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Miscibility studies of the blends of chitosan with some cellulose ethers

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Abstract

The polymeric films have been prepared based on blends of chitosan with two cellulose ethers—hydroxypropylmethylcellulose and methylcellulose by casting from acetic acid solutions. The films were transparent and brittle in a dry state but an immersion of the samples in deionized water for over 24 h leads to their disintegration or partial dissolution. The miscibility of the polymers in the blends has been assessed by infrared spectroscopy, wide-angle X-ray diffraction, scanning electron microscopy and thermal gravimetric analysis. It was shown that although weak hydrogen bonding exists between the polymer functional groups the blends are not fully miscible in a dry state.

Keywords: Chitosan; Cellulose ethers; Blends; Miscibility; Hydrophilic films

1. Introduction

The blending of polymers, which results in preparation of new materials with improved physicochemical and mechanical properties, has received considerable attention of researchers in the past several decades. The final properties of the blends are determined by the miscibility of the polymers, which is greatly favored by formation of intermolecular hydrogen bonds between the component polymers (Coleman & Painter, 1995; He, Zhu, & Inoue, 2004; Jiang, Mei, Maoliang, & Hui, 1999).

Chitosan is a polyaminosaccharide, which is produced by partial *N*-deacetylation of chitin. Chitosan exhibits unique physicochemical properties and it is highly suitable for biomedical application due to its biocompatibility, non-toxicity, biodegradability, etc. In the past few years a number of publications appeared on the blending of chitosan with various polymers such as poly(vinyl alcohol) (Mucha & Pawlak, 2005; Pawlak & Mucha, 2003), poly(*N*-vinyl pyrrolidone) (Sakurai, Maegawa, & Takahashi, 2000), poly(ethylene oxide) (Amiji, 1995), starch (Pawlak & Mucha, 2003), cellulose (Twu, Huang, Chang, & Wang, 2003; Wu, Yu, Mi, Wu, Shyu and Peng, 2004) and its derivatives (Mucha & Pawlak, 2005; Pawlak & Mucha, 2003), etc.

Earlier Suto and Ui (1996) have reported on the chemical cross-linking of chitosan/hydroxypropylcellulose blends with glyoxal and glutaraldehyde. Based on the similarity of the backbones of chitosan (CHI) and hydroxypropylcellulose (HPC) they assumed that these polymers are miscible in the blend. The cross-linked films were shown to be amorphous, although the uncross-linked films retained cholesteric liquid crystalline order.

Pawlak and Mucha (2003) reported that the CHI/HPC blends form transparent homogeneous films at any polymer ratio, which is the result of strong hydrogen bonding interactions between the functional groups of the component polymers. Moreover, the presence of HPC in the blend was found to improve the thermal stability of CHI. The blends exhibited two stages of decomposition characteristic for both polymers. Later on the same authors (Mucha & Pawlak, 2005) have studied the CHI/HPC blending by dynamic mechanical thermal analysis and differential scanning calorimetry and found that this system undergoes phase separation, which occurs more drastically upon removal of water traces. The water molecules in this system were found to be an active compatibilizer, which works as a 'glue' acting by formation of additional hydrogen bonds.

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In the present work, we have attempted to clarify the question on miscibility of chitosan with two cellulose ethers—hydroxypropylmethylcellulose (HPMC) and methylcellulose (MC) by infrared spectroscopy, wide-angle X-ray diffraction, scanning electron microscopy and thermal gravimetric analysis.

2. Experimental part

2.1. Materials

Chitosan of food grade with M_w 105 kDa and deacetylation degree 95.7% was purchased from Shanghai Seaflag Biochemistry Product Co. Ltd (The viscosity of its 1% solution in 1% acetic acid at 20 °C was 50 cp).

HPMC with viscosity of 2% aqueous solution at 20 °C is 60 cP and MC with viscosity of 2% aqueous solution is 550 cP were purchased from Shanghai Chemical Agent Corp.

2.2. Preparation of the films

CHI-MC and CHI-HPMC blends were prepared by casting 0.1 M solutions of polymers in 1% acetic acid on 2×2×1 cm poly(tetrafluoroethylene) surface with subsequent drying on air at room temperature for several days. Before casting the solution mixtures were sonicated using 200-W probe-type sonicator (JHN-M-4E, Shanghai Jump Ultrosonica Equipment Co., China).

