Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Oriented Gelatin—A New Source for High-Performance Materials

Wenyan Zhao[a]; Andrzej Kloczkowski[a]; James E. Mark[a]; Burak Erman[b]; Ivet Bahar[b]
[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH, USA [b] School of Engineering and the Polymer Research Center Bogazici University and the TUBITAK Advanced Polymeric Materials Research Center, Bebek, Istanbul, Turkey

To cite this Article Zhao, Wenyan , Kloczkowski, Andrzej , Mark, James E. , Erman, Burak and Bahar, Ivet(1996) 'Oriented Gelatin—A New Source for High-Performance Materials', Journal of Macromolecular Science, Part A, 33: 5, 525 — 540

To link to this Article: DOI: 10.1080/10601329608010876
URL: http://dx.doi.org/10.1080/10601329608010876

J.M.S.—PURE APPL. CHEM., A33(5), pp. 525–540 (1996)

ORIENTED GELATIN—A NEW SOURCE FOR HIGH-PERFORMANCE MATERIALS

WENYAN ZHAO, ANDRZEJ KLOCZKOWSKI,
and JAMES E. MARK*

Department of Chemistry and the Polymer Research Center
The University of Cincinnati
Cincinnati, OH 45221-0172, USA

BURAK ERMAN and IVET BAHAR

School of Engineering and the Polymer Research Center
Bogazici University and the TUBITAK Advanced Polymeric
Materials Research Center
Bebek 80815, Istanbul, Turkey

ABSTRACT

Two types of gelatin with different gel-forming capabilities ("bloom values") were used in a novel processing technique to improve their mechanical properties when in the form of films. Networks consisting of the water-soluble gelatin chains were prepared by diisocyanate crosslinking in 2,2,2-trifluoroethanol—in which gelatin forms no collagen folds (physical junctions) at room temperature. The liquid-crystalline behavior of both the uncrosslinked gelatin and its networks were studied with regard to the effects of molecular weight and nature of the solvent. Mechanical property measurements indicated dramatic increases in tensile strength, tensile modulus, and toughness after drying the swollen films under stain, both uniaxial and equi-biaxial. The improvements in mechanical properties were determined as a function of polymer concentration at stretching, elongation during drying, and molecular weight of the gelatin. In all cases the improvements increased monotonically with the increase of elongation during drying. Furthermore, equi-biaxial orientation resulted in almost twofold improvements in tensile strength and modulus compared to those from uniaxial orientation (at essentially the same extension ratio during drying). Additional characterization, in terms of the extent of ordering in these oriented networks, was obtained from birefringence measurements. In overall performance the oriented gelatin films can be described as tough plastics, with tensile strengths between 65 and 140 MPa and elongations at break of 15-20%.

INTRODUCTION

In the search for suitable biodegradable materials to replace conventional synthetic polymers, gelatin and starch are of particular interest since these biopolymers have no adverse impact on human or environmental health. Furthermore, the introdution of gelatin and starch as partial replacements for synthetic polymers will contribute to the preservation of limited nature resources such as oil, because these biopolymers are, of course, continuously being replaced by nature [1].

The principal uses of gelatins at present are categorized as food products (55%), pharmaceutical (25%), photographic films (15%), and other technical applications (5%) [2]. Usually gelatin is considered mechanically useless because of its brittleness. In fact, it is only recently that attempts have been made to extrude gelatin into granules suitable for packaging applications [1].

