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Mechanical properties and transition temperatures of crosslinked-oriented gelatin

II. Effect of orientation and water content on transition temperatures

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Abstract This second part of a systematic study of the properties of crosslinked-oriented gelatin involves the effects of orientation and water content on the glass transition temperature T_g and on the melting behavior. The samples were the same as those in the preceding study, and their transition temperatures were determined by both differential scanning calorimetry and dynamic mechanical thermal analysis. The crosslinked gelatin which had been room-conditioned showed two transition temperatures: the lower one was attributed to T_g of the water-plasticized gelatin, and the higher one was interpreted as T_g of dried gelatin superimposed by melting. A rather unusual situation arose because of the fact that the T_g and melting temperatures T_m (217 and 230 °C, respectively) are so similar. Using water as plasticizer not only decreases T_g but produces imperfect crystallites which melt below the T_g of the system. The presence of the amorphous phase in the glassy state would presumably make it essentially impossible to define a melting point or crystallization temperature in the normal manner, as an equilibrium between crystalline and amorphous phases.

Key words Gelatin – crosslinking – drawing – oriented films – dynamic mechanical properties – glass transition

Introduction

A series of chemically crosslinked films and fibers of gelatin were prepared in the first part [1] of this systematic study of the mechanical properties and transition temperatures of crosslinked, oriented gelatin. These samples are now investigated by following the effect of the draw ratio during drying and water content on the transition temperatures of these materials. The films had been swollen, deformed, and then dried according to the requirements of a novel orientation technique designed for semi-rigid polymers [2–9]. This resulted in improvements in Young's modulus E, and tensile strength σ_b, by factors of nearly three, and the dynamic modulus by a factor of nearly six. These and further attempts to the improvement of the originally very poor mechanical properties of gelatin are motivated by its very attractive characteristics as material for fibers, films, composites, etc. Gelatin is attractive material for various applications since its sources and processing conditions are environmentally friendly [10].

At the same time, in contrast to synthetic polymers, gelatin has two important peculiarities: (i) it is distinguished by very close values of glass transition and melting temperatures and T_g is extremely sensitive to the water content in gelatin since water plays the role of a plasticizer [10]. These very preliminary results deserve more attention since the better understanding of the effect of drawing and water content in gelatin on its thermal behavior can shed some light on the improvement of the orientation and mechanical properties. The aim of this second part of our study was to follow the glass transition T_g and melting behavior of crosslinked gelatin films and fibers as a function of the draw ratio during their drying and of the water content during the measurements.

Experimental

Materials

The samples used in this work were the same as those used in the previous study, and the materials, sample preparation, and reaction conditions have been described previously [1, 13].

The room-conditioned films and fibers typically contain 15–17% water. Samples with a higher water content were prepared by swelling for 10–15 min between moistened filter papers and thereafter tested in the DSC instrument. Samples with less than 15–17% water were prepared by varying the drying temperature and duration.

Techniques

The glass transition temperature of the crosslinked gelatin samples was determined by means of DMTA instrument of Polymer Laboratories in tensile mode. The measurements were performed in the temperature range between 25 and 250 °C, at 5 Hz and a heating rate of 10 °C/min.

The glass transition and melting temperatures of the crosslinked gelatin films were determined by the DSC technique using the Polymer Laboratories calorimeter and a Mettler TA-3000 instrument. In the first case, the sample was open to the air, the temperature ramp was 10 °C/min in the range 25–250 °C. In the second case, the measurements were carried out in nitrogen atmosphere and a heating and cooling rate of 20 °C/min was applied in the range −100 to 250 °C.

Thermogravimetric measurements were performed on a Perkin–Elmer instrument both in air and in argon atmosphere, from 25 to 300 °C, at a heating rate of 10 °C/min.

