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Controllable antioxidative xylan–chitosan Maillard reaction products used for lipid food storage

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ABSTRACT

Controllable antioxidative xylan–chitosan Maillard reaction products (MRPs) were prepared by co-heating xylan and chitosan at different time periods and used for lipid food storage in lecithin model system and refrigerated pork meat. The results of antioxidant protective effect on lecithin liposome peroxidation induced by 2,2′-azobis(2-methylpropionamidine) dihydrochloride revealed that the MRPs heated for 120 min and 180 min showed much higher inhibitory activity than chitosan or MRP heated for 60 min. In the experiment of fresh pork protection, the MRPs heated for 60 and 120 min retarded the growth of spoilage organisms more effectively. Lipid oxidation potential of the meat, determined by thiobarbituric acid reactive substances, also showed that the samples treated by the MRPs heated for 60 and 120 min had higher acceptance than others. These results demonstrate that the MRPs of xylan and chitosan are promising controllable antioxidative preservatives for lipid food formulations, and the antioxidant behavior depends not only on the antioxidant substances, but also on the interaction of the food systems.

1. Introduction

Hemicelluloses, representing about 20–35% of lignocellulosic biomass, have emerged as an immense renewable resource of biopolymers. Xylan-type polysaccharides are the main hemicellulose components of secondary cell walls and account for 50% of the biomass of annual and perennial plants, but their application potential has not yet been exploited commercially, compared to other polysaccharides, due to the source-dependent diversity, branching, and varying chemical composition (Ebringerova, Hromadkova, & Heinze, 2005). During the latest decade, xylan resourced from different plants have been explored by some research groups and used to produce many novel functional materials (Hansen & Plackett, 2008). For example, xylan from corn cobs is a promising polymer for drug delivery as it could be biodegraded by colon microflora but not be digested in the stomach (Oliveira et al., 2010). Also, many hydrophilic and hydrophobic xylan derivatives, which may have promising applications in plastic and papermaking industries, have been produced by chemical modifications (Fredon et al., 2002; Ren, Peng, & Sun, 2008). Besides, the relatively low molecular weight and structural heterogeneity may offer xylan some special functions, however, until now little information is available in literatures.

Chitosan, the deacetylated derivative of chitin, is a linear aminopolysaccharide. Maillard reaction between the amino groups of chitosan and the aldehydes or ketones of reducing sugars has been reported, and some Maillard reaction products (MRPs) are used as natural emulsifiers, antimicrobial, and antioxidative agents (Kato, 2002). Taking into account the potential exploitation of xylan and the functional properties of chitosan-based MRPs, we have prepared xylan–chitosan conjugates by heating the two biopolymers (Li, Shi, Wang, & Du, 2011). In this report, the antioxidant and antimicrobial activities of the xylan–chitosan MRPs, together with the color and fluorescence changes, were also investigated in order to gain more insight on the Maillard reaction between the two polysaccharides.

Meat and meat products are comparatively highly susceptible to rancidity due to microbial and oxidative spoilage. Thus, delaying lipid oxidation and preventing bacterial growth can have a significant contribution toward the extension of shelf life. In order to achieve these goals, food additives, especially natural products such as plants phenol extract, essential oil, and honey, have been used because of their antioxidative and antibacterial effects (Kerry, McCarthy, Kerry, Lynch, & Buckley, 2001). Chitosan exhibits antimicrobial activity against a range of food-borne microorganisms in several meat products and consequently has attracted attention as a potential natural food preservative (No, Meyers, Prinyawiwatkul, & Xu, 2007). Though it is documented that chitosan minimizes lipid oxidation in different food commodities,

