

THERMAL AND ATOMIC FORCE MICROSCOPY (AFM) STUDIES OF MICROCRYSTALLINE CHITOSAN/POLY(VINYL ALCOHOL) MIXTURES

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Abstract

In the present paper, the results of thermal analysis (DSC and TGA) and atomic force microscopy studies of microcrystalline chitosan (MCCh) with poly(vinyl alcohol) (PVA) are presented. Microcrystalline chitosan is blended with poly(vinyl alcohol) in acetic acid solution and this solution is cast to prepare the blend film. From thermal curves the thermal transitions: T_g , T_m and characteristic temperatures of decomposition: T_{di} , T_{max} have been determined and compared. The influence of the degree of PVA hydrolysis on the thermal properties of blend systems has been discussed. The surface properties of the MCCh and PVA films and their blends have been studied by tapping-mode atomic force microscopy (AFM). The changes of topography images were considered by determining the root mean square (RMS) deviation in the image data. The obtained results suggested that in solid MCCh/PVA mixtures the components are poorly miscible.

Key words: *microcrystalline chitosan, poly(vinyl alcohol), polymer blends, AFM, thermal analysis.*

1. Introduction

Blending is one of the often applied method in modification of high molecular weight compounds. This method is usually cheaper and less time-consuming for the creation of polymeric materials with new properties than the development of new monomers and/or new polymerization routes. Poly(vinyl alcohol) (PVA) is a synthetic, non-ionic polymer soluble in water. PVA is recognized as a biodegradable polymer [1 - 2]. Its properties mainly depend on the degree of hydrolysis.

Microcrystalline chitosan (MCCh) is a special form of chitosan which is prepared via its physicochemical modification using aqueous hydroxides and their salts [3]. Unique properties of microcrystalline chitosan such as bioactivity, biocompatibility and biodegradability have resulted in an increasing interest of its investigation and application e.g. in medicine, pharmacy and food and cosmetic industries.

The purpose of this study was to evaluate the thermal stability and miscibility of microcrystalline chitosan with poly(vinyl alcohol). The influence of PVA degree of hydrolysis (DH) on the properties of MCCh/PVA blend was investigated.

2. Materials and methods

The thermal behaviour of microcrystalline chitosan (MCCh) with poly(vinyl alcohol) (PVA) have been investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) measurements were performed on ca 2 mg samples with a Perkin Elmer Pyris Diamond apparatus with the power compensation using new DSC technique: high speed DSC (Hyper DSC) [4]. The instrument was calibrated with an indium standard. DSC curves of samples under helium atmosphere were recorded at heating rate 300 °C/min in two scans between 25 °C - 200 °C (298 K - 473 K). The reported T_g are those from the second scan. The melting temperature (T_m) and the enthalpy of fusion (ΔH_f) of each sample were determined from the maximum and the area of the melting peak, respectively. Thermogravimetric analysis (TGA) was carried out using Thermal Analysis SDT 2960 Simultaneous TGA-DTA analyser of TA Instruments Firm in the temperature range of 25 °C - 500 °C (298 K - 773 K) at heating rate 5 °C/min in nitrogen atmosphere. Topographic imaging were performed using a commercial AFM a MultiMode Scanning Probe Microscope Nanoscope IIIa (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA) operating in the tapping mode in air. Surface images, using scan widths ranging from 1 μ m to 5 μ m with a scan rate of 1.97 Hz were acquired at fixed resolution (512 \times 512 data points).

The investigated blend system contained: poly(vinyl alcohol): PVA(99) (degree of hydrolysis DH = 99%, $M_v = 1.2 \times 10^5$ g/mol), PVA(88) (DH = 88%, $M_v = 1.1 \times 10^5$ g/mol) with microcrystalline chitosan: MCCh (degree of deacetylation DD = 84% $M_v = 1.0 \times 10^6$ g/mol).