Results

Effect of the draw ratio on the transition temperatures of chemically crosslinked gelatin

The DMTA technique is one of the most sensitive methods for following the changes in the amorphous part of a polymer. From the curves of E', E'', and tan δ, the glass transition temperature of the gelatin films was determined. It turned out that T_g is resolved most effectively from the E'' curves. Figure 1 shows the E'' curves for gelatin crosslinked at 14% water solution, with different draw ratios λ. For a better visual presentation the curves were shifted with respect to the E''-axis. First of all it should be noted that two rather well-resolved transition temperatures are observed: a lower one at about 50–100 °C and a higher one at about 200 °C. While the first transition depends on the draw ratio (changing its value between 50–60 and 100–120 °C), the second one seems to be insensitive to λ (Fig. 1). For this reason the numerical values of the lower-temperature transition, evaluated from the curves displayed in Fig. 1 are summarized in Table 1 together with those for gelatin chemically crosslinked in a 10% aqueous solution.

In order to understand the nature of both transitions, one has to take into account the two important peculiarities of gelatin as a polymeric material: the unusually close

Fig. 1 Temperature dependence of the tensile modulus E'' for undrawn and drawn gelatin, chemically crosslinked in a 14% solution. The draw ratio λ is specified for the various curves

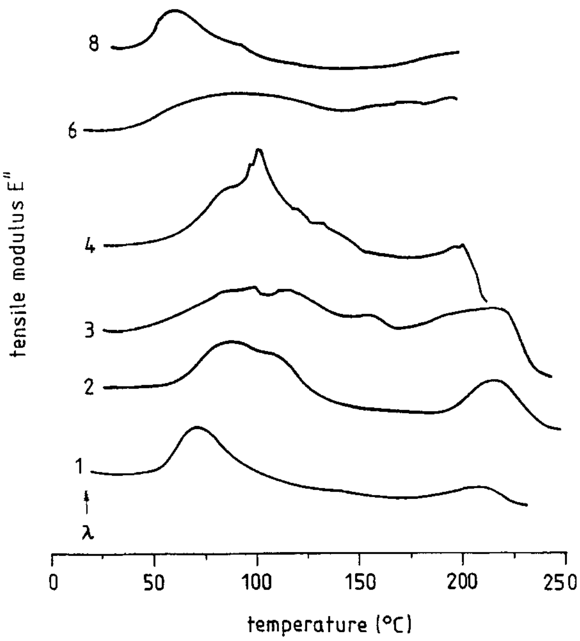

Table 1 Glass transition temperature T_g (from E'') as evaluated from DMTA measurements of E'' on chemically crosslinked (in 10% and 14% solutions) gelatin with different draw ratio λ

λ	1	2	3	4	6	8
Crosslinking in 14% solution						
T_g(°C)	65	86	90	99	104	84
Crosslinking in 10% solution						
T_g(°C)	62	75	78	96	106	94

values of T_g and T_m, 217 and 230 °C, respectively [10], as well as the extremely strong plasticizing effect of water on gelatin (gelatin containing 20% water has a T_g of about 25 °C). Considering this second characteristic feature of gelatin, one can assign the first transition to water-plasticized gelatin, T'_g. Determination of the water content of room-conditioned crosslinked undrawn gelatin showed a value of about 15%. Isotropic, chemically non-crosslinked gelatin with the same water content is known to exhibit a T_g of about 55 °C [10], in agreement with our finding for undrawn chemically crosslinked gelatin (Fig. 1, curve for $\lambda = 1$; Table 1).

Keeping in mind that the samples with different λ (Fig. 1) are room-conditioned (i.e. they are expected to be plasticized to the same extent), the curves displayed in Fig. 1 allow one to follow the effect of the draw ratio on T_g. One can easily see that the increase of the draw ratio up to $\lambda = 4$–5 causes a rise in the T'_g values, while a further increase of up to $\lambda = 8$ leads to a decrease of T'_g.

Such a relationship can be explained by the restricted segment mobility of plasticized gelatin induced by crosslinking and mostly by orientation, as generally observed with other crosslinked and/or oriented polymers. This restriction effect is available only up to $\lambda = 4$–5. At higher draw ratios (up to $\lambda = 8$–10) the freedom of movement is partially restored as proven by X-ray scattering and discussed in details in the first part of this study [1].

Also of considerable interest is the second, high-temperature transition (Fig. 1). Taking into account the above-mentioned fact that the T_g and T_m of dried gelatin are very close to each other, the high transition temperature can be interpreted as glass transition of dry gelatin superimposed by the melting. In order to verify this assumption, an attempt was made to separate the two processes by following the crystallization and melting behavior of the same samples in the same temperature interval as in the case of DMTA measurements, but this time using DSC.