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research on the use of chitosan as an antioxidant in muscle foods is still limited compared to other food products (Suman et al., 2010). Combination of chitosan with natural antioxidants is one way of extending shelf life of the meat products (Georgantelis, Blekas, Katikou, Ambrosiadis, & Fletouris, 2007; Kanatt, Chander, & Sharma, 2008). MRPs also exhibited promising antioxidative and antimicrobial effects and have been used to develop food preservatives. For example, the glucose–lysine MRPs showed higher antioxidant activity than plant phenolics such as cloves, ascorbic acid, and cinnamon in terms of decreased warmed-over-flavor and lipid peroxidation (Jayathilakan, Sharma, Radhakrishna, & Bawa, 2007). Also, the addition of chitosan–glucose Maillard complex to lamb meat increased the shelf life by more than two weeks during chilled storage (Chander, Kanatt, & Sharma, 2008). Similarly, in the study of Chang, Chen, and Tan (2011), pork loins dipped in chitosan–glucose MRPs tended to retard lipid oxidation and microbial spoilage during refrigerated storage, however, little influence was observed on the change of the reactant concentration. We consider that the rapid reaction of small molecular glucose made the Maillard reaction into higher or even final stages in short time at high temperature and this may conceal the difference of the antioxidative ability of the chitosan–glucose MRPs. In our previous study, it has been shown that the xylan–chitosan MRPs with good antioxidant capacity and antimicrobial activity can be used as promising food preservatives (Li et al., 2011). In the present study, the controllable antioxidant activities of xylan–chitosan MRPs, including the inhibition of lipid peroxidation in lecithin liposome systems and the preservative effect on fresh pork during refrigerated storage, were investigated.

2. Materials and methods

2.1. Materials

Chitosan was obtained from Qingdao Yunzhou Ltd. (China) with the deacetylation degree of 95%. Xylan isolated by alkaline extraction of corn cobs was obtained from Shanghai Hanhong Ltd. (China) and the properties were investigated in our last study (Li et al., 2011).

2.2. Preparation of xylan–chitosan MRPs

Chitosan was dissolved in 0.5% (v/v) aqueous acetic acid to obtain 1% (w/v) solution, and filtered to remove insoluble residues. Xylan 1% (w/v) was then dissolved in the chitosan solution and refluxed at 100 °C in an oil bath. After 0 min, 60 min, 120 min, and 180 min, the reaction mixture was cooled to an ice bath. The solutions with different heating time were used directly and coded as XC-0, XC-60, XC-120, XC-180, respectively. Pure xylan and chitosan with the concentration of 1% (w/v) in 0.5% (v/v) aqueous acetic acid were prepared as controls and coded as xylan and CS respectively.

2.3. X-ray diffraction of the MRPs

Diffractograms were recorded in reflection mode in the angular range of 5–40° (2θ) with a D8 Advance X-ray Diffractometer. The Cu Kα radiation generated at 40 kV and 40 mA was monochromatized using a 20 μm Ni filter. Solutions were tested after being freeze-dried and without grinding, while xylan powder was measured directly.

2.4. Molecular weight (M_w) measurements

The M_w profiles of the MRPs were estimated by gel permeation chromatography (GPC) using a TSK-G3000PW gel filtration column and monitored by RI 150 refractive index detector. 0.2 M CH_3COOH/0.1 M CH_3COONa was used as the eluent, and the flow rate was maintained at 1.0 mL/min. Three-fold dilutions of the samples were tested. Pullulan standards (Shodex Standard P-82, Japan) were used for a calibration curve. All data provided by the GPC system were collected and analyzed using the Jiangshen Workstation software package (Dalian, China).

2.5. Reducing power of the MRPs

Measurement of reducing power was the same as our previous report: 1.0 mL of the solution was mixed with 1.0 mL water and 1.0 mL of 1% potassium ferricyanide, and then incubated at 50 °C for 20 min. Trichloroacetic acid (TCA, 10%, 2.5 mL) was added to the mixture and centrifuged at 10,000 × g for 5 min. Then the supernatant (2 mL) was mixed with 2 mL of water and 1 mL of 0.1% ferric chloride. The absorbance at 700 nm was measured, and higher value indicated greater reducing power. There were three parallel samples in each group of the measurements.