Microcrystalline chitosan were prepared by means of the original methods described in literature [3]. MCCh and PVA were solubilized separately in 0.1 M aqueous acetic

acid. Ternary solutions for each system were prepared by mixing the appropriate quantity of polymer solutions in the weight ratios $w_A : w_B$ of 0.2 : 0.8, 0.5 : 0.5 etc. The solution blends were poured on the glass plate covered with polyethylene film and evaporated at room temperature (298 K). Films of homopolymers were prepared in the same manner.

3. Results and discussion

DSC

Differential scanning calorimetry (DSC) was used to assess the miscibility of MCCh/PVA solid blends [5 - 7]. The values of T_g , T_m , ΔH_f and w_c (degree of crystallinity) are collected in **Table 1**.

As can be observed, the T_g of MCCh/PVA blends remain almost unchanged with the blend composition. This behaviour suggests that in solid MCCh/PVA(99), MCCh/PVA(88) blends the components are not miscible. If the content of MCCh in a MCCh/PVA(99) blends is than higher 50%, the glass transition temperature values could not be determined precisely. However, the experimental melting temperature T_m and the enthalpy of fusion ΔH_f corresponding to PVA(99), PVA(88) and MCCh/PVA blends given in **Table 1** show important depression of the melting temperature of PVA with the increase of MCCh content. This means the decrease of PVA crystallinity in MCCh/PVA blends.

TGA

On the basis of analysis of the thermogravimetric curves some characteristic parameters of blend thermodegradation were determined as: the temperature of initial decomposition (T_{di}), the temperature at maximum decomposition rate (T_{max}) and the mass loss (Δm). **Table 2** shows TGA parameters for PVA, MCCh and their blends {MCCh/PVA(99) and MCCh/PVA(88)}.

TGA curves of samples of MCCh and MCCh/PVA 80/20 blends show a weight loss in two stages. In the case of other samples, the decomposition proceeds in three stages. The first weight loss at 20 -130°C is due to the moisture vaporization. Further stages corresponded to the thermal degradation of samples. For the MCCh/PVA(99) and MCCh/

Table 1. The values of the glass transition (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_f) and degree of crystallinity (w_c) of MCCh/PVA mixtures.

Sample	w_{MCCh}	T_g , °C	T_m , °C	ΔH_f , J/g	w_c , %
MCCh/PVA(99)	1.0	146	-	-	-
	0.8	-	-	-	-
	0.5	90	206	10.3	7.3
	0.2	87	218	33.2	23.4
	0.0	87	231	52.4	36.9
MCCh/PVA(88)	1.0	146	-	-	-
	0.8	140	-	-	-
	0.5	81	-	-	-
	0.2	81	181	1.3	0.9
	0.0	82	188	21.2	14.9

Table 2. Thermogravimetric parameters of MCCh, PVA and their mixtures.

Sample	w _{MCCh}	I stage			II stage			III stage		
		T _{di}	T _{max} , °C	Δm, %	T _{di}	T _{max} , °C	Δm, %	T _{di}	T _{max} , °C	Δm, %
MCCh/PVA(99)	1.0	22	37	16	203	265	39	–	–	–
	0.8	31	71	14	202	260	58	–	–	–
	0.5	30	71	17	202	252	53	376	416	10
	0.2	37	77	11	195	248	64	383	419	12
	0.0	40	76	5	182	248	63	365	419	16
MCCh/PVA(88)	1.0	22	37	16	203	265	39	–	–	–
	0.8	19	33	11	200	265	46	–	–	–
	0.5	32	63	15	192	261	56	372	421	11
	0.2	34	57	10	190	260	69	388	419	10
	0.0	40	60	4	223	303	70	388	425	16

Table 3. The root-mean-square (Rms) surface roughness for MCCh, PVA and their mixtures

w _{MCCh}	Root-mean-square (Rms) surface roughness, nm	
	MCCh/PVA(99)	MCCh/PVA(88)
1.0	2.22	2.22
0.8	4.98	3.73
0.5	1.92	5.38
0.2	1.61	1.61
0.0	2.33	1.92

PVA(88) blends, the T_{di} and T_{max} of blends is practically constant. These results indicate that the influence of MCCh on the thermal stability of PVA is negligible.

