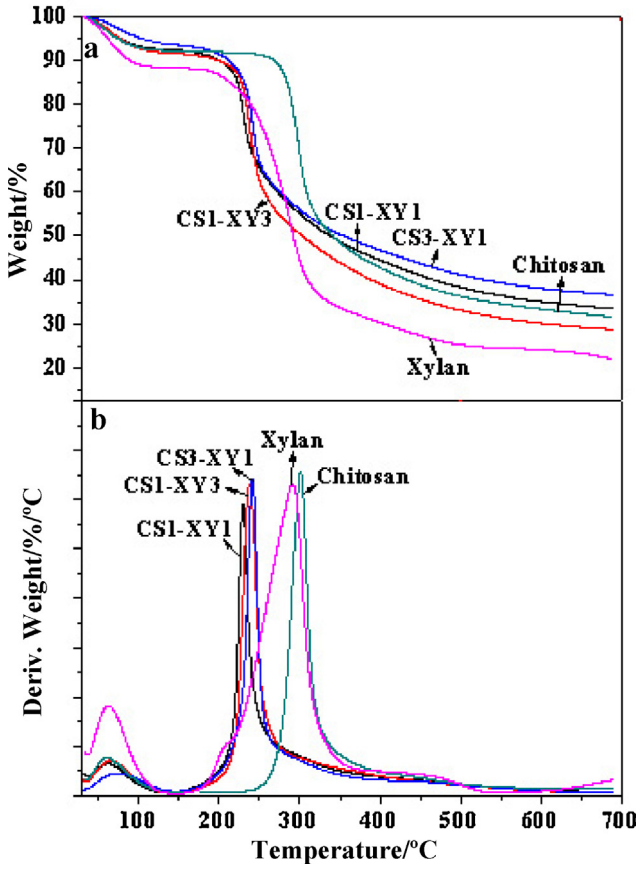

Fig. 6. TG (a) and DTG (b) curves of chitosan, xylan and chitosan–xylan MRPs.

3.7. Antioxidant activity

In this study, four different systems were applied to investigate the antioxidant ability of the chitosan–xylan MRPs. The results are shown in Fig. 7. Chitosan showed relatively high reducing power and scavenging activity and certain chelating capacity, it is not surprising that chitosan *per se* is good antioxidant agent. Chitosan has two hydroxyl groups and one amino group in each monosaccharide unit. The hydroxyl groups can react with free radicals by the typical H-abstraction reaction (Xue, Hirata, Terao, & Lin, 1998). On the other hand, according to free radical theory, the amino groups in chitosan can react with free radicals to form additional stable macroradicals. Therefore, the active hydroxyl and amino groups in the chains are the origin of the scavenging ability of chitosan (Feng, Du, Li, Hu, & Kennedy, 2008).

As shown in Fig. 7(a), it seems that the ability to scavenge peroxyl radical of the MRPs did not improve a lot as compared to chitosan. This may induced by the decrease of amino groups of chitosan after Maillard reaction. However, CS1–XY1 had a significantly ($p < 0.05$) high H_2O_2 scavenging activity compared with chitosan, which reveals that scavenging activity of hydrogen peroxide of CS1–XY1 MRP improved greatly as compared to chitosan.

Superoxide radical scavenging capacity of the chitosan–xylan MRPs was significantly increased ($p < 0.05$) compared with chitosan (Fig. 7(b)). The results may be related to hydroxyl groups in chitosan, intramolecular hydrogen-bond interaction was strong in the original chitosan so that there were not much enough free hydroxyl