2.6. Inhibition of liposome lipid peroxidation

For the antioxidant protection of test compounds, 2 mM 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH) was added into the lecithin liposome (10.0 mg/mL in 0.01 M, pH 7.4 phosphate buffered saline) to initiate lipid oxidation, and the result was measured by the TBA assay modified from Yin, Hwang, and Chan (2002). Briefly, 1 mL of sample was mixed with 0.5 mL of 30% TCA, and then centrifuged at 5000 × g for 5 min. 1 mL of supernatant was mixed with 1 mL of 0.02 M 2-thiobarbituric acid solution (TBA) and heated in water bath at 90–100 °C for 30 min. The absorbance of the pink supernatant was read at 532 nm, and called as A_s. The blank was made with 1.0 mL deionized water substitution for 1.0 mL sample, named as A_c. In order to exclude the interference of aldehydes produced in the Maillard systems, the conjugates were measured directly by the above assay without the addition of AAPH and lecithin, and the absorbance was named as A_m. There were three replicate samples in each group for the measurements, and the inhibition percentage (%) was calculated as formula:

$$\text{Inhibition percentage } (\%) = \left[1 - \frac{A_s - A_m}{A_c}\right] \times 100$$

2.7. Treatment of pork meat with the MRPs

Fresh porcine longissimus muscle, which was obtained from a local meat processing company, was cut into cubes of 1 cm^3, and dipped in the chitosan or MRP solutions for 10 min. Samples without any dipping treatment was used as control. The treated meats were then gently drained on a tissue paper, placed in plastic bags, and stored in the refrigerator at 4 °C for 20 days.

2.8. Microbiological analysis and pH of meat

Total viable counts (TVC) were determined by the pour-plate method. A 10-g sample and 90 mL of sterilized distilled water were homogenized by a meat grinder. Several ten-fold serial dilutions were diluted with sterilized saline. 1 mL of each serial dilution was mixed evenly with 15 mL of liquefied agar. After solidification, it was incubated at 35–37 °C for 48 h. Microbiological data were transformed as $\log_{10}$ colony forming units (cfu) per gram of sample. The pH was measured using a pH meter by adding nine parts of deionized distilled water into one part of homogenized sample. All counts were performed in duplicate.

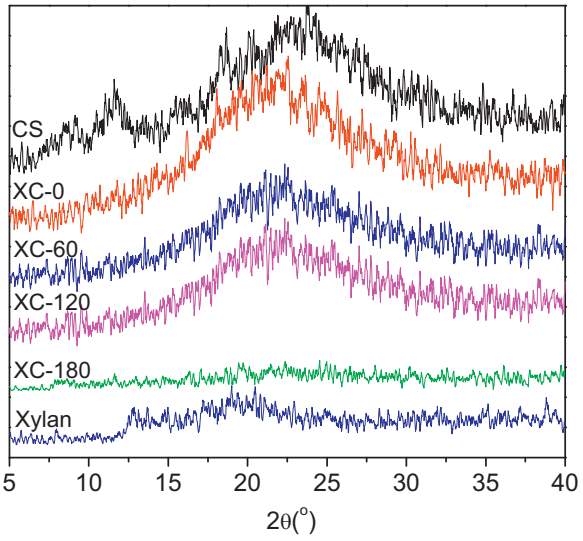

Fig. 1. XRD patterns of xylan, chitosan, and the xylan–chitosan MRPs heated for different time.

2.9. Lipid oxidation of meat

Lipid oxidation was assessed on the basis of the concentration of malondialdehyde (MDA) in the samples according to the thiobarbituric acid reactive substance (TBARS) assay modified from that of Witte, Krause, and Bailey (1970): one gram of the homogenized meat was blended with 5 mL of distilled water and 5 mL of 20% TCA for 5 min, and then centrifuged at 12,000 × *g* for 5 min. 1 mL of supernatant was combined with 2 mL of 0.02 M TBA, heated in a boiling water bath for 30 min, and chilled in ice water for 10 min. The absorbance was read at 532 nm against a blank that contained all the reagents but no meat. The samples were analyzed in triplicate and the results were expressed as μg MDA/kg sample, using a standard curve with serial dilutions of 1,1,3,3-tetramethoxypropane.