Gelatins are high molecular weight polypeptides derived from collagen, the primary protein component of animal connective tissues, such as bone, skin, and tendon [2]. The collagen molecules consist of three helical peptide chains (alpha chains) held in close, parallel association; they form rigid rods, with dimensions of 1.4 × 300 nm. In the most common collagen variety, type I, two alpha chains, called $\alpha 1$, are identical; the other chain, $\alpha 2$, is very similar to these both structurally and chemically. These chains contain 1054 and 1038 amino acids, respectively, resulting in a collagen total molecular weight of 290,000 g/mol. Collagen is commonly transformed into gelatin by thermal denaturation [2], and dissolved gelatins are in the conformationally-disordered sol states above 40°C in water. Below 35-40°C, gelatin molecules slowly change conformation and aggregate, but gel formation depends on both concentration and temperature. When gelatin is above ca. 0.5 wt%, the interchain associations begin to predominate, and chilled solutions eventually set to viscoelastic gels. These thermally-induced changes are caused by segments of gelatin chains organizing intermolecularly into partial collagen folds. These physical junctions have limited length and nonnative alignments compared to the original collagen folds, but still a consideration with regard to compliance. Two of the three amino acids of gelatin—proline and hydroxyproline—are in high abundance and restrict the rotational freedom of the polymer backbone [3]. Considering the stiffness of these polypeptide backbones, if a suitable solvent (in which gelatin stays in the conformationally disordered state at room temperature) is found, it would be possible to perform a novel orientation technique developed for such materials [4-9]. This technique involves drying stretched networks of relatively stiff chains so as to increase the orientation of the domains into which the chains aggregate. Possibly, the mechanical properties of gelatin films could be improved (e.g., brittleness would be reduced), which could lead to rather strong biodegradable materials.

There is now theory underlying this idea that swollen networks consisting of semirigid chains acquire dramatically-improved mechanical properties after drying in the deformed state [4, 5]. The practical outcome of these theories was the devising of a series of steps [6–9] in which polymer chains of sufficient stiffness are identified for obtaining liquid-crystalline domains, and the crosslinking of these chains is performed in a solvent. Due to the presence of crosslinks, the polymer chain dynamics are greatly slowed so the polymer chains can remain in a deformed state for almost any length of time. Segmental orientation is achieved by uniaxial or biaxial deformation of the swollen networks. Finally, by removing the solvent, a homogeneous and highly-ordered material is obtained. Results supporting this theory have now been obtained on networks consisting of cellulose derivatives [10–12], polyisocyanates [13, 14], and starch ethers [14]. In brief, the mechanical properties of films of these materials have been greatly improved by this orientation technique, resulting in high-performance materials. This approach is now being extended to gelatin [14–16].

In a search for suitable solvents, 2,2,2-trifluoroethanol (CF_3CH_2OH) became of particular interest since gelatin displays high solubility in it without forming the collagen folds at any concentration at room temperature [14]. In addition, this solvent's miscibility with some diisocyanates enables preparation of the networks with urea linkages, which should have no adverse impact on the environment upon disposal. In the present study the results on mechanical properties of oriented gelatin networks prepared in trifluoroethanol are discussed. Their biodegradability and their potential uses are also addressed.

EXPERIMENTAL

Materials

Samples of gelatin were purchased from Sigma and used as received. They were designated type A (from porcine skin, approximately 300 bloom, where "bloom values" characterize gel-forming capabilities) and type B (from bovine skin, approximately 225 bloom). 2,2,2-Trifluoroethanol (99+ %) was purchased from Aldrich and also used as received. Hexamethylene diisocyanate was purchased from Aldrich, and distilled from CaH_2 before use. Triethylamine was purchased from Fisher, and distilled from barium oxide before use.

Diisocyanate Crosslinking of Gelatin in 2,2,2-Trifluoroethanol

Gelatin (type A or type B, 2.0 g) was dissolved in 20–25 mL of 2,2,2-trifluoroethanol over 2–3 days. Hexamethylene diisocyanate (60 μL) was added via a syringe, followed by 20 μL of triethylamine. The mixture was stirred for about 1–2 hours before transferring to a round Teflon pan (3-inch diameter). The gelation was completed in this container for 2–3 days at 40–50°C.

Cross-Polarized Optical Microscopy

Samples for optical studies were studied between two cover glasses placed between two cross polarizers. A Nikon polarizing optical microscope (model: DPT-PHOT-PDL, Diagnostic Instrument, Inc.) equipped with an Olympus camera was used to study the phase separations. The magnifications of the lens used were 10× and 40×, respectively, and the camera lens had an additional magnification of 2.5×.