Table 1
FTIR absorption bands in CHI-HPMC and CHI-MC blends

Blend CHI/cellulose ether, wt%					
100:0	80:20	50:50	20:80	0:100	Assignment
CHI/HPMC					
3448	3312	3394	3377	3415	OH- and NH-stretching
3363					
3313					
2907	2918	2918	2912	2927	CH-stretching
2867	2842	2842	2847	2858	
1650	1634	1634	1640	1634	C=O stretching (amide I), water in the amorphous region
1578	1542	1553	1547	–	NH-bending (amide II)
1413	1416	1405	1410	1402	CH- and OH-vibrations
	1309	1317	1318		
1148	1153	1153	1153	1110	Anti-symmetric stretching of the C-O-C bridge
1066	1071	1061	1055	1055	Skeletal vibrations involving the C-O stretching
	1017				
CHI/MC					
3448	3350	3383	3306	3454	OH- and NH-stretching
3363					
3313					
2907	2918	2918	2924	2907	CH-stretching
2867	2864	2876	2847	2836	
1650	1646	1634	1635	1645	C=O stretching (amide I), water in the amorphous region
1578	1541	1553	1558	–	NH-bending (amide II)
1413	1405	1410	1405	1377	CH- and OH-vibrations
	1340	1340	1336	1306	
1148	1148	1150	1150	1188	Anti-symmetric stretching of the C–O–C bridge
1066	1071	1066	1061	1055	Skeletal vibrations involving the C–O stretching

2.3. Infrared spectra

The FTIR spectra of the polymeric films were recorded using a FT-IR spectrophotometer (AVATAR370, Nicolet, USA) in the region of 4000–500 cm^{-1}.

2.4. Wide-angle X-ray diffractograms

X-ray diffraction patterns of the polymers and their blends were determined with a diffactometer (D/MAX2550, Rigaku, Japan). The operation conditions were as follows: power 12 kW; range from 5 to 80° and scanning speed, $2\theta = 8°$/min.

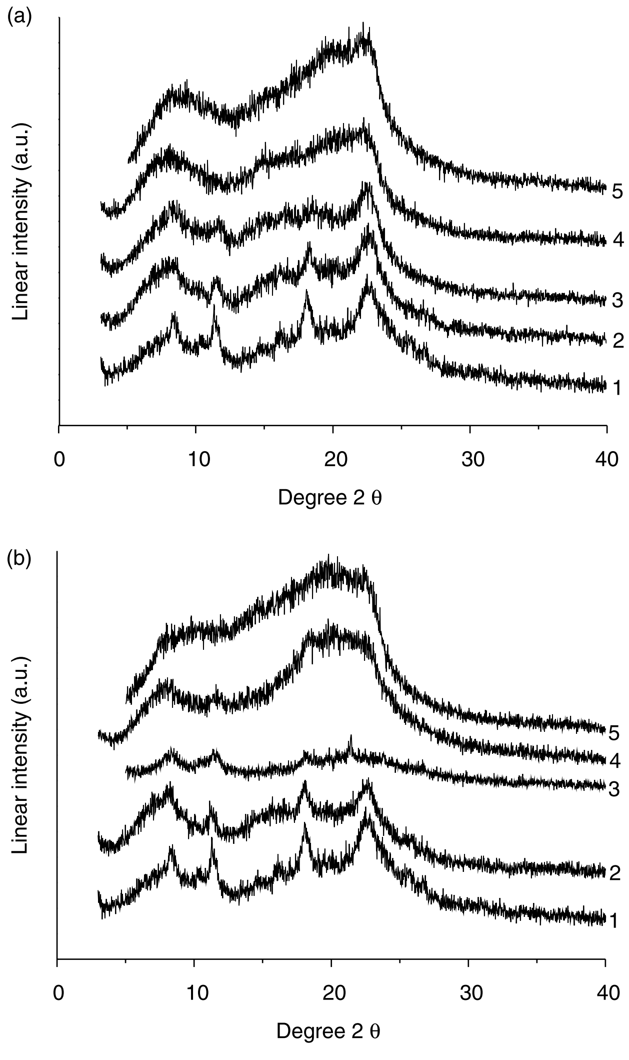


Fig. 1. (a) WAXD diffractograms of CHI/HPMC blends containing 0 (1), 20 (2), 50 (3), 80 (4), 100 wt% (5) of HPMC. (b) WAXD diffractograms of CHI/MC blends containing 0 (1), 20 (2), 50 (3), 80 (4), 100 wt% (5) of MC.