2.10. Statistical analysis

An average value of the replicate analyses was used in calculations of sample variation and significance testing. One-way analysis of variance (ANOVA) was done, and values are presented as means ± standard deviations (SD).

3. Results and discussion

3.1. Structure changes of the MRPs

XRD patterns of xylan, chitosan, and their MRPs heated at different time are shown in Fig. 1. It has been reported that the crystallization behavior of the xylan-rich hemicelluloses depends on the substituted regions on their main chains. For example, the xylan from aspen was found to have a relatively higher crystalline peak in the region of 2θ at 17–20° (Grondahl, Eriksson, & Gatenholm, 2004), while the xylan power isolated from bamboo is amorphous but the xylan films are semicrystalline (Peng, Ren, Zhong, & Sun, 2011). Similarly, the arabinoxylans from barley husks was mainly amorphous with small crystalline peaks in the region of 17–20° (Hoije, Grondahl, Tommeraas, & Gatenholm, 2005). Same to the barley husks, the cob-resourced xylan in our experiment was also amorphous because of the low molecular weight and the high ratio of arabinose and xylose. Chitosan exhibited typical crystalline peaks at 13 and 22°. After mixing with xylan, broader peak was showed and the position was shifted to about 21°. For the MRPs of xylan and chitosan, as the heating time prolonged, the intensity of the peak became weaker, for example, the patterns of XC-180 was nearly amorphous, indicating that Maillard reaction reduced the crystallinity of the reactants (Su, Huang, Yuan, Wang, & Li, 2010; Ying, Xiong, Wang, Sun, & Liu, 2011).

Table 1
Change of molecular weight M_w (g/mol) for xylan and chitosan before and after Maillard reaction.

	M_w	M_w
Xylan		2100
CS	118×10^3	
XC-0	118×10^3	2000
XC-60	109×10^3	1900
XC-120	92×10^3	1800
XC-180	77×10^3	1600

Change of the molecular weight of xylan, chitosan, and their MRPs is shown in Table 1. Both of chitosan and xylan appeared unimodal distribution with the weight average M_w of around 118×10^3 and 2100 respectively. When the two polysaccharides mixed together, the molecular weight exhibited bimodal distribution pattern. With the heating time prolonging, the molecular weights of both the bimodal distribution decreased, especially of chitosan. During the Maillard reaction process, a Schiff's base is formed between the carbonyl group and an available amino group, following by an irreversible Amadori rearrangement. The Amadori compounds may then undergo several degradation reactions with the cleavage in sugar unit and produce many colored and high molecular weight compounds called melanoidins in the subsequent advanced and final stages (Silvan, van de Lagemaat, Olano, & del Castillo, 2006). The M_w of sugar–protein Maillard conjugates was usually higher than the corresponding unconjugated sugars due to the combination with proteins (Yadav, Strahan, Mukhopadhyay, Hotchkiss, & Hicks, 2012), but a decrease of the M_w of chitosan was observed in our experiment, perhaps due to the Strecker degradation of amino group residues in the final stages of Maillard reaction.

3.2. Evaluation of pH and antioxidative properties of the MRPs

The pH values the MRPs at different heating time are depicted in Fig. 2. Before heating, the pH of the chitosan–xylan mixture was adjusted to the same as that of chitosan at 4.92. With increasing the heating time to 180 min, the pH was decreased to 4.7. Similar observation has been reported in previous studies. For example, the reaction of porcine plasma protein–sugar MRPs also induced

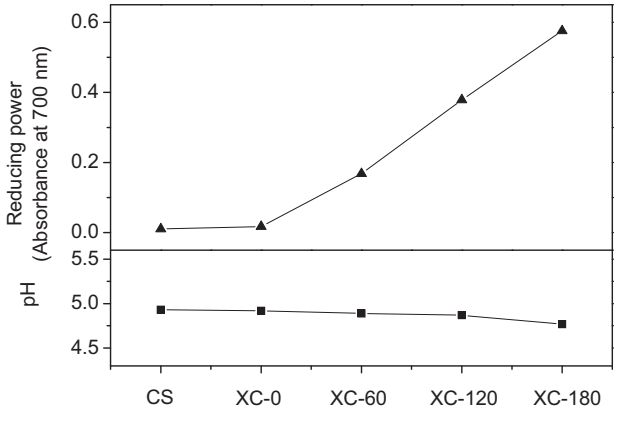

Fig. 2. Change of pH (■) and reducing power (▲) of chitosan and xylan–chitosan MRPs heated for different time.

