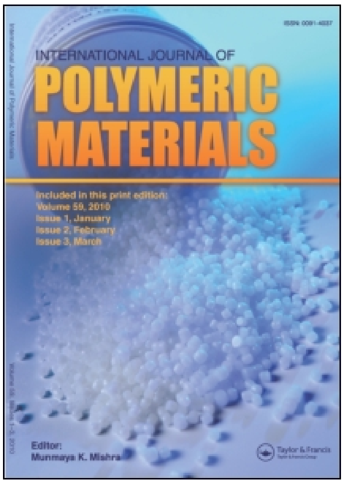

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Effect of Processing Conditions on Mechanical Properties of Pretreated Gelatin Samples*

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The mechanical behavior of seven gelatin samples, chemically crosslinked by bifunctional agents have been studied. The latter were two aldehydes (glyoxal and glutaric aldehyde), two diepoxides (1,2,3,4-butadiene diepoxide and 1,2,7,8-diepoxyoctane) as well as three diisocyanates (1,4-diisocyanato butane, 1,6-diisocyanato hexane and 1,12-diisocyanato dodecane). The first four agents lead to both physical and chemical network in gelatin, whereas the last three – to only chemical one. Several sets of unoriented samples, room conditioned or dry, as well as annealed at various annealing temperatures and duration, were prepared. In addition, samples were drawn in a swollen state and subsequently dried at fixed ends showing draw ratios between $\lambda = 1$ and $\lambda = 9$. The dependences of the universal microhardness, indentation modulus as well as the Vicker's microhardness on the annealing temperature and duration were obtained for room conditioned and dry unoriented crosslinked gelatin samples. An attempt was make to establish a relationship between the indentation modulus as obtained from universal microhardness measurements and the Young's modulus as obtained from static mechanical tests and it was found that this relationship strongly deviates from the theoretically derived one which is explained by the extremely high microhardness of gelatin. The dependence of the indentation modulus on the molecular weight between two crosslinking points for annealed room conditioned samples showed a clear minimum due to the competition between the two processes, taking place with the decrease of the network density – loosening of the network and increasing of the degree of crystallinity.

For the oriented samples it was found that the drawability strongly depends on the type of networks present in the sample and the highest values were obtained for the

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[*] The authors dedicate this paper to Prof. Dr. S. Fakirov on occasion of his 65th birthday wishing him good health and further enjoyable team work.

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samples, containing only chemical network and the sample, crosslinked with 1,2,3,4-butadiene diepoxide (characterized by the loosest network among the samples with both types of networks). Finally, the dependences of the Young's modulus, tensile strength and elongation at break on the draw ratio were obtained from static mechanical tests.

Keywords: Gelatin; Mechanical properties; Drawability; Crosslinking; Microhardness

1. INTRODUCTION

In our previous studies [1, 2] it was found that the microhardness of native gelatin being relatively high as compared to other polymeric materials, dramatically increases with temperature and duration of thermal treatment of the samples. As native gelatin we consider chemically uncrosslinked gelatin films obtained by casting of water solution at room temperature. It was demonstrated that the microhardness increase is due to the crosslinking reactions, taking place at elevated temperatures [2].

Also, it is well known [3] that native gelatin is very brittle and has relatively poor mechanical properties since it contains a physical network-collagen triple helixes which act as junctions for this type of network. The mechanical properties can be improved by orientation but the physical network hinders the cold drawing. Basically, the gelatin can be made less rigid if the physical network is replaced by a more loose and flexible chemical network. A chemical network can be created by crosslinking the gelatin by various bifunctional crosslinkers. By varying the nature and length of the crosslinker one can control the flexibility of the chemical network. In addition, the formation of the physical network can be avoided by crosslinking in some specific solvents, *e.g.*, 2,2,2-trifluoroethanol, a solvent which suppresses the triple helix formation at room temperature [4]. Thus, some initial network density will be established in the samples characterized by some level of the microhardness. Furthermore, by annealing at elevated temperatures for certain time, additional condensation reactions will take place leading to an increase of the network density. Hence, an increase of the microhardness is expected to occur.

Another way to improve some static mechanical characteristics, namely the Young's modulus, the tensile strength and the deformation at break, can be achieved by orientation [5, 6]. Since gelatin can not be cold drawn, a new orientation technique described in detail elsewhere [7] and already successfully applied to gelatin [6] allowed to obtain very good orientation at relatively low draw ratios and at the same time to preserve the oriented structure for a long enough time by introducing of a loose chemical network. Draw ratios up to $\lambda = 15$ were achieved for these samples and as was shown by wide-angle X-ray analysis [6] that the drawing affected positively the orientation only up to $\lambda = 4 - 5$. The network structure and the orientation were destroyed at higher draw ratios. Two mechanisms of the network destruction were suggested – pulling out of gelatin macromolecules from the crystallites as well as chain scission which probably takes place at higher draw ratios [6].

Since the drawing is effective only to certain degree it was important to obtain draw ratios as high as possible, *i.e.*, the highest drawability and thus to assure that the respective relationship between some mechanical characteristic and the draw ratio will pass through a maximum in accordance with previous observations [6]. For this reason an attempt was made to influence the drawability through the density and the flexibility of the network by changing the type and the chain length of the crosslinker as well as the number of the networks.

It is the aim of this work to shed some light on the relationship between the processing conditions like type of crosslinking, draw ratio, annealing temperature and annealing time of gelatin from one hand, and some mechanical characteristics like microhardness, indentation modulus, Young's modulus, tensile strength and elongation at break, on the other. Some additional properties will also be considered where necessary.

2. EXPERIMENTAL

2.1. Sample Preparation

Native gelatin was chemically crosslinked by the use of seven bifunctional crosslinkers, differing in the type of the functional groups as well as in their chain length (which reflects on their chain flexibility and the molecular weight between two crosslinking points M_c, respectively. (Further on in this paper we will simply say "molecular weight'' or M_c when discussing the network density for the sake of simplicity). The conditions of crosslinking are shown in Table I and the procedure is thoroughly described in [8]. In summary, all the samples were crosslinked at 5.5 wt% gelatin concentration and 0.0128 M concentration of the crosslinker and could be separated into two sets: (1) gelatin samples containing both chemical and physical network (samples 1–4, Tab. I), and (2) samples containing only chemical network (samples 5–7, Tab. I). The latter were prepared by using a suitable solvent (2,2,2-trifluoroethanol) suppressing the formation of physical network during crosslinking [4].

After the crosslinking with each of the agents (Tab. I) the cast dry isotropic 0.2–0.4 mm thick films were cut into pieces, and separated into three groups: (i) unannealed; (ii) annealed for 5 h at 70, 100, 130, 150, 180 and 210°C or (iii) annealed for 5, 10, 15, 20 or 25 h at 180°C. Subsequently the samples of all three groups were held for several days at room conditions in order to get the equilibrium moisture content (15–17 wt% [6]). These samples were used to investigate the effect of the annealing temperature T_a (for fixed annealing time of 5 h) or the effect of the annealing time t_a (at $T_a = 180°C$) on the microhardness. Part of the already annealed for 5 h at various temperatures crosslinked samples were dried for 24 at 105°C and subsequently for another 24 h at 105°C in vacuum according to a procedure described elsewhere [9]. The obtained dry samples were kept in a dessicator prior the respective measurement of the effect of the annealing temperature (for fixed time of 5 h) on the microhardness.

In order to obtain oriented samples the new orientation technique [7] consisting of swelling the crosslinked gelatin samples, drawing to various draw ratios in a swollen state and drying in the oriented state at fixed ends was used. The maximum draw ratio (drawability) depends on the nature of the sample and it turned out to be as high as $\lambda = 9$ for the case of 1,2,3,4-butadiene diepoxyde and $\lambda = 8-9$ for all diisocianato crosslinked samples.