2.5. Scanning electron microscopy

The images were taken from the fracture surface of the materials, which were preliminary frozen in liquid nitrogen and covered by gold vapours.

2.6. Thermal gravimetric analysis

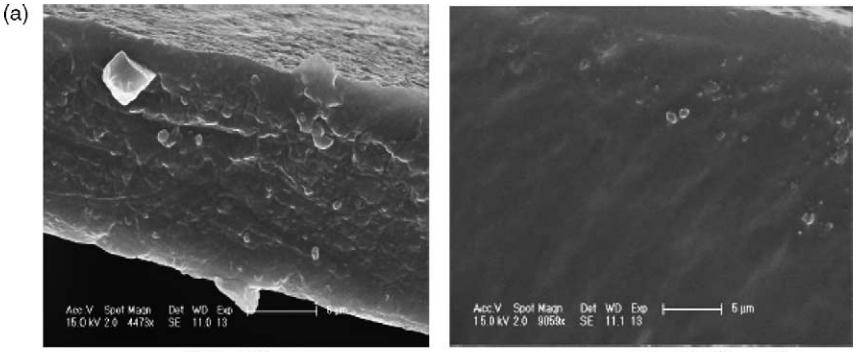
The thermal analysis experiments were conducted using simultaneous thermal analysis (STA 409 PC, Netzsch, Germany).

3. Results and discussion

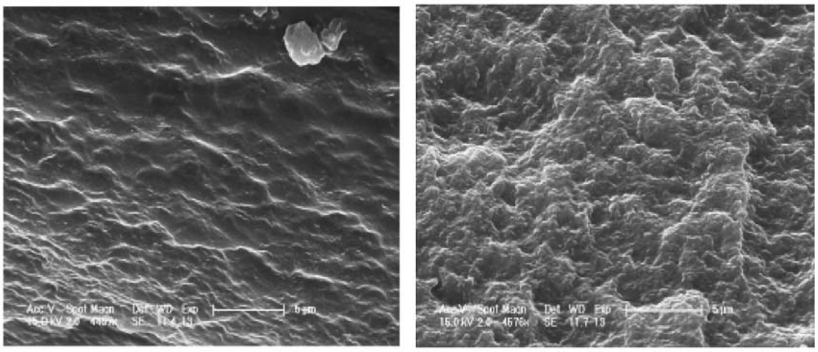
The films prepared based on blends of CHI and cellulose ethers (HPMC and MC) were transparent and brittle in a dry state. An immersion of the films in deionized water for over 24 h leads to their disintegration or partial dissolution.

The films were examined by Furrier-transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA).

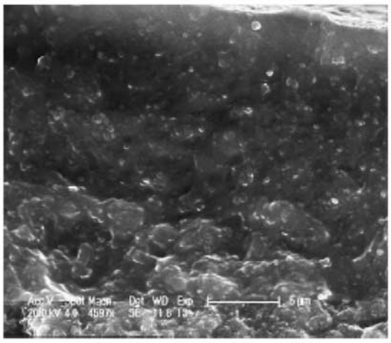
The data on infrared spectra of the pure components and the blends are summarized in Table 1 with assignment of the absorption bands. The spectrum of pure CHI film shows the presence of the absorption bands at 3452, 3363, 3313, 2907, 2867, 1650, 1578, 1413, 1390, 1336, 1263, 1148, 1066, 1032 and 999 cm^{-1}. The bands at 3452, 3363 and 3313 cm^{-1} can be due to the OH-stretching, which overlaps with NH-stretching in the same region. The peaks at 2907 and 2867 correspond to CH-stretching. The bands at 1650 and 1578 cm^{-1} are C=O stretching (amide I) and NH-bending (amide II). The absorption bands at 1148 cm^{-1} (anti-symmetric stretching of the C–O–C bridge), 1066 cm^{-1} and 1032 cm^{-1} (skeletal vibrations involving the C–O stretching) are characteristics of chitosan polysaccharide structure. The spectral features of pure