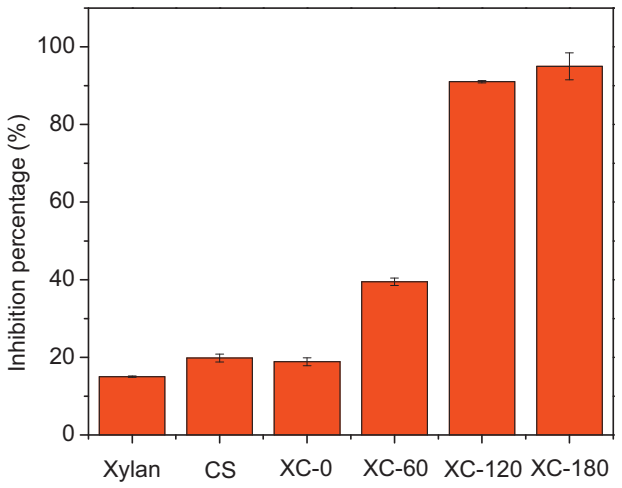

Fig. 3. Lipid peroxidation inhibition percentage of xylan, chitosan, and xylan–chitosan MRPs heated for different time.

pH decreasing as the heating time increased up to 5 h (Benjakul, Lertittikul, & Bauer, 2005), and the phenomena may be due to the production of formic, acetic acid, lactic, levulinic, propionic, citric, and saccharinic acids (Brands & van Boekel, 2002). The difference was that, for the polymers of chitosan and xylan, the variation was not obvious because there were a great quantity of available amino binding sites on the chitosan molecules (deacetylation degree of 95%), and the decrease of amino groups in the reaction were not enough to change the pH in short time. Though Maillard reaction is well-known to progress efficiently at higher pH in aqueous medium, the pH was selected at 4.9 in our experiment because the mixture of acid soluble chitosan and xylan would be gelled at higher pH when heating time was longer (Kosaraju, Weerakkody, & Augustin, 2010).

The antioxidant capacity of the MRPs was evaluated by the measurement of reducing power, with the result shown in Fig. 2. The xylan–chitosan MRPs exhibited an increasing reducing power when prolonging the heating time, while there was no any noteworthy reducing activity of chitosan. The better antioxidative activity of the Maillard reaction products are generally associated with the presence of reductones of the advanced product melanoidins, which act through a chain breaking, oxygen scavenging, free radical direct scavenging, and metal chelating mechanism (Silvan et al., 2006). Under the same conditions, the reaction rate of polysaccharides between chitosan and xylan was lower than that of low molecule reactants, which would result in a slower change of antioxidant activity, for the steric hindrance of the long chains of the polymers delayed the formation of intermediate compounds. Thus it is beneficial to prepare a controllable antioxidant by the two polysaccharides.

3.3. Antioxidant effectiveness of the MRPs in lecithin liposome system

MRPs were reported to have the capability of forming stable free radicals thus causing the inhibition of lipid oxidation. Fig. 3 shows the antioxidant effect of the xylan–chitosan MRPs in an AAPH-initiated lecithin liposome system. Xylan, CS, and XC-0 exhibited low inhibition. While increasing the heating time of MRPs, the inhibition effect increased, indicating better antioxidative characteristics. For example, the inhibition percentage of XC-120 and XC-180 were 91.0 and 95.0% respectively, much higher than 39.4% of XC-60. Similar Maillard reaction conjugate has been found to evolve stable free radicals, and interact with lipid free radicals, causing an inhibition of the lipid oxidation in methyl linoleate system (Jayathilakan & Sharma, 2006).