2.2. Testing Techniques

Microhardness measurements: The universal microhardness (HU) and the Vicker's microhardness (HV) of some of the samples were measured using Dynamic Ultra Microhardness tester DUH-202

TABLE I Sample designation, crosslinking conditions and molecular weight between two crosslinking points M_c

No.	*Crosslinking agent*	*Solvent*	*Temperature of cross-linking* [°*C*]	*Time of cross-linking* [*min*]	*Molecular weight* M_c [*g/mol*]
1	Glyoxal	Phosphate buffer, pH = 5.8	45	120	650 ± 30
2	Glutaric aldehyde	Phosphate buffer, pH = 5.8	45	5	840 ± 20
3	1,2,3,4-Butadiene diepoxide	Phosphate buffer, pH = 5.8	45	120	3600 ± 170
4	1,2,7,8-Diepoxyoctane	Phosphate buffer, pH = 5.8	45	120	–
5	1,4-Diisocyanato butane	2,2,2-Trifluoro-ethanol	25	120	4450 ± 170
6	1,6-Diisocyanato hexane	2,2,2-Trifluoro-ethanol	25	120	3200 ± 260
7	1,12-Diisocyanato dodecane	2,2,2-Trifluoro-ethanol	25	80	1400 ± 150

(Shimadzu). This instrument allows an instant computer recording of the indentation depth as a function of the applied load and its subsequent removal. Hence, the HU could be determined from the force-indentation depth-curve and the elastic properties of the material could be investigated as well. The measurements were performed with a Vickers indenter. A load range of 500 mN, a loading and unloading speed of 23.5 mN/s and a holding time of 6 s after completing the indentation were used.

On the other hand, the other more common technique for measurement of the microhardness can be applied and by evaluation of the residual impression area left on the material surface after the unloading the Vicker's microhardness could be determined. Since an elastic recovery of the material takes place immediately after the unloading, the HV could provide information only about the permanent plastic deformation of the material. Thus, the universal microhardness method has the advantage, as compared to the optical evaluation of the indentation, that the measurement of the depth is fully automatic and in comparison to the visual evaluation the subjective influence is omitted.

During the experiments the two types of microhardnesses were measured but since it turned out that the data of HV were much scattered, only the data of HU were presented. It is worth noticing that generally the HV is higher than the HU and that the difference, due to the elastic recovery of the material, is an estimate for the elastic component of the deformation.

Furthermore, a smooth surface is necessary in order to get good and reproducible results. It turned out that with the increase of the annealing temperature T_a, the gelatin samples change. For example, for samples 5–7 (Tab. I), the highest T_a (210°C) was not reachable without bubbles to appear in the samples which made the respective measurements impossible regardless of the fact if HU or HV is measured. Generally, five measurements were performed to get the mean value and the mean square error of the microhardness for every T_a or t_a.

In addition, using a technique described in the literature [10] of fitting of force-indentation depth-curve at unloading, obtained by universal microhardness measurements, it was possible to calculate the indentation modulus E^* for the crosslinked samples for various T_a

or t_a. Further, E^* values were also compared with the Young's modulus E of unannealed gelatin samples as evaluated by means of static mechanical measurements. The comparison was made on the basis of two well known relations [11–13]. The cited in [11] relationship is $E^* = E/(1 - v^2)$, where v denotes the Poisson ratio, whereas in [12, 13] correlation and even equality of these moduli has been demonstrated for metals and metal alloys.

Static mechanical measurements: Young's modulus E, tensile strength σ and elongation at break ε in a tensile mode were obtained at room temperature by the use of testing machine Zwick 1464, Germany. The Young's modulus was calculated from the linear part of the stress-strain curve in the strain interval from 0.05 to 0.5 mm and sample length between the clamps equal to 20 mm.

The DSC measurements were performed on a Mettler – Toledo Star System (Switzerland), in the range 0–250°C with a heating rate of 10°C/min in a nitrogen atmosphere. Sample weight was 5–10 mg. Only samples 1 and 2, annealed at different temperatures and duration were investigated.

2.3. Data Evaluation

Some words about the way the results were evaluated. Almost in all the cases there is only a statistical relationship between the function and the argument. In some cases such a connection can be seen and then it is described. Very often, though, the points are scattered and then we tried to linearly fit with the straight line $Y = Y_o + AX$, where Y is the function, X is the argument, Y_o is the value of Y for $X = 0$, and A is a coefficient. As an output of the linear fit one gets also the respective mean square errors ΔY_o and ΔA. Obviously when $A = 0$ there is no dependence of Y on X, but what happens if zero is in the experimentally found region of $A \pm 2\Delta A$? In this work we consider Y *dependent* on X if zero is *outside* the region $A \pm 2\Delta A$. In this case the changes in Y are significant. If zero is *within* the region $A \pm 2\Delta A$ then Y is considered *as independent* of X (or a constant within the experimental error). As is well known such a choice of the region leads to approximately 96% probability that Y is *really* independent of X.

Generally, if there are only few points on a plot, we did not connect them. In some cases, though, when the dependence is well expressed or when there are more points, a fitting function in vicinity of these points was drawn. The case simplifies for linear fit. Then we say whether it is increasing or decreasing and also characterize it by a respective factor. The later is the ratio of the function for maximal and minimal value of the argument in the range of the argument in question. This factor is always larger than unity since if the linear dependence is decreasing we simply take the reciprocal of the above ratio. This factor equals unity for a lack of dependence.

3. RESULTS

3.1. Dependence of Universal Microhardness, Vicker's Microhardness, and Indentation Modulus on Annealing Conditions

As was already mentioned, the crosslinked gelatin samples, described in Table I, could be separated into two sets: (1) gelatin samples containing both chemical and physical networks (samples 1–4, Tab. I) and (2) gelatin samples containing only chemical network (samples 5–7, Tab. I). In Figure 1a the dependence of the HU for room conditioned samples 1–4 (Tab. I) on T_a for $t_a = 5\,h$ are shown. An increase of the HU by a factor of 1.3 or 1.6 with T_a can be seen for samples 1 and 2, respectively. There is no clearly pronounced dependence for sample 3, whereas an decrease of the microhardness for high T_a can be seen for sample 4.

Generally, the microhardness is related to the perfection of the crystallites in crystalline polymers provided the degree of crystallinity is constant. The perfection may be estimated by the melting temperature of the crystals. DSC curves were obtained for samples 1 and 2, being considered as representative also for the rest of the samples (Tab. I) regarding the conclusions drawn below. In these curves two minima, situated at relatively high temperatures of 125–240°C, can be seen. The lower-temperature minimum position depends strongly on the annealing conditions, whereas the high-temperature minimum position practically does not change and reflects the melting of the dry gelatin at 230°C [3]. In Table II the temperature of the lower-melting minimum for unannealed and annealed for 5 h at several

