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Thermal analysis of chitosan and its blends

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Abstract

The present work is concerned with experimental results of DMTA and DSC techniques, which are used to study phase relaxation behavior of chitosan having various DD and its blends with polyvinyl alcohol (PVAL) and hydroxypropylcellulose (HPC). The analysis of DMTA spectra of chitosan leads to recognition of a few molecular relaxations in chitosan and in its blends. A strong effect of water presence on the macromolecular dynamics is observed. Double "wet" relaxations (close to ambient temperature) are observed. Optical film transparency of the chitosan blends with PVAL and HPC allows us to predict good miscibiliry of components in the complex systems. However, unchanged temperatures of the glass transitions of PVAL and isotropization of HPC in the blends indicate separation of components. However, a low content of PVAL or HPC can be molecularly distributed in a chitosan matrix giving a miscible system of good mechanical properties.
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1. Introduction

Chitosan is a biodegradable polysaccharide having active amino groups. Many papers have recently been published on the utilization of chitosan as a functionalized polymer [1,2]. A method of blending chitosan with other polymers by using cosolvents is often applied. Such polymers as polyvinyl alcohol, hydroxypropylcellulose, polyethylene oxide [3,4] are recognized as materials supporting chitosan to obtain material with sufficient mechanical strength of films and fibers prepared.

The question of whether the polymers are partly or well miscible is of paramount importance. The results of our previous studies on the structure and application of chitosan blends with polyvinyl alcohol or polyethylene oxide used for templated membrane production and paper impregnation [5–7] support good miscibility of the polymeric components in water solutions and partial miscibility in casting films.

It is known that various hydrophilic biological systems absorb water molecules creating hydrogen bonds. The prop-

erties of the systems are strongly affected by the water content. A number of papers deal with the influence of water on the relaxation properties of biopolymers [8–12]. Distinction is made between free water known as "freezing" water, which has the bulk properties of water showing a separate melting transition on DSC thermogram and "non-freezing" water which is difficult to remove by drying under vacuum at moderate temperatures and unrecorded by DSC. Thus, the double scanning applied here in both DMTA and DSC thermal experiments allows us to compare the results for "as cast" and preheated samples. In this paper, the effect of a residual water on phase relaxations of chitosan macromolecules also in film blends with polyvinyl alcohol (PVAL) and hydroxypropylcellulose (HPC) is studied.

2. Experimental

2.1. Materials

- Chitosan (CH) samples (prepared from krill chitin) of various deacetylation degree DD = 59–86% were purchased from the Sea Fishery Institute in Gdynia.

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- Polyvinyl alcohol (PVAL) sample was supplied by the Polish Chemical Reagents.
- Hydroxypropylcellulose (HPC) of $M_w = 1 \times 10^5$ g/mol was supplied by Sigma–Aldrich.

2.2. Preparation of polymer blends

The blends were prepared by mixing of chitosan acidic solution (in 1% acetic acid) with PVAL and HPC aqueous solutions in required ratios to obtain the blends of various compositions. Blend films 50 μm thick were prepared by casting. The samples were dried at room temperature for 24 h and then for 1 h at 80 °C. However, residual water was still present in the films. The samples used for DSC and DMTA studies are characterized in Table 1.

2.3. Thermal analysis

Dynamic mechanical thermal analysis (DMTA) was performed on DMTA Mk III (with head powers and dual cantilever of E geometry damping) of Rheometric Scientific Firm. The dynamic mechanical spectra were recorded under the following conditions: frequency 1 Hz, amplitude 32 μm, heating rate 2°/min, two times scanning over the temperature range from −50 to 130 °C and from −50 to 220 °C.

Thermograms from du Pont DSC Apparatus TA 2920 were obtained for observation of heat effects of all samples in the heating process equal to 10 °C/min. They were recorded for original—"as cast" (first scan ranging from −50 to 170 °C) and preheated (secondary scan ranging from −50 to 220 °C) samples.

3. Results and discussion

3.1. DMTA results

The dynamic-mechanical thermal analysis of polymer materials is of great interest and importance resulting from its great sensitivity in detecting changes of internal molecular

Table 1
Characterization of samples under study

No.	Sample	Symbol
1	Chitosan of DD = 59%	$(CH)_1$
2	Chitosan of DD = 67%	$(CH)_2$
3	Chitosan of DD = 78%	$(CH)_3$
4	Chitosan of DD = 86%	$(CH)_4$
5	Polyvinyl alcohol	PVAL
6	Hydroxypropylcellulose	HPC
7	Chitosan of DD = 78%/polyvinyl alcohol blends of various weight fractions of chitosan: 0.2, 0.4, 0.6, 0.8	$(CH)_3$/PVAL
8	Chitosan of DD = 78%/hydroxypropylcellulose blends of various weight fractions of chitosan: 0.2, 0.4, 0.6, 0.8	$(CH)_3$/HPC

mobility and in probing a phase structure and morphology of polymers.