The DSC measurements were carried out with chemically crosslinked (in 10% and 14% solutions) undrawn and drawn ($\lambda = 2$, 5, 10, and 15) gelatin in a heating–cooling–heating mode. Typical curves are presented in Fig. 2 and the numerical data of all measurements are summarized in Table 2. The entire heating–cooling–second heating cycle is presented only for the sample with $\lambda = 5$.

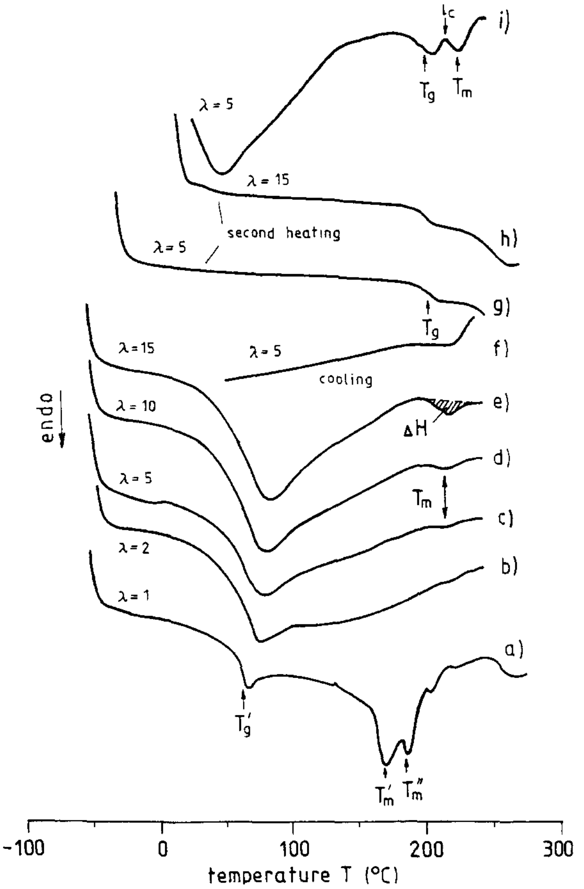

Fig. 2 DSC curves in a heating–cooling–heating mode for chemically crosslinked (4% solution) undrawn and drawn gelatin. The complete heating–cooling–second heating cycle is given only for the sample with $\lambda = 5$. All curves are obtained by means of Mettler calorimeter except for curve i, where a Polymer Laboratories calorimeter and heating rate of 2 °C/min were used

Table 2 Calorimetric data on chemically crosslinked (in 14% solution) gelatin with different draw ratios λ

Draw ratio	1	2	5	10	15
First heating					
First transition T'_g(°C)	64	66	66	66	70
Second transition T_m(°C)	–	223	220	220	220
Heat of fusion ΔH(kJ · kg^{-1})	–	0.7	1.7	3.5	7.8

The first important observation is the rather different behavior of the undrawn ($\lambda = 1$) sample, compared to the drawn ones (curves b–e, Fig. 2). The undrawn sample

(Fig. 2, curve a) exhibits a well-expressed low-temperature transition (at about 64 °C) followed by two low-temperature melting peaks, T'_m and T''_m, respectively. This undrawn sample deserves special attention and its behavior will be discussed in more detail below.

The curve profiles for all the drawn samples is nearly the same – a very broad endothermic peak (between 30 and 170 °C) with a minimum at about 80 °C, followed by another, relatively small high-temperature endothermic peak at T_m = 200–220 °C. The area of the latter increases with increase of the draw ratio (Table 2).

The large low-temperature endothermic peak can originate from overlapping of two processes: glass transition and mostly water evaporation of the room-conditioned samples (water content 15–17%). This assumption is supported by the results of the DMTA measurements (Fig. 1) which clearly demonstrate a glass transition for the same samples between 65 °C and 104 °C depending on the draw ratio (Table 1). Additional support can be found in the behavior of the undrawn sample (Fig. 2, curve a), where a well-developed transition at about 64 °C is observed. Thus, it can be concluded that the left parts of the curves in the area of the minimum (between 30 °C and 85 °C) incorporate the glass transition and its inflection point could be considered as the glass transition temperature T'_g (Table 2).

