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Miscibility and thermal stability of poly(vinyl alcohol)/chitosan mixtures

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ABSTRACT

The miscibility and the thermal behaviour of chitosan acetate (ChA) with poly(vinyl alcohol) (PVA) have been investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). 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.

Based upon the observation on the DSC analysis, the melting point of PVA is decreased when the amount of ChA in the blend film is increased. Though some broadening of the transition curves could be noticed (DSC, TGA and DMA), the obtained results suggest that in the solid ChA/PVA blends the components are poorly miscible. Only PVA sample with relatively low DH = 88% and hence low degree of crystallinity shows partial miscibility with ChA of relatively low molecular weight.

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 (DMA) are widely employed in both scientific and industrial sector. The thermal properties of polymers give valuable information regarding stiffness, toughness, stability and miscibility in blends [1–6].

Chitosan (ChA) is a linear polysaccharide which consists of 2-amino-2-deoxy-β-D-glucopyranose and 2-acetamido-2-deoxy-β-D-glucopyranose. This biopolymer is obtained by the process of alkaline *N*-deacetylation of chitin. Chitosan is a weak polybase, showing a polyelectrolytic effect in aqueous dilute acidic solutions [7,8]. Unique properties of chitosan such as bioacitivity, biocompatibility and biodegradability have resulted in an increasing interest of its investigation and application e.g. in medicine, pharmacy and food and cosmetic industries.

Poly(vinyl alcohol) (PVA) is a synthetic, non-ionic polymer soluble in water. PVA is recognized as a biodegradable polymer [9–11]. Its properties mainly depend on the degree of hydrolysis.

Studies of physico-chemical properties of chitosan with poly(vinyl alcohol) in solid state have been reported [12–19]. Mechanical properties and FTIR characterization of ChA/PVA films have been studied by Miya et al. [12], Guthrie and co-workers [13], Marsh and co-workers [16] and Tharanathan and co-workers [17]. Mucha et al. [14,18,19] has reported the results of thermal and rheological properties. These studies have shown that ChA with PVA are poorly miscible. Moreover, FTIR analysis has revealed the existence of weak hydrogen bonding interactions between PVA and chitosan [12,16,17]. Young and co-workers [15] has studied the ChA/PVA blending by DSC, SEM and electron spectroscopy for chemical analysis (ESCA) and found that this system undergoes phase separation. The SEM photographs shown the ChA/PVA blended membrane undergoes dramatic changes on the surface and bulk structure during the membrane formation [15]. However, the authors of these investigations did not frequently give full characteristics of the used polymer samples. Thus, some interesting aspects still remain to be elucidated such as the influence of the degree of hydrolysis of PVA and the molecular weight of the homopolymers (ChA) on the miscibility in the blend.

The purpose of this work is the evaluation of the miscibility of chitosan acetate differing in molecular weight with poly(vinyl alcohol) of different degrees of hydrolysis on the basis of differential scanning calorimetry (Hyper DSC), thermogravimetric analysis and dynamic mechanical thermal analysis (DMA).

2. Experimental

2.1. Materials

The high molecular weight compounds used in this work were commercial products whose properties are given in Table 1. Distilled water and 0.1 M aqueous acetic acid were used as solvent.

The viscosity average molecular weight $\overline{M}_v$ of chitosan and PVA was measured with an Ubbelohde viscometer. The

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Table 1
Characteristics of polymer samples.

Polymer	$\overline{M}_v \times 10^{-3}$(g/mol)	DH (%)	DD (%)	Source
PVA(88)	136[1][a]	87.7[a]		Loba
PVA(99)	110[2][a], 85–145[b]	99.4[a], 99[b]		Aldrich
ChA I	471[3][a]		83[a]	Institute of Sea Fisher (Poland)
ChA II	1400[3][a]		79[a]	Aldrich

$\overline{M}_v$ is the viscosity average molecular weight, DH is the degree of hydrolysis of PVA, DD is the degree of deacetylation of ChA, [a]determined in this study; [b]producer's value; [1]$K = 8.0 \times 10^{-4}$ dl/g, $a = 0.58$, $T = 298$ K, solvent: water [20]; [2]$K = 6.9 \times 10^{-4}$ dl/g, $a = 0.61$, $T = 298$ K, solvent: water [20]; [3]$K = 1.81 \times 10^{-2}$ dl/g, $a = 0.93$, $T = 298$ K, solvent: 0.1 M CH_3COOH/0.2 M NaCl [21].

temperature of viscosity measurement, the solvent and the Mark–Houwink–Kuhn–Sakurada constants K and a for evaluating $\overline{M}_v$ are specified in Table 1.

The degree of deacetylation (DD) of chitosan was estimated according to Polish Standards (PN-87/A-86850). The method relies on chitosan acidic hydrolysis in 40% (v/v) H_3PO_4 and titration with 0.1 M NaOH the obtained acetic acid distilled over from the reaction mixture (up to 433 K). A blank sample is needed.

The degree of hydrolysis (DH) of PVA refers to the content of residual vinyl acetate groups. It was determined titrimetrically according to the Japan Industrial Standard [9].

2.2. Preparations

The solution of PVA were prepared in the following way: in the bottle fitted with a plastic rim seal, weighted amounts of PVA and solvent were mixed. The slurry was kept for swelling at 298 K, shaken at regular intervals. After 12 h of swelling, the slurry was heated up to 368 K with stirring to obtain a clear solution.