The DMTA spectra: loss modules E'' or loss factor $T_g \delta = E''/E'$ can show few peaks, which are attributed to the relaxation processes: the main of them being known as α and β. The β process has been assigned to the local mode of relaxation in the amorphous phase. The α relaxation related to the glass transition of the amorphous phase, is controlled by both intra- and intermolecular interactions. It is accompanied by a distinct decrease of the storage modules E' with increasing temperature and the presence of E'' peak.

Data obtained over a broad temperature range can also be used to ensure the molecular response of a polymer in blends with other polymers. In heterogeneous (phase separated) blends the molecular motions of the components remain unchanged, whereas in miscible blends the motions should be strongly affected and a single α transition appears [13].

3.1.1. Chitosan of various DD

DMTA complex spectra E', E'' and $T_g \delta$ of chitosan samples $(CH)_1$–$(CH)_4$ of various DD were registered. Fig. 1a and b, presents, for example, two scan spectra (taken directly form the apparatus) of "as cast" chitosan sample of $(CH)_3$ (first scan I ranging from −50 to 130 °C) and of the same preheated sample (second scan II ranging from −50 to 200 °C). Moreover, Fig. 2a and b has shown the storage modulus spectra E' of chitosan samples $(CH)_1$–$(CH)_4$ drawn in the two scans, respectively.

Loss modulus E'' spectra of $(CH)_3$ (first and second scans) and $T_g \delta$ spectra of $(CH)_1$–$(CH)_4$ samples (second scan) are shown in Fig. 3a and b.

The clear differences in the DMTA curves obtained in the first and the second scans are seen. In the case of "as cast" sample, loss factor peaks (E'') occur at $T_1 = -21$ °C, $T_2 = 24$ °C and $T_3 = 43$ °C. They move to higher temperatures at $T_1 = -12$ °C, $T_2 = 32$ °C and $T_1 = 45$ °C, in the second scan. The respective peaks on $T_g \delta$ curves are observed at some lower temperatures. Clearly seen broad $T_g \delta$ peak at 156–170 °C denoted as temperature T_4 (see Fig. 3b) is recognized as α relaxation at T_g of chitosan. T_4 value decreases with increasing DD of chitosan (Fig. 4b). At such comparable high temperature, chain mobility of chitosan increases also by weakening intermolecular interactions due to dissociation of hydrogen bonds. Probable starting of a molecular chain scission due to breaking of glycosidic bonds occurs [17,18].

The transition occurring at a temperature close to $T_1 = -21$ °C can be recognized as β relaxation, associated with local motions of side groups in chitosan. In general, pure polysaccharides broad relaxation, observed by dielectric spectroscopy [14–16] at low temperature range (−120 to −5 °C) is recognized as due to orientational motions of local segments via the glycosidic bonds. It was found for cellulose, starch and dextran in the wet and dried state. The molecular similarity between these polysaccharides and chitosan and the presence of the glycosidic linkage in their polymer back-
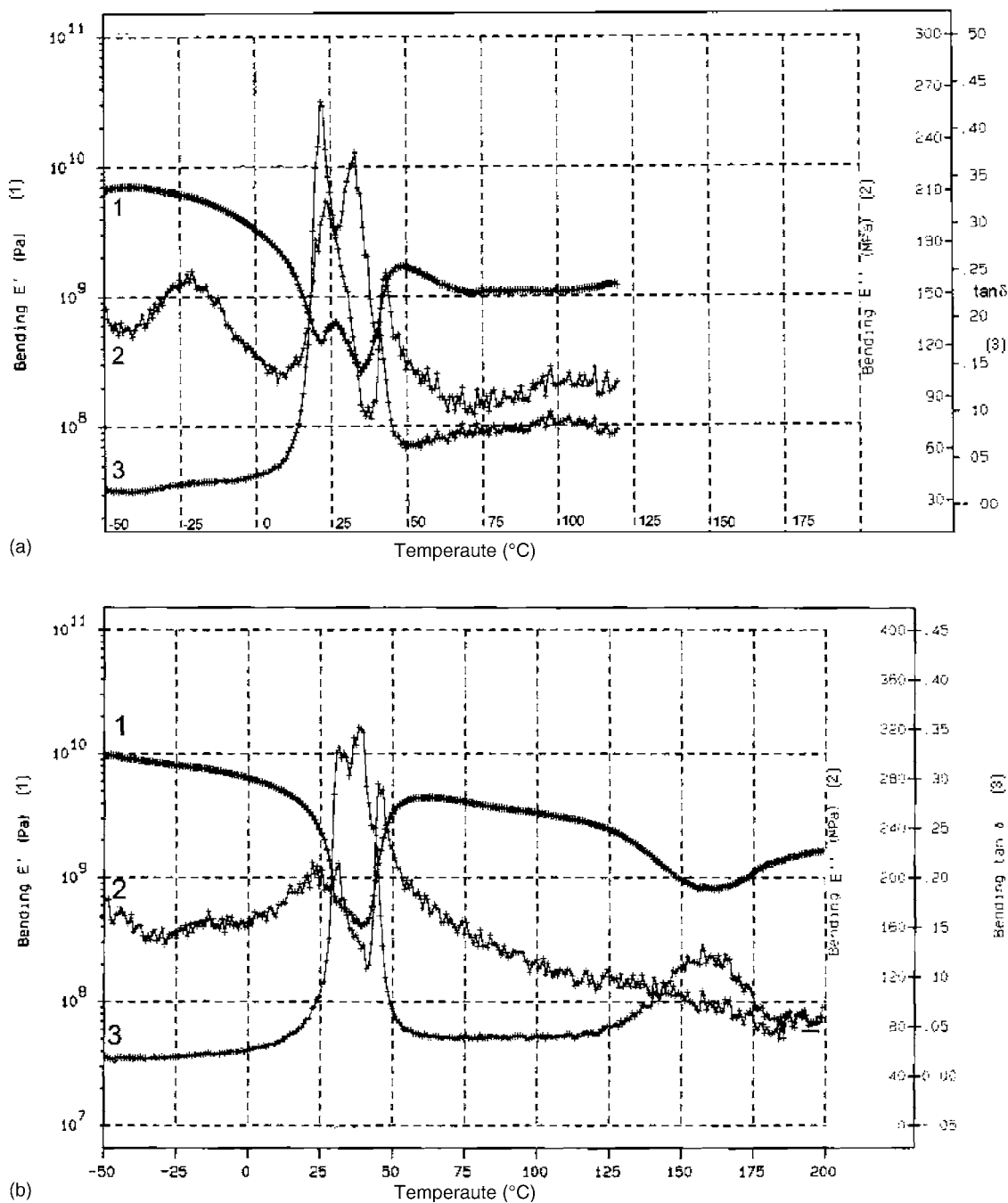
Fig. 1. DMTA spectra E' (1), E'' (2) and T_g δ (3) vs. temperature taken for $(CH)_3$: (a) first scan; (b) second scan.

