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S. Fakirov
Z. Sarac
T. Anbar
B. Boz
I. Bahar
M. Evstatiev
A.A. Apostolov
J.E. Mark
A. Kloczkowski

Mechanical properties and transition temperatures of cross-linked oriented gelatin

1. Static and dynamic mechanical properties of cross-linked gelatin

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Dr. S. Fakirov (✉)
Sofia University
Laboratory on Structure and
Properties of Polymers
1 J. Bourchier Ave.
1126 Sofia, Bulgaria

Z. Sarac · T. Anbar · B. Boz · I. Bahar
Polymer Research Center
School of Engineering
Bogazici University
and TUBITAK Advanced Polymerica
Materials Research Center
80815 Bebek, Istanbul, Turkey

M. Evstatiev · A.A. Apostolov
Sofia University
Laboratory on Structure and
Properties of Polymers
1126 Sofia, Bulgaria

J.E. Mark · A. Kloczkowski
Department of Chemistry and
the Polymer Research Center
The University of Cincinnati
Cincinnati, Ohio 45221-0172, USA

Abstract This study is an extension of previous work on cellulosics [(1994) *Colloid Polym Sci* 272:284, 393] that showed that unusually good mechanical properties can be obtained by drying a swollen network of semirigid chains in a state of strain. This novel approach is applied in this investigation to gelatin, because of its attractive environmental characteristics but poor mechanical properties in the unmodified form. Since drawing of non-crosslinked gelatin is not practical, crosslinking by formaldehyde was used, followed by swelling, drawing and drying at fixed length. Mechanical tests were performed in static and dynamic modes. In this way improvements of Young's modulus E, and stress at break σ_b, were determined as a function of gelatin concentration during drying. An increase in E and σ_b up to 2–3 times, and in the dynamic modulus E' up to 6 times, was obtained when the draw ratio λ reached 4–5, after which E, E', and σ_b were found to decrease. Such behavior is explained by the highest orientation being achieved at $\lambda = 4$–5, as proved by x-ray analysis. At $\lambda = 10$–20 the orientation is lost due to relaxation of chain segments, which is preceded by partial destroying of the network structure (chemical and physical), possibly via chain scission, but probably mostly by the pulling out of chains from crystallites. In any case, the mechanical properties become poor again.

The improvements reported above were referred to the undrawn but crosslinked gelatin. Compared to the starting isotropic non-crosslinked material, the improvement is slightly higher. The observation that the improvements are less than those obtained for the cellulosics is explained by the coexistence of interpenetrating chemical and physical networks, which is typical of gelatin. This structural feature drastically reduces the orientability of the chains and the improvements that can be expected in the mechanical properties.

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

Introduction

Anisotropic materials are very attractive because of the improved mechanical properties they acquire in the direction of orientation. Polymers are suitable for drawing processes because their anisotropy can be controlled. Segmental or molecular orientation is induced by external means and is described as the anisotropic distribution of chain segment orientations in space.

Segmental orientation can be induced by methods such as cold or hot drawing [1, 2], solid-state extrusion [1–3], zone drawing [4, 5] and rapid drawing from melts or solutions [1, 6, 7]. However, these methods have some disadvantages: when the external field is removed, the chains relax and lose some or all of their anisotropy. Thus a need has appeared to develop various orientation techniques.

There is now considerable theoretical work that is helpful in this regard. One approach describes techniques by which swollen, deformed, and dried networks of semirigid chains become materials having very good mechanical properties [8, 9]. In this novel processing method [8, 9], suitable polymeric chains are identified, with preference for those of sufficient stiffness to give anisotropic, liquid-crystalline phases. The chains are then cross linked, preferentially in the presence of a solvent. The cross links confer the solidity required to keep the chains in the deformed state during drying and the solvent prevents premature collapse of the chains into domains not themselves oriented in the direction of deformation. The segmental orientation can be induced by either uniaxial or biaxial deformation of the swollen network, and the solvent can be removed by either evaporation or by diffusion into another solvent miscible with the first, but immiscible with the polymer. The result should be a homogeneous and highly ordered material with greatly improved mechanical properties.