3.4. pH measurement of pork meat during storage

The effect of MRPs on pork meat storage during 20 days was then studied by the measurement of pH, microorganisms, and lipid oxidation. It can be seen from Fig. 2 that the chitosan and MRP solutions had the same pH value, but the meats treated with these solutions showed large differences during storage. As shown in Table 2, the pH of the control was decreased to 5.81 from 6.03 in the first day, followed thereafter by slight increase to 5.94 at the 9th day, and jumped to 7.55 at the 15th day. All treatments exhibited a distinct decrease of pH in the first day; from 1st day to 6th day, a gradual increase was showed and there were no significant differences ($p > 0.05$) among them, while the pH began to increase with different speeds after 9 days. The initial pH decrease of the control may be attributed to the dissolution of CO_2 in the sample, while the lower pH value of the treated samples in the first few days was evidently influenced by the solvent of the treating solutions, acetic acid. The increase of pH was due to the accumulation of basic compounds such as ammonia derived from microbial action. Though the groups treated by MRPs showed lower pH than that by chitosan during the storage, it can be easily seen that the samples treated by XC-180 had significantly higher pH than that by XC-60 and XC-120, which meant that the over-reacted xylan–chitosan MRPs could not protect the fresh meat from deterioration, while the initial MRPs exerted higher effectiveness.

3.5. Microbiological analysis of pork meat during storage

The results of microbiological analysis of the meats during 20 days storage period are presented in Table 3. At the first day, the total viable counts of the samples treated with chitosan or MRPs were approximately 1 log cfu/g, which was lower than the control. After 9 days storage, the total counts in the control samples nearly exceeded the maximum acceptable level (10^7 cfu/g) (Chris & Melody, 1999), while the values in chitosan and the MRPs addition samples were below the level during 20 days storage, indicating significant inhibition of microbial growth ($p < 0.05$). Taking into consideration of the pH value of the treated samples in the first day, it is apparent that the growth inhibition of microorganisms became stronger if some acidifying substance (acetic acid) was added. The groups treated with XC-60 and XC-120 had comparatively lower microbial counts, whereas the counts of samples containing CS and XC-0 slightly exceeded 10^7 cfu/g at the 20th day of storage, demonstrating that the xylan–chitosan MRPs retarded the growth of microorganisms of fresh pork samples during refrigerated storage. In literatures, the MRPs have been shown to exhibit antibacterial activities, for example, Huang, Huang, Huang, and Chen (2007) have found that MRPs from chitosan and xylose had antibacterial activity in the storage of fresh noodle. Different antibacterial mechanisms of the MRPs were reported: Nakamura, Kato, and Kobayashi (1992) believed that the MRPs can destabilize the outer membrane and inhibit the growth of bacterial cells due to their excellent surfactant properties, while Rufián-Henares and Morales (2006) have proved that melanoidins of MRPs could be responsible for the antimicrobial activity. In spite of this, the meat treated with XC-180 had much higher microbial counts than that with XC-60 and XC-120 during the storage, indicating the ineffectiveness of longer time heated xylan–chitosan MRPs in inhibiting the growth of microbial. The reason was that when prolonging the heating time, the small molecular compounds of final stage Maillard products could not inhibit the microbial growth, which was consistent with the result of pH above.

Table 2
pH change of fresh pork treated with xylan–chitosan MRPs during refrigerated storage at 4 °C for 20 days.