bone allows to predict the same behavior. The T_1 temperature of chitosan decreases with increasing DD (Fig. 4a). It means an increasing number of substitutions of amide group present in chitin chain by a smaller and more mobile amino group.

The strongest complex relaxations at T_2 and T_3 occurring at ambient temperature (any heat effects in calorimetric studies are observed) can be recognized as a structural reorganization of packing of chitosan molecules due to an increase of residual water mobility, volume expansion and following change of hydrogen bond strength. Thus after initial strong decrease of E' an increase at about 50 °C is observed. At the second heating scan the amount of water in chitosan film is lower. Thus, the values of T_1, T_2 and T_3 temperatures increase because the system appears stiffer. Also the amplitude of E'' at the relaxation temperatures is found lower by 30%. When the samples were heated to 200 °C the residual water was removed and the chitosan molecular degradation and crosslinking were observed [17,18]. Thus, in the following heating scans the relaxations at T_1, T_2 and T_3 completely disappeared.
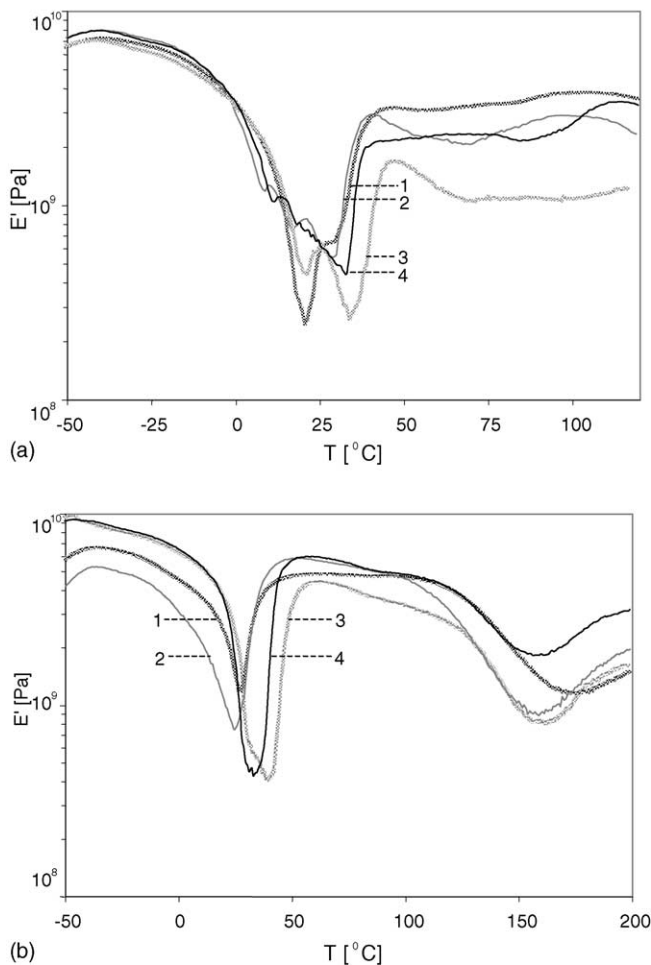
Fig. 2. Storage modulus E' spectra of chitosan samples of various DD: (1) $(CH)_1$; (2) $(CH)_2$; (3) $(CH)_3$; (4) $(CH)_4$; (a) first scan (I); (b) second scan (II).