The solution of ChA were prepared by shaking the polymer with the solvent at room temperature for 24 h. After this time the solution were clear. The two solutions were mixed in at different rations. 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. The thickness of films was about 100 μm for DMA measurements. The solid films were further dried at 323 K for 24 h under vacuum and stored in a desiccator. All the blend films cast from stable mixed polymer solutions were visually homogeneous irrespective of composition.

2.3. DSC measurements

Differential scanning calorimetry measurements were performed on ca. 2 mg samples with a PerkinElmer Pyris Diamond apparatus with the power compensation using new DSC technique: high speed DSC (Hyper DSC) [22,23]. The instrument was calibrated with an indium standard. The application of high heating or cooling rates has been presented by Mathot and co-workers [22] and is know as high speed DSC or high performance DSC. Conventional DSC analysis often does not provide the high sensitivity required for the determination of weak glass transitions in highly crystalline materials or polymers. Power compensation Diamond DSC instrument has very low mass furnaces and thus is capable to achieve linearity in temperature, even when heating rates of up to 500 °C/min are applied. This also provides very high resolution or high definition of DSC transitions. Using very small sample masses, of about 2 mg or less for fast heating, thermal lag is effectively minimized. DSC curves of samples under helium atmosphere were recorded at heating rate 300 °C/min in two scans between 25 °C and 200 °C (298–473 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.

2.4. TG analysis (TGA)

Thermogravimetric analysis was carried out using Thermal Analysis SDT 2960. Simultaneous TGA-DTA analyser of TA Instruments Firm in the temperature range of 25–500 °C (298–773 K) at heating rate 5 °C/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 [24].

2.5. DMA measurements

Dynamic mechanical analysis (DMA) was carried out using a Dynamic Mechanical Analyzer DMA 2980 of TA Instruments Firm with standard bending head at a frequency of 1 Hz in the range 25–250 °C (298–523 K) and heating rate of 3 °C/min. In the DMA instrument, a film sample is longitudinally deformed by small sinusoidal stress. The resulting strain, which lags behind the applied force by phase angle δ, is measured. The values of the storage modulus E' (in-phase component), the loss modulus E'' (out-of-phase component), and bending loss tangent $\tan\delta = E''/E'$ were obtained as function of temperature.

3. Results and discussion

3.1. DSC

Generally, the observation of a single glass transition temperature (T_g) for a blend, between T_g temperatures of the used high molecular weight components is regarded as an evidence of polymer miscibility. The DSC curves obtained for the different pairs of blends presented in this paper are shown in Fig. 1. The values of T_g, T_m, ΔH_f and w_c (degree of crystallinity) are collected in Table 2. Each DSC curve was shifted in relation to the other to facilitate the presentation of the results. The homopolymer PVA showed T_g at 82 °C (355 K) and at 92 °C (365 K) for the 88% {Fig. 1(c and d)} and 99% {Fig. 1(a and b)} hydrolysed PVA, respectively. An endothermic peak, due to the melting of the crystalline phase present in this polymer can be observed at 191 °C (464 K) in PVA(88) and at 240 °C (513 K) in PVA(99). The differences in the observed T_m values are due to the different DH of PVA samples. In general, the crystalline melting temperature of partly hydrolysed poly(vinyl alcohol) decreases with increasing residual acetate content [9]. For the PVA samples was observed also the small peak at ca 140 °C (413 K) bigger in the case of PVA(88), which may be attributed to the motions within the residual acetate region of PVA.

As for the T_g of chitosan the reported data are in discrepancy. Ogura et al. [25] observed a peak at ~157 °C (430 K) in DMTA curves and attributed it to the T_g values chitosan. Pizzoli et al. [26] and Blumstein and co-workers [27] for dry neutral chitosan observed some relaxations at approximately 130 °C (403 K) and 90 °C (363 K),