CHI 100 wt % HPMC 100 wt %

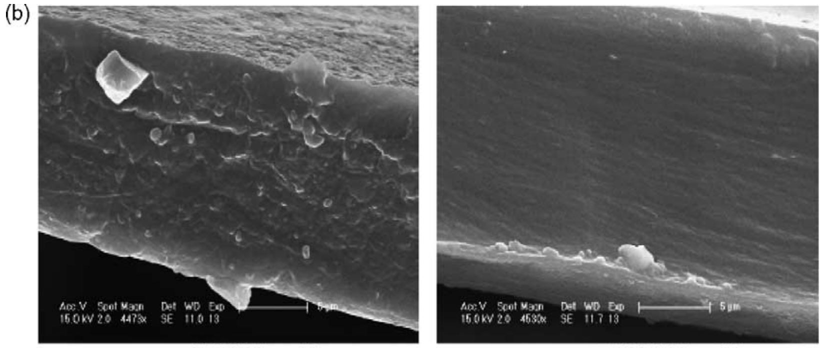


CHI/HPMC 20:80 wt % CHI/HPMC 50:50 wt %

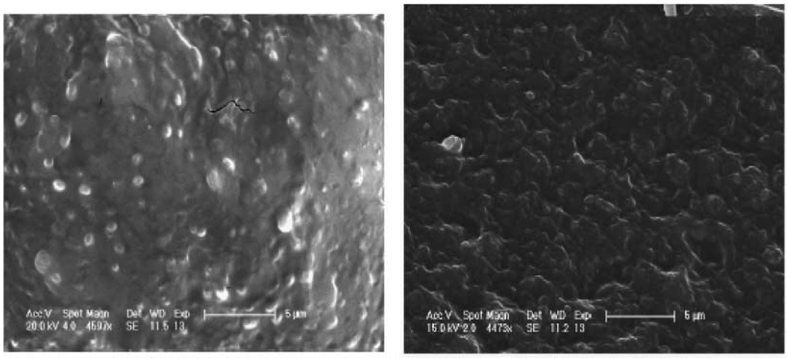


CHI/HPMC 80:20 wt %

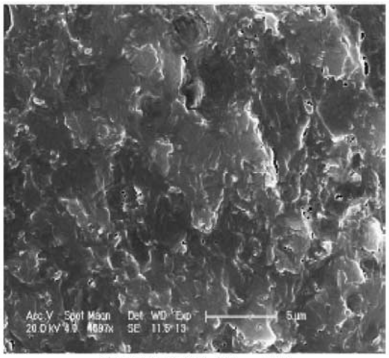
Fig. 2. (a) SEM images of CHI/HPMC blends. (b) SEM images of CHI/MC blends.



CHI 100 wt % MC 100 wt %



CHI/MC 20:80 wt % CHI/MC 50:50 wt %



CHI/MC 80:20 wt %

Fig. 2 (*continued*)

CHI are in agreement with our previous results (Bo, Khutoryanskiy, Kan, Gabdulina, Mun and Nurkeeva, 2001) and the literature data (Xu, Kim, Hanna & Nag, 2005).

The spectrum of pure HPMC film shows the presence of the bands at 3415, 2927, 2858, 1634, 1402, 1375, 1316, 1110, 1055, 947 cm^{-1}. The broad band centered at 3415 cm^{-1} corresponding to the OH stretching vibration and 2927 cm^{-1} are responsible for C–H stretching. The band at 1634 cm^{-1} has previously been assigned to water in the amorphous region (Liang & Marchessault, 1959). The strong band at 1055 cm^{-1} is assigned, respectively, to the C–O–C stretching. The spectrum of pure MC film shows similar bands at 3454, 2907, 2836, 1645, 1377, 1306, 1055, 946 cm^{-1}. The difference between the absorption bands of two cellulose ethers could be attributed to a different degree of hydration (presence of water traces).