Above T'_g one can expect some crystallization and further water evaporation (Fig. 2, curves b–e). The crystals formed melt at about 220 °C (Fig. 2, Table 2), whereas the melting temperature of dry gelatin is 230 °C [10]. It is important to note that the high-temperature maximum in the E'' curves (Fig. 1, Table 1) is in the same temperature interval. Furthermore, the T_m values from the DSC curves do not change with increase in draw ratio (Table 2). Comparing the E'' curves (Fig. 1) and DSC curves (Fig. 2, curves b and c for drawn samples in their high-temperature regions), one can conclude that the maximum on the E'' curves (Fig. 1) around 220 °C comprises the melting process assumed above. Unfortunately, the DSC traces (Fig. 2, curves b–e) show no clear evidence for the existence of a glass transition, as can be assumed from the DMTA measurements (Fig. 1). For this reason, additional experiments were performed in order to separate the glass transition from melting, in case they overlap the heating curves (Fig. 2, curves b–e).

Figure 2 shows the cooling curve (curve f), obtained immediately after the melting of the sample with $\lambda = 5$ (curve c). Immediately after cooling, the same sample was reheated (curve g). Another reheating curve is that for sample with $\lambda = 15$ (curve h). Finally, the first-heating curve for a fresh sample again for $\lambda = 5$ (but at a much lower heating rate of 2 °C/min), is also displayed (curve i).

These additional experiments allow one to draw an important conclusion concerning the number and type of transitions in drawn gelatin at higher temperatures (around 200 °C). First, it should be noted that the cooling curve (Fig. 2, curve f) does not offer any information about the processes taking place just in this temperature interval. The same curve, though, does not show any indication of crystallization during the cooling. This is a rather important fact which will be interpreted later. Interesting enough, the curves of the second heating offer the most important information (Fig. 2, curves g and h). In conformity with the cooling curve, the second heating of the same sample does not show any melting peak. The only transition observed is the well-developed glass transition at 210 °C, which should be assigned to the glass transition of dry gelatin, i.e. T_g (since the sample has been subjected to two heatings up to 200 °C and is supposed to be completely dry). The sample with λ = 15 which was subjected to the same treatment in the calorimeter behaves in the same way. In addition to the clearly evidenced glass transition, on the curve of reheating (Fig. 2, curve h), an indication of a second transition situated above T_g can be detected. Obviously, this can originate from melting. Taking into account the fact that during the cooling (Fig. 2, curve f) and subsequent heating (Fig. 2, curves g and h) no crystallization is observed, one can conclude that the assumed crystallization (Fig. 2, curve h) takes place above the glass transition, T_g = 210 °C. The absence of a crystallization peak above T_g in curve h can be explained by the well-known recrystallization processes during scanning in the calorimeter [14]. In order to avoid this to some extent, the experiment was repeated with a fresh sample at a lower heating rate of 2 °C/min. The resulting curve (Fig. 2, curve i) exhibits a very well-resolved glass transition of the dry gelatin T_g = 214 °C, a peak of crystallization T_c, and a peak of melting T_m = 233 °C. Both the T_g and the T_m values are in excellent agreement with those which have been reported for dry gelatin [10].

At first glance the assignment of the observed changes in the thermogram in such a narrow temperature interval to the three basic transitions of polymers seems ambiguous. The interpretation given is supported by similar behavior of other polymers distinguished also by close T_g and T_m values. A good example is the behavior of polyethylene oxide blocks (with molecular weight of 2000) in the polyetheresters, where T_g is approximately −50 °C, crystallization peak occurs at −35 °C, and melting at 15 °C is reported [14].

One can conclude that the DSC measurements in a heating–cooling–second heating mode (Fig. 2), performed with the same undrawn and drawn samples used for DMTA tests, unambiguously support the assumption that the lower temperature transition should be assigned to the glass transition temperature T'_g of the water-plasticized (15–17%) gelatin and the higher temperature maximum (Fig. 1) originates from the overlapping of the glass transition of dry gelatin T_g and melting of gelatin crystallites at temperature T_m. This assignment is confirmed also by the DSC results, gained from experiments on undrawn gelatin containing different amounts of water, as discussed below.