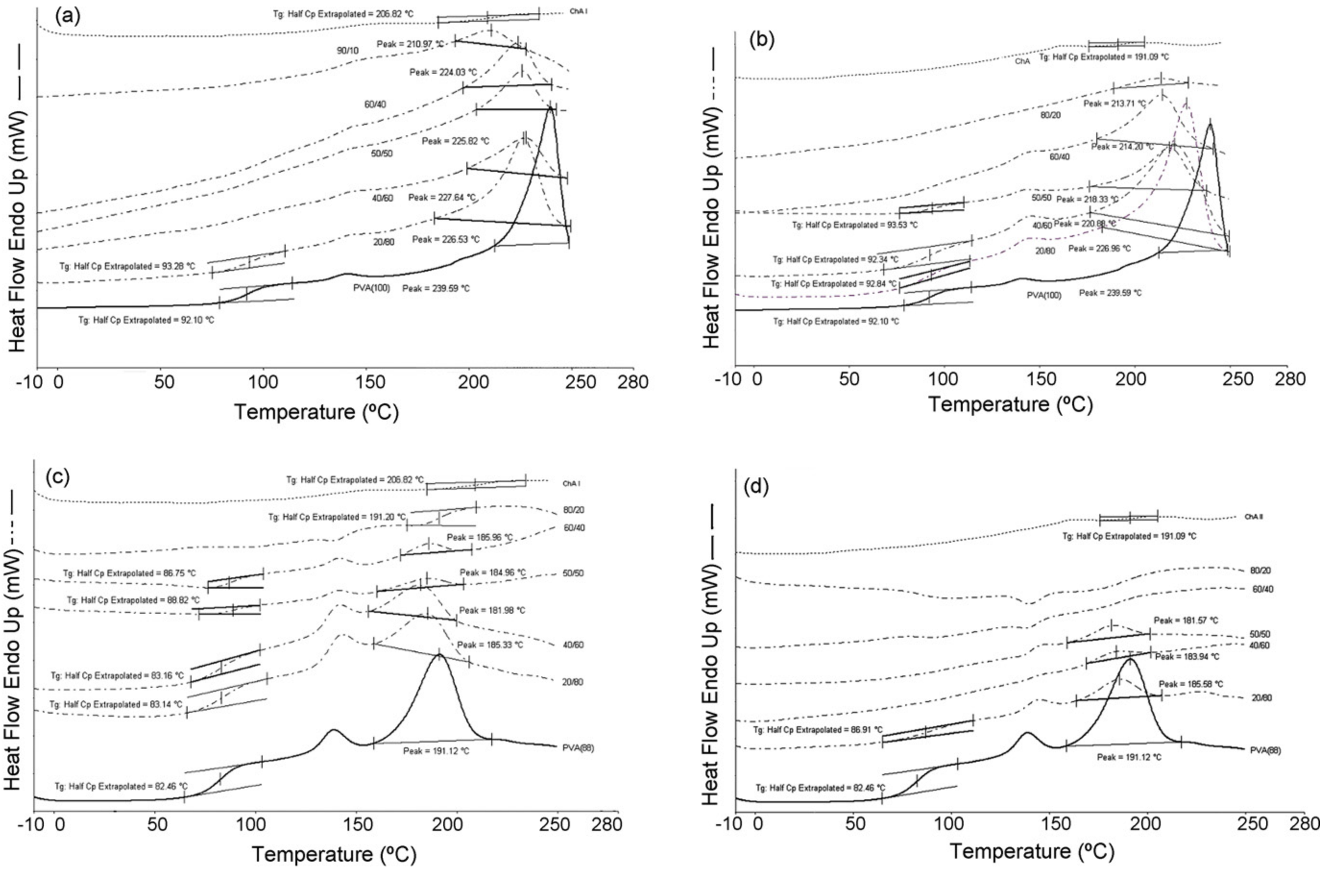

Fig. 1. DSC curves for PVA, ChA and their blends: (a) ChA I/PVA(99); (b) ChA II/PVA(99); (c) ChA I/PVA(88); (d) ChA II/PVA(88).

respectively. Blumstein and co-workers [27] conclude that these relaxations are mainly caused by the local motions within the amine region and it is not the glass transition of chitosan chains. Pizzoli et al. [26] suggested the T_g of chitosan close to that of dextran at 220 °C (493 K). Recently, the effect of water on the macromolecular dynamics in chitosan is reported by Mucha et al. [19]. The α-relaxation (T_g) of preheated chitosan is estimated at 140–160 °C (413–433 K) in DSC and DMTA measurements [19].

In the present paper the DSC curves for both chitosan samples are flat up to about 135–150 °C (408–433 K), where the first relaxation is observed (at ~135 °C for ChA I and at ~145 °C for ChA II). Following Blumstein and co-workers [27] this relaxation is assumed to be connected with the local motions within the amine groups in chitosan. At higher temperature the DSC curves of chitosan show the second transition – at ~207 °C (480 K) and 191 °C (464 K) for ChA I and ChA II, respectively. These temperatures may be considered to be the α-transition of chitosan chains, as for unmodified cellulose the T_g is estimated at 250 °C [28].

In the case of ChA I/PVA(88) blends the thermograms showed a single glass transitions temperature between the T_g's of the two homopolymers for blends with $w_{\mathrm{ChA}} \geq 0.5$. The presence of a single T_g suggests miscibility in these systems. From Fig. 1(a, b and d), it is observed that the T_g of ChA/PVA {ChA I/PVA(99), ChA II/PVA(99), ChA II/PVA(88)} blends remain almost unchanged with the blend composition. This behaviour suggests that in solid ChA I/PVA(99), ChA II/PVA(99), ChA II/PVA(88) blends the components are not miscible. If the content of ChA in a ChA/PVA blends is than higher 40%, 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 ChA/PVA blends given in Table 2 show important depression of the melting temperature of PVA with the increase of ChA content. This means the decrease of PVA crystallinity in ChA/PVA blends. Based on the experimental heat fusion values and the fusion of 100% crystalline PVA, the degree of crystallinity (w_c) of ChA/PVA blends is calculated. As can be observed, the degree of crystallinity of PVA in blends decreases with the increase of ChA content (cf. Table 2). The addition of ChA reduces the PVA crystallinity and as a consequence the decreases of PVA melting point is observed. Thus, partial miscibility in blends of ChA/PVA may be considered when the value of w_c lowers from about 17% to about 2% and the molecular weight of chitosan is not to high ($\overline{M}_v$ of ChA I amounts of about 470×10^3 g/mol).

