

THERMAL STUDY OF CHITOSAN BLENDS WITH VINYL POLYMERS

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1. Introduction

Techniques of thermal analysis have been used for many years for characterization of polymer materials. Thus, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA) are widely employed in both scientific and industrial sectors.

In the present paper, the thermal studies (DSC and TGA) of chitosan acetate (ChA) with poly(vinyl alcohol) (PVA) or polyacrylamide (PAM) blends were discussed.

Recently Mucha and coworkers [1, 2] have reported the results on miscibility of chitosan and poly(vinyl alcohol) by thermogravimetric analysis, FTIR [1], differential scanning calorimetry (DSC) and the dynamic mechanical thermal analysis (DMTA) [2]. The authors [1, 2] did not consider the influence of the hydrolysis degree of PVA on the miscibility of chitosan with PVA.

The purpose of this study was to evaluate the thermal stability and miscibility of chitosan with PVA or PAM, on the basis of differential scanning calorimetry (Hyper DSC) and thermogravimetric analysis (TGA). The influence of PVA degree of hydrolysis (DH) on the thermal properties of ChA/PVA blend was investigated.

2. Materials and methods

The characteristics of polymer samples are given in Table I.

Table I. Characteristics of high molecular weight compounds used; DH is the degree of hydrolysis of PVA, DD is the degree of deacetylation of Ch, *producer's determination, **determined in this study, 1a – $A_2 = 8.0 \times 10^{-3} \text{ ml} \cdot \text{mol/g}^2$, 1b – $K = 8.93 \times 10^{-3} \text{ dl/g}$, $a = 0.71$ $T = 303 \text{ K}$, solvent: 0.2 M $\text{CH}_3\text{COOH}/0.1 \text{ M NaCl}/4 \text{ M Urea}$, 1c – $K = 1.81 \times 10^{-2} \text{ dl/g}$, $a = 0.93$, $T = 298 \text{ K}$ solvent: 0.1 M $\text{CH}_3\text{COOH}/0.2 \text{ M NaCl}$.

Compound	Molecular weight, g/mol		DD**, %	DH**, %	Producer
	$M^* \times 10^3$	$M_v^{**} \times 10^3$			
Ch	84.6 _{1a}	116 _{1b} 471 _{1c}	83	-	Institute of Sea Fisher (Poland)
PVA(99)	145	120	-	99	Aldrich
PVA(88)	-	110	-	88	Loba Austria
PAM	5000	3000	-	-	Acros

Hyper differential scanning calorimetry (HyperDSC) measurements were performed on ca 2 mg samples with a Perkin Elmer Pyris Diamond apparatus with the power-compensation [3]. The instrument was calibrated with an indium standard. DSC curves of samples under helium atmosphere were recorded at heating rate of 300 K/min in two scans between 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 a Thermal Analysis SDT 2960 Simultaneous TGA-DTA analyser of TA Instruments Firm in the temperature range of 298 K – 773 K at heating rate 5 K/min in nitrogen atmosphere. From thermogravimetric curves the characteristic temperatures of decomposition: temperature of initial decomposition T_{di} and temperature at maximum decomposition rate T_{max} , of the investigated blends were determined. Activation energy of decomposition E_{ad} was calculated from TG curves using the Horowitz – Metzger method [4].

Chitosan, PVA and PAM were solubilized separately in 0.1 M aqueous acetic acid and then mixed at different ratios. The casting solution blends were poured on a glass plate covered with polyethylene film and evaporated at room temperature (298 K). Films of homopolymers were prepared in the same manner.

3. Results

3.1. DSC

Differential scanning calorimetry (DSC) was used to assess the miscibility of ChA/PVA and ChA/PAM solid blends. Generally, the observation of single glass transition temperature T_g for a blend, between those temperatures of the used high molecular weight components, is regarded as an evidence of polymer miscibility. Table 2 and Table 3 shows DSC data

for ChA/PVA and ChA/PAM respectively. The results of Hyper DSC studies of ChA/PVA blends show that in chitosan/PVA(88) solid blends an increase of the recorded T_g is observed in comparison with the T_g of sole PVA(88). These data (Table 2) show also important depression of the melting temperature of PVA(99) with the increase of ChA content, which means the decrease of PVA crystallinity in ChA/PVA blends. The degree of crystallinity of the PVA component in the blend films was found to monotonically decrease with increase of chitosan acetate content.

In the case ChA/PAM blends (Table 3), the values of glass transition temperature (T_g) of ChA/PAM blends, showing the nonmonotonical change with the change in blend composition suggest that in the solid ChA/PAM blends the components are poorly miscible.

Table 2. The values of the glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_f) and degree of crystallinity (w_c) of ChA/PVA blends.