Naturally-occurring polymers are attractive objects for this new orientation technique since many, such as the cellulosics and proteins, consist of semi-rigid chains. There has, in fact, been relevant experimental work on a cellulose ester (cellulose acetate) and a cellulose ether (hydroxypropyl-cellulose). The drying-under-deformation technique gave a 4-5-fold increase in Young's modulus and tensile strength relative to the isotropic untreated material [10, 11].

Another example in which the mechanical properties of a natural polymer have been improved by orientation is a calcium alginate gel fiber [12]. In this work, the higher modulus of fibers of calcium alginate after drawing was explained by the higher degree of polymer chain alignment. Although this does involve orientation of networks, it differs from the present approach in that the network is only temporary (physical) since the junctions are crystallites rather than chemical linkages.

Gelatin is a good candidate for extension of the drying-under-deformation approach [8–11] because of its very attractive characteristics [13–16]. It satisfies all basic requirements for a contemporary material for commodity purposes, since it is produced from natural sources (typically a waste product of meat and skin), and its manufacturing and further processing are carried out under very mild conditions (without the necessity of aggressive chemicals and processing procedures). Gelatin in the crosslinked state is insoluble is water but is swollen by it, it is biodegradable, it can serve as a foodstuff, and its price (food grade) is competitive with those of synthetic polyolefins [13]. The most serious disadvantage of gelatin as a material is its poor mechanical properties. In fact, gelatin film in the dried state is extremely brittle.

The purpose of the present study was therefore to apply this orientation technique for the convertion of gelatin to a material useful in applications requiring significant strength and toughness.

Experimental part

Preliminary attempts to orient gelatin which was held in a network structure only by means of temporary crystallites failed. The present work, therefore, focuses on gelatin having a more permanent network structure because of the presence of covalent crosslinks. The reaction conditions to achieve this crosslinking were adopted from the extensive study of Davis and Tabor on the crosslinking of gelatin by formaldehyde [14].

Materials

Food-grade gelatin powder (Merck) was used, and the crosslinking reagent was a water solution containing a minimum of 37 wt% formaldehyde (Merck). The gelatin was used in a solution with distilled water.

Sample preparation

The gelatin was soaked overnight at 5 °C, then dispersed at 50 °C (water bath) in the presence of a phosphate buffer. A buffered solution of the crosslinking agent was added at 50 °C, with thorough mixing. In this way, the concentration of formaldehyde in the final solution varied between 0.02 and 0.1 M, and the pH of the solution between 5.5 and 6.5. Gelatin concentrations varied between 2 and 14 wt%. (All of these ranges are optimal for the effective crosslinking of gelatin [14]). Portions of the resulting gelatin solution were dried in order to obtain isotropic, chemically crosslinked films. These films were cut into strips, which were then swollen and drawn uniaxially as much as 20 fold, mostly at 50 °C. The drawn samples were dried at room temperature at fixed length. At the highest draw ratios, they were actually fiber-like in appearance.

Techniques

Young's modulus E, the stress at break σ_b, and the strain at break ε_b of the drawn strips were measured in a static mode at room temperature. Their lengths were approximately 50 mm, and they were tested using a crosshead speed of 5 mm/min on a Zwick 1464 machine equipped with an incremental extensometer. For each draw ratio, measurements were made on at least 5 (and more often 10) samples.

The dynamic mechanical behavior of the crosslinked gelatin samples was determined using a dynamic mechanical thermal analyzer (DMTA), of Polymer Laboratories. The tensile mode was applied, and the sample was mounted with its long side (corresponding to the deformation direction during drying) placed parallel to the drive direction. The measurements were performed at 5 Hz between 25 and 250 °C, using a heating rate of 10 °C/min. The strain level was chosen as x1. The values of the glass transition T_g refer to the inflection point of the sections of the storage modulus E' vs. temperature curves reflecting the softening process, using the standard software of the DMTA instrument. From the same curves, the value of E' at 30 °C was taken for sake of comparison. Since the T_g of gelatin is extremely sensitive to water content [13], all DMTA measurements were performed on samples with the same water content, differing only in their draw ratios for a given concentration during cross linking.