3.2. TGA

Fig. 2 shows TG and DTG curves obtained for PVA, ChA and ChA I/PVA(99), ChA II/PVA(99), ChA I/PVA(88) and ChA II/PVA(88) blends. TGA curves of both samples of ChA show a weight loss in two stages. The first stage ranges between 30 °C (303 K) and 165 °C (438 K) and shows about 12% loss in weight for both ChA samples. This may correspond to the loss of adsorbed and bound water and the residue of acetic acid. The second stage of weight loss starts at 200 °C (473 K) and continues up to 360 °C (633 K) during which there was ~41% in ChA I and ~45% in ChA II weight loss due to the degradation of chitosan. Decomposition of PVA proceeds in three stages. The first weight loss at 50–130 °C (323–403 K) is due to the moisture vaporization. The second stage, which begins at 200 °C (473 K), mainly involves dehydration accompanied by the formation of some volatile products. In the third stage, the polyene residues are further degraded at 400 °C (673 K) to yield carbon and hydrocarbons. From the results shown in Fig. 2 it is evident the TGA curve of PVA(99) is different in comparison with PVA(88). The reason is that these samples differ in their molecular structure.

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.

Blend composition ChA I/PVA(99)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	w_c (%)
ChA I/PVA(99)				
100:0	207 ± 2	–	–	–
90:10	–	211 ± 2	7.5 ± 0.5	5.3 ± 0.5
60:40	–	224 ± 2	16.2 ± 2	11.4 ± 1
50:50	–	226 ± 2	17.0 ± 2	12.0 ± 1
40:60	–	228 ± 2	22.7 ± 2	16.0 ± 1
20:80	93 ± 1	227 ± 2	40.5 ± 4	28.6 ± 2
0:100	92 ± 1	240 ± 2	47.0 ±4	33.1 ± 2
Blend composition ChA II/PVA(99)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	w_c (%)
ChA II/PVA(99)				
100:0	191 ± 2	–	–	–
80:20	–	214 ± 2	3.3 ± 0.5	2.3 ± 0.2
60:40	–	214 ± 2	20.9 ± 2	14.7 ± 1
50:50	94 ± 1	218 ± 2	21.3 ± 2	15.0 ± 1
40:60	92 ± 1	221 ± 2	33.5 ± 2	23.6 ± 2
20:80	93 ± 1	227 ± 2	51.5 ± 4	36.3 ± 2
0:100	92 ± 1	240 ± 2	47.0 ± 2	33.1 ± 2
Blend composition ChA II/PVA(99)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	w_c (%)
ChA I/PVA(88)				
100:0	207 ± 2	–	–	–
80:20	191 ± 2	–	–	–
60:40	87 ± 1	186 ± 2	1.0 ± 0.1	0.7 ± 0.2
50:50	89 ± 1	185 ± 2	3.0 ± 0.5	2.1 ± 0.2
40:60	83 ± 1	182 ± 2	9.0 ± 0.5	6.4 ± 0.5
20:80	83 ± 1	185 ± 2	13.0 ± 1	9.2 ± 0.5
0:100	82 ± 1	191 ± 2	24.6 ± 2	17.3 ± 1
Blend composition ChA II/PVA(99)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	w_c (%)
ChA II/PVA(88)				
100:0	191 ± 2	–	–	–
80:20	–	–	–	–
60:40	–	–	–	–
50:50	–	182 ± 2	3.5 ± 0.5	2.5 ± 0.5
40:60	–	184 ± 2	3.0 ± 0.5	1.9 ± 0.5
20:80	87 ± 1	186 ± 2	6.7 ± 0.5	4.8 ± 0.5
0:100	82 ± 1	191 ± 2	24.6 ± 2	17.3 ± 1

TGA curves of all blend films show the greatest weight loss in the range 210–380 °C (483–653K), which are believed to the disintegration of intermolecular and partial breaking of the molecular structure. However, in the case of ChA/PVA blends containing 20% ChA (Fig. 2a and b), the behaviour of weight loss with temperature is peculiar. Above 200 °C, a three-step degradation process is recognizable in these blends. The two mirror peaks, at ~230 °C and ~420 °C show that degradation behaviours of pure PVA is retained in the blend. The major peak at ~340 °C may correspond to the decomposition of chitosan. Such a shift to higher temperature indicates on some interactions between polymer components in the blend.

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}) and the temperature at maximum decomposition rate (T_{max}). Fig. 3 shows the T_{di} and T_{max} of ChA/PVA blend versus composition for the second stage of both components. In the case of ChA I/PVA(99) and ChA II/PVA(99) blends, the T_{di} and T_{max} of blends increases (approximately linear) with the increase in the ChA content. This provides evidence of some improvement of PVA(99) stability in the investigated blends. Similar results were observed by Mucha and Pawlak [18] at different experimental conditions: in the temperature range of 100–450 °C, in air atmosphere; the degree of hydrolysis of PVA sample was not specified. For the ChA I/PVA(88) and ChA II/PVA(88) blends, the T_{di} and T_{max} of blends is practically constant for blends with $w_{ChA} > 0.2$ (w – the weight fraction of ChA I and II in the blend). These results indicate that the influence of ChA I and ChA II on the thermal stability of PVA(88) is negligible.

Activation energies of decomposition (E_a) have been calculated for the second stage (200–380 °C, 473–653 K) using the Horowitz–Metzger equations [24]. Fig. 4 shows that E_a does not depend very much on the properties of the ChA sample {small difference in chemical structure of (ChA 79% ≤ DD ≤ 83%)}. In the case of PVA sample, the E_a value of PVA(99) is higher than that of PVA(88). The reason is, that these two commercially PVA samples differ in their molecular structure (different DH), which as could be expected, influenced their physico-chemical properties. The PVA(99) sample falls into a fully hydrolyzed PVA group with the degree of hydrolysis of about 99%, whereas the PVA(88) sample belongs to a partly hydrolyzed PVA group with 88% of hydrolysis.