Storage time (days)	Control	Treatment				
		CS	XC-0	XC-60	XC-120	XC-180
0	6.03 ± 0.02	–	–	–	–	–
1	5.81 ± 0.01	5.56 ± 0.03^{x}	5.54 ± 0.02^{x}	5.50 ± 0.04^{x}	5.53 ± 0.02^{x}	5.52 ± 0.02^{x}
3	5.73 ± 0.02^{a}	5.60 ± 0.04^{ax}	5.65 ± 0.01^{x}	5.64 ± 0.01^{ax}	5.65 ± 0.01^{ax}	5.65 ± 0.01^{ax}
6	5.77 ± 0.03^{a}	5.62 ± 0.03^{ax}	5.65 ± 0.03b^{xy}	5.63 ± 0.02^{ax}	5.66 ± 0.02^{axy}	5.68 ± 0.02^{axy}
9	5.94 ± 0.03	5.65 ± 0.01^{ax}	5.67 ± 0.02^{axy}	5.69 ± 0.03^{xy}	5.69 ± 0.01^{axy}	5.74 ± 0.04^{b}
15	7.55 ± 0.04	5.98 ± 0.02	5.70 ± 0.03^{ax}	5.72 ± 0.02^{x}	5.70 ± 0.02^{ax}	5.80 ± 0.02^{b}
20	–	6.34 ± 0.05^{x}	6.26 ± 0.07^{x}	5.82 ± 0.02	5.98 ± 0.03	6.51 ± 0.03

^{ab} Means within the same column without the same superscripts are significantly different ($p < 0.05$).
^{xy} Means within the same row without the same superscripts are significantly different ($p < 0.05$).

Table 3
Total viable counts ($\log_{10}$ cfu/g) in fresh pork treated with xylan–chitosan MRPs during refrigerated storage at 4 °C for 20 days.

Storage time (days)	Control	Treatment				
		CS	XC-0	XC-60	XC-120	XC-180
0	4.85 ± 0.15	–	–	–	–	–
1	5.05 ± 0.20	3.95 ± 0.16^{x}	3.96 ± 0.04^{x}	3.94 ± 0.08^{x}	3.94 ± 0.23^{x}	3.99 ± 0.06^{x}
3	5.72 ± 0.09	4.82 ± 0.23^{x}	4.85 ± 0.16^{x}	4.76 ± 0.16^{xy}	4.55 ± 0.11^{ay}	4.65 ± 0.11^{y}
6	6.24 ± 0.11	5.38 ± 0.06^{x}	5.31 ± 0.24^{x}	5.18 ± 0.14^{xy}	4.78 ± 0.22^{ay}	5.65 ± 0.09
9	6.88 ± 0.04	5.73 ± 0.39^{x}	5.73 ± 0.02^{x}	5.67 ± 0.28^{axy}	5.32 ± 0.16^{by}	5.91 ± 0.21^{x}
15	10.74 ± 0.67	5.90 ± 0.11^{x}	6.10 ± 0.13^{x}	5.71 ± 0.03^{ay}	5.64 ± 0.22^{by}	6.33 ± 0.31^{x}
20	–	7.28 ± 0.23^{xz}	7.60 ± 0.35^{x}	5.98 ± 0.18^{y}	6.02 ± 0.12^{y}	7.06 ± 0.16^{z}

^{ab} Means within the same column without the same superscripts are significantly different ($p < 0.05$).
^{xyz} Means within the same row without the same superscripts are significantly different ($p < 0.05$).

3.6. Lipid oxidation of pork meat during storage

Results of the TBARS values in meat are presented in Table 4. Sheard et al. (2000) indicated MDA concentration of 500 μg/g was the threshold value of rancidity perception by consumers. Control samples in the present study had the MDA of 476.0 and 597.7 μg/g at 9 and 15 days respectively, and would therefore be perceived as rancid already after the 9 days of storage, whereas in the remaining four treatments, TBARS values were well below the limiting threshold for the acceptability until the end of the storage period. Among them, the MDA concentration of the chitosan treated sample reached 337.8 μg/g at 20 days, close to the value of XC-0 at 305.8 μg/g. The effectiveness of chitosan on the oxidative stability of meat has already been demonstrated (Georgantelis et al., 2007; Kanatt et al., 2008), and the mechanism is related to the chelation on free iron released from hemoproteins (Shahidi, Arachchi, & Jeon, 1999). The incorporation of xylan into chitosan solution did not improve the protection of the meat samples against lipid oxidation. In comparison with the control and chitosan treated groups, MRPs of XC-60 and XC-120 prevented peroxidation of the meat by extending the induction period, which indicated that the tested MRPs added to the pork meat showed good antioxidant properties. However, the TBARS value of the XC-180 treated group was higher than the XC-60 and XC-120 treated samples, indicating that the longer reacted MRPs could not prevent the oxidation of the pork meat in long time storage, which was well consistent with the results of pH and microbiological analyses.