Effect of water content on the transition temperatures of chemically crosslinked gelatin

There are at least two reasons for carrying out these experiments: (i) the rather different profile of the DSC curve for undrawn sample (Fig. 2, curve a) relative to the drawn ones (Fig. 2, curves b–e), both types being room-conditioned, and (ii) to make use of the interesting peculiarity of gelatin, related to its strong plasticizability, for a better separation of the transition temperatures. For this purpose, chemically crosslinked undrawn gelatin was subjected to swelling in order to obtain samples with a higher water content (31% and 50%), or to different drying regimes for the preparation of samples with a lower water content (between 0% and 10%). The resulting DSC curves, taken only in a heating mode, are shown in Fig. 3, and their numerical evaluation can be found in Table 3.

A common characteristic feature of all the curves obtained is that they display a glass transition and one or more melting peaks. What is more important, both types of transitions are very sensitive to the water content of gelatin; they shift to higher temperatures with decrease of water content. The sample richest in water has the lowest T'_g and T'_m values, $-9\,^\circ C$ and $124\,^\circ C$, respectively (Fig. 3, curve a). For the sample with 31% water and the room-conditioned one (17.7%, Fig. 3, curves b and c, respectively), T'_g and T'_m increase significantly (Table 3). When the water content decreases to 10%, a transition at approximately $65\,^\circ C$ and melting between $160\,^\circ C$ and $180\,^\circ C$ are observed (Fig. 3, curve d). Both transitions shift to higher temperatures, 110–120 °C and 180–220 °C, respectively, for the sample with even lower water content (7%, Fig. 3, curve e). In addition, the melting peak is preceded by a shoulder at about 180 °C. For the completely dried sample (Fig. 3, curve f), the two transitions are well resolved and a glass transition temperature of 195 °C as well as a melting temperature of 225 °C are obtained. The fact that the T_m value obtained in this study corresponds to that reported in the literature is related to the drying conditions applied to this particular sample: it was dried at 140 °C for 5 h. This treatment, being sufficiently long, can be considered also as annealing for the crystalline phase, and a considerable improvement in the crystalline order is thus expected.

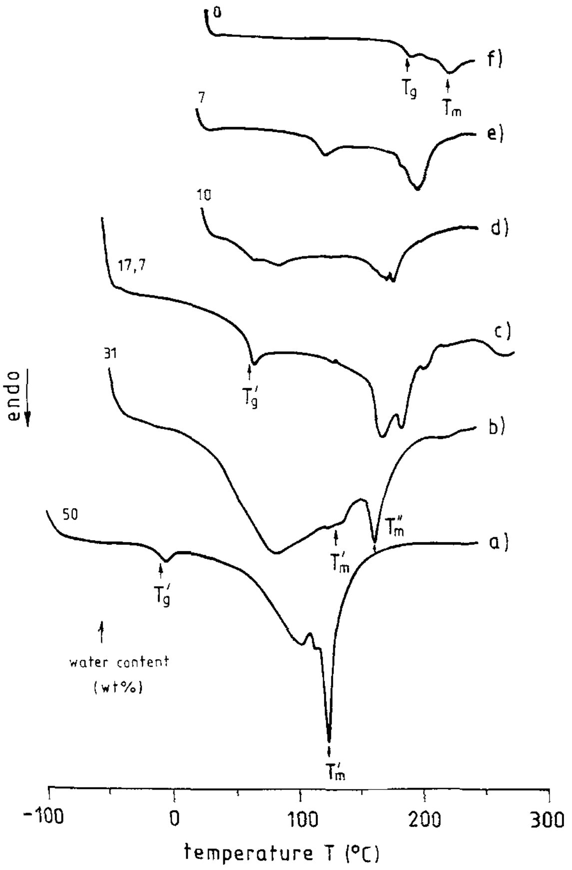

Fig. 3 DSC curves for chemically crosslinked (0% and 14% solutions) undrawn gelatin having different water contents as specified, before starting the measurement: (A and B) by additional swelling; (D and E) by drying at 60 °C; (F) by drying at 140 °C for 5 h