All the characteristic bands of the component polymers are present in the spectra of their blends and the intensities of the bands vary depending on their composition in the mixture. Earlier Xu et al. (2005) have reported a shift the amino-group band of chitosan from 1578 to 1584 cm^{-1} in the composite films with starch and attributed this shift to the interaction between the component polymers confirming their molecular miscibility. Although, in our case this band is even more significantly shifted, which shows some interaction between the component polymers, we abstain from the conclusion about the complete miscibility of these polymers based on just infrared data. Additionally before the analysis all samples were just air dried, which means that water content in the materials is still high and exerts strong effect on FTIR spectra.

Wide angle X-ray diffractograms of CHI/HPMC and CHI/MC are shown in Fig. 1(a) and (b), respectively. A pure CHI film shows four main diffraction peaks ($2\theta = 8.3$, 11.28, 18.1, 22.44), confirming the presence of crystalline domains in its structure, which is in a good agreement with the results reported by Ritthidej, Phaechamud and Koizumi (2002).

The diffractograms of pure HPMC and MC show that these materials are mostly amorphous. The diffractograms of CHI/HPMC and CHI/MC blends containing 80 and 50% of CHI show the presence of the diffraction peaks typical for pure chitosan, which can be considered as an indication on immiscibility of the polymers. The diffractograms of the blends containing 20% of CHI are similar to pure cellulose ether, which indicate that this blend is more miscible than the other two. Perhaps the miscibility of this blend can result from the presence of hydrogen bonding via residual water molecules. This is in agreement with Mucha and Pawlak results (2005), who demonstrated that residual water molecules can act as an active compatibilizer in the blend.

The morphology of the polymer films cross-sections was studied by scanning electron microscopy. It can be seen from Fig. 2(a) and (b) the films of pure CHI, HPMC and MC have homogeneous morphology. However, the cross-sections of blends have rough structure and cavities, which confirms the partial immiscibility of the polymers. However, it should be noted that the morphology of the blends between chitosan and cellulose ethers is more homogeneous compared to the morphology of the blends between hydroxyethylcellulose and poly(sodium acrylate) we reported before (Khutoryanskiy, Cascone, Lazzeri, Barbani, Nurkeeva and Mun, 2004), where the possibility of hydrogen bonding was completely prevented. Hence, we can conclude that the blends of chitosan and cellulose ethers show some partial immiscibility.

Fig. 3(a) and (b) show the results of thermogravimetric analysis of CHI/HPMC and CHI/MC blends, respectively. The pure CHI film thermal degradation consists of two stages and the first thermal event is a weight loss of up to 20% with maximum rate at 109 °C, which is related to the evaporation of water present in a sample. The second thermal event starts at 220 °C with the maximum at 264 °C and it is related to depolymerisation of chitosan chains. This degradation profile of CHI is in good agreement with the results of Wanjun, Wang and Donghua (2005). The pure HPMC and MC also show the first thermal event centered at 65.5 and 57.8 °C, respectively,