Soluble Fraction Measurements

Representative samples from each of the above chemically crosslinked gelatin films were accurately weighed after drying the crosslinked networks for 1-2 days in vacuo. All of the samples were then swollen in 2,2,2-trifluoroethanol and extracted for 2 days in order to remove any unreacted materials. The networks were then slowly deswollen with chloroform and dried in air for 2 days followed by in vacuo for 2 more days and reweighed. Values for the soluble fraction of polymer, S_f, were then calculated from the original and final weights.

Equilibrium Swelling Measurements

The extent of maximum (equilibrium swelling), expressed as the volume fraction of polymer v_{2m} in the swollen gel, was determined for each gelatin network crosslinked by the different methods. Initial weights of extracted samples were accurately determined prior to swelling. The samples were weighed periodically until there was no further appreciable change in swollen weight as a function of time.

The resulting values of the maximum swollen weight were then used to calculate v_{2m}, where W_p is the initial weight of the dry extracted sample and W_s is the weight of the solvent in swollen sample. The quantity ρ_p is the density of polymer and ρ_s is the density of the solvent. Assuming simple additivity of volumes, v_{2m} is given by

$$v_{2m} = \frac{\left(\dfrac{W_p}{\rho_p}\right)}{\left(\dfrac{W_p}{\rho_p}\right) + \left(\dfrac{W_s}{\rho_s}\right)} \tag{1}$$

Orientation Procedures

Crosslinked gelatin sheets were swollen in water or 2,2,2-trifluoroethanol at a chosen composition ratio for a few days. The swollen film was uniaxially deformed to a desired extension by moving two clamps attached at their ends, or by simply stretching them with one's hands. The extension ratio used to characterize the strain imposed is defined as

$$\text{Extension (\%)} = (L - L_0)/L_0 \times 100 \tag{2}$$

where L is the final length of the stretched sample and L_0 is the original length.

The stretched films were dried at constant length in vacuo at 50°C for several days, and then stored in a desiccator.

Biaxial orientation was performed by stretching swollen networks simultaneously in two directions to the same extension ratio, as defined above. The resulting equi-biaxially oriented films were dried at constant lengths (of the two stretched directions).

Mechanical Property Measurements

Values of the tensile strength and modulus of dried samples having dimensions of 50 × 5 × 0.2 mm^3 were obtained using an Instron mechanical tester (model 1122). The crosshead speed was 0.1 in./min with the initial gauge length of 0.7 inch. The force and deformation were recorded with an x-y recorder.

RESULTS AND DISCUSSION

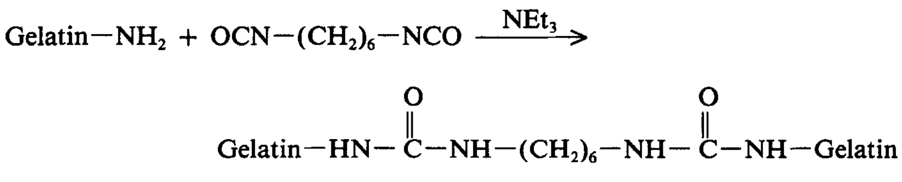
Dialdehyde crosslinking has long been widely used industrially for hardening gelatin media in photographic materials [17]. For this orientation study, the crosslinking was first attempted on gelatin using glutaric dialdehyde [13]. Because of the presence of collagen-fold crystallites in water and the rigid imine linkage (Scheme 1), however, the resulting networks were extremely hard and brittle. The swollen specimens were extremely fragile in water at room temperature, and the desired orientation was impossible to perform.

$$\text{Gelatin}{-}\text{NH}_2 + \text{OHC}{-}(\text{CH}_2)_3{-}\text{CHO} \longrightarrow$$

$$\text{Gelatin}{-}\text{N}{=}\text{CH}{-}(\text{CH}_2)_3{-}\text{CH}{=}\text{N}{-}\text{Gelatin}$$

SCHEME 1. Dialdehyde crosslinking of gelatin in water.