Wide-angle x-ray scattering (WAXS) patterns were obtained for undrawn and drawn crosslinked gelatin films by means of a flat camera using Ni-filtered Cu K_α radiation.

Results

In the case of the static mechanical results, the focus was on Young's modulus E, the stress at break σ_b, and the strain at break ε_b, as a function of the draw ratio during drying. Although the gelatin concentration was systematically varied between 2 and 14 wt%, for simplicity pairs of values of the mechanical parameters were averaged (specifically 2 and 4%, 5 and 7%, and 10 and 14%).

Figure 1 shows typical static stress-strain curves, for crosslinked samples dried at various values of the draw ratio. Included for purposes of comparison are results for isotropic crosslinked and isotropic non-crosslinked samples. One can see that both isotropic crosslinked samples and non-crosslinked samples behave rather similarly. Their stress at break is of about 50 Mpa and deformation at break is around 2–3%. The isotropic crosslinked sample and particularly the non-crosslinked one are obviously very brittle materials, in dire need of improvements in mechanical properties.

The samples of the highest draw ratio ($\lambda = 10$–15) show a significant improvement – both the maximum stress (ultimate strength) and the deformation at break (maximum extensibility) increase up to twofold (Fig. 1, curves for $\lambda = 10$ and 15). The most essential changes in the mechanical behavior are found with the samples with intermediate draw ratios ($\lambda = 4$ or 5). In this case the stress increases three-fold, and the elongation at break up to five-fold (Fig. 1, curves for $\lambda = 4$ or 5).

In Figs. 2–4, the dependencies of Young's modulus E, the stress at break σ_b, and the strain at break ε_b on the draw ratio for various gelatin concentrations during crosslinking are shown. These results allow a more detailed

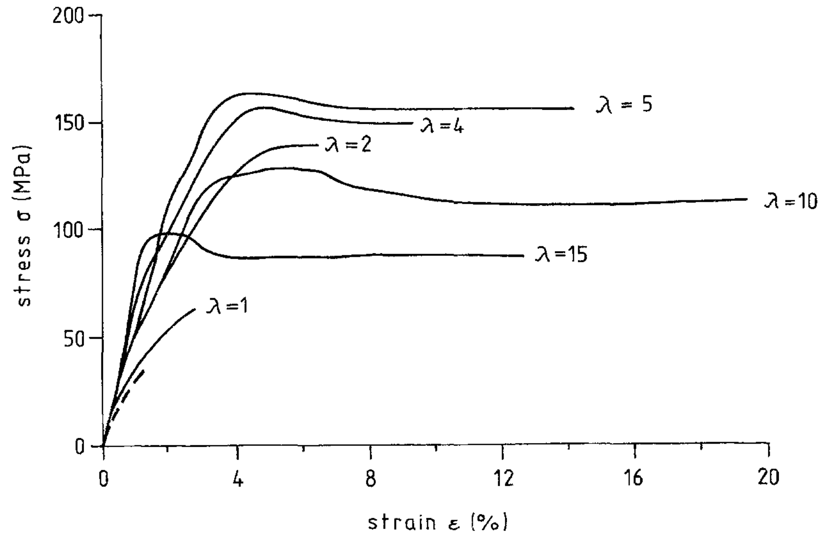


Fig. 1 Stress-strain curves for non-crosslinked (dashed line) and crosslinked undrawn as well as crosslinked drawn gelatin (the draw ratio λ is given in the respective curves). The concentration of gelatin in water during crosslinking is 14 wt.%

Fig. 2 Dependence of Young's modulus E on the draw ratio λ for gelatin, chemically crosslinked in solution with different concentration as follows: □-2 and 4%; ○-5 and 7%; △-10 and 14%; ●-non-crosslinked undrawn sample