Table 3 Glass transition T_g and melting T_m (from DSC) of chemically crosslinked (in a 10% solution) gelatin with various initial water content

Water content (wt%)	50	31	17.7	10	7	0
First transition T_g(°C)	−9	46	64	65	120	195
Second transition T_m(°C)	124	161	185	178	198	225

The effect of water content on the transition temperatures is better expressed in Fig. 4, which shows this dependence for chemically crosslinked undrawn gelatin. The first conclusion from these results is that the completely dry sample reveals T_g and T_m values close to those reported [10] as well as to those obtained in this study for drawn, dry samples (Fig. 2, Table 3). One has to mention also that T_g is more sensitive to the water content than T_m. T'_g varies between $-9\,^\circ C$ and $195\,^\circ C$, and T_m between

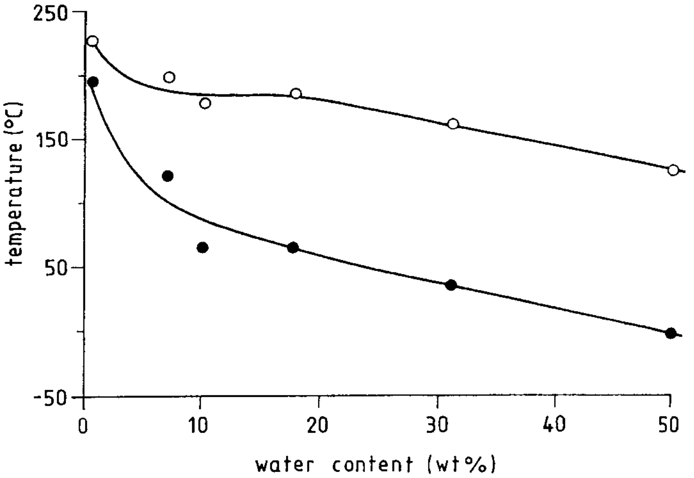

Fig. 4 Dependence of the glass transition temperature T_g (●) and melting temperature T_m (○) on the water content in chemically crosslinked gelatin. T_g and T_m were evaluated from the DSC curves in Fig. 3

124 °C and 225 °C for the whole range of water content (50–0%, Fig. 4, Table 3). This clearly demonstrates that the observed depression in T_g is actually a result of the plasticizing effect of water.

The nature of this depression should be completely different in the case of T_m, although the two depressions are very closely related. The observed decrease in T_m' for samples with increasing water content can be explained by the well-known effect of crystallization temperature on T_m. One has to bear in mind that the melting observed originates from crystals which appear under very unfavorable crystallization conditions. For example, for the room-conditioned gelatin containing at least 15% water (Fig. 3, curve c), T_g is expected to be of about 60 °C [10]. This strong depression in T_g (from 217 °C to 60 °C) makes possible the crystallization of gelatin taking place at 80–100 °C, which is far below $T_m = 230$ °C. Therefore, rather small and imperfect crystallites should be expected, as was actually observed from their melting behavior. Heating in the calorimeter in this case can contribute to only an insignificant increase in perfection of the existing crystals. Additional crystallization cannot take place since above 100–120 °C the gelatin crystals are assumed to be embedded in a solid glass, i.e. in the amorphous part of gelatin which softens only at about 200 °C [10]. In this way, melting of polymer crystals below T_g of the same polymer can occur.

In order to determine more precisely the temperature interval in which water leaves gelatin as well as to check the thermal stability of the samples studied, i.e. to what extent the observed high-temperature transitions can be affected by thermal decomposition processes, gravimetric measurements of chemically crosslinked undrawn gelatin were performed in the range 25–300 °C. The curves taken in air and in nitrogen atmosphere are shown in Fig. 5.

