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COMPATIBILITY OF FIBROIN/CHITOSAN AND FIBROIN/CELLULOSE BLENDS STUDIED BY THERMAL ANALYSIS

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The compatibility of fibroin with chitosan was confirmed by means of the DSC method, measuring thermal characteristics of blends of these components in the form of films obtained from solutions in a common solvent such as HFIP. Polymers have the general temperatures of glass transition and the beginnings of degradation of crystal areas. The TG analysis of fibroin/cellulose blends in the form of films obtained from NMMO solutions has shown that the thermal stability of such blends is higher than that of cellulose owing to the strong interaction between the components, which is also shown by the decreased mass loss rate of the blend during thermal treatment, as compared to that of individual components.

Keywords: *blends, cellulose, chitosan, DSC, fibroin, TG*

Introduction

The formation of polymeric blends constitutes a perspective way of making materials with new properties, especially from natural polymers that are of special importance. Fibroin, a component of silk, with its unique characteristics can be used for biotechnological and biomedical applications such as powders, gels and films [1–3]. The basic disadvantage of films obtained by the coagulation of fibroin solution is their increased fragility: in a dry condition, they are practically unsuitable for use [4, 5]. Fibroin in silk fibres is plasticised by other natural polypeptide such as sericin and therefore silk fibres are strong and elastic. The formation of fibroin blends with other polymers is one of the ways to improve the properties of fibroin films. Taking into consideration the area of application, film-forming polysaccharides such as cellulose and chitosan seem to be very promising as the second component of such blends. They have many active groups capable of interacting with fibroin macromolecules, which is a necessary condition for the compatibility of polymers in solutions and films. Fibroin/cellulose blends from solutions in cuoxam [6] and fibroin/chitosan blends coagulated from the mixtures of dialysed solutions of fibroin in LiBr-water and solutions of chitosan in acetic acid have been investigated [1, 7]. The capability of these components to interact through the formation of hydrogen bonds has been shown by FTIR. This interaction should become apparent in the examination of the blends by the methods of thermal analysis, which play the major role in the assessment of component compatibility in polymer blends. The amorphous part of polymers is characterised by the glass transition temperature, whose value depends on the composition of blend [8]. Fibroin and chitosan have the glass transition temperature of amorphous regions ranging from 130 to 190°C [9, 10]. The glass transition temperature of cellulose is equal to 220–240°C, being above the temperature of initial degradation, which begins at 150°C [11, 12]. Therefore, to make the characteristic of thermal behaviour of blends fibroin with chitosan is very important the modification of temperature of glass transition components. In the case of fibroin blends with cellulose it is expedient to use thermal stability parameters. The thermal stability of cellulose in blends with synthetic polymers decreases in conformity with the degree of compatibility, as shown by Nishioka *et al*. [13–15].

Experimental

Materials

The fibroin of *Bombyx mori* silk in the form of short fibres with a length of 3.6 mm and a diameter of 34.6 μm was washed to remove fatty, wax and mineral substances. Cellulose with a DP of 495 was used. Its α-cellulose content was 95.8%, dry substance 89.8% and degree of whiteness 91.8%. The chitosan used had the following characteristics: deacetylation degree 95%, moisture content 7.5%, viscosity of 2% solution in 2% acetic acid at 25°C, 30.8 mPas.

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Hexafluorisopropanol (HFIP) from Merck-Schuchardt was used as solvent for the preparation of fibroin blends with chitosan, while the fibroin blends with cellulose were prepared with the use of N-methylmorpholine-N-oxide (NMMO) from Merck-Schuchardt.

Sample preparation

Fibroin and cellulose were dissolved in NMMO at 95°C for several hours under constant stirring. Films were prepared by casting 2% solutions on polyethylene plates followed by their coagulation with a water-alcohol mixture. After coagulation, the films were washed with deionised water before the complete removal of solvent and dried 48 h in air at room temperature 23°C and relative humidity *RH*=65%.