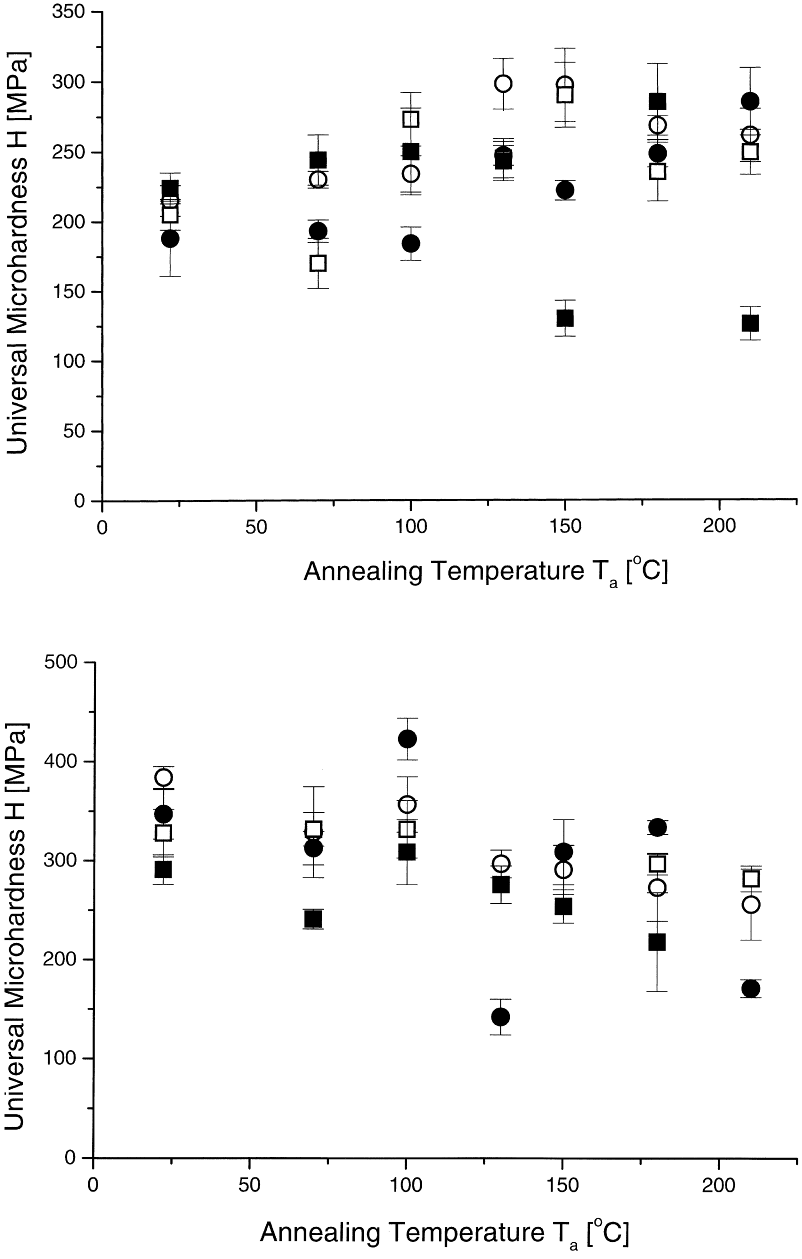

FIGURE 1 Dependence of the universal microhardness on the annealing temperature for crosslinked gelatin by: (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde and (□) 1,2,7,8-diepoxyoctane; (a) room conditioned samples and (b) dry samples.

TABLE II Temperature of the lower-melting minimum for crosslinked gelatin samples, annealed for 5 h at temperature T_a

	T_a [°C]				
*Sample No.**	*Unannealed*	130	150	180	210
1	– **	165	175	196	– **
2	123	170	175	170 ***	200

* For sample designation see Table I.
** Sample not measured.
*** Very weak flat minimum.

temperatures crosslinked gelatin samples 1 and 2 is given. One can clearly see the moving of the lower-temperature minimum towards high temperatures with the increase of T_a.

For all the samples containing physical and chemical networks the HV values (not shown) are usually higher by about 40–45% than the HU values.

In Figure 1b the dependence of the universal microhardness of dry samples 1–4 (Tab. I) on T_a for $t_a = 5$ h are shown. A decrease of the HU by a factor of 1.5 with T_a can be seen for sample 1. For sample 2 there is no definite dependence. A decrease of the microhardness at high T_a can be seen for sample 3. Due to the larger error bars it is best to consider the microhardness of sample 4 as a constant. Generally, the dry gelatin microhardness values are higher by 25–50% than the room conditioned gelatin microhardness values.

The respective dependences for gelatin samples containing only chemical network look similar. In Figure 2a the dependence of the HU for the room conditioned samples 5–7 (Tab. I) on T_a for $t_a = 5$ h are shown. The points are rather scattered and HU practically does not change with T_a. Again, as in the case of samples containing both types of networks, a comparison between the values of both microhardnesses obtained for one sample was done. For every sample containing only chemical network the HV values (not shown) are about 30–40% higher than the HU values.

In Figure 2b the dependences of the HU for the dry samples 5–7 (Tab. I) on T_a for $t_a = 5$ h are shown. Whereas the microhardness is constant within the experimental error for samples 5 and 6, it slightly decreases by a factor of 1.2 for sample 7 with the increase of T_a. Generally, the dry gelatin microhardness values of samples 5–7 are by

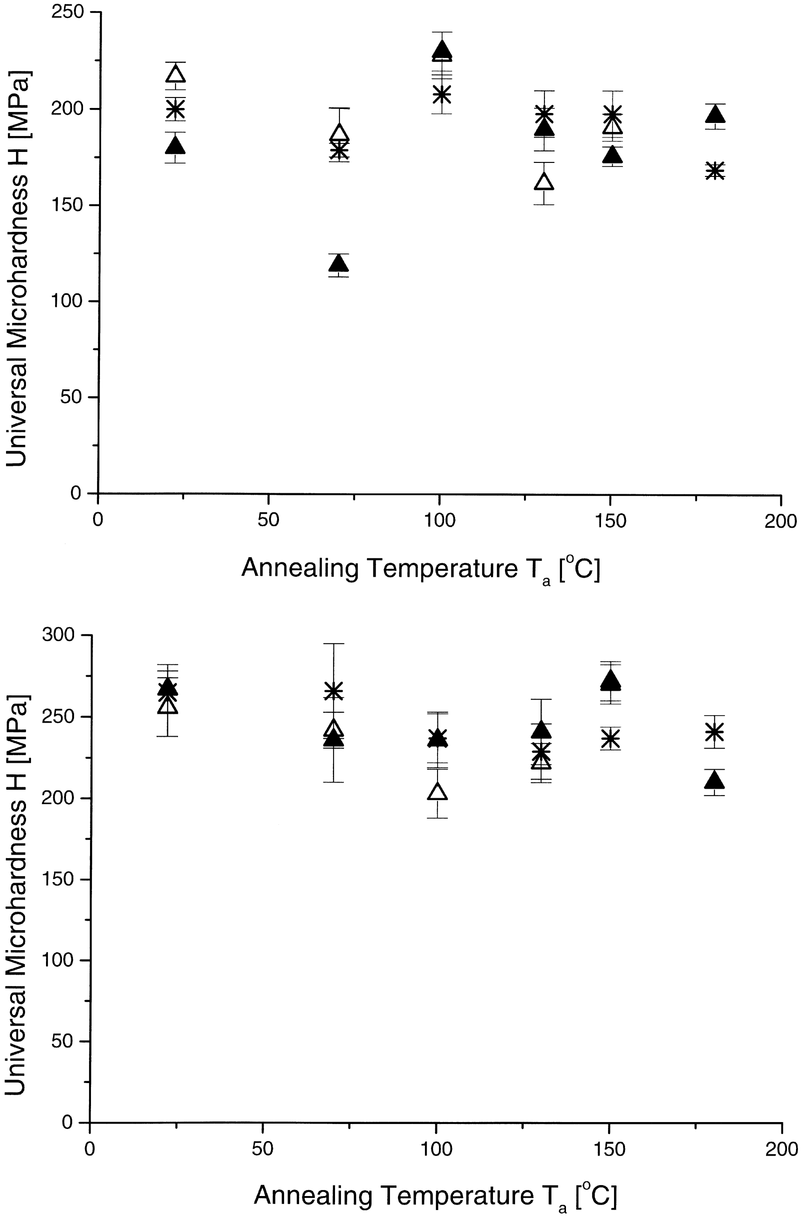

FIGURE 2 Dependence of the universal microhardness on the annealing temperature for crosslinked gelatin by: (△) 1,4-diisocianato butane, (▲) 1,6-diisocyanato hexane, and (✳) 1,12-diisocianato dodecane; (a) room conditioned samples and (b) dry samples.

30–35% higher than the room conditioned gelatin microhardness values.

The dependence of HU on t_a at $T_a = \text{const}$ was measured only for room conditioned gelatin samples containing both chemical and physical network (samples 1–4, Tab. I) and the corresponding curves are given in Figure 3. HU of samples 1, 3 and 4 does not depend on t_a, whereas for sample 2 a slight increase by a factor of 1.3 can be detected. This could be explained with a process of increasing of the crystallites perfection assuming a more or less constant degree of crystallinity. As above, the crystallite perfection is reflected in their melting temperature, given in Table III, as dependent on t_a at constant $T_a = 180°C$.

As was mentioned in the experimental part, from the unloading curve during the measurement of HU also the indentation modulus E^* can be obtained. Since a substantial difference between E^* *vs* T_a dependences for the room conditioned and dry samples was not found, they will be monitored together.