The ChA I/PVA(99) and ChA II/PVA(99) blends showed the positive and negative deviations of E_a (Fig. 4) from additivity rule. For ChA II/PVA(88) blends the negative deviations are observed. The increase of activation energy of decomposition calculated on the basis of TGA analysis is shown in the case of ChA I/PVA(88) blends at $w_{ChA} \geq 0.5$. The deviation from the additive rule may be related to the hydrolysis degree of PVA and molecular weight of ChA in the blend. Negative or positive deviations have been related to polymer miscibility/immiscibility that is: miscible systems show nearly linear curves or positive deviation and immisible systems showing negative deviations [29]. Thus, the increase in homogeneity of PVA(88) sample with ChA I may be deduced. The conclusion is in agreement with DSC results (for $w_{ChA} \geq 0.5$).

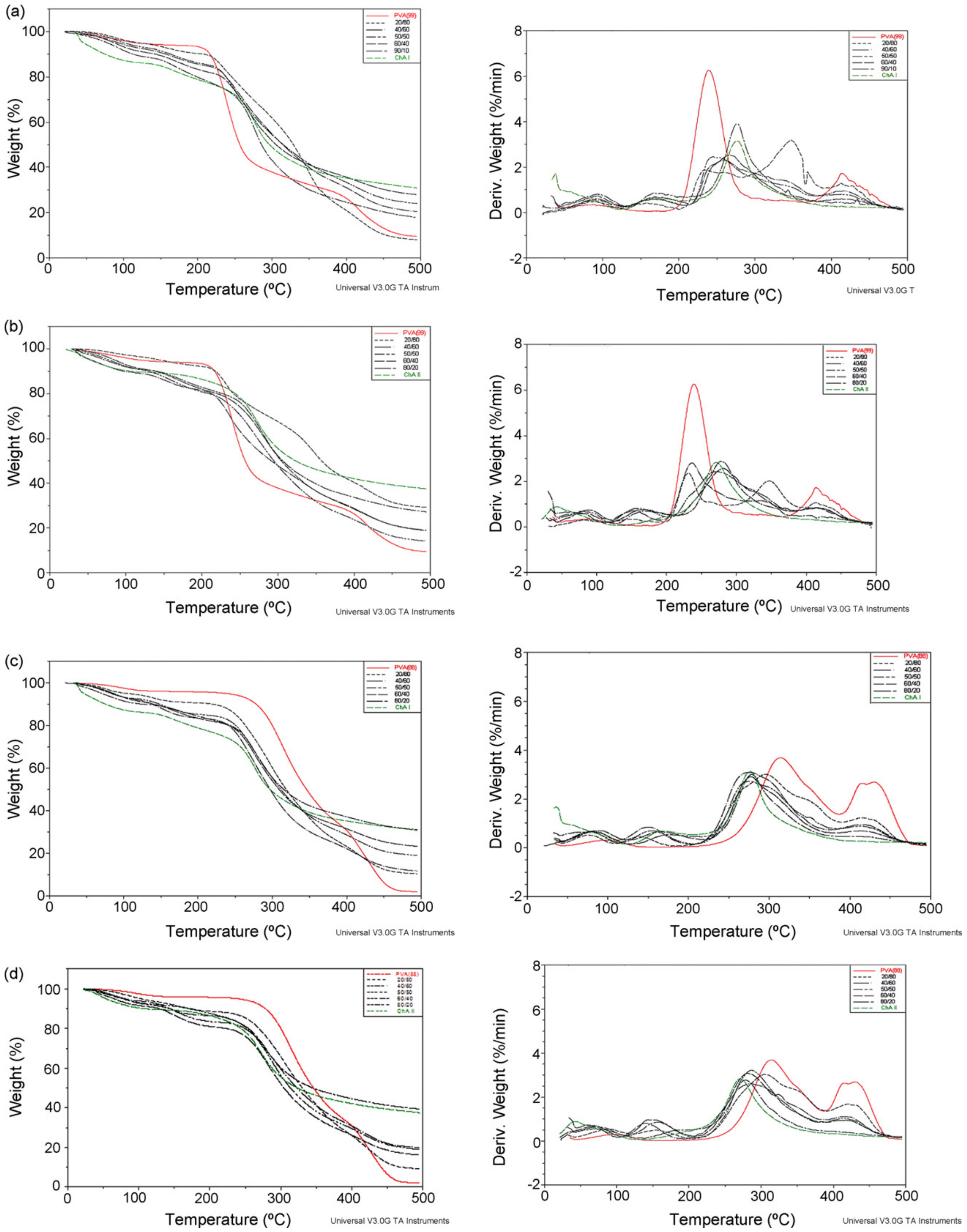

Fig. 2. TGA curves for PVA, ChA and their blends: (a) ChA I/PVA(99); (b) ChA II/PVA(99); (c) ChA I/PVA(88); (d) ChA II/PVA(88).