The films of fibroin–chitosan blends were prepared according to [16] and the solvent was removed by evaporation 24 h in air at 23°C and relative humidity *RH*=65%.

The thickness of films 0.04–0.06 mm.

Measurements

Differential scanning calorimetry measurements were carried out by means of a DSC-204 micro-calorimeter of Netzsch within the temperature range from 30 to 500°C under nitrogen (50 mL min^{-1}) at a heating rate of 10°C min^{-1} and sample mass 2–3 mg.

Thermogravimetry (TG) was carried out in air with the use of a MOM Q-1500 D thermogravimetric system (Hungary) within the temperature range from 23 to 500°C at a heating rate of 2.5°C min^{-1} and sample mass 100 mg.

Results and discussion

Fibroin/chitosan blends

The results of DSC measurements of fibroin, chitosan and their blends are given in Table 1. The DSC curve of a pure fibroin film (Fig. 1, curve 7) shows an endothermic peak at 78°C ($T_{1\text{fibr}}$), attributed to the evaporation of adsorbed water. Glass transition of the fibroin amorphous regions was also observed at 152°C ($T_{2\text{fibr}}$), then one can observe a small exothermic effect of transition during heating by forming the β-sheet structure from a random-coil conformation [9, 17]. The small endothermic peak at 246°C is attributed to the strong molecular motion within the α-helix crystals [18]. It is known [19, 20] that in fibroin solutions in HFIP, 50% of macromolecules are positioned in α-helix conformation, which remain in fibroin films. The endothermic peak at about 280°C is connected with the thermal degradation of the crystal regions of fibroin [9]. Figure 2 shows the TG curve of the film fibroin, measured in the same conditions (heating rate of 10°C min^{-1} under nitrogen). Onset of intensive mass loss correspond with the endothermic

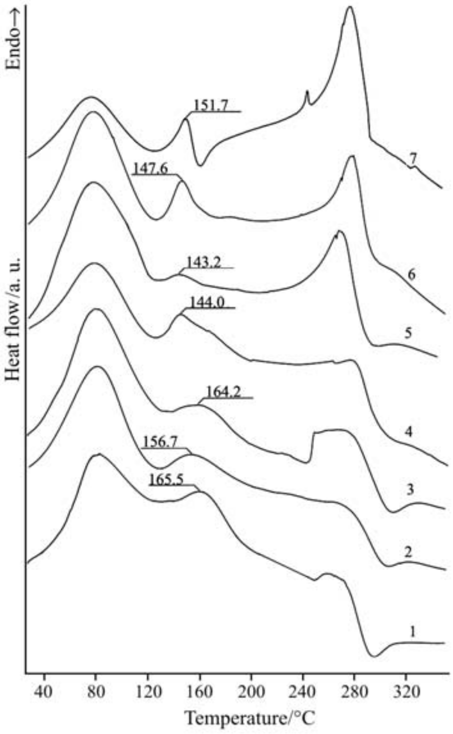

Fig. 1 DSC curve of films chitosan/fibroin: 1 – 100/0, 2 – 80/20, 3 – 60/40, 4 – 40/60, 5 – 30/70, 6 – 20/80, 7 – 0/100 mass%

Table 1 DSC data of fibroin/chitosan blend films

Content of chitosan/mass%	$T_{1\text{fibr}}$/°C	$T_{1\text{chit}}$/°C	ΔH_1/J g^{-1}	$T_{2\text{fibr}}$/°C	$T_{2\text{chit}}$/°C	$T_{\alpha\ \text{fibr}}$/°C	$T_{\text{degr.fibr}}$/°C	$T_{\text{degr.chit}}$/°C
–	78.2	–	106.3	151.7	–	246.4	280	–
20	79.4		134.9	147.6		–	280	
30	88.3		119.2	143.2		–	277	
40	78.9		124.5	144.0		–	276	
60	96.8		236.1	164.2		–	275	
80	81.7		267.5	156.7		–	268	
100	–	101.0	109.3	–	165.5	–	–	262