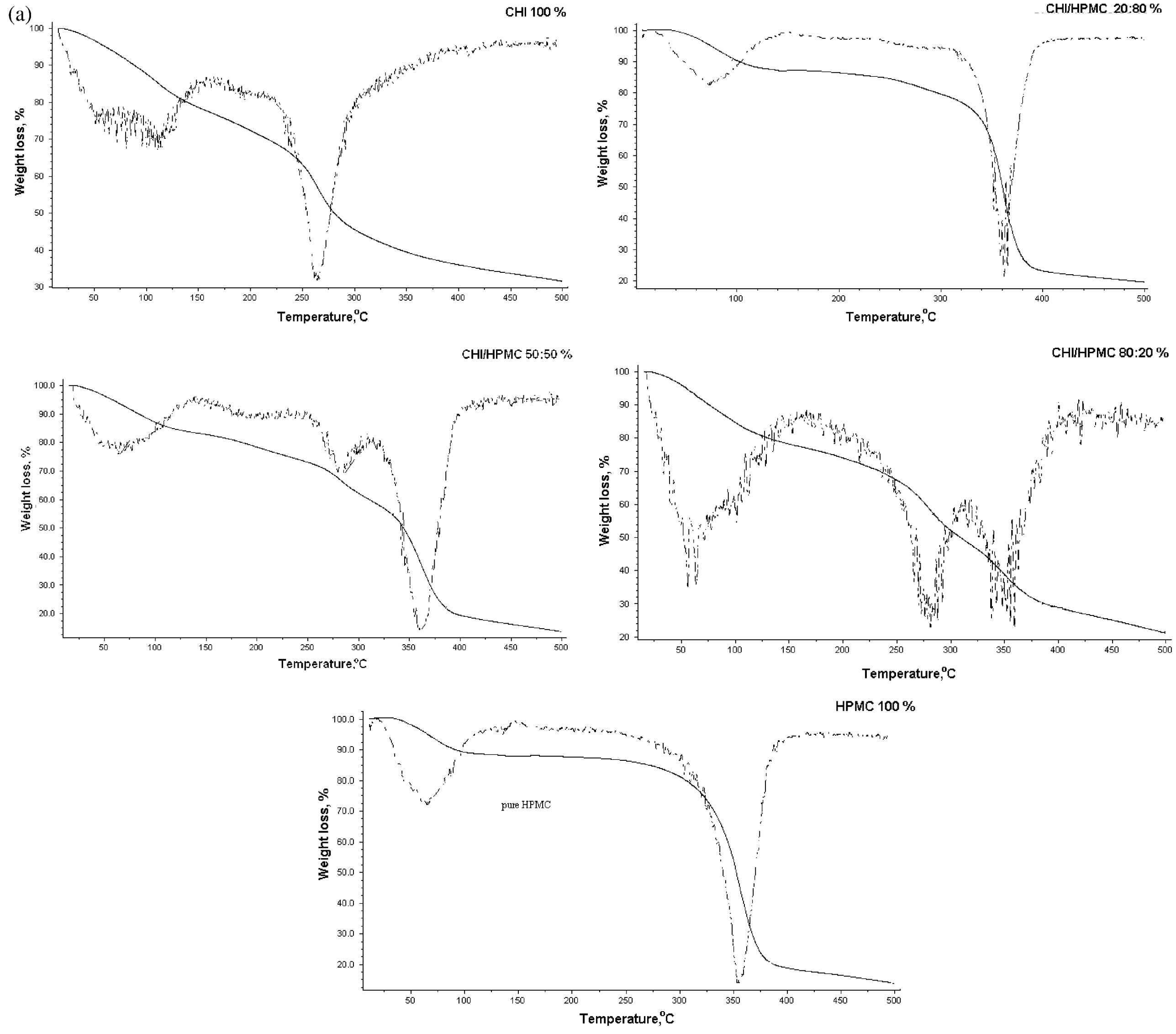


Fig. 3. (a) Thermogravimetric analysis of CHI/HPMC blends. (b) Thermogravimetric analysis of CHI/Mc blends.