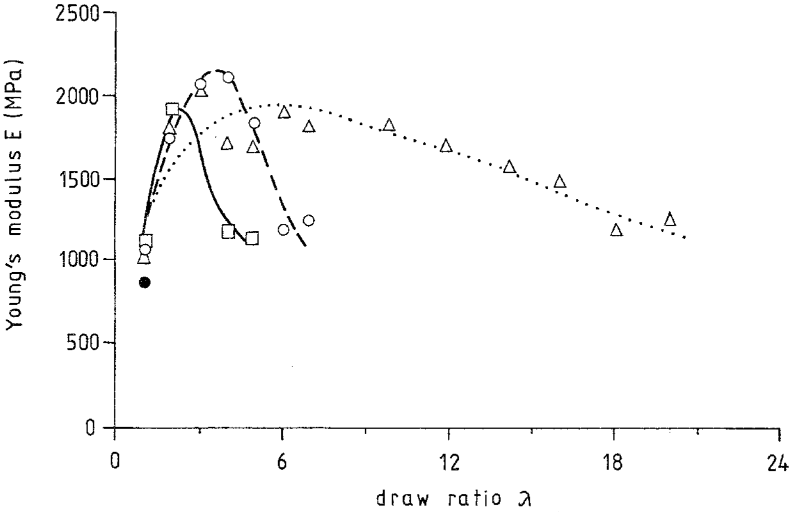
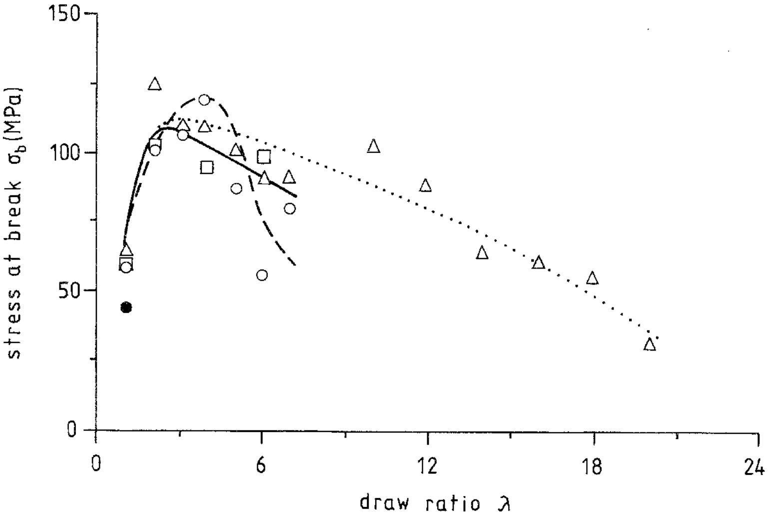


Fig. 3 Dependence of the stress at break σ_b on the draw ratio λ for gelatin chemically crosslinked in solution with different concentration as follows: □-2 and 4%; ○-5 and 7%; △-10 and 14%; ●-non-crosslinked undrawn sample



analysis of the mechanical properties of crosslinked drawn gelatin.