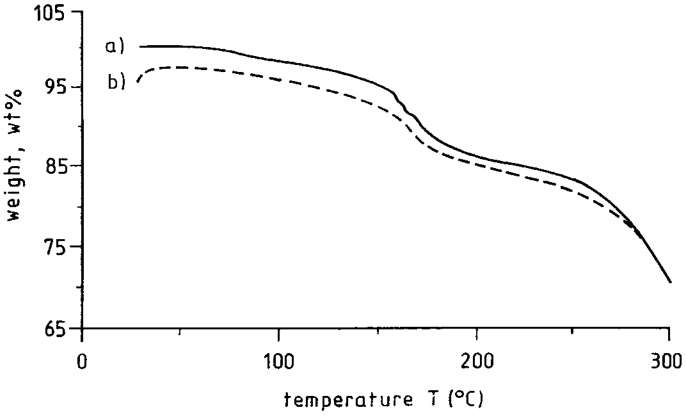

Fig. 5 Thermogravimetric measurements of chemically crosslinked undrawn gelatin, performed in air (curve a) and nitrogen (curve b)

The first conclusion drawn from this experiment is that the water leaves gelatin at temperatures considerably higher (150–170 °C) than the common drying temperatures (100–120 °C). The reason for this observation is related to the ability of gelatin to form hydrogen bonds with water. Thus, higher temperatures are required for water removal, compared to the drying of substances which do not form such bonding.

The second important conclusion from the same measurements is based on the fact that no substantial changes in the sample weight occur in the temperature range between 25 and 150 °C, except for a steady loss of about 5% of the starting weight. Between 150 and 170 °C an abrupt drop of about 10% in sample weight occurs, and the total loss of 15% due to heating up to 170 °C corresponds to the starting amount of water. With further rise in temperature (from 170 °C to 250 °C), a continuous loss in weight of about 2–3% total can be observed. It can be concluded from the TGA measurements (Fig. 5) that weight losses of 15% in the temperature range up to 170 °C should be related to the removal of hydrogen-bonded water and only the small losses of 2–3% at higher temperatures (up to 250 °C) can originate from thermal decomposition processes. It is important to note here that the majority of transition temperatures (T_g and T_m) observed (Table 3) are outside the temperature interval (150–170 °C) in which an abrupt drop in the weight is registered (i.e. the transitions observed do not originate from the drying process). Such behavior means that the well-developed endothermic peaks at about 220 °C (Table 2) are not caused by drying or thermal decomposition processes. It is worth noting that the TGA curves taken in the inert atmosphere and in air are the same, i.e. crosslinked undrawn gelatin shows a relatively high thermal stability even in the presence of oxygen (compare curves a and b, Fig. 5). This fact can be considered as an additional important advantage of gelatin as material and makes it even more attractive object for modification in order to avoid its basic disadvantage – poor mechanical properties in the unmodified state.

It should be mentioned here that the TGA measurements were carried out only for a room-conditioned sample (Fig. 5), i.e. a sample with more or less equilibrium water content. Thus, these results help the interpretation of the DSC curve of the same sample (Fig. 3, curve c) or, in the best case, those of the samples with lower water content (Fig. 3, curves d–f). Gelatin with water content higher than a conventional sample should behave differently in a calorimeter (Fig. 3, curves a and b). When there is much more water in the sample (50% and 31%, respectively), one can expect that the drying process will start intensively at lower temperatures. Only the rest, amounting to about 10%, will be removed at 150–170 °C, in accordance with the TGA measurements of the sample with 15–17% water content (Fig. 5). In this way, one can explain the very broad endothermic peak for samples with higher water contents (Fig. 3, curves a and b). Obviously, in the temperature range between 50 and 150 °C, one deals with overlapping of drying, the glass transition, and the melting of imperfect crystals. The dominance of one or another of these processes will depend on the characteristics of the samples: water content, predrying conditions (temperature and duration), degree of orientation, etc.

Discussion

It is a basic postulate in polymer physics that crystallization is possible only above the glass transition temperature, since the ordering process presumes some chain mobility [15]. Actually, the crystallization processes take place (with different rates) in the temperature interval between T_g and T_m, T_g being always below T_m (according to the experimentally derived rule $T_g = (\frac{2}{3} T_m, \mathrm{K})$. For the majority of synthetic polymers, the interval between T_g and T_m in which crystallization occurs is at least 150–200 °C. It is also well known and generally accepted that the lower the crystallization temperature T_c, or more precisely the larger the undercooling $\Delta T = T_m - T_c$, the less perfect the crystallites (distinguished by lower T'_m). For these reasons the situation when polymer crystals melt below T_g of the same polymer seems to be rather unphysical.