AFM

The AFM images of MCCh, PVA their blends {MCCh/PVA(99) and MCCh /PVA(88)} are shown in **Figure 1** and **Figure 2**. As can be seen, the AFM images show differences in surface properties of homopolymer films and their blends. The MCCh and PVA films have relatively smooth and flat surfaces, whereas their blends show two separated phases. This observation agrees very well with the results of thermal analysis.

The values of the Rms surface roughness are collected in **Table 3**. As can be observed, the Rms surface roughness of blends increases with the increase in the MCCh content (for w_{MCCh} > 0.2).

4. Conclusions

1. The T_g of MCCh/PVA blends remain almost unchanged with the blend composition. This behaviour suggests that in solid MCCh/PVA blends the components are not miscible.
2. The DSC data show the depression of the melting temperature of PVA with the increase of MCCh content.
3. The degree of crystallinity of the PVA component in the blend films was found to monotonically decrease with increase of microcrystalline chitosan content.
4. TGA data indicates that the influence of MCCh on the thermal stability of PVA is negligible.

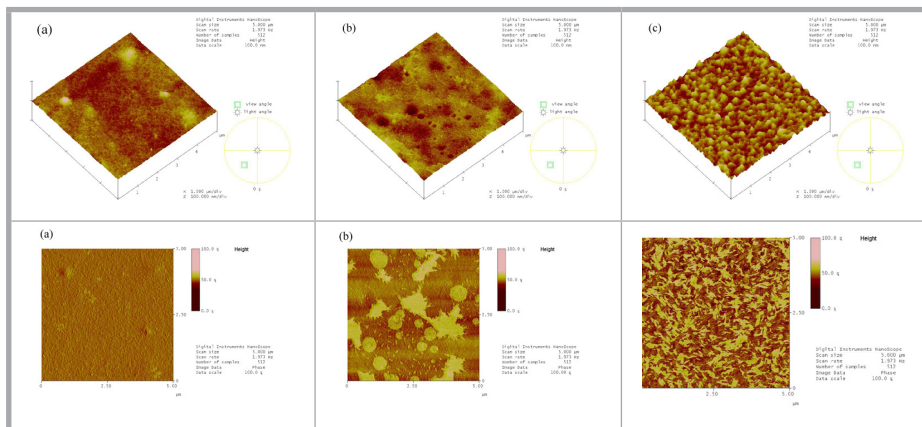


Figure 1. AFM images of (a) pure MCCh, (b) pure PVA(99), (c) 80/20 MCCh/PVA.

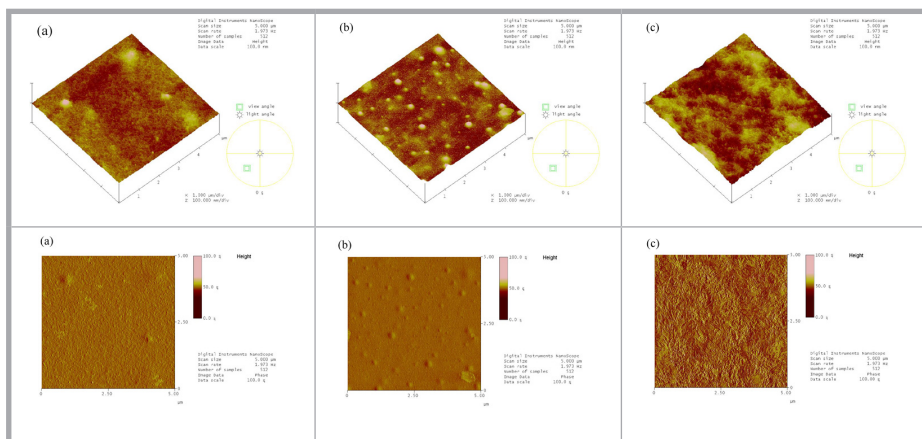


Figure 2. AFM images of (a) pure MCCh, (b) pure PVA(88), (c) 80/20 MCCh/PVA.

5. The MCCh, PVA(99) and PVA(88) films have relatively smooth and flat surfaces, whereas their blends show two separated phases.

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6. References

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