The gelatin films prepared by diisocyanate crosslinking in 2,2,2-trifluoroethanol were still brittle in the dry state (probably because of gelatin's high glass transition temperature), but much softer in the swollen state. Due to the very flexible nature of the hexamethylene unit (Scheme 2) and the complete amorphous nature of the gelatin chains, the swollen networks were much easier to stretch.



$$\text{Gelatin}{-}\text{NH}_2 + \text{OCN}{-}(\text{CH}_2)_6{-}\text{NCO} \xrightarrow{\text{NEt}_3}$$

$$\text{Gelatin}{-}\text{HN}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\text{NH}{-}(\text{CH}_2)_6{-}\text{NH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\text{NH}{-}\text{Gelatin}$$

SCHEME 2. Diisocyanate crosslinking of gelatin in 2,2,2-trifluoroethanol.

Phase separation was studied in both gelatin solutions and gels using 2,2,2-trifluoroethanol as the solvent. It was found that all types of gelatin (type A and B, with different bloom values) failed to exhibit phase separation at any concentration

(Fig. 1). For diisocyanate crosslinked gelatin networks, both water and 2,2,2-trifluoroethanol were used as swelling solvent. The gelatin networks usually can be swollen to 4–5 times their original volume in water at room temperature, and 20–24 times of their original volume in 2,2,2-trifluoroethanol. For these gelatin gels, strain-induced birefringence was observed, as is illustrated in Fig. 2(a). Unfortunately, there was no evidence for mesomorphic birefringence in either gelatin or its gels, probably because of the strong interactions between the amino acid groups in those peptide chains. The existence of strong hydrogen bonding between the

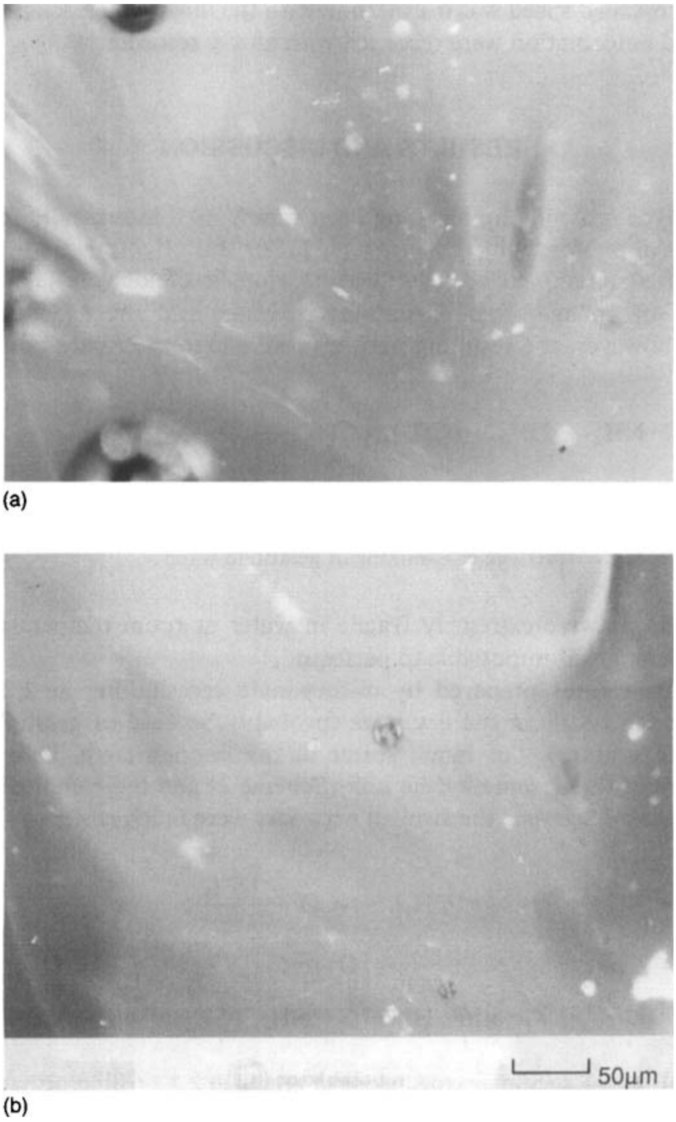


FIG. 1. (a) Microphotograph of 20 wt% type B gelatin in 2,2,2-trifluoroethanol. Magnification: 350×. (b) Microphotograph of 20 wt% type A gelatin in 2,2,2-trifluoroethanol. Magnification: 350×.