The XC-120 and XC-180 solutions showed higher antioxidant activities than XC-60 from the reducing power result of Fig. 2, and this was the same as the antioxidant effectiveness in lecithin model system shown in Fig. 3, but the pork meats treated with XC-60 and XC-120 exhibited better acceptance than that with XC-180. It is demonstrated that the antioxidant behavior of MRPs depends not only on the antioxidant substances, but also on the interaction of the food systems. Longer time heating resulted in relatively higher antioxidant activity contributed by both intermediate and melanoidins, but the low molecular weight aldehydes and other carbonyl compounds in the intermediates may influence the antioxidant effect because of their interaction with the systems. In the measurement of lecithin liposome system detection, the interference of aldehydes produced in the Maillard systems on the TBA detection has to be excluded, though the method has been widely employed in the determination of autoxidative alterations of fats and oils (Guillen-Sans & Guzman-Chozas, 1998). When the MRPs were used for meat storage, the small molecules would permeate into the local pork tissue and lost the protective effect in wide range for long time, and this may be the reason which made XC-180 treated group deteriorated rapidly. Also, it can be found that

Table 4
Thiobarbituric acid value (TBA; μg MDA/kg sample) of fresh pork treated with xylan–chitosan MRPs during refrigerated storage at 4 °C for 20 days.

Storage time (days)	Control	Treatment				
		CS	XC-0	XC-60	XC-120	XC-180
0	104.5 ± 3.2	–	–	–	–	–
1	138.9 ± 7.2^{x}	131.3 ± 32.1^{x}	133.0 ± 3.3^{x}	125.7 ± 10.9^{x}	124.9 ± 17.6^{x}	125.3 ± 14.4^{x}
3	223.3 ± 20.9	186.0 ± 10.5^{ax}	193.3 ± 21.3^{ax}	171.7 ± 33.3^{ax}	133.8 ± 8.8	174.3 ± 6.5^{ax}
6	357.9 ± 24.8	215.8 ± 21.0^{abx}	212.8 ± 21.8^{abx}	185.7 ± 7.8^{aby}	183.9 ± 11.1^{y}	194.5 ± 40.3^{abxy}
9	476.0 ± 85.1	237.8 ± 11.5^{bx}	230.0 ± 16.4^{bx}	214.2 ± 20.5^{bx}	207.8 ± 1.0	238.1 ± 34.0^{bcx}
15	597.7 ± 79.9	282.0 ± 11.5^{x}	274.9 ± 5.0^{cxy}	251.7 ± 6.9^{cz}	240.6 ± 12.2^{z}	261.9 ± 30.1^{cyz}
20	–	337.8 ± 5.6^{x}	305.6 ± 26.2^{cx}	280.4 ± 14.4^{cy}	284.2 ± 11.9^{y}	329.7 ± 14.0^{x}

^{abc} Means within the same column without the same superscripts are significantly different ($p < 0.05$).
^{xyz} Means within the same row without the same superscripts are significantly different ($p < 0.05$).

the oxidation protection of the MRPs was responsible for insignificant difference in the detection of microorganisms and pH during the storage.

4. Conclusions

In this work, a controllable antioxidative xylan–chitosan MRPs has been evaluated and developed for lipid food preservation. The crystal form of the two polymers changed much with the molecular weights decreased for the long time reaction MRPs. The antioxidative effects on lipid peroxidation showed that the MRPs tended to protect the peroxidation of lecithin liposome induced by AAPH. The fresh pork treated by the early MRPs after 60 and 120 min of reaction deteriorated less rapidly and was judged more acceptable than all the other samples from the detection of pH, microbiological analysis, and lipid oxidation. Thus, the Maillard reaction xylan–chitosan MRPs can be used as a promising candidate material for lipid food storage.

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