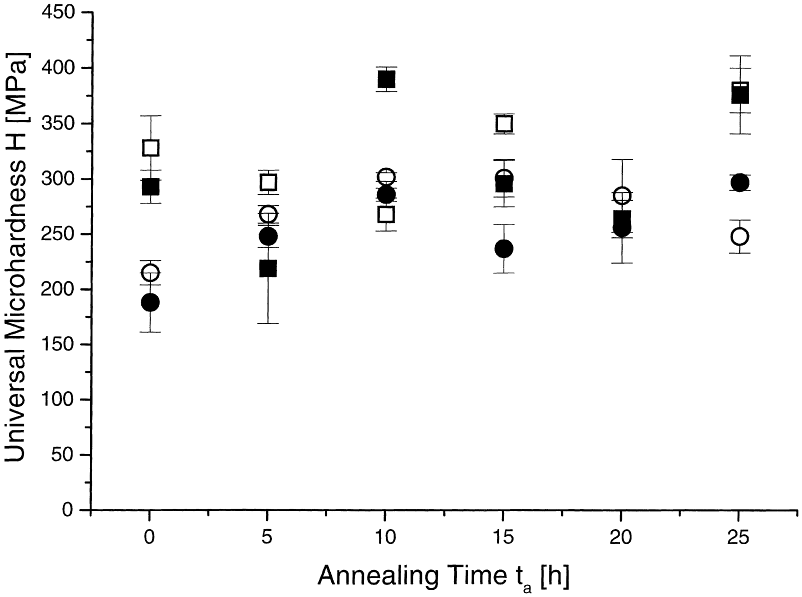

FIGURE 3 Dependence of the Universal microhardness on the annealing time for room conditioned crosslinked gelatin samples by: (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde and (□) 1,2,7,8-diepoxyoctane.

TABLE III Temperature of the lower-melting minimum for crosslinked gelatin samples, annealed at 180°C for various duration t_a

	t_a [*h*]			
*Sample No.**	0	5	10	15
1	– **	195	215	225***
2	124	172***	215	210 + 225

* For sample designation see Table I.
** Sample not measured.
*** Very weak flat minimum.

In Figures 4a and b the dependence of E^* on T_a for room conditioned and dry gelatin samples, respectively, containing both chemical and physical network, are shown. For all four samples the points are very scattered and no systematic change of E^* on T_a can be detected. The only difference is that its values for the dry samples are at average by 20–25% higher than the respective values for the room conditioned samples.

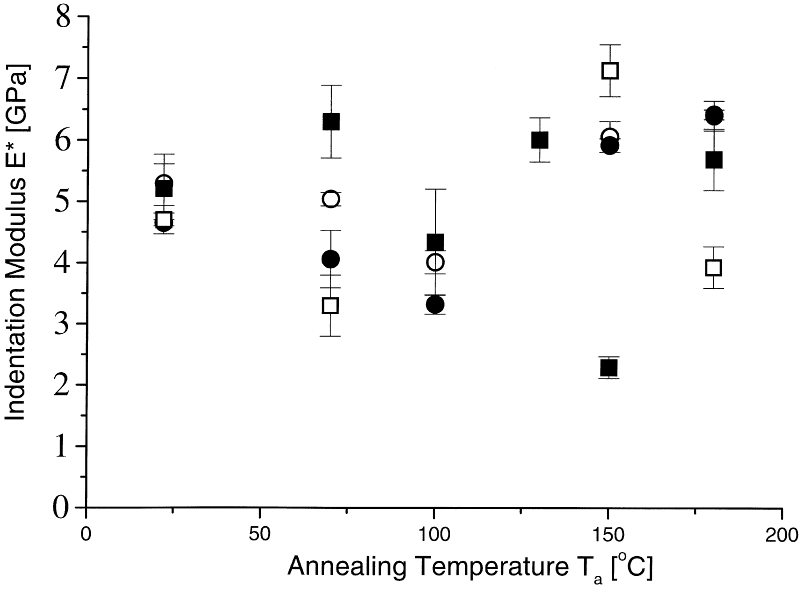

FIGURE 4 Dependence of the indentation modulus on the annealing temperature for crosslinked gelatin by: (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde and (■) 1,2,7,8-diepoxyoctane; (a) room conditioned samples and (b) dry samples.

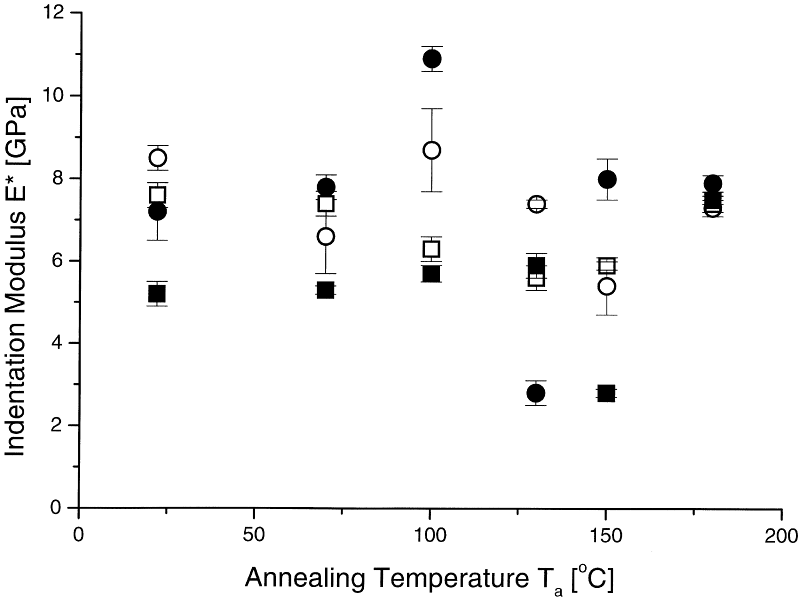

FIGURE 4 (Continued).

In Figures 5a and b the dependences of the indentation modulus E^* on T_a for room conditioned and dry gelatin samples, respectively, containing only chemical network, are shown. Again, as in the previous case (Fig. 4a) the points for the room conditioned samples are very scattered and there is no clearly pronounced tendency for any of these samples. After annealing (Fig. 5b) the scattering of the points decreases and for sample 5 a linear increase by a factor of 1.4 of E^* with T_a can be detected. For gelatin samples containing only chemical network there is a large difference in the values of E^* for the samples before and after the drying: the values of E^* for the dry samples are at average higher by 40–50% than the respective values for the room conditioned samples.

3.2. Relationship between Young's Modulus and Indentation Modulus

Since both Young's modulus E and the indentation modulus E^* express the elastic behavior of the material it seems interesting to

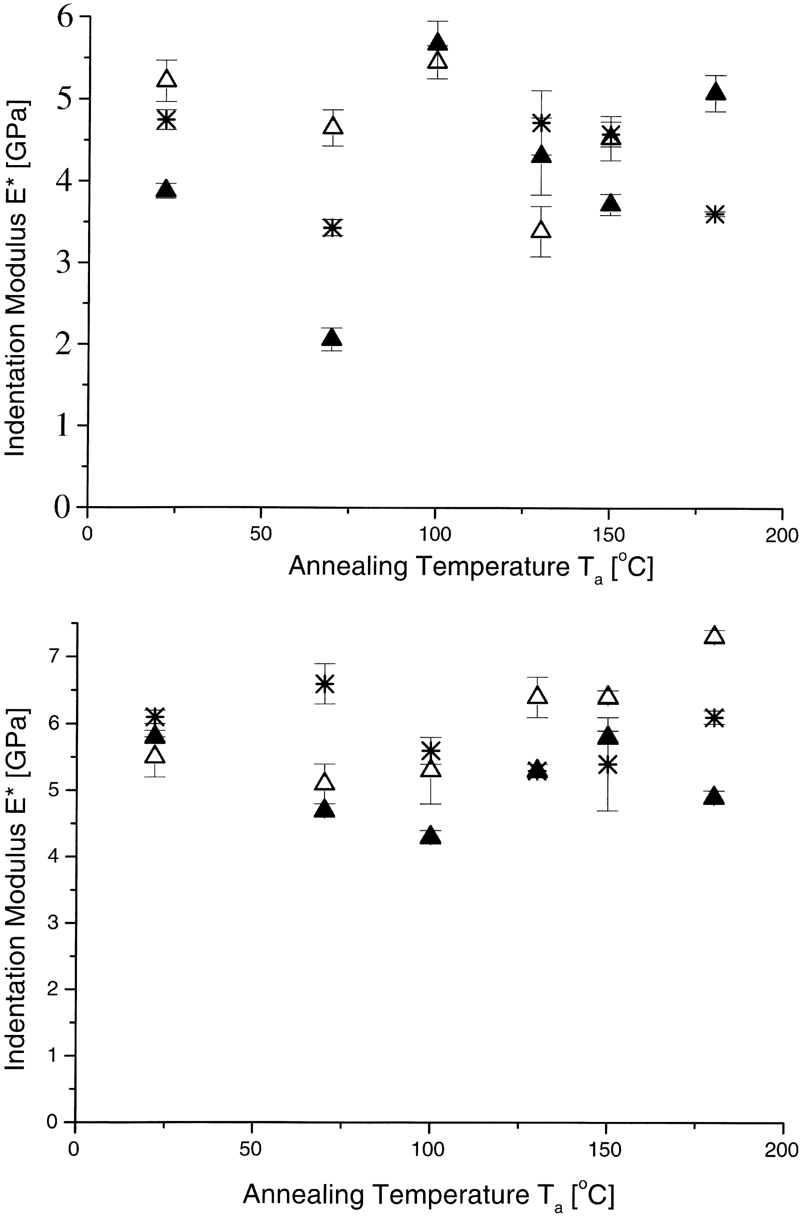

FIGURE 5 Dependence of the indentation modulus on the annealing temperature for crosslinked gelatin by (△) 1,4-diisocianato butane, (▲) 1,6-diisocyanato hexane, and (✻) 1,12-diisocianato dodecane; (a) room conditioned samples and (b) dry samples.