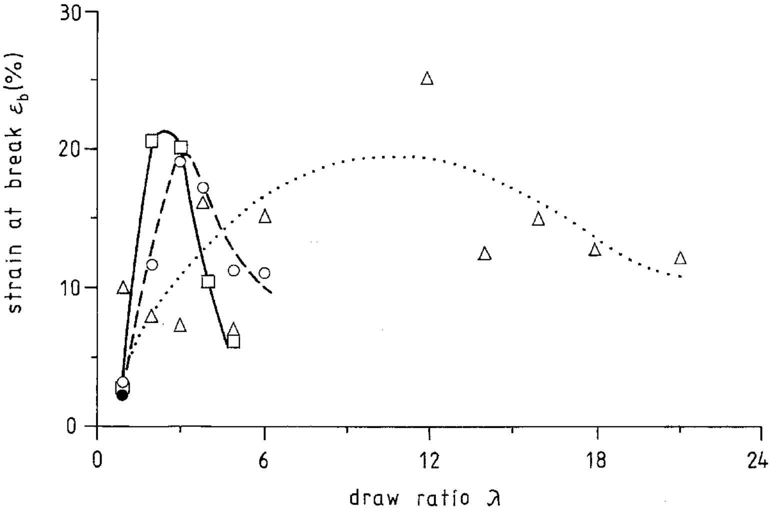
Figure 2 shows Young's modulus as a function of the draw ratio during drying. For all gelatin concentrations, Young's modulus of undrawn crosslinked gelatin films is around 1000 MPa. For the sake of comparison, the E value of the isotropic chemically non-crosslinked gelatin is also plotted, its value being about 800 MPa. As the draw ratio increases up to $\lambda = 4$, a twofold increase of E is observed. At higher draw ratios, the modulus *decreases* for all gelatin concentrations, almost decreasing back to its initial value for $\lambda = 15$–20 (for 10–14%).

The effect of the draw ratio on the stress at break σ_b of gelatin films is shown in Fig. 3. The value for the undrawn crosslinked films is around 60 Mpa, and for the isotropic chemically non-crosslinked samples it is somewhat lower. Regardless of the concentration, a twofold increase of σ_b is observed until λ reaches 4, followed by a continuous decrease for all concentrations, reaching its initial value for $\lambda = 15$–20.

The strain at break ε_b is presented as a function of the draw ratio for various gelatin concentrations in Fig. 4. The strain at break of both chemically crosslinked and non-crosslinked undrawn films is around 3%. As the deformation during drying is increased to three-fold, ε_b also increases up to six-fold, compared to the undrawn films, reaching a value of about 20%.

From the data displayed in Figs. 2–4 it is not possible to deduce an unambiguous relationship between mechanical properties and gelatin concentration in solution while

Fig. 4 Dependence of the strain at break ε on the draw ratio λ for gelatin chemically crosslinked in solution with different concentration as follows: □-2 and 4%; ○-5 and 7%; △-10 and 14%; ●-non-crosslinked undrawn sample



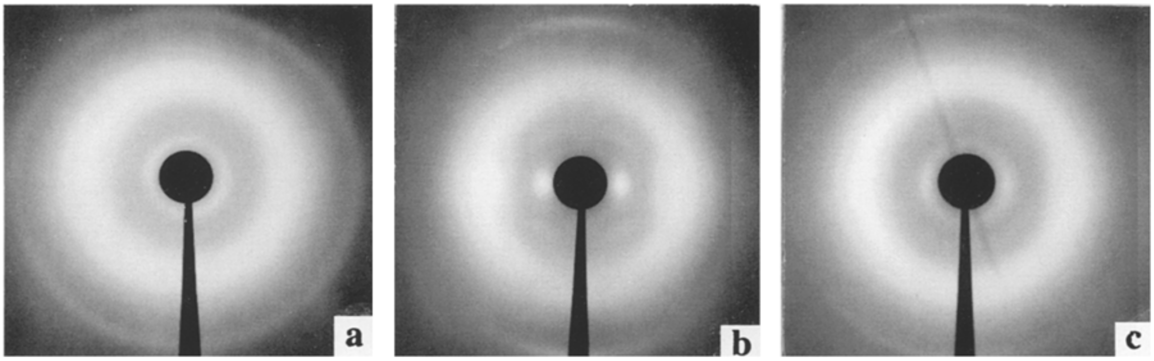


Fig. 5 WAXS pattern of chemically crosslinked gelatin: a - undrawn; b - drawn, $\lambda = 5$; c - drawn, $\lambda = 15$

the crosslinking was carried out. In contrast to this, a rather well expressed tendency with respect to the drawability can be observed. When the gelatin concentration during the crosslinking stage does not exceed 5–7%, the maximum draw ratio achieved is around $\lambda = 7$ and only for concentrations up to 14% one obtains $\lambda = 20$ (Figs. 2–4).