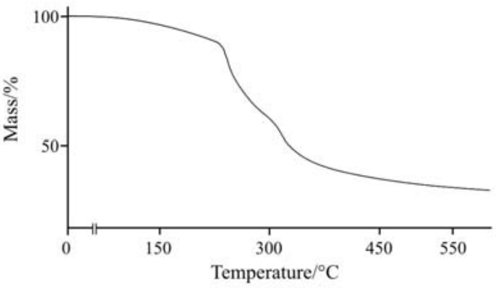

Fig. 2 TG of a film fibroin prepared from HFIP

peak about 246°C. The mass loss rate increases and attains its maximum at 280°C, when the degradation in β-crystal regions begins. During further heating until about 310°C the degradation rate slows down and later on it increases.

The chitosan film shows some endo-effects in the DSC (Fig. 1, curve 1), which are attributed to the removal of adsorbed water ($T_{1\text{hit}}$ at 101°C), glass transition ($T_{2\text{hit}}$ at 165°C). Beginning of thermal decomposition of chitosan can observed at 262°C ($T_{\text{degr.hit}}$) [10, 21].

The DSC curves of polymer blends with different compositions (Fig. 1, curves 2–6) show general thermal effects T_1, T_2 and T_{degr} that attest to the compatibility of components. If the content of chitosan is 20–40%, one can observe a decrease in the glass transition temperature. It may be connected with decreased sizes of amorphous domains due to the formation of a more homogeneous structure at this composition. If the content of chitosan in the blend is 60%, the endo-effect of the glass transition increase. It is possible that the structure of the blends becomes more amorphous. The increase in the thermal effects of water evaporation also testifies to it. When chitosan is added, the peak at 246°C disappears. This peak is attributed to the motion of fibroin α-crystals. One may believe that the presence of chitosan prevents the formation of crystal α-helix conformation of fibroin macromolecules, where mainly hydrogen bonds can be formed inside the spiral due to the preferable interaction of diverse macromolecules [22, 23]. The formation of intermolecular fibroin–chitosan bonds leads to coordinated polymers in respect of glass transition. The formation of both hydrogen and ionic bonds is probable as chitosan is a weak base [10] and fibroin – a weak polyacid [9]. The blend conforms to known Fox's equation for compatible polymers with a deviation from T_2 of no more than 15%:

$$1/T_g=\omega_1/T_{g1}+\omega_2/T_{g2}$$

where T_g, T_{g1} and T_{g2} are glass transition temperatures of the blend, polymer 1 and polymer 2, respectively; ω_1 and ω_2 – mass fraction of polymer 1 and 2 in the blend, respectively.

The behaviour of components in crystal regions is also coordinated. This is confirmed by the temperature of intensive degradation of the crystal regions changing proportionally to the change in the blend composition.

Thus, in addition to other methods, the DSC data of fibroin/chitosan blends, precipitated from HFIP solutions, allow one to draw a conclusion on the compatibility of polymers.

Fibroin/cellulose blends

TG curves of fibroin, cellulose and fibroin/cellulose films coagulated from solutions in NMMO are shown in Fig. 3. The thermal decomposition of the polymers and their blends under investigation, accompanied by mass losses, takes place in several stages (Table 2).

At the first stage, the mass loss of fibroin films (curve 6) during heating in air at 100°C is connected with the evaporation of water (6%). Until reaching 250°C, a slight mass loss occurs due to the changes in amorphous regions. At 250°C, the mass loss rate increases and attains its maximum at 280°C, when the degradation of H-bonds in β-crystal sites of the polymer begins. At 500°C, the mass loss of fibroin film amounts to 77%.