compare them. E is obtained by static mechanical tests in a tensile mode and E^* – from universal microhardness measurements. The result is shown in Figure 6 both with some theoretical lines. The two straight lines ($v = 0.2$ and $v = 0.5$) represent the known [11] relation $E^* = E/(1 - v^2)$ between the indentation modulus E^* and the Young's modulus E, where v denotes the Poisson ratio. Since the Poisson ratio of gelatin may change with the degree of crosslinking, the two extreme cases of $v = 0.2$ and 0.5 [12] were taken and the respective straight lines were drawn in Figure 6. The lowest straight lines corresponds to the case $E^* = E$ [13, 14]. For the experimentally measured points there is also a least square linear fit of the data drawn in Figure 6 (the line at the top). In the case of crosslinked unoriented gelatin samples all points are situated in a region far above the theoretical straight lines, *i.e.*, the experimentally measured indentation modulus is 4–5 times larger than that calculated from the Young's modulus.

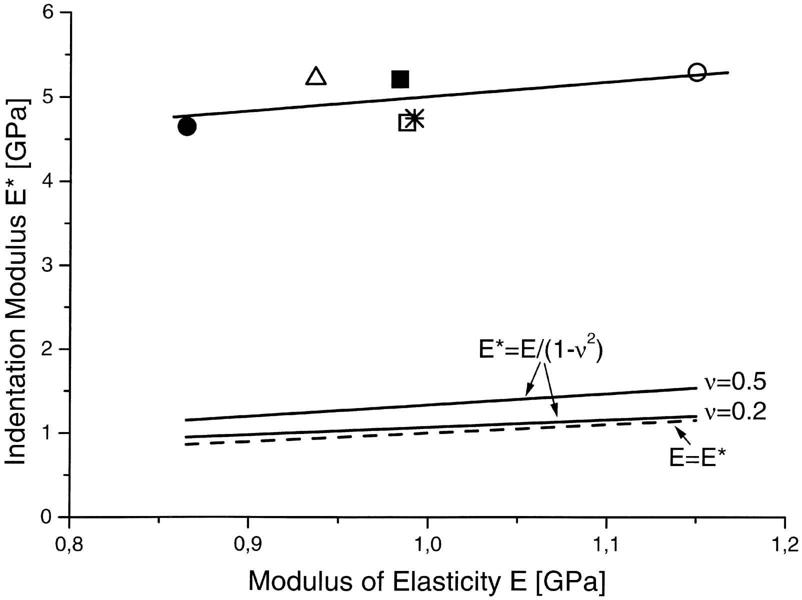

FIGURE 6 Comparison between Young's modulus and the indentation modulus. The experimental points are as follows: (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde, (□) 1,2,7,8-diepoxyoctane, (△) 1,4-diisocyanato butane and (✱) 1,12-diisocianato dodecane. The lines represent theoretical relations and least square fit (see text); ν is the Poisson's ratio.

So far, the two types of networks were regarded separately. The network present in the sample may be characterized by only one parameter, namely the molecular weight between two crosslinking points M_c without considering if the net is physical, chemical or both. Up to now, the different samples were characterized by different values of M_c (Tab. I) hence differences in their mechanical behavior should be expected. From the data of Figures 1 and 2 the dependence of the indentation modulus on M_c can be readily derived. Figure 7 shows the dependence of E^* on M_c for unannealed and annealed for 5 h at 70°C room conditioned samples 1–3, 5–7 (Tab. I). A slight minimum at $M_c = 2600$ g/mol can be seen for the unannealed samples, which becomes very well expressed at approximately the same M_c after annealing.

It is worth mentioning here that for every sample the network density should increase starting from the initial one (given in Tab. I) with the course of annealing, due to condensation reactions taking

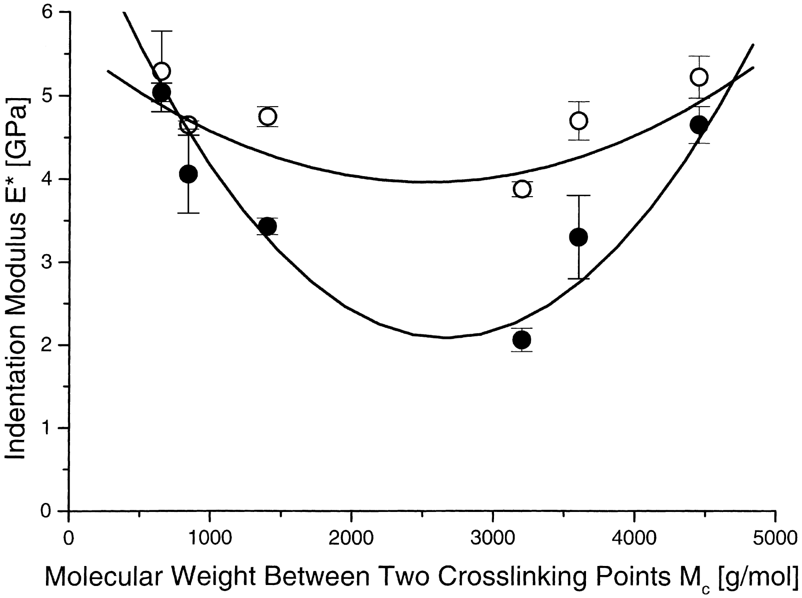

FIGURE 7 Dependence of the indentation modulus on the molecular weight between two crosslinking points for room conditioned crosslinked gelatin samples: (○) unannealed and (●) annealed for 5 h at 70°C.

place [9]. Thus, the dependence for the unannealed samples given in Figure 7 reflects only the initial state of crosslinking, *i.e.*, before any additional condensation reactions occur during the subsequent annealing.

3.3. Static Mechanical Properties Dependences on the Draw Ratio

Up to now we dealt with unoriented gelatin samples trying to improve their mechanical characteristics by variation of the annealing conditions. We will show the effect on some static mechanical properties as Young's modulus E, tensile strength σ and elongation at break ε of the draw ratio λ for oriented, room conditioned crosslinked samples. We will start with the dependence of E on the draw ratio λ of samples 1–4, (Tab. I), containing both chemical and physical network, shown in Figure 8a. Drawability $\lambda =$ of 2.5–4 is achieved for samples 1, 2

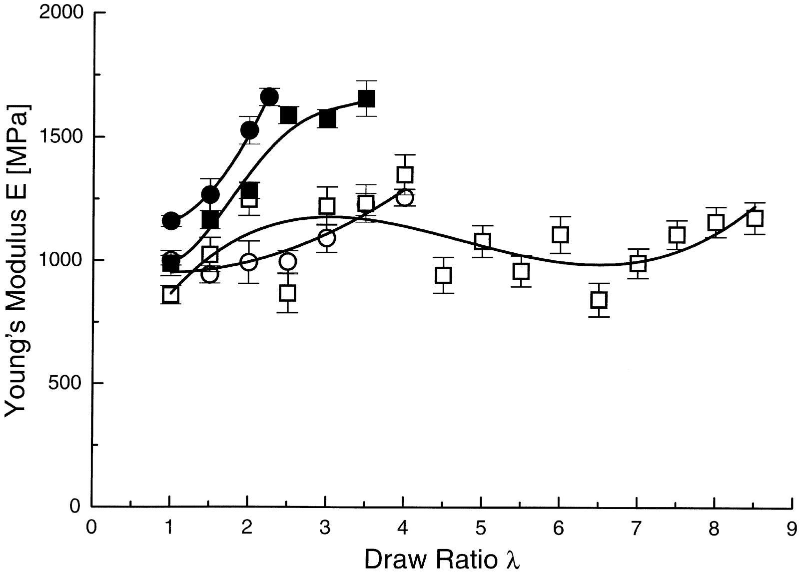

FIGURE 8 Dependence of the Young's modulus on the draw ratio of room conditioned crosslinked gelatin samples by: (a) (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde, (□) 1,2,7,8-diepoxyoctane and (b) (△) 1,4-diisocianato butane, (▲) 1,6-diisocyanato hexane and (✻) 1,12-diisocianato dodecane.