Also dielectric spectra of the wet polysaccharides [12] show an additional relaxation process at ambient temperatures named as "β wet relaxation". It vanishes after drying but appears again after rewetting. The shape of this relaxation process and the Arrhenius plot of its relaxation time characterize this relaxation process as more Debye-like referring to a non-cooperative motion. The authors assume that this relaxation belongs to reorientation process in gel-like phases of a polymer-water system.

Fig. 3. (a) Loss modulus E'' spectra of chitosan sample $(CH)_4$; first scan (I) and second scan (II). (b) T_g δ spectra of chitosan samples of various DD (second scan): (1) $(CH)_1$; (2) $(CH)_2$; (3) $(CH)_3$; (4) $(CH)_4$.

3.1.2. Chitosan/PVAL blends

E'' spectra of chosen $(CH)_3$/PVAL blend (for clarity) having weight ratio of components equal to 2/8 as well as those of two homopolymers are shown in Fig. 5a and b. They are obtained in the first scan ("as cast" samples) and in the second scan (preheated samples), respectively.

The following observations have been made.

1. The transitions in the blends spectra are broad. It is due to close placements of PVAL α relaxation at $(T_{g1}(I))$ and

Fig. 4. Relaxation temperatures of chitosan: (a) T_1, β relaxation (first scan) and (b) T_4, α relaxation (second scan) drawn vs. chitosan DD.

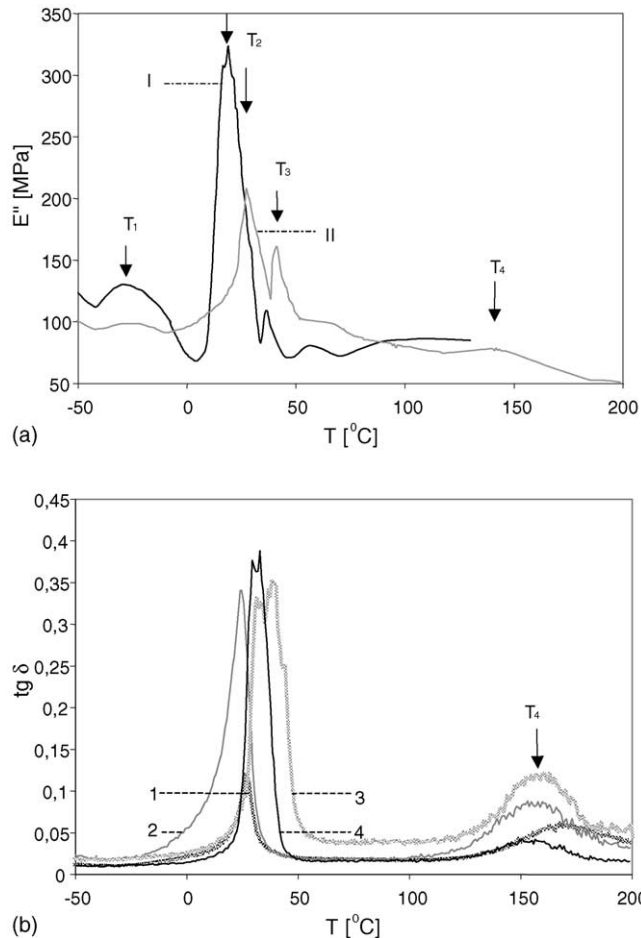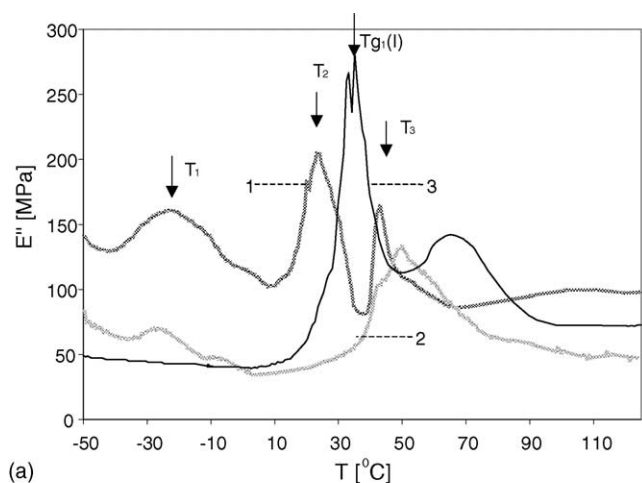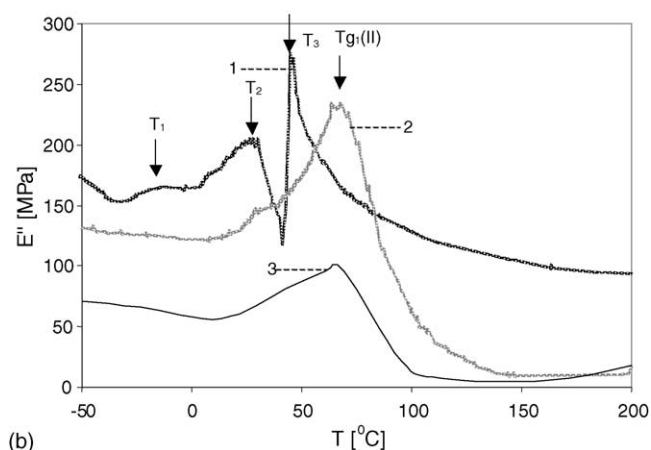(a)