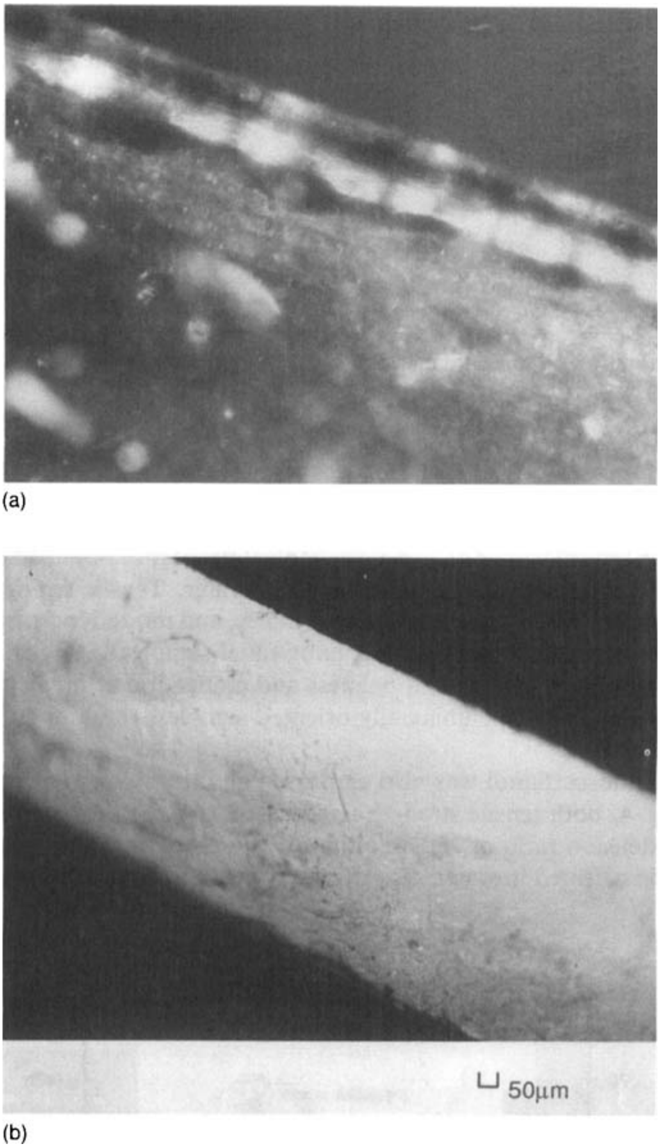


FIG. 2. (a) Microphotograph of a 20-wt% type A gelatin specimen in water before orientation. Magnification: 90×. (b) Microphotograph of the above specimen after orientation and drying. Magnification: 90×.

solvents and the polar groups on gelatin could interfere with the self-assembling of the chains into mesomorphic phases.

For orientation purposes, gelatin was crosslinked using hexamethylene diisocyanate in very dilute trifluoroethanol solution (~10.0 wt/vol%). Dilute solution crosslinking had the advantage of reduced chain entangling and giving more homogeneous crosslink densities. All of the type B gelatin networks that had been diisocyanate crosslinked had a maximum swollen ratio ($1/v_{2m}$) of 20–22 in trifluoroethanol,

TABLE 1. Orientation Conditions for the Gelatin Networks

	Maximum swelling ratio, $1/v_{2m}$[a]	Polym concentration at stretching, v_2	Sol fraction, %
Type B in water (uniaxial)	20-22	0.2-0.25	10-15
Type B in CF_3CH_2OH	20-22	0.7	10-15
Type A in water (uniaxial)	22-24	0.2-0.25	8-10
Type A in water (biaxial)	22-24	0.2-0.25	8-10

[a] The maximum swelling ratio measured in 2,2,2-trifluoroethanol is a volume ratio.

as shown in Table 1. The relatively low crosslink density obtained allowed high chain extensibility.