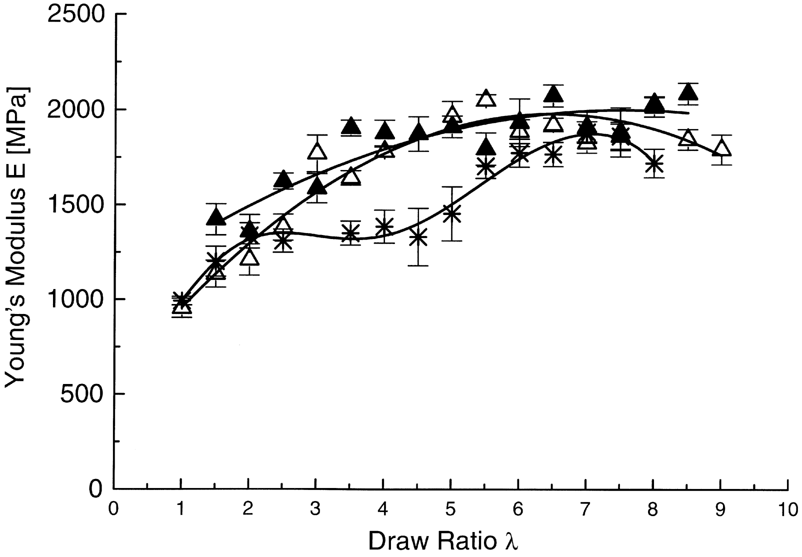

FIGURE 8 (Continued).

and 4, whereas it is surprisingly high ($\lambda = 8.5$) for sample 3, characterized by the loosest network (Tab. I). E modulus increases by a factor of 1.6 for sample 1, changes slightly as shown for sample 3, and increases by a factor of 1.7 for samples 2 and 4 (Fig. 8a).

In Figure 8b the dependence of E on λ of gelatin samples 5–7, (Tab. I) containing only chemical network are shown. As expected, due to the absence of the physical network very high and practically one and same drawability of $\lambda = 8-9$ was achieved for all three samples. E increases by a factor of almost 2 for samples 5 and 7, and by 1.6 for sample 6.

In Figure 9a the dependence of the tensile strength σ on λ of gelatin samples 1–4, (Tab. I) containing both chemical and physical network is shown. σ decreases twofold for sample 3, increases by a factor of 1.7 for samples 2 and 4, and changes as indicated for sample 1.

In Figure 9b the dependence of σ on λ of gelatin samples 5–7, (Tab. I) containing only chemical network are shown. A remarkable increase of σ with the draw ratio in comparison to the respective unoriented samples can be seen as follows: 5 × for sample 5 and 3.7 × for samples 6 and 7.

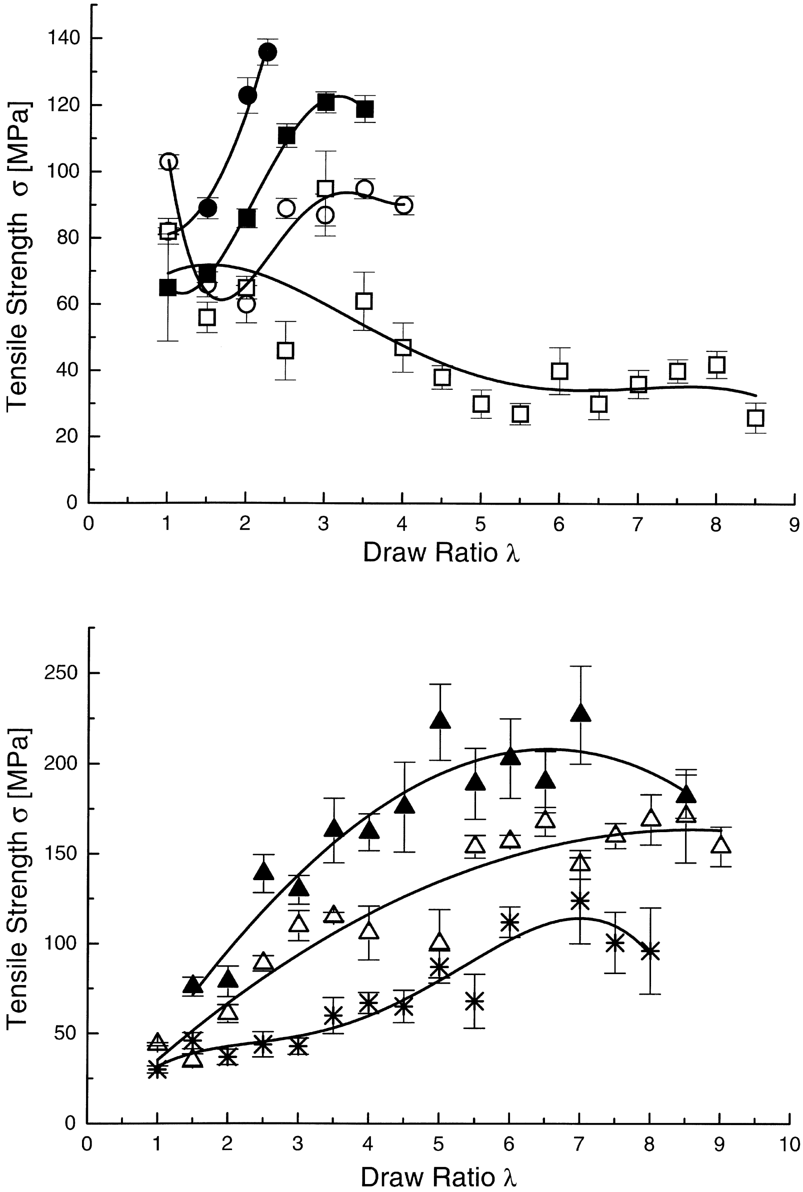

FIGURE 9 Dependence of the tensile strength on the draw ratio of room conditioned crosslinked gelatin samples by: (a) (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde, (□) 1,2,7,8-diepoxyoctane and (b) (△) 1,4-diisocianato butane, (▲) 1,6-diisocyanato hexane and (✱) 1,12-diisocianato dodecane.

The dependence of the elongation at break ε on λ of oriented crosslinked gelatin samples 1–4, (Tab. I) containing both chemical and physical network is shown in Figure 10a. ε increases almost linearly from 13 (unoriented sample) to 34% ($\lambda = 8.5$) for sample 3, decreases linearly by a factor of 1.7 for sample 1 and passes through a maximum at a certain draw ratio of about 2 for samples 2 and 4.

In Figure 10b the dependence of ε on λ of gelatin samples 5–7, (Tab. I) containing only chemical network is shown. Due to the absence of the physical network the effect of λ on ε can be clearly seen. The three curves are bell-shaped, *i.e.*, a maximum ε is reached for certain λ smaller than the drawability. The λ value at maximum ε later equals 7, 6 and 5 × for samples 5, 6 and 7, respectively (Tab. I), *i.e.*, the looser the network the higher the draw ratio at which the peak appears. From all seven samples (Figs. 10a, b) the highest elongation at break reached is 65% for sample 7.