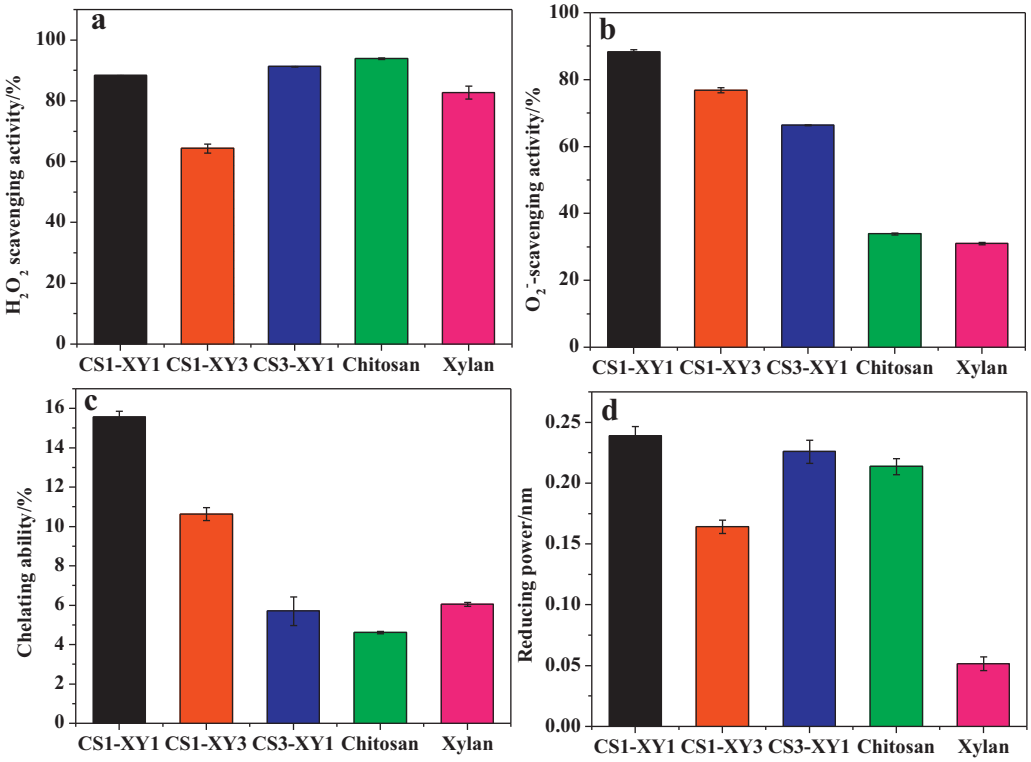

Fig. 7. Antioxidant activity of chitosan, xylan and chitosan–xylan MRPs: (a) scavenging activity of hydrogen peroxide; (b) scavenging activity of superoxide radical; (c) metal ion-chelating capacity; (d) reducing power.

groups. After chitosan reacted with xylan, the intramolecular hydrogen bonds in chitosan were destroyed greatly, more hydroxyl groups might be exposed, which would account for the stronger scavenging activity. In addition, it has been reported that compounds responsible for antioxidant activity are formed during thermolysis of Amadori products in the primary phase of Maillard reaction or could be the heterocyclic products of Maillard reaction (Rao, Chawla, Chander, & Sharma, 2011). Therefore, the MRPs play an important role in antioxidant activity.

In addition, we can find that the chitosan–xylan MRPs showed significantly higher ($p < 0.05$) metal chelating activity than original xylan and chitosan. It coincides with the previous study in which MRPs have been found to be effective as metal-chelating compounds (Rufian-Henares & Morales, 2008). The chelating activity of the MRPs may possibly be attributed to hydroxyl or pyrrole groups originating from the Maillard reaction. Furthermore, it can find that the chelating property of CS1–XY1 was the strongest and that of CS3–XY1 was the weakest, which is in agreement with the above results.

The reducing power of chitosan, xylan and the chitosan–xylan MRPs were determined by the potassium ferricyanide reduction method. From Fig. 7(d), CS1–XY1, CS3–XY1 and chitosan showed relatively high reducing power. Among the MRPs, CS1–XY1 MRP had a significant ($p < 0.05$) reducing power compared with chitosan, which indicates that CS1–XY1 had a relatively high reducing power. The reducing capacity might be due to hydrogen-donating ability, which has exerted antioxidant action by breaking the free-radical chain and donating a hydrogen atom (Niki, 2010). There are many hydroxyl radicals in chitosan chain, which can contribute to the hydrogen-donating ability. After Maillard reaction, the intramolecular hydrogen bonds in chitosan were destroyed, more hydroxyl groups might be exposed, resulting in stronger hydrogen-donating ability. Moreover, intermediate MRPs are known as reductones, these reductones compounds exhibit high reducing power due to their ability to donate hydrogen atoms. So CS1–XY1 showed higher reducing power than chitosan.

In summary, compared with chitosan and xylan, the MRPs shows relatively high antioxidant ability, the better radical-scavenging activity of the conjugates can be contributed to the advanced Maillard reaction product melanoidins, which showed high antioxidant capacity through the formation of reductones, oxygen-scavenging and metal-chelating mechanism (Silvan, van de Lagemaat, Olano, & del Castillo, 2006). Among all the MRPs, CS1–XY1 had the best antioxidant ability.

4. Conclusions

In this study, the Maillard reaction occurred between chitosan and xylan with different mass ratios in ionic liquid, resulting in the destruction of the hydrogen bonds in chitosan and the ring-cleavage reaction in xylan resulted from β→(1–4) glycosidic bond. In all the MRPs, CSI–XY1 turned out to be the best MRP according to the results of UV absorbance, fluorescence changes, FT-IR and solid-state ^{13}C NMR spectra, and CS1–XY1 product showed better antioxidant capacity activity.

Acknowledgements

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