Mechanical properties were first measured on oriented type B gelatin films. Figure 3 shows typical values of some mechanical properties obtained after uniaxial orientation of swollen networks of this type in water. Tensile strengths increased more than threefold at an extension ratio of 145%, and moduli increased almost the same amount (compared to crosslinked unoriented samples). As can be seen from the stress-strain curves in Fig. 5, toughness and elongation at break also increased substantially for most of the uniaxially-oriented samples, resulting in tough plastic materials.

2,2,2-Trifluoroethanol was also employed as the swelling solvent. As can be seen from Fig. 4, both tensile strength and modulus increased approximately three times at an extension ratio of 150%, although the absolute values were lower than those of gelatin oriented in water. The reason for this is that the polymer concentra-

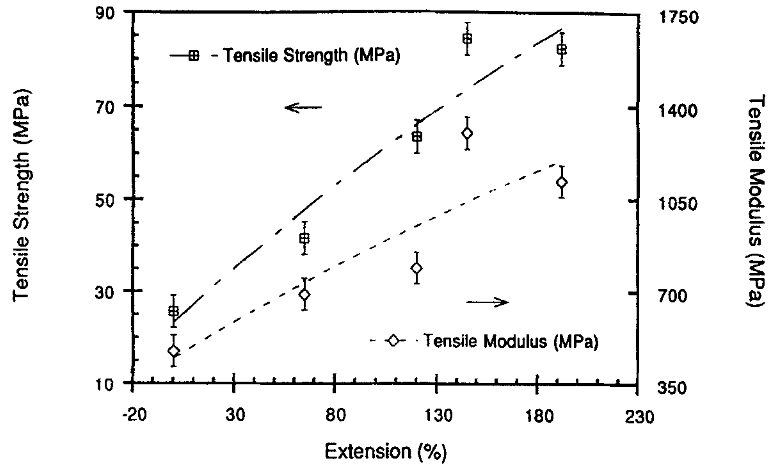


FIG. 3. Tensile strength (⊞) and modullus (◇) as a function of extension ratio during drying for oriented type B gelatin; Swelling solvent: water; v_2 at stretching: 0.2-0.25.

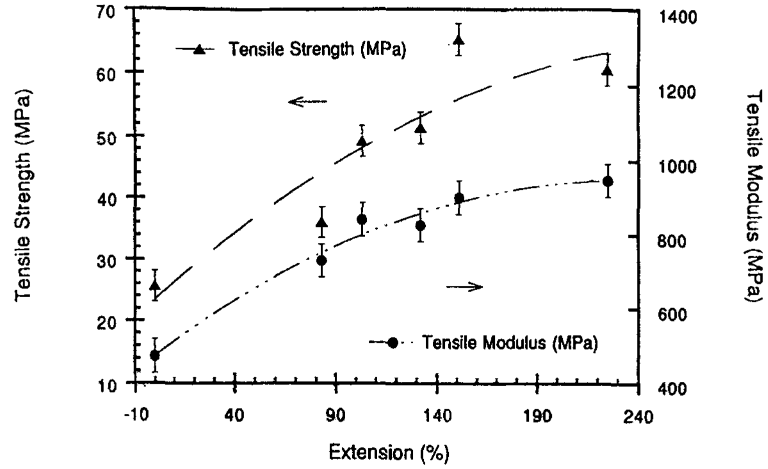


FIG. 4. Tensile strength (▲) and modulus (●) as a function of extension ratio during drying for oriented type B gelatin. Swelling solvent: CF_3CH_2OH; ν_2 at stretching: 0.7.

tion of the swollen network in 2,2,2-trifluoroethanol ($\nu_2 = 0.7$) was higher than that in water ($\nu_2 = 0.2\text{–}0.25$). This suggests that higher orientations are achieved in the case of networks stretched at higher dilutions.