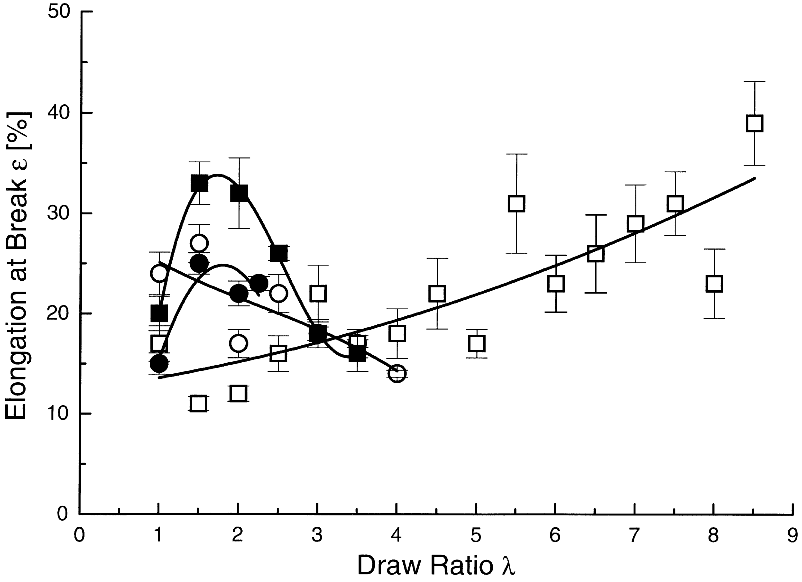

FIGURE 10 Dependence of the deformation at break on the draw ratio of room conditioned crosslinked gelatin samples by: (a) (○) glyoxal, (●) glutaric aldehyde, (■) 1,2,3,4-butadiene diepoxyde, (□) 1,2,7,8-diepoxyoctane and (b) (△) 1,4-diisocianato butane, (▲) 1,6-diisocyanato hexane and (∗) 1,12-diisocianato dodecane.

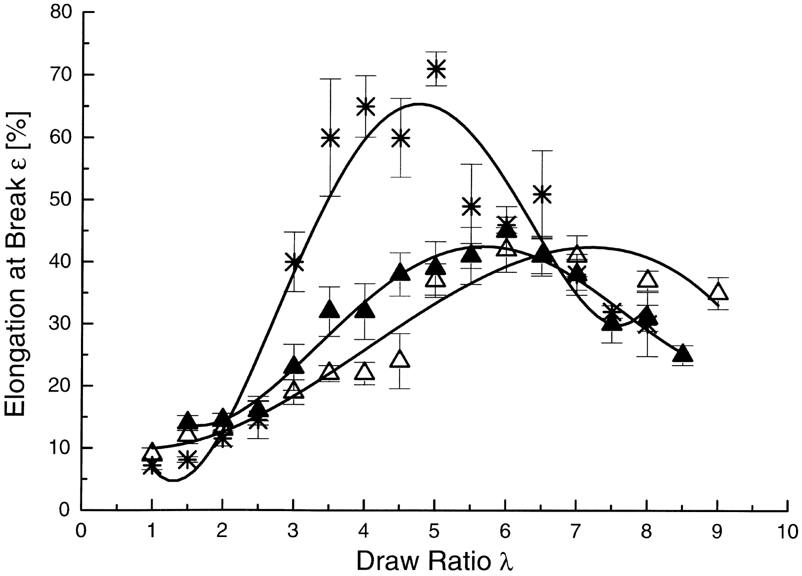

FIGURE 10 (Continued).

4. DISCUSSION

Before starting the discussion it is worth recalling the main differences between HU and HV. It is a common practice to measure HV by estimation of the length of the residual impression diagonals left by the indentor on the material surface *after* removing the load whereas the HU can be calculated from the deepest penetration of the indentor. Both microhardnesses are obtained by applying certain load for a certain time. Since after removal of the load elastic recovery takes place and it is to be expected that the HU will be lower than the HV when the material is elastic. The other way round-the difference between the HV and the HU can be a measure of the elastic part of the deformation.

4.1. Dependence of the Universal Microhardness on the Annealing Temperature and Annealing Time

Let us try to analyze in this light the results for the HU as a function of T_a. For all room conditioned samples containing physical and chemical networks the HV values are by about 40–45 % higher than the HU values, whereas for all samples containing only chemical network this difference is about 30–40%. As a next step the fraction of the plastic, elastic and viscoelastic contribution to the total deformation (indentation depth) caused by the indentor was estimated. These contributions were obtained as an output of the measuring program. The dependence of the indentation depth together with the dependences of these three contributions on the molecular weight between two points of crosslinking M_c are plotted in Figure 11. All three magnitudes remain constant with M_c within the experimental error. The values of the later are taken from Table I. The total indentation depth can be considered as a sum of 57% plastic, 37% elastic and 6% viscoelastic contribution and these values do not vary with the density of the network. It is a rather strange observation keeping in mind that the samples containing only chemical network are characterized by much higher molecular weight (smaller network density, Tab. I, sample 3 is an exception) and they are expected to be

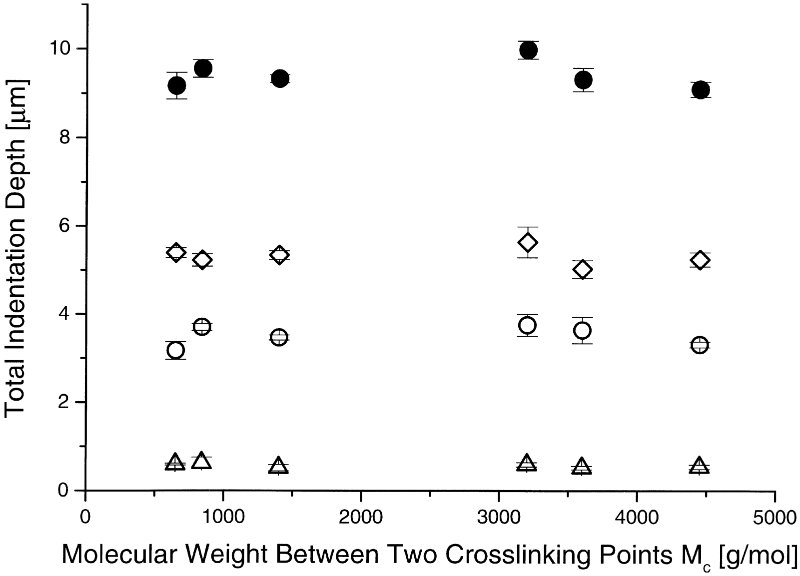

FIGURE 11 Dependence of the (●) total indentation depth and its components: (◇) plastic, (○) elastic and (△) viscoelastic contribution on the molecular weight between two crosslinking points for room conditioned crosslinked unannealed gelatin samples.

more flexible. It may be due to the fact that M_c of the samples under investigation changes in a relatively narrow interval between 600 and 4500 g/mol (Tab. I).

If, on the other hand, we compare the microhardness values obtained for both types of samples, we can conclude that the samples containing both physical and chemical network have values higher by 70 – 80 MPa for both room conditioned and dry samples. This is to be expected, since the physical network junctions are actually crystallites which always have higher microhardness than the amorphous phase. The samples containing only chemical network must show lower microhardness since they do not contain crystalline phase [15]. This was shown in our previous investigations by the use of X-ray diffraction where we explained that the samples having chemical network were not able to crystallize since the presence of chemical network hinders the crystallization [17].

Let us go back to Table II. As is clearly seen, the temperature of the lower-melting minimum for crosslinked gelatin samples, annealed for 5 h, strongly increases with T_a for both crosslinked with glyoxal (sample 1) or glutaric aldehyde (sample 2). Since higher perfection leads to higher microhardness [15] this way the observed increase of HU with T_a (Fig. 1) can be explained at least for samples 1 and 2 (Tab. I).

As was already shown the data points of the HU *vs.* t_a (Fig. 3) are very scattered, the only exception being the glutaric aldehyde crosslinked sample (2) where the microhardness increases linearly by a factor of 1.3 and this can be connected with the process of getting crystallites more perfect with the increase of the t_a. This is confirmed by the data for sample 2 in Table III. Although the data for sample 1 in Table III are consistent, they do not lead to the expected increase of the HU (Fig. 3, sample crosslinked by glyoxal).

It can be concluded that no obvious influence of the annealing time on the HU can be seen for room conditioned samples containing only chemical network and very slight one is observed in the case of two of the room conditioned samples, containing both chemical and physical networks.