(b)

Fig. 5. E'' spectra of $(CH)_3$ (curve 1), PVAL (curve 3) and chitosan/PVAL blend of $w_f = 0.2$ (curve 2); (a) first scan (I); (b) second scan (II); w_f: weight fraction of chitosan.

a "wet" relaxation of "as cast" chitosan sample at T_2 and T_3.

2. In the second scan, chitosan relaxation peak at T_2 is weakly seen in the blends. It moves slightly to lower temperature with increasing PVAL content.

3. The β relaxation at T_1 of chitosan in the blend is weakly seen and its temperature does not change with increasing PVAL in blends.

4. The temperature of α relaxation T_{g1} of PVAL slightly increases in blends with rising chitosan content. It indicates some interactions of both macromolecules by hydrogen bonds [19]. T_{g1} value of PVAL is equal to 40–50 °C (max E'') for "as cast" sample. It is known from literature that the T_g of PVAL is strongly affected by a water content. Water exerts a plasticizing effect on the polymer, lowering its glass transition temperature. The T_g value increases to 65–75 °C (or 75–85 °C from $T_g \delta$) in the second scan for an anhydrous sample. The results are in agreement with DSC ones.

5. The temperature of chitosan α relaxation (T_{g2}) in the blends equal to 160–170 °C is found. The plots
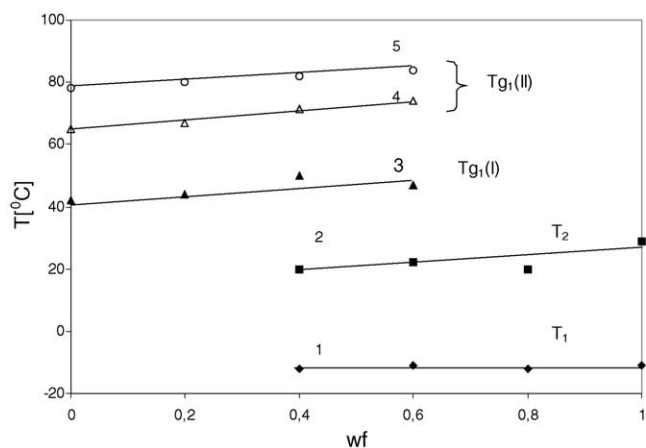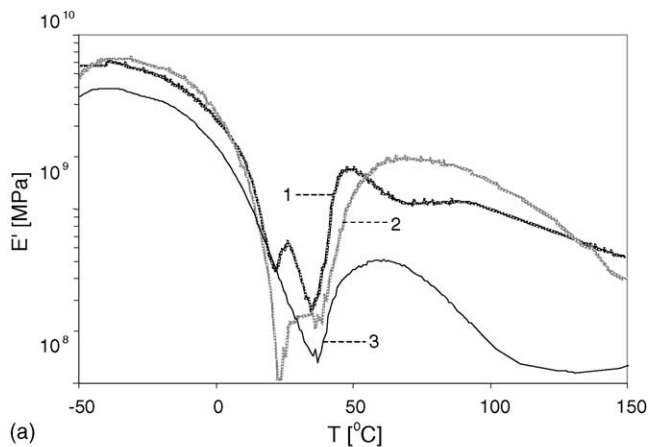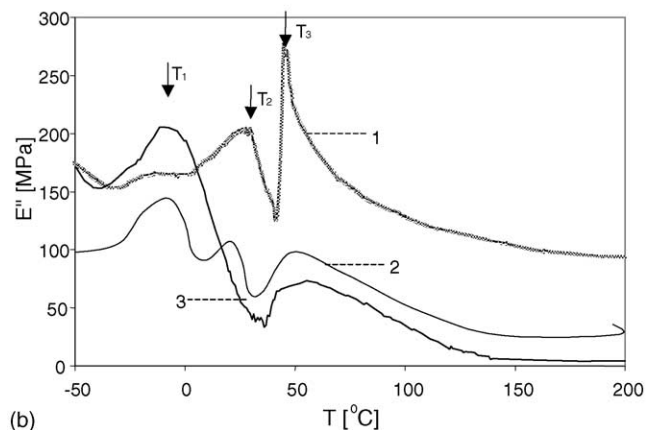