The improvement of the modulus and the stress at break of the material as the draw ratio during drying increases up to $\lambda = 4$ can be explained by the effective orientation in the network. At higher draw ratios a decrease in the mechanical properties is observed, instead of continuing improvements. The reason for this can be related to the different effectiveness of drawing with respect to the final draw ratio on orientation. In order to test this assumption, WAXS patterns taken from crosslinked undrawn and drawn films ($\lambda = 5$ and 15) were analyzed. The results are displayed in Fig. 5.

The WAXS pattern of an undrawn gelatin film is shown in Fig. 5a. The film is isotropic and of poor crystallinity, as can be concluded from the cloudy rings. In Fig. 5b, which displays the x-ray pattern of a gelatin film with $\lambda = 5$, the rings now appear as arcs especially in the central part, thus indicating that the chains are oriented. Figure 5c, in which the x-ray pattern of a gelatin film with $\lambda = 15$ is displayed, there is again a different picture. The arcs typical of $\lambda = 5$ (Fig. 5b) have disappeared, and again continuous rings are seen. The chains are no longer as oriented as in the previous case (Fig. 5b), and are closer to the case of undrawn films (Fig. 5a).

These scattering results show that drawing leads to an effective orientation only up to $\lambda = 5$ (Fig. 5b). Neither orientation nor crystallinity (Fig. 5c) is improved by the further increases of the draw ratio. On the contrary, these two characteristics both approach their initial values (Fig. 5a). At first glance such behavior seems to be very unusual, and a possible explanation for it will be given in the Discussion. In order to explain these observations, one has to assume that with increased drawing (above $\lambda = 5$), drastic changes in the network take place, affecting mostly the contacts between larger structural entities (e.g. crystallites, microfibrils, etc.). There are at least two ways these contacts could be destroyed, specifically chain scission and the pulling out of chains from crystallites, the second mechanism being more probable. The elimination of contacts makes possible the relaxation and disorientation of the larger morphological units. In this way, additional drawing (up to $\lambda = 20$) will result in slippage of ensembles of relatively disconnected and disoriented morphological elements containing highly defective crystallites, due to the pulling out of chains. The last statement is supported by the disappearance of the relatively sharp crystalline reflections (Fig. 5c).

Further support in favor of this explanation of the decreases of orientation at the highest draw ratios can be obtained from the recent study of the deformation behavior of thermoplastic elastomer (PEE type) by means of small-angle x-ray scattering (SAXS) [16], including synchrotron radiation [17]. This system has structural features that are quite similar to the present one, i.e., coexistence of interpenetrating physical and chemical networks. In this case, the deformation mechanism at the highest draw ratios is related exclusively to slippage of assemblies of microfibrils being in relaxed state due to destroying of the interfibrillar contacts, mostly via pulling out of chains from crystallites as demonstrated by decreasing crystallinity visualized by WAXS [16]. A possible explanation of this observation will be given in the following section.

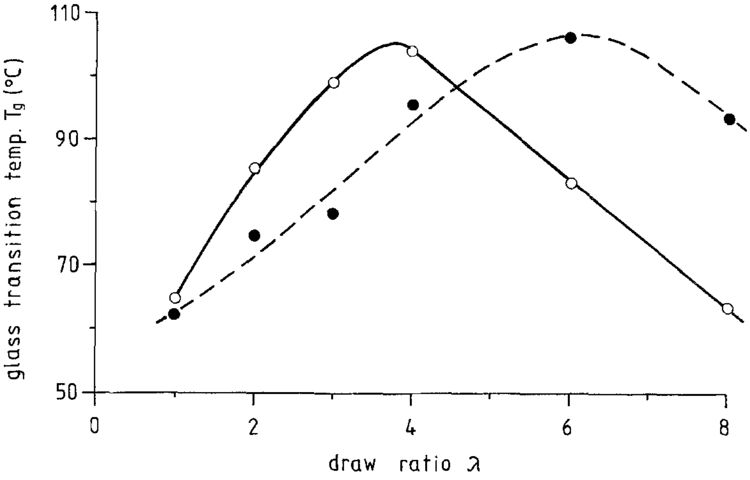
Concluding, one has to note that the observed improvement in the mechanical properties (up to twofold for E and σ_b) as a result of chemical crosslinking and drawing in the swollen state is referred to the undrawn but chemically crosslinked gelatin. Recalling that this study aimed at the improvement of mechanical properties of gelatin (i.e., an undrawn and non-crosslinked product), and considering the crosslinking as a stage of the processing, one should rather use the properties of the totally untreated gelatin as a basis for comparison. The extent of improvement on this basis is now increased, corresponding to threefold improvements in E and σ_b (relative to the chemically non-crosslinked undrawn sample).