The stress–strain curves shown in Fig. 5 demonstrate the special utility of equi-biaxial orientation. To put the advantages into context, it should be noted that in uniaxial orientation properties along the transverse direction usually decrease. Also, as indicated in Fig. 5, a uniaxially oriented sample with a 180% extension ratio during drying has values of tensile strength which show no apparent increase.

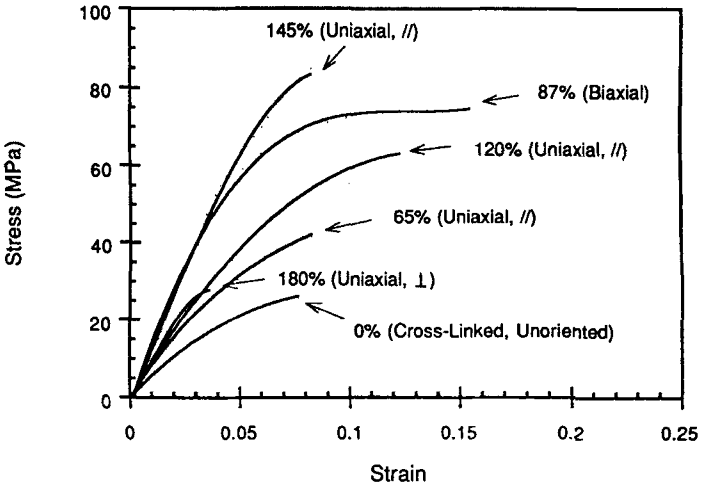


FIG. 5. Stress–strain behavior of uniaxially and biaxially oriented type B gelatin. Swelling solvent: water; ν_2 at stretching: 0.2–0.25.

Finally, the elongation at break was decreased, indicating that the transverse direction of uniaxially-oriented film exhibited even more brittleness. A biaxially-oriented specimen with an extension ratio of 87%, however, showed enormous improvements in terms of strength and modulus. Even more impressively, the toughness increased about four times for *all* test directions.

Those results on type B gelatin were encouraging, given the fact that pure gelatin is extremely brittle and usually considered as mechanically useless. It seemed possible that if a higher molecular weight gelatin were used, the mechanical properties could be further improved. Type A gelatin with a higher bloom value was employed for this purpose. All of the type A gelatin networks used for orientation had a maximum swelling ratio ($1/v_{2m}$) of 22–24, slightly higher than the type B gelatin networks, as documented in Table 1. Orientation was performed in water, with a polymer concentration during stretching of 20–25 vol%. The gels used for orientation have better extensibility in the swollen state than the type B gels, and they can be stretched to 210% of their original length. This is probably due to the fact that the type A materials have a higher bloom value than the type B, the higher bloom values usually corresponding to higher molecular weights [2].

Figure 6 shows some mechanical properties of type A gelatin networks after uniaxial orientation in water. Both tensile strengths and moduli increased monotonically with an increase of extension ratio during drying (from 0 to 210%). There are approximately 5-fold increases in tensile strength and a 270% increase in tensile modulus at an extension ratio of 190%. From the stress–strain curves in Fig. 7, it can be seen that toughness increased about 20 times and elongation at break increased about 3 times at this extension ratio. This demonstrates that the orientation greatly reduces the brittleness of the gelatin. The oriented gelatin films are markedly more flexible and tougher.