Fig. 6. Chitosan relaxation temperatures T_1 and T_2 (curves 1, 2) and T_{g1} (curves 3: T_{g1}(I) and 4: T_{g1}(II) (from E''), 5: T_{g1}(II) (from $T_g \delta$)) vs. weight fraction w_f of chitosan: I, first scan; II, second scan.

of T_1 and T_2 (relaxation temperatures in chitosan) and T_{g1} (α relaxation of PVAL) versus weight fraction of chitosan in the blends are presented in Fig. 6.

(a)

(b)

Fig. 7. E' and E'' spectra of $(CH)_3$ (curve 1), HPC (curve 3) and chitosan/HPC blend of $w_f = 0.2$ (curve 2); (a) first scan (I); (b) second scan (II).
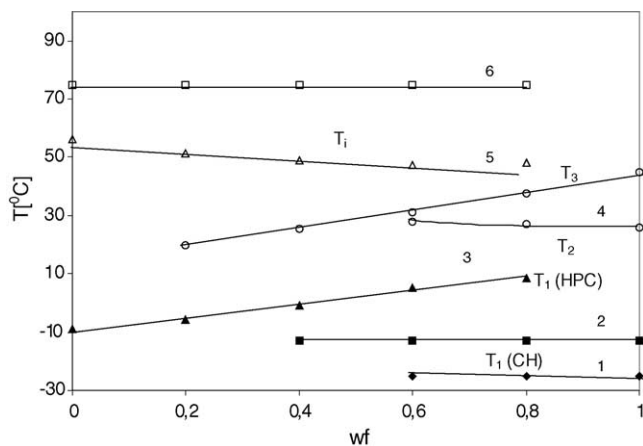
Fig. 8. Relaxation temperatures vs. weight fractions of chitosan in the blends (chitosan//HPC): curve 1, $T_1(I)$; curve 2, $T_1(II)$ and curve 4, $T_2(II)$, $T_3(II)$; curve 3, HPC β relaxation at T_1, 5-HPC isotropisation transition at T_i (taken from E''); and 6 (taken from T_g δ). I: first scan, II: second scan.

3.1.3. Chitosan/HPC blends

DMTA spectra of chosen chitosan/hydroxypropyl-cellulose blend ($w_f = 0.2$) as well as CH and HPC are shown in Fig. 7. Relaxation temperature observed in the blends are drawn versus weight fraction of chitosan in Fig. 8.

The following conclusions can be drawn from the analysis of the spectra.

1. The β relaxations with a maximum at T_1 are observed in chitosan, HPC and in their blends. T_1 value of "wet" chitosan is about $10\,°C$ lower than the ones of preheated sample. However, T_1 of HPC appears few degrees higher than T_1 of $(CH)_3$ and its value increases with increasing chitosan content in the blends.