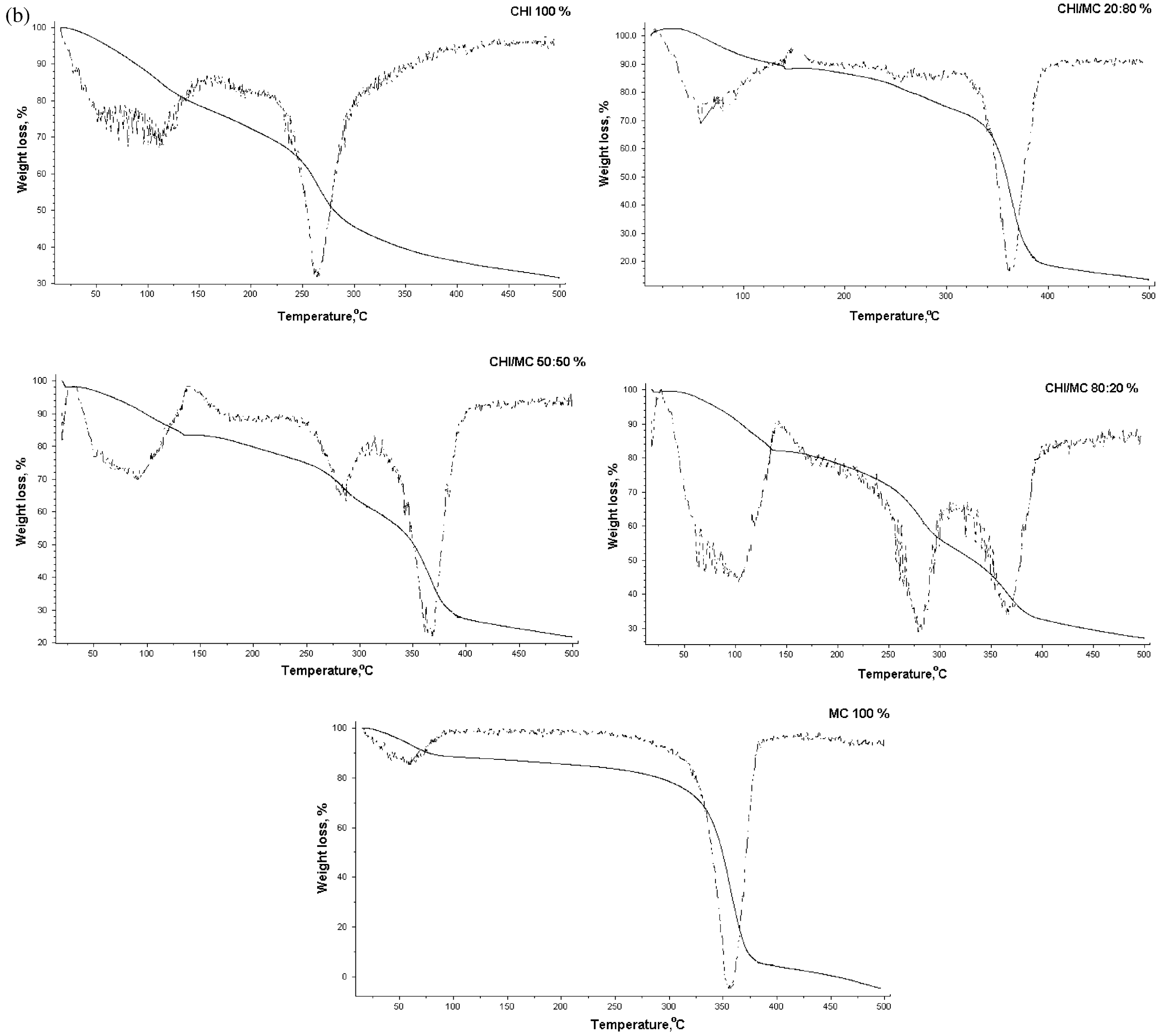


Fig. 3 (*continued*)

which are related to the evaporation of unbound water. The second thermal event for pure HPMC and MC is observed at about 300°C with the maximal rate at 355–356 °C and is related to cellulose ethers degradation, which includes the parallel processes of dehydration and demethoxylation. The degradation profile of MC is in good agreement with our previous results (Khutoryanskiy, Cascone, Lazzeri, Nurkeeva, Mun and Mangazbaeva, 2003). The degradation profile of the blends containing 50 and 80% of CHI consists of the events typical for both pure CHI and pure cellulose ether. This behavior could be observed for degradation of mechanical mixtures of the polymers and indicate on their immiscibility in the blend. However, the degradation of the blend containing 20% of CHI shows only events characteristic for pure cellulose ether. The absence of the event typical for pure CHI at 250–350 °C in this blend indicates on some interactions between the polymers and may be considered as a proof of their partial miscibility.

4. Conclusions

The examination of the properties of the films based on chitosan and two cellulose ethers–hydroxypropylmethylcellulose and methylcellulose revealed that the polymers are not miscible in the blends. However, the presence of weak hydrogen bonding between the components is demonstrated. Earlier similar situation was observed for the blends of hydroxypropylcellulose with poly(vinyl methyl ether) (Nurkeeva et al., in press), where the presence of intermacromolecular hydrogen bonding could not provide complete miscibility between the polymers. Based on the results obtained in this work as well as our earlier data we can conclude that if the hydrogen bonding between the component polymers is relatively weak the full miscibility cannot be achieved. However, the miscibility of chitosan with cellulose ethers is much better than the miscibility between hydroxyethylcellulose and poly(sodium acrylate) (Khutoryanskiy et al., 2004), where the possibility of hydrogen bonding is completely prevented.