The relatively large scattering of the HU data for room conditioned samples (Figs. 1a, 2a, 3, 4a and 5a) can possibly be explained by the presence of moisture in the samples, since the process of evaporation (hindered by the network) is time consuming and so the total annealing time is not long enough to cause changes in the samples. The use of dry samples simplifies the case a little. Generally the scattering of the points decreases after drying (compare Figs. 1a and 1b; Figs. 2a and 2b; Figs. 4a and 4b; Figs. 5a and 5b). Since the water in gelatin acts as a plasticizer [16] forming a phase with a lower density than the dry gelatin the exclusion of it during the drying process should lead to higher microhardness as well as to more uniform density of the sample, which in turn would decrease the mean square error in the microhardness.

4.2. Dependence of the Indentation Modulus on the Annealing Temperature and M_c

A comparison between the E^* for both types of samples shows that the samples containing both physical and chemical network have values higher by 1 GPa for both room conditioned and dry samples than the samples containing only chemical network. By analogy of the microhardness [15], this is to be expected and could be explained by the absence of any crystalline structure in the samples containing only chemical network [17].

Let us now comment on the dependence of the E^* on the molecular weight M_c. The plot for annealed for 5 h at 70°C crosslinked gelatin samples given in Figure 7 shows a very specific dependence. One can speculate that: i) decrease of the indentation modulus with increasing M_c for its low and middle values is due to loosening of the network (decreased network density), and ii) increase of the indentation modulus with increasing M_c for its middle and high values is due to increased degree of crystallinity after annealing in the samples with higher M_c. As a result the dependence of the indentation modulus on M_c would have a minimum somewhere for the middle values of M_c, which is actually the case (see Fig. 7). Although for the unannealed sample the points are scattered a similar dependence could be seen.

4.3. Relationship between Young's Modulus and Indentation Modulus

As seen in Figure 6, there is quite a large difference between the experimental points and the theoretically derived lines $E^* = E/(1 - v^2)$.

The agreement between the experimental points and the theoretical line $E = E^*$ is also very poor. This line has been proven to fit the experimental data in the case of many metals and alloys [13, 14]. The E^* values for crosslinked unannealed samples are unusually high-around 5 GPa. What is important to mention in this respect is the fact that the values of E^* for the annealed samples are even higher, around 8 GPa. Having in mind that E values of the gelatin samples under investigation are in the range of the typical ones for the majority of synthetic polymers, the value of E^* in the present case are unusually high for polymeric materials.

What could be the reason for this striking difference? In order to answer this question one should recall our previous results on microhardness measurements on thermally treated gelatin samples. It was found [1] that these samples show extremely high Vickers microhardness surpassing all known synthetic polymers and soft metals and approaching the value of some metals as for example zinc. Since E^* (Fig. 6) is derived from microhardness measurements, *i.e.*, it reflects the modulus only on the surface of the sample, it is also unusually high in contrast to the tensile Young's modulus E, which reflects the mechanical behavior of the whole sample. In this way one can explain, at least qualitatively, the deviation of the experimental points in Figure 6 from the theoretical lines.

4.4. Improvement of Some Mechanical Properties as Obtained from Static Mechanical Tests

As already said, avoidance of the physical network formation should improve to a significant extent the mechanical properties of gelatin since it will enhance the orientation. In order to directly follow the influence of the network on some mechanical properties of gelatin the same two groups of samples, containing both types of networks and samples containing only chemical network, were investigated. We tried to influence the density of the network, hence the flexibility and the drawability of these samples by changing the type and the chain length of the crosslinker.

Basically, the mechanical properties can be improved by orienting the gelatin. Since it can not be oriented by cold drawing this was performed by drawing in a swollen state according to [7]. A very good orientation and significant improvement of the mechanical properties was achieved earlier [6] at relatively low draw ratios for gelatin samples crosslinked by formaldehyde, *i.e.*, containing both types of networks. In some cases the mechanical parameter in question (E, σ or ε) passes through a maximum for certain draw ratio in vicinity of $\lambda = 5$. Hence, in order to detect such a maximum, if there is one, it is necessary to obtain as high as possible drawability.

By studying oriented samples it was found that the drawability strongly depends on the type of network present in the sample as the highest values of $\lambda = 8-9$ were obtained for the samples containing only chemical network (samples 5–7, Tab. I) and the sample, crosslinked with 1,2,3,4-butadiene diepoxide (sample 3) and containing the loosest network. The typical drawability of the other three samples, containing both physical and chemical network (samples 1, 2 and 4, Tab. I) was in the range of $\lambda = 2.5-4$. As expected, an increase was found of the drawability due to the suppression of the physical network formation. In brief, the drawability of all samples was drastically improved, thus allowing a following of the dependences of E, tensile strength and elongation at break on the draw ratio and respective improving of these parameters. As a measure of this improvement the maximal ratio of every parameter to its value for unoriented sample was taken. The results derived from Figures 8–10 and showing this improvement are given in Table IV.

TABLE IV Ratio of the maximal Young's modulus E_{max}, maximal strength at break σ_{max} and maximal elongation at break ε_{max} for oriented gelatin samples, to their respective values E, σ and ε for unoriented samples. Both unoriented and oriented samples are crosslinked

*Sample No.**	E_{max}/E	σ_{max}/σ	$\varepsilon_{max}/\varepsilon$
Samples containing both chemical and physical networks			
1	1.6	1*	1*
2	1.7	1.7	1.7
3	1.3	1*	2.6
4	1.7	1.7	1.7
Samples containing only chemical network			
5	1.9	5.0	4.2
6	1.6	3.7	3.1
7	1.9	3.4	8.1

* For sample designation see Table I.

As can be seen in Table IV, an increase of E in the range of 1.3 – 1.9 was found for all seven samples. These values are a little higher for the samples containing only chemical network, as compared to the samples containing both types of networks. σ increases relatively poorly for the samples crosslinked with both networks, and increases significantly for the samples, containing only chemical network, to reach an increasing by a maximum factor of five in comparison to unoriented samples for the 1,4-diisocyanato butane crosslinked sample. This is probably due to the much better orientation in comparison to the samples containing both types of networks for both the Young's modulus and the tensile strength. ε is also higher for the samples containing only chemical network reaching an increase by a maximum factor of eight in comparison to unoriented samples for the 1,12-diisocyanato dodecane crosslinked sample.

It is interesting to compare the samples containing only chemical network having in mind their network density, expressed by M_c (Tab. I). ε *vs.* λ dependences (Fig. 10) pass through a well expressed maximum which is in correspondence with our earlier observations on gelatin crosslinked by formaldehyde [6] where it was shown that an improvement of the orientation in gelatin takes place only up to a draw ratio $\lambda = 4 - 5$. For higher draw ratio it is not more effective since a destruction of the network occurs during the drawing. The destruction of the network structure which causes disorder at high draw ratios for gelatin samples crosslinked by formaldehyde [6] was explained as mainly due to pulling out gelatin chains from the crystallites as these samples contain both physical and chemical network. In the case of samples containing only chemical network however the mechanism of network destroying by chain scission seems more appropriate since these samples do not contain physical junctions. This is implicitly proved by the fact that the observed maxima in ε are shifted to higher draw ratios, *i.e.*, the chain scission should start at higher draw ratio $\lambda = 5 - 7$ and should generally depend on the network density – the denser the network the lower the draw ratio at which the network destruction begins. This is the actually the case with the samples containing only chemical network. Such maxima, although not so very well expressed, can also be seen in σ *vs.* λ dependence (Fig. 9b) as well as in E *vs.* λ dependences (Fig. 8b).

5. CONCLUSIONS

From the measurements on the room conditioned crosslinked unoriented gelatin samples, it can be concluded that only in some cases dependence of the universal microhardness on the annealing conditions can be established. The relations between HU and the annealing conditions becomes better defined after drying the samples (the scattering of the points decreases). The relation between the indentation modulus as obtained from universal microhardness measurements and the Young's modulus as obtained from static mechanical tests was found to strongly deviate from the theoretical one. A very well expressed minimum exists in the dependence of the indentation modulus on the molecular weight between two cross-linking points due to the competition of two processes, namely loosening of the network with the increase of the molecular weight, on one hand, and increasing the degree of crystallinity, on the other. Finally, a significant increase of the Young's modulus, tensile strength and elongation at break together with a high drawability was achieved for oriented, chemically crosslinked gelatin samples in which the physical network formation was suppressed.

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