2. The characteristic "wet" relaxation of chitosan macro-molecules is broad and consists of two peaks T_2 and T_3 perhaps connected with various mobility of both comonomers present in chitosan structure in "wet" con-
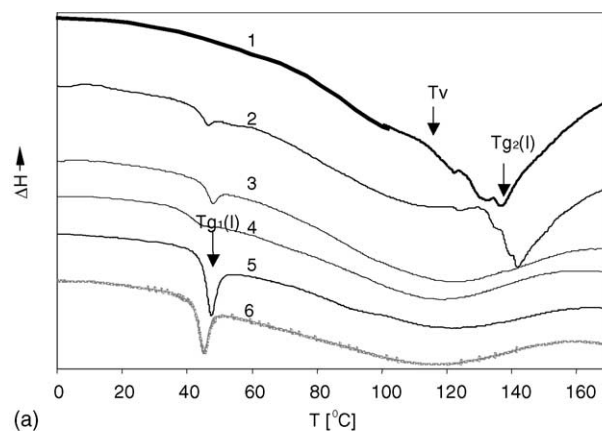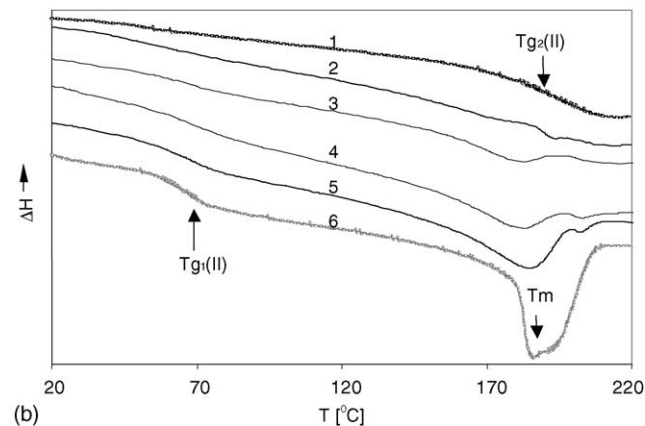
Fig. 10. DSC thermograms of chitosan/PVAL blends of various weight fractions of chitosan w_f: curves: (1) (CH) $w_f = 1$; (2) $w_f = 0.8$; (3) $w_f = 0.6$; (4) $w_f = 0.4$; (5) $w_f = 0.2$; (6) $w_f = 0$ (PVAL), $T_{g1}(I)$: glass transition temperature of PVAL; $T_{g2}(I)$: glass transition temperature of CH; T_v: temperature of water evaporation; T_m: melting point of PVAL (a) first scan; (b) second scan.

ditions. T_3 temperature of chitosan moves with changing the blend composition.

3. Both components of the blends are polysaccharides and have a similar chemical structure. Solvent-cast blend films
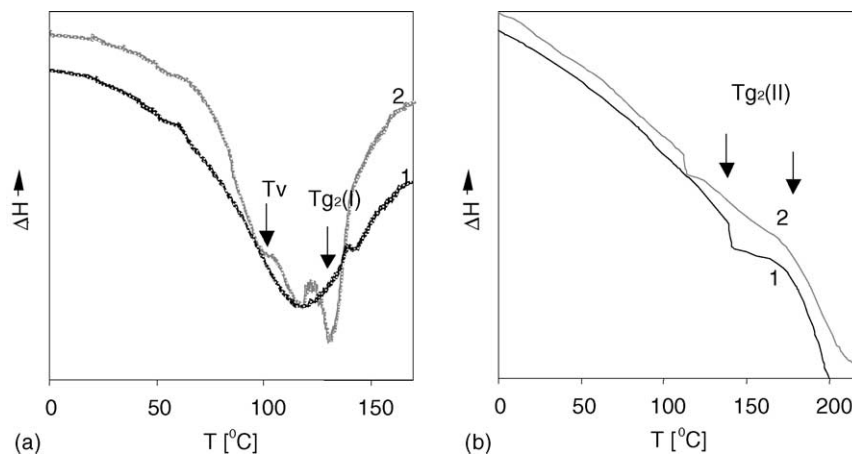

Fig. 9. DSC thermograms of two chitosan samples of various DD: $(CH)_1$ (curve 1); $(CH)_4$ (curve 2); (a) first scan; (b) second scan.
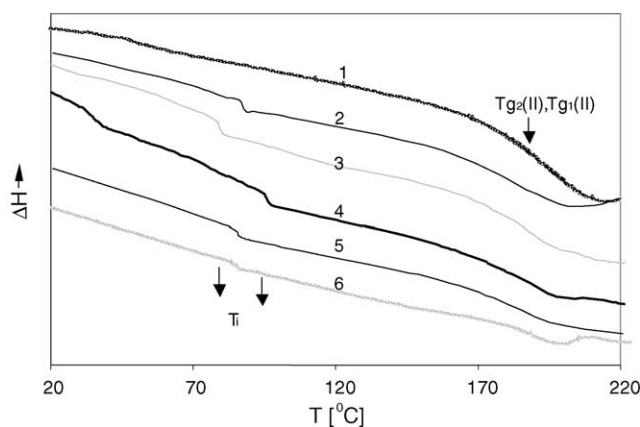
Fig. 11. DSC thermograms (second scan) of CH/HPC blends of various weight fractions of chitosan w_f: curves (1) (CH) $w_f = 1$; (2) $w_f = 0.8$; (3) $w_f = 0.6$; (4) $w_f = 0.4$; (5) $w_f = 0.2$; (6) $w_f = 0$ (HPC). $T_{g2}(II)$ and $T_{g1}(II)$ glass transitions of chitosan and HPC at second scan. T_i: critical (isotropisation) temperature of HPC.

are transparent in a macroscopic optical scale. The relaxation at $T = 60–70\,°C$ can be identified as the isotropization temperature of HPC and it is seen also in the blends. The DSC second scan curve has shown also a heat capacity jump at about $70–90\,°C$.