Acknowledgements

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References

Amiji, M. M. (1995). Permeability and blood compatibility properties of chitosan–poly(ethylene oxide) blend membranes for haemodialysis. *Biomaterials*, *16*, 593–599.

Bo, Y. J., Khutoryanskiy, V. V., Kan, V. A., Gabdulina, Y. R., Mun, G. A., & Nurkeeva, Z. S. (2001). Interaction of chitosan with hydrogel of poly(acrylic acid) and preparation of encapsulated drugs. *Eurasian Chemical Technological Journal*, *3*, 191–194.

Coleman, M. M., & Painter, P. C. (1995). Hydrogen bonded polymer blends. *Progress in Polymer Science*, *20*, 1–59.

He, Y., Zhu, B., & Inoue, Y. (2004). Hydrogen bonds in polymer blends. *Progress in Polymer Science*, *29*, 1021–1051.

Jiang, M., Mei, L., Maoliang;, X., & Hui, Z. (1999). Interpolymer complexation and miscibility enhancement by hydrogen bonding. *Advances in Polymer Science*, *146*, 121–196.

Khutoryanskiy, V. V., Cascone, M. G., Lazzeri, L., Barbani, N., Nurkeeva, Z. S., Mun, G. A., et al. (2004). Morphological and thermal characterization of interpolymer complexes and blends based on poly(acrylic acid) and hydroxypropylcellulose. *Polymer International*, *53*, 307–311.

Khutoryanskiy, V. V., Cascone, M. G., Lazzeri, L., Nurkeeva, Z. S., Mun, G. A., & Mangazbaeva, R. A. (2003). Phase behaviour of methylcellulose–poly(acrylic acid) blends and preparation of related hydrophilic films. *Polymer International*, *52*, 62–67.

Liang, C. Y., & Marchessault, R. H. (1959). Infrared spectra of crystalline polysaccharides. *Journal of Polymer Science*, *39*, 269–278.

Mucha, M., & Pawlak, A. (2005). Thermal analysis of chitosan and its blends. *Thermochimica Acta*, *427*, 69–76.

Nurkeeva, Z. S., Tyukova, I. S., Suvorova, A. I., Mun, G. A., Dzhusupbekova, A. B., & Khutoryanskiy, V. V. (in press). Miscibility studies in poly(methyl vinyl ether)/hydroxypropylcellulose binary system in aqueous solutions and solid state. *Carbohydrate Polymers*, vol. 62, 80–86.

Pawlak, A., & Mucha, M. (2003). Thermogravimetric and FTIR studies of chitosan blends. *Thermochimica Acta*, *396*, 153–166.

Ritthidej, G. C., Phaechamud, T., & Koizumi, T. (2002). Moist heat treatment on physicochemical change of chitosan salt films. *International Journal of Pharmaceutics*, *232*, 11–22.

Sakurai, K., Maegawa, T., & Takahashi, T. (2000). Glass transition temperature of chitosan and miscibility of chitosan/poly(*N*-vinyl pyrrolidone) blends. *Polymer*, *41*, 7051–7056.

Suto, S., & Ui, N. (1996). Chemical crosslinking of hydroxypropyl cellulose and chitosan blends. *Journal of Applied Polymer Science*, *61*, 2273–2278.

Twu, Y.-K., Huang, H.-I., Chang, S.-Y., & Wang, S.-L. (2003). Preparation and sorption activity of chitosan/cellulose blend beads. *Carbohydrate Polymers*, *54*, 425–430.

Wanjun, T., Cunxin, W., & Donghua, C. (2005). Kinetic studies on the pyrolysis of chitin and chitosan. *Polymer Degradation and Stability*, *87*, 389–394.

Wu, Y.-B., Yu, S.-H., Mi, F.-L., Wu, C.-W., Shyu, S.-S., Peng, C.-K., et al. (2004). Preparation and characterization on mechanical and antibacterial properties of chitosan/cellulose blends. *Carbohydrate Polymers*, *57*, 435–440.

Xu, Y. X., Kim, K. M., Hanna, M. A., & Nag, D. (2005). Chitosan–starch composite film: Preparation and characterisation. *Industrial Crops and Products*, *21*, 185–192.