3.3. DMA

The DMA curves for homopolymers PVA(99), ChA I, ChA II and their blends are shown in Figs. 5 and 6. The temperature corresponding to the maximum of the peaks in the plot of tan $\delta = f(T)$ are assumed to be the relaxation temperature: glass transition (T_g) or secondary relaxation. The largest peak is generally the α-peak, which is associated with the glass transition temperature.

PVA(99) presents an intensive relaxation with maximum at 95 °C (368 K) attributed to the glass transition and a broader relax-

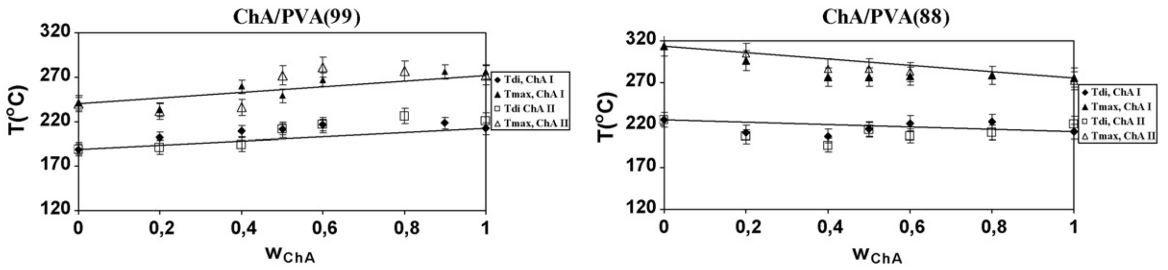

Fig. 3. Temperature of initial decomposition T_{di} and temperature at maximum decomposition rate T_{max} of ChA/PVA blends. Solid line – the values calculated according to the additivity rule.

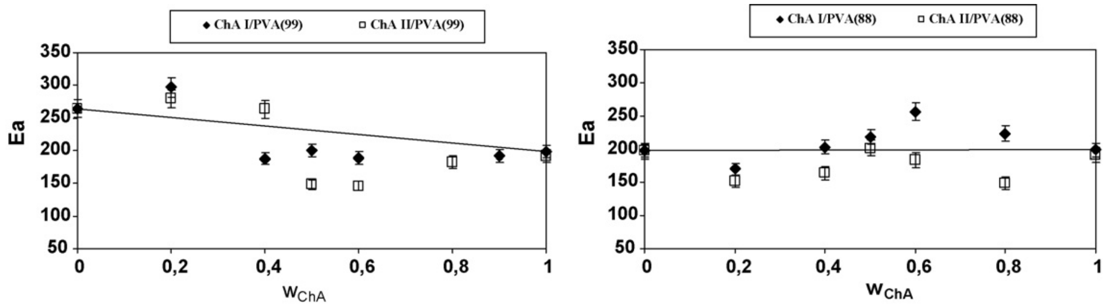

Fig. 4. Activation energy of decomposition (E_a, kJ/mol) versus ChA content (w_{ChA}) in ChA/PVA blends. Solid line – the values calculated according to the additivity rule.

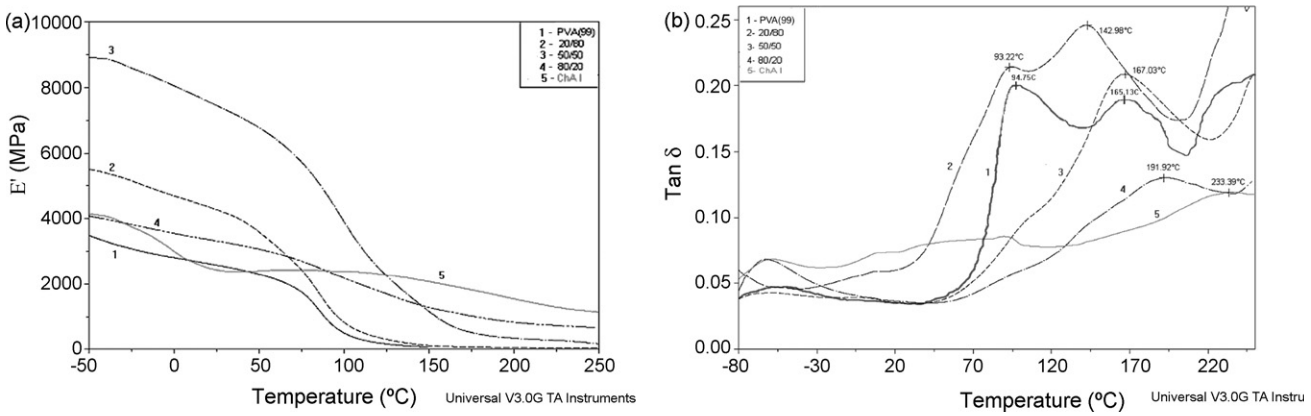

Fig. 5. DMA curves of ChA I, PVA(99) and ChA I/PVA(99) blends. (a) E'; (b) tan δ.

ation with maximum at 165 °C (438 K) (Fig. 5). The relaxation at 165 °C (438 K) is called α_c or α'-dispersion. Takayanagi attributed the α_c relaxation to molecular motion within crystalline phase [30,31]. ChA I and ChA II showed a relaxation at 233 °C (506 K) and at 229 °C (502 K) which is related to the glass transition, respectively. As can be observed the DMA measurements usually give higher values of T_g in comparison with DSC method. In the case of ChA I/PVA(99) and ChA II/PVA(99) blends, the transitions in the blend curves are broad. This indicate an increase in heterogeneity in the samples. The tan δ curves of the blend at $w_{ChA} \leq 0.5$ show small intensive relaxation at ca. 90 °C (363 K), which may correspond to the glass transition of the PVA. This behaviour indicates the lack of miscibility. The conclusion is in agreement with DSC results, where the T_g of blends do not change with the blend composition or could not be determined precisely. It is known that DMA analysis detects molecular relaxations such as the α, T_g processes with a sensitivity higher by factor of approximately 1000 than DSC/DTA. The maximum of tan δ lies between the maxima of the two homopolymers suggesting some interaction in the blend. The shift of the maximum of tan δ in the ChA II/PVA(99) blends is lower than the shift for ChA I/PVA(99).