4. The α relaxation of chitosan ($T_{g2}(II)$) in the blends is observed at the temperature range $158–162\,°C$.

3.2. DSC results

Figs. 9–11 present DSC thermograms of two chitosan samples $(CH)_1$ and $(CH)_4$ and chitosan $(CH)_3$ blends with PVAL and HPC taken for "as cast" (first scan) and for preheated samples (second scan).

A broad endothermic peak close to $100–120\,°C$ observed on the first scan curves (Figs. 9a and 10a) is attributed to evaporation of residual water, from "as cast" samples. In the case of chitosan samples the endothermic peak is extremely irregular. In the vicinity of $110–140\,°C$ the glass transition temperature $T_{g2}(I)$ of water-plasticized chitosan macromolecules is assumed to appear. The T_g temperature of chitosan preheated samples moves to a higher value ($T_{g2}(II)$) equal to about $170\,°C$. However, at high magnification (Fig. 10b) residual peaks at $110–140\,°C$ are also visible. Some part of samples stays still plasticized by water.

The glass transition $T_{g1}(I)$ of PVAL in the blends is determined on the first scan thermogram in Fig. 10a as a hysteresis peak in the vicinity of $45\,°C$. The T_{g1} value is low due to plasticizing effect of water. In the second scan of preheated samples the hysteresis disappears and $T_{g1}(II)$ of PVAL increases to $70\,°C$. The transition is getting broader and weaker for rich chitosan blends. At the same time, the $T_{g2}(II)$ of chitosan in the blends with PVAL moves to higher temperature equal to about $170\,°C$.

A strong endothermic peak? in the vicinity of $190\,°C$ resulting from melting of PVAL crystalline phase is seen in Fig. 10b. The melting enthalpy decreases with decreasing PVAL content in the blends. Also the peak position moves to lower temperature value indicating diluent effect due to the influence of interactions of both macromolecules probably by hydrogen bonds.

Fig. 11 presents DSC (second scan) thermograms of chitosan $(CH)_3$ blends with HPC. Both polysaccharides have shown broad jump at $170–180\,°C$ which can be recognized as their T_g reflecting increase of molecular movement due to dissociation of hydrogen bonds and starting of molecular chain scissions.

The origin of a jump located at $T_1 = 80–90\,°C$ observed on DSC thermograms (and DMTA) of HPC and the blends is not precisely resolved (observed also in DMTA results). It can be recognized as HPC critical temperature in which transformation from anisotropic (mesomorphic liquid crystalline order) to an isotropic phase of the HPC macromolecules occurs [21,22].

4. Conclusions

1. The presented of DMTA spectra of chitosan and its blends are complicated due to complex molecular dynamics in the complex structure of polysaccharides. Hydrophilic nature of the polysaccharides is reflected in a strong effect of absorbed water on the macromolecular mobility. The analysis of DMTA spectra of chitosans indicated a few molecular relaxations existing in chitosan and in its blends.
2. The broad peak of β relaxation is recognized in the vicinity of $T_1 = -20$ to $-10\,°C$. The β relaxation is due to local side chain movement of polysaccharides. The temperature of the β relaxation decreases with increasing deacetylation degree (DD) of chitosan and changes with water content.
3. Chitosan is a copolymer, partly deacetylated chitin. The "wet" relaxations, at T_2 and T_3 associated with water presence are dependent on amino groups content and their distribution in chitosan. Double "wet" relaxation at T_2 and T_3 can result probably from various water affinities of both comonomers in the copolymer. The water content in chitosan depends on DD and it is the higher the lower is DD. It reaches about 16 wt.% at 60% air humidity [20].
4. The α relaxation in the region of glass transition temperature of chitosan depends on water acting as a plasticizer. A broad water evaporation peak in the vicinity of $100–130\,°C$ covers T_g of water-plasticized chitosan. It seems that a free, weak bonded water molecules are removed from the system by heating in first scan to $130\,°C$. It still stays a stronger bonded water which affects DMTA behavior in the second scan. The α relaxation of preheated chitosan samples moves to higher temperature equal to $140–160\,°C$. At such comparable high temperature intermolecular interactions of hydrogen bonds break allowing molecular motion. Perhaps molecular chain scissions can

start at the temperatures. Heating to 200 °C has caused a degradation and crosslinking of chitosan molecules leading to a stiffer system. In the following scans most of the previously observed relaxations disappear.

5. Good optical transparency and good mechanical strength of films made from chitosan blends with PVAL and HPC resulted in prediction of good miscibility of components in the system. However, the presence of both T_g of PVAL and T_i of HPC in the blends at almost the same temperatures indicates the separation of components. Low content of PVAL or HPC (up to 15 wt.%) can be molecularly distributed in a chitosan matrix giving a miscible system of specific mechanical properties [6]. The phase separation of components occurs more drastically after water removal. The water molecules in such a system are an active compatibilizer which works as a "glue" acting by formation of additional hydrogen bonds.

Acknowledgments

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