ChA/PVA(99)				
Blend composition ChA/PVA	T_m , K	ΔH_f , J/g	w_c , %	
90:10	483	7.5	5.3	
60:40	497	16.2	11.4	
50:50	498	17.0	12.0	
40:60	500	22.7	16.0	
20:80	502	40.5	28.6	
0:100	512	47.0	33.1	
ChA/PVA(88)				
Blend composition ChA/PVA	T_g , K	T_m , K	ΔH_f , J/g	w_c , %
60:40	384	469	0.99	0.7
50:50	362	458	3.0	2.1
40:60	356	455	9.0	6.4
20:80	356	458	13.0	9.2
0:100	355	464	24.6	17.3

Table 3 The values of the glass transition temperature (T_g) of ChA/PAM blends.

ChA/PAM	
Blend composition ChA/PAM	T_g , K
60:40	439
50:50	437
40:60	451
20:80	457
0:100	452

3.2. TGA

The results of TGA measurements carried out for ChA/PVA blends are shown in Figure 1 and Figure 2. The characteristic temperatures (T_{max} and T_{di}) vs composition curves for ChA/PVA(99) blends follow the dependence according to the additivity rule (Figure 1), whereas in the case of ChA/PVA(88) blends (Figure 2) the same plots shows the tendency to negative deviations.

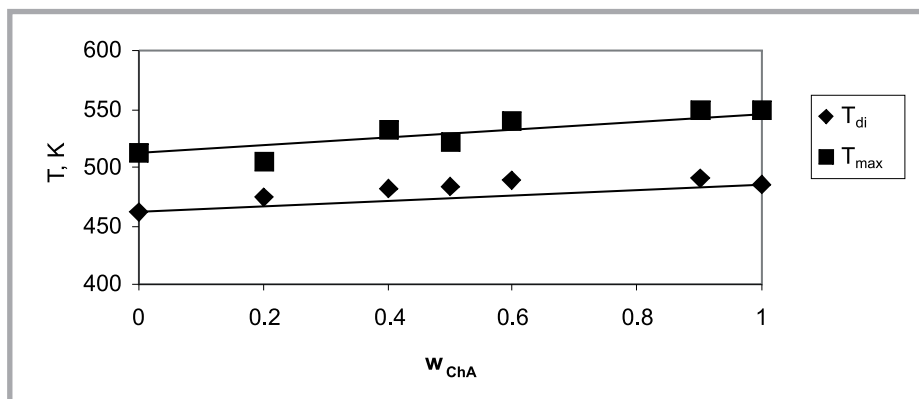


Figure 1. Temperature of initial decomposition T_{di} and temperature at maximum decomposition rate T_{max} of ChA/PVA(99) blends (TGA); Solid line - the values calculated according to the additivity rule.

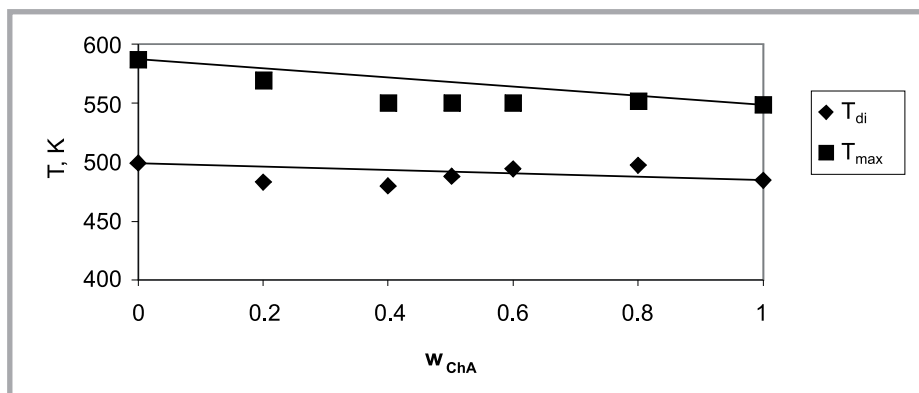


Figure 2. Temperature of initial decomposition T_{di} and temperature at maximum decomposition rate T_{max} of ChA/PVA(88) blends (TGA); Solid line - the values calculated according to the additivity rule.

Figure 3 shows the plots of T_{max} and T_{di} vs. composition w_{ChA} for ChA/PAM blends. The T_{max} values show positive deviation from additive rule. This provides evidence of some improvement of thermal stability of the investigated blends.

Figure 4 and Figure 5 show the E_a versus blend composition for ChA/PVA(99) and ChA/PVA(88) respectively. The ChA/PVA blends showed the positive and negative deviations of E_{ad} from additive rule. The increase of activation energy of decomposition E_{ad} calculated on the basis of TGA analysis is observed in the case of ChA/PVA(88) blends at $w_{ChA} \geq 0.5$ (w_{ChA} is the weight fraction of ChA in the blend). These behaviours suggest that deviation from additive rule may be related to the hydrolysis degree of the PVA in the blend.