At the first stage of heating cellulose film (curve 1) at a temperature of 105°C, the mass loss is 11.2% corresponding to the evaporation of ad-

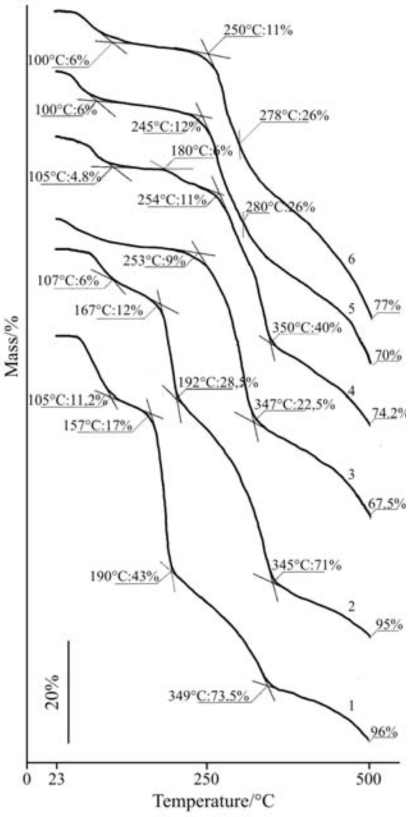

Fig. 3 TG of films cellulose/fibroin: 1 – 100/0, 2 – 90/10, 3 – 70/30, 4 – 50/50, 5 – 10/90, 6 – 0/100 mass%

Table 2 TG data of fibroin/cellulose blend films

Content of cellulose/mass%	Stages of the thermal decomposition/°C				Δm (500°C)/%
	cellulose			fibroin	
–	–	–	–	250	77
10	–	–	–	245	70
50	–	–	350	254	74.2
70	–	–	347	253	67.5
90	167	192	345		95
100	157	190	349	–	96

sorbed moisture. During heating above 157°C, the degradation rate sharply increases to reach its maximum at 190°C. At this temperature the mass loss of the sample is 43%. During further heating, the degradation rate slows down and later on it increases again to reach a new maximum at 349°C (the mass loss amounts then to 73.5%). Probably at the first stage of degradation, amorphous areas decompose by the dehydroxylation of cellulose units, while at higher temperatures decomposition takes place in the crystal areas of the polymer [24–30]. At a temperature of 500°C the mass loss amounts to 96%, which corresponds to the evaporation of volatile products of polymer chemical degradation.

When some fibroin is added to cellulose (TG curve 2–5), the intensive mass loss begins at a higher temperature as compared with that of 100% cellulose, being characteristic of the thermal degradation of fibroin crystals. The character of curve changes with the increase in the fibroin content. The mass loss rate of blends is lower than that of individual components.

The loss of mass decreases with the increase in the content of fibroin.

At 500°C the mass loss of samples containing less than 90% of cellulose amounts to 67.5–74.2%, while the mass loss of 100% cellulose film at this temperature is 96% and that of 100% fibroin amounts to 77%. The fibroin/cellulose blend in proportion 30/70 has turned out to be the most stable during heating up to 500°C. Thus, the addition of fibroin increases the thermal stability of cellulose, slowing down its thermal degradation. The results obtained confirm the presence of strong interaction between diverse macromolecules. Strong contacts between –OH groups of cellulose and –NH-groups of fibroin that have been formed in solution remain in films after the removal of solvent.

Conclusions

The compatibility of fibroin with chitosan was confirmed by means of the DSC method, measuring thermal characteristics of blends of these components in the form of films obtained from solutions in a common solvent such as HFIP. Polymers have the general temperatures of glass transition and the beginnings of degradation of crystal areas. The relationship between glass transition temperature and the composition of polymer blend can be described by Fox's equation with a maximal deviation of 15%. If the content of chitosan in a blend is 60% or more, the increase in the amorphous part of samples as the result of interaction, at the same time the values of enthalpy of evaporation of water and glass transition increase.

The TG analysis of fibroin/cellulose blends in the form of films obtained from NMMO solutions has shown that the thermal stability of cellulose in such blends is higher than that of cellulose owing to the strong interaction between the components, which is also shown by the decreased mass loss rate of the blend during thermal treatment, as compared to that of individual components.

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