Nevertheless, one can expect such behavior when dealing with polymers characterized by (i) high T_g and T_m, and (ii) T_g and T_m close to one other. In this case, a plasticizer can decrease the glass transition to a value T'_g ($T'_g \ll T_g$) and to carry out crystallization at high undercooling ΔT (but still above T'_g of the plasticized polymer!). This would yield crystallites of rather low perfection, their T'_m being much lower than T_m. Furthermore, the plasticizer can be removed by drying at low temperatures and as a result T'_g will increase, approaching the T_g value typical of the neat polymer (i.e. without plasticizer). The temperature of drying should be low enough to avoid recrystallization, i.e. formation of more perfect crystals with higher T'_m. At this stage, a rather unusual structure of the material could be realized: imperfect crystallites embedded in a solid polymer glass with T_g possibly higher than the melting temperature of crystallites T'_m.

The described experiments (Fig. 3) with chemically crosslinked undrawn gelatin containing different amounts of water can help one check this interpretation. Considering again the sample with the highest water content (50%, Fig. 3, curve a), a very well-resolved glass transition temperature T'_g can be seen around −9 °C. This value is in good agreement with the literature results [10] for gelatin containing approximately 50% water. Furthermore, at about 20 °C there is the start of an endothermic peak, which ends at 200 °C. In this rather broad interval another very sharp peak (between 110 and 150 °C) can be seen. While the onset and the first part of the large and broad endothermic peak could originate from the overlapping of melting of the most defective crystallites and most of the water evaporation, the second sharp one (located at $T' = 124$ °C) should be assigned to melting of gelatin crystallites. Regardless of whether these crystallites existed in the sample before the DSC measurements or appeared during the measurement in the calorimeter as a result of recrystallization processes, it is important that their melting temperature $T'_m = 124$ °C is far below T_g of dry gelatin (217 °C [10]). This is similar to the situation with the neat samples, plasticized by larger amounts of water (31 and 17.7%, respectively. They exhibit a T'_m of 161 and 185 °C, respectively (Fig. 3, curves b and c, Table 3).

Dry amorphous gelatin really exhibits a glass transition temperature around 200 °C as can be concluded from Figs. 2 and 3. In the curves for the second heating there is no indication of another transition up to 240 °C (Fig. 2, curves g and h). After softening of the completely dried gelatin above $T_g = 195$ °C, no crystallization occurs during subsequent cooling (Fig. 2, curve f) and second heating (Fig. 2, curves g and h). Such behavior is in agreement with the basic rule that no crystallization takes place below T_g (217 °C in the case of dry gelatin [10]). According to curves g and h in Fig. 2, it is 206 °C, and according to curve i, it is 214 °C.

Thus, taking advantage of the two peculiarities of gelatin, namely high T_g and T_m, close to one other, as well as the easy depression of T_g to very low values using water as plasticizer (Fig. 3), it is possible to realize the unusual situation: melting of polymer crystals below the glass transition temperature of the same polymer. The observed phenomenon does not contradict the basic concepts concerning the temperature intervals in which crystallization can occur. On the contrary, it confirms them since the glass transition temperature T'_g of the system gelatin–water strongly differs from T_g of dry gelatin. The crystallization observed takes place above T'_g of the system gelatin–water. Another question is, after creating low-temperature melting crystallites, can T'_g be shifted (by removing the plasticizer) up to temperatures far above T'_m of the imperfect crystallites but close to T_g of the neat polymer (dried in the present case).

The observed phenomenon of melting below the glass transition has another peculiarity. Since the imperfect crystallites are surrounded by a glassy matrix after removing the water, the melting process results in the formation of a solid amorphous phase rather than of a liquid phase as in the usual case. That is, a "crystalline solid–amorphous solid" transition could be observed. This quite unusual situation offers the rare opportunity for the obtaining of highly ordered polymer glasses. The exploration of this possibility with the appropriate structural characterization, as well as application of the described approach to other polymer–plasticizer systems, is in progress.

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