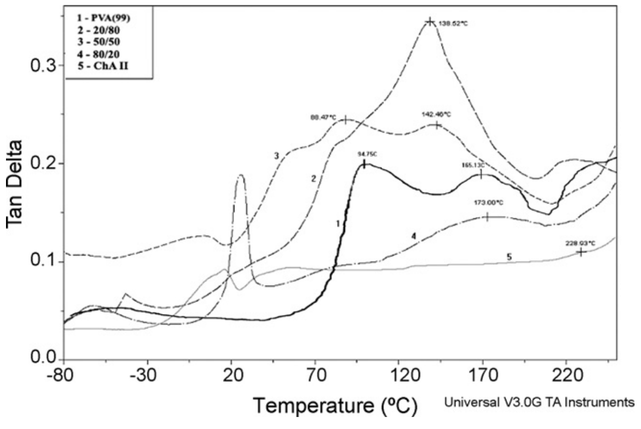

Fig. 6. The tan δ thermograms of ChA II, PVA(99) and ChA II/PVA(99) blends.

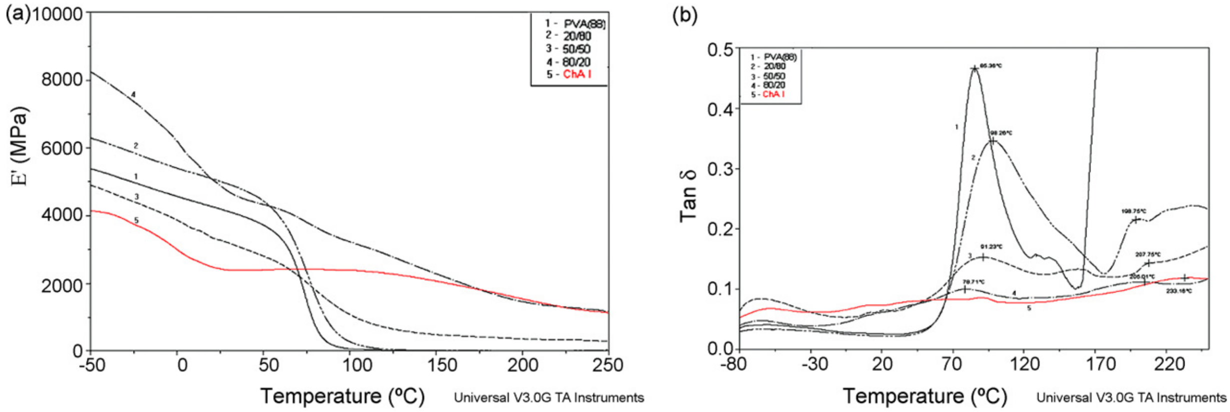

Fig. 7. DMA curves of ChA I, PVA(88) and ChA I/PVA(88) blends. (a) E'; (b) tan δ.

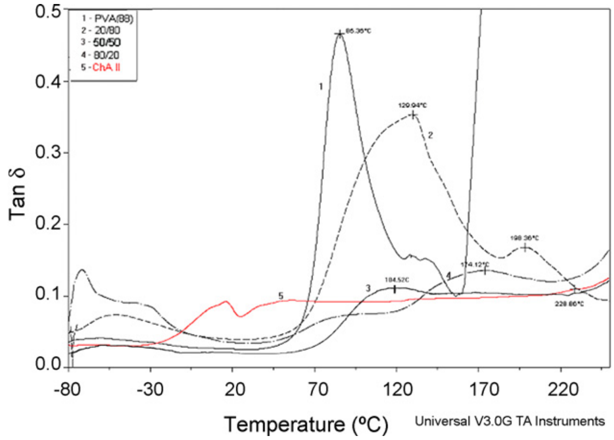

Fig. 8. The tan δ thermograms of ChA II, PVA(88) and ChA II/PVA(88) blends.

The behaviour of tan δ curves for blends containing PVA(88) is similar to that observed for the blends of PVA(99) (Figs. 7 and 8). PVA(88) presented only a relaxation at ca. 85 °C (358 K), which was attributed to the glass transition. In the ChA I/PVA(88) and ChA II/PVA(88) blends the maximum of tan δ shift to higher temperatures with an increase in the ChA content. The blend containing 50% of ChA I or ChA II presented a small shift of glass transition indicating an increase in heterogeneity in the amorphous region.