This conclusion, derived from static mechanical measurements, is also supported by dynamic mechanical measurements. The values of E', evaluated from these curves (as well as those for 10% concentration of gelatin during crosslinking) are summarized in Table 1. Included are data for the first, low-temperature transition T_g evaluated from the E'' curves for the same samples. The samples obtained from crosslinking at a 10% concentration have a three-fold increase in E' when the draw ratio increases to $\lambda = 3$, and the samples prepared from a 14% solution exceed this value for $\lambda = 4$ (showing a six-fold increase of E' (from 1000 to 5890 MPa, Table 1)). Further increase in λ to 6 and 8 results in a strong decrease of E' (Table 1), which is similar to the results of the static measurements (shown in Figs. 2 and 3 and interpreted above). The postulated improvement of the orientation up to $\lambda = 4$–5, followed by a progressive disorientation at higher values of λ (as supported by the WAXS measurements) is further supported by changes in the value of T_g in the range $\lambda = 1$–8. This can be concluded from Fig. 6 which shows the data from Table 1, reflecting the effect of the draw ratio λ on T_g for gelatin concentrations of 10 and 14% during crosslinking. Generally, improvement of the orientation leads to an increase of T_g, and disorientation to a decrease. A decrease is what was observed, as shown in Fig. 6 and Table 1. The two maxima for T_g are located between $\lambda = 4$ and 6, where the WAXS results show the highest orientation. Also, these values of λ are a little larger than the value for which the optimal mechanical properties are observed (Figs. 2–4). It is interesting to note that the two bell-shaped curves, reflecting the dependence of T_g on the draw ratio, are shifted with respect to the λ axis. The samples chemically crosslinked at higher gelatin concentration displays a T_g maximum at lower λ and vice versa (Fig. 6), which could be related to the crosslinking density. The higher gelatin concentration during crosslinking suggests a higher crosslinking density, resulting in a lower orientability. In such a case the expected maximum in the T_g values should appear at lower draw ratios. In the case of lower crosslinking density, one needs higher draw ratios in order

Table 1 Storage modulus E' at 30 °C and T_g (from E'') as evaluated from DMTA measurements on chemically crosslinked (from 10 and 14% solutions) gelatin with different draw ratios λ

λ	1	2	3	4	6	8
crosslinking in 14% solution						
E' (30 °C) (MPa)	1000	4810	4350	5890	3570	2880
T_g (°C)	65	86	99	104	84	63
crosslinking in 10% solution						
E' (30 °C) (MPa)	1520	3890	4420	4420	5310	4130
T_g (°C)	62	75	78	96	106	94

Fig. 6 Dependence of the glass transition temperature T_g on the draw ratio λ for chemically crosslinked (from 10 or 14% solution) gelatin. The data are evaluated from the curves reflecting the temperature dependence of the loss modulus E'' for samples having the same starting water content; gelatin concentration during crosslinking (in %) is: ○-14; ●-10



to achieve the optimal orientation of the chain segments, as was actually observed (Fig. 6).