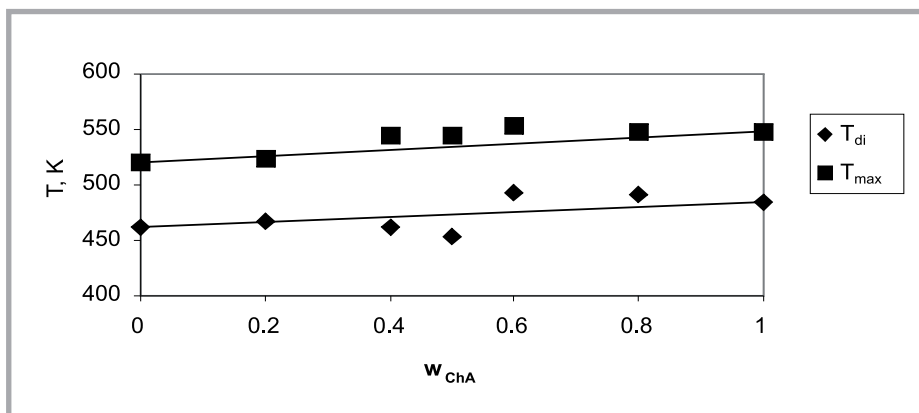


Figure 3. Temperature of initial decomposition T_{di} and temperature at maximum decomposition rate T_{max} of ChA/PAM blends (TGA); Solid line - the values calculated according to the additivity rule.

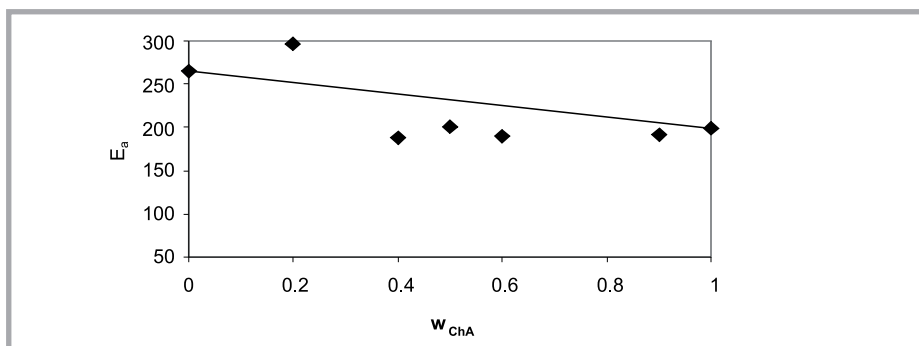


Figure 4. Activation energy of decomposition E_{ad} (kJ/mol) versus ChA content (w_{ChA}) in ChA/PVA(99) blends; Solid line - the values calculated according to the additivity rule.

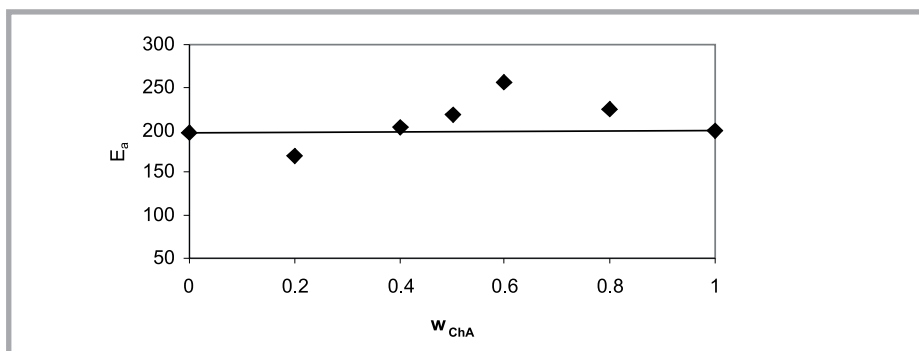


Figure 5. Activation energy of decomposition E_{ad} (kJ/mol) versus ChA content (w_{ChA}) in ChA/PVA(88) blends; Solid line - the values calculated according to the additivity rule.

4. Conclusions

1. The obtained results of DSC measurements may indicate some degree of miscibility of ChA/PVA blends of suitable composition [5 - 6].
2. The results of DSC measurements on ChA/PAM blends reported in this paper suggest that in the solid blends both components are poorly miscible.
3. For the ChA/PVA blends, their decomposition behaviour (T_{di} and T_{max}) was found to be intermediate to those of the pure components.
4. Thermogravimetric analysis of ChA and its blends with PAM revealed improving stability of ChA in the ChA/PAM blends (positive deviation of T_{max}).
5. The obtained results of the thermal studies suggested that the miscibility of ChA with vinyl polymers depend on the blends composition and degree of PVA hydrolysis.

The study was partly financed by the Nicolaus Copernicus University within the scope of the grant UMK nr 345.

5. References

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