4. Conclusions

The thermal properties of ChA/PVA blend films are studied. The DSC results show a single T_g value for the ChA I/PVA(88) blends with $w_{ChA} \geq 0.5$. In the case of other blends {ChA I/PVA(99), ChA II/PVA(99), ChA II/PVA(88)} the value of T_g is practically constant for blends with $w_{ChA} \leq 0.5$, or could not be determined precisely. The DSC data show the depression of the melting temperature of PVA with the increase of ChA content. Only for ChA/PVA(99) blends the results of TGA show the enlargement of thermal stability of PVA in the blends. The activation energy of decomposition (E_a) show positive and negative deviations from the linearity. The negative deviations of E_a mainly depend on the molecular weight of chitosan and are the greater the higher is the molecular weight of chitosan. In the case of ChA I/PVA(88) blends at $w_{ChA} \geq 0.5$, the increase of E_a is observed. This may indicate an increase in homogeneity of PVA(88) sample with ChA I. DMA studies confirm the poor miscibility of ChA/PVA blends. In the investigated system of ChA/PVA blends the degree of miscibility (homogeneity) between the polymeric components mainly depends on the degree of PVA hydrolysis (the miscibility sets mainly in the amorphous region), moreover on the blend composition and on the molecular weight of chitosan. Thus, the PVA sample with relatively low DH = 88% and low degree of crystallinity (w_c) of ~17% shows partial miscibility (single value of T_g) with ChA, when the value of w_c in the blend lowers up to about 2% at $w_{ChA} \geq 0.5$, and the $\overline{M}_v$ of chitosan is not to high, as is the case of ChA I ($\overline{M}_v \cong 470 \times 10^3$ g/mol).

References

[1] Z.H. Ping, Q.T. Nguyen, J. Neel, J. Macromol. Chem. 189 (1988) 437.
[2] Y. Nishio, T. Haratani, T. Takahashi, J. Polym. Sci. Part B: Polym. Phys. 28 (1990) 355.
[3] X. Qu, A. Wirsén, A.-C. Albertsson, Polymer 41 (2000) 4841.
[4] R.V. Rao, P.V. Ashokan, M.H. Shridhar, Polym. Degrad. Stab. 70 (2000) 11.
[5] J.F. Mano, D. Koniarova, R.L. Reis, J. Mater. Sci.- Mater. Med. 14 (2003) 127.
[6] K. Lewandowska, Eur. Polym. J. 41 (2005) 55.
[7] G.A.F. Roberts, Chitin Chemistry, first ed., Macmillan Press Ltd., London, 1992.
[8] C.J. Brine, P.A. Sanford, J.P. Zikakis (Eds.), Advances in Chitin and Chitosan, Elsevier Applied Science, London, 1992.
[9] C.A. Finch, in: C.A. Finch (Ed.), Poly(vinyl alcohol), Wiley, New York, 1973.
[10] E. Chiellini, A. Corti, R. Solaro, Polym. Degrad. Stab. 64 (1999) 1346.
[11] A. Corti, R. Solaro, E. Chiellini, Polym. Degrad. Stab. 75 (2002) 447.
[12] M. Miya, S. Yoshikawa, R. Iwamoto, J. Appl. Polym. Sci. 22 (1984) 1149.
[13] H.S. Blair, J. Guthrie, T.-K. Law, P. Turkington, J. Appl. Polym. Sci. 33 (1987) 641.
[14] M. Mucha, React. Funct. Polym. 38 (1998) 19.
[15] W.-Y. Chuang, T.-H. Young, Ch.-H. Yao, W.-Y. Chiu, Biomaterials 20 (1999) 1479.
[16] S.Y. Park, S.T. Jun, K.S. Marsh, Food Hydrocolloids 15 (2001) 499.
[17] P.C. Srinivasa, M.N. Ramesh, K.R. Kumar, R.N. Tharanathan, Carbohydr. Polym. 53 (2003) 431.
[18] A. Pawlak, M. Mucha, Thermochimica Acta 396 (2003) 153.
[19] M. Mucha, A. Pawlak, Thermochimica Acta 427 (2005) 69.
[20] A. Beresniewicz, J. Polym. Sci. 39 (1959) 63.
[21] G.A.F. Roberts, J.G. Domszy, Int. J. Biol. Macromol. 4 (1982) 374.
[22] T.F.J. Pijpers, V.B.F. Mathot, B. Goderis, R.L. Scherrenberg, E.W. van der Vegte, Macromolecules 35 (2002) 3601.
[23] G.Z. Papageorgiou, D.S. Achilias, G.P. Karayannidis, D.N. Bikiaris, Ch. Roupakias, G. Litsardakis, Eur. Polym. J. 42 (2006) 434.
[24] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.
[25] K. Ogura, T. Kanamoto, M. Itoh, M. Miyashioro, K. Tanaka, Polym. Bull. 2 (1980) 301.
[26] M. Pizzoli, G. ceccorulli, M. Scandola, Carbohydr. Res. 222 (1991) 205.
[27] J.A. Ratto, C.C. Chen, R.B. Blumstein, J Appl. Polym. Sci. 59 (1996) 1451.
[28] K. Kamide, M. Saito, Polym. J. 17 (1985) 919.
[29] P.P. Lizymol, S. Thomas, Polym. Degrad. Stab. 41 (1993) 59.
[30] M. Takayanagi, Viscoelastic Properties of Polymers, Mem. Fac. Eng. 23 (1963) 1.
[31] T. Murayama, Dynamic Mechanical Analysis of Polymeric Material. Materials Science Monograph, vol. 1, Elsevier Scientific Publishing Company, Amsterdam, 1978.