Discussion

As was shown in Figs. 2–4, the improvements in mechanical properties achieved in this study are lower than those obtained by application of the same techniques to other systems [10, 11]. In order to understand this, one has to take into account the peculiarities of gelatin as a polymeric material. It is obtained from collagen as a result of transformation by denaturation and physical and chemical degradation. The collagen molecule itself consists of three helical peptide chains (α chains) held in close, parallel association, in the form of a rigid rod. Thermal denaturation occurs near 40 °C for solutions of most mammalian collagens and is marked by abrupt changes in intrinsic viscosity, specific optical rotation, sedimentation, and light scattering intensities [15].

Because of intramolecular crosslinks near the ends of the α chains, three distinct gelatin species can be formed. Frequently, they are referred to as protogelatins, and have been designated α, β, and γ gelatin and correspond approximately to monomer, dimer, and trimer, respectively. The conversion of collagen to gelatin by thermal denaturation involves the disruption of only noncovalent bonds, such as coulombic, hydrophobic, or hydrogen bonds, and van der Waals forces. The thermal denaturation of protogelatins is partially reversible, a fact that is used to explain the gelling properties of gelatin [13]. Among proteins, the last-mentioned property of gelatin is unique, suggesting that it depends upon the primary structure of collagen, which survives the denaturation and degradation of the conversion processes. The crosslinking centers in gelatin represent crystallites of helical chains which melt around 40 °C and the physical network disappears (melts) at higher temperatures.

Due to the large number of side functional groups it contains, gelatin readily undergoes chemical reactions including chemical crosslinking when a multifunctional reagent is used, as was the case in this investigation. This complicates the situation in the case of chemically crosslinked gelatin, since physical crosslinking will generally occur as well, but to an uncontrolled extent. The presence of these two types of networks can greatly limit the controlled deformation and orientation of the chain segments, relative to systems in which there is only carefully introduced chemical crosslinking. In addition, the physical crosslinks can be of relatively large volume, and involve significant sections of chains that could otherwise participate in the orientation.

These considerations are supported by the results of Mark et al. [11] on application of the novel orientation technique to hydroxypropyl cellulose. They found basically a twofold increase in E and σ_b; only in case of long primary chains (i.e., in the highest molecular weight polymer which had been slightly crosslinked in dilute (isotropic) solution), did the increase in ε and σ_b became fivefold to sevenfold [11]. Due to the greatly reduced orientability of gelatin, arising from the coexistence of two types of interpenetrating networks, the improvements in the mechanical properties are decreased, relative to systems [10, 11] in which only a chemical network is present.

These peculiarities of gelatin can explain the atypical relationship between draw ratio and orientation; i.e., instead of a steady increase of orientation with deformation in the interval $\lambda = 1$–20, a maximum is observed at $\lambda = 4$–5.

In order to overcome this limiting peculiarity of gelatin, one should apply the drying-under-deformation technique [8, 9] under conditions suppressing the formation of the additional physical crosslinks. There are at least three approaches that could bring this about: i) increased temperatures during all steps of the procedure; ii) use of a solvent that interferes with the associations, and iii) changes in solvent pH to those that destabilize protein helical conformations. In all cases a complete control of the chain conformation is required. Preliminary results in this direction are rather promising [18].

Conclusions

By means of the chemical crosslinking, followed by drawing in a swollen state and drying, it is possible to improve the otherwise poor mechanical properties of non-crosslinked isotropic gelatin. This improvement is observed only up to a draw ratio λ of about 4, however, after which the effective orientation is lost. This decrease in orientation has been proven by x-ray analysis for samples with $\lambda = 15$–20, and as a result, the mechanical properties approach those of the undrawn material. Similarly, the glass transition temperature T_g increases up to $\lambda = 4$–6, and then decreases for higher λ, for the same reason.

The fact that the improvement obtained was lower than in the case of other polymers is explained by one of the peculiarities of gelatin, specifically its ability to form coexisting chemical and physical networks. For this reason the orientation effect and the expected improvement in the mechanical properties are drastically reduced. Ways for overcoming this peculiarity of gelatin were suggested, and are being actively explored.

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