In contrast to the direction parallel to the orientation direction, the mechanical properties showed insufficient improvements. As indicated in Fig. 7, a twofold

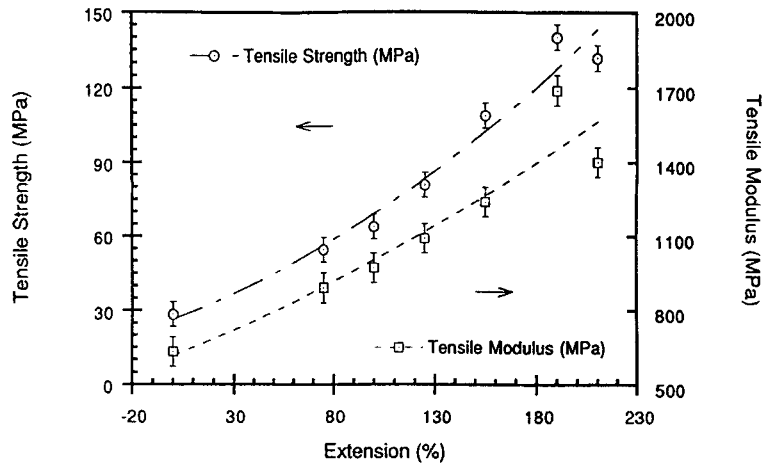


FIG. 6. Tensile strength (○) and modulus (□) as a function of extension ratio during drying for oriented type A gelatin. Swelling solvent: water; v_2 at stretching: 0.2–0.25.

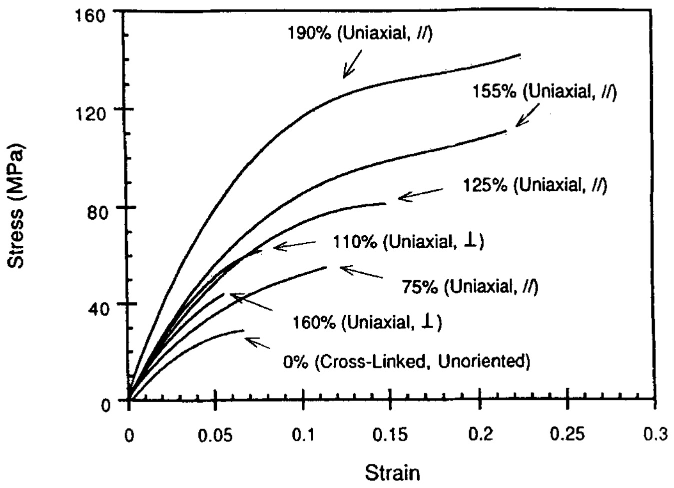


FIG. 7. Stress-strain behavior of uniaxially oriented type A gelatin. Swelling solvent: water; v_2 at stretching: 0.2-0.25.

increase in strength, a 200% increase in modulus, and a twofold increase in toughness at an extension ratio of 110% in the perpendicular direction were obtained. This is to be compared to a 1.5-fold increase in strength, a 50% increase in modulus, and a 1.5-fold increase in toughness at an extension ratio of 160% in the perpendicular direction. As can be concluded from these data, an increase of orientation degree causes changes in the perpendicular direction that are the opposite of those in the parallel direction.

Equi-biaxial extension was performed to achieve good mechanical properties in all directions. The biaxially-oriented samples were prepared by deforming the swollen type A gelatin gels in two perpendicular directions at the same time to equal extension. Similar to the uniaxial orientation, mechanical properties increased with the increase of extension ratio during drying time (from 0 to 115%) (Figs. 8 and 9). A 4-fold increase in tensile strength, a 150% increase in modulus, and a 14-fold increase in toughness were observed for films with an extension ratio during drying of 115%. The profound effect of biaxial extension is clearly presented in Figs. 10 and 11. At a similar extension ratio, both tensile strength and modulus for biaxial orientation increased twice as much as uniaxial orientation.

As can be realized from the above results, substantial increases in mechanical properties were obtained for both type B and type A networks at relative low stretching ratios (100-200%). In the case of other orientation techniques [18, 19], effective orientation could be obtained only after stretching the polymer solutions or melts to 15-20 times their original lengths. This comparison demonstrates the utility of the novel orientation technique. With the help of crosslinking (which prevents chain sliding), the segmental orientation can be induced by stretching the semirigid networks in the swollen state, and the degree of orientation can thus be controlled by varying the extension ratio during drying. The chain dynamics also greatly slowed down, and the ordering is preserved after the force which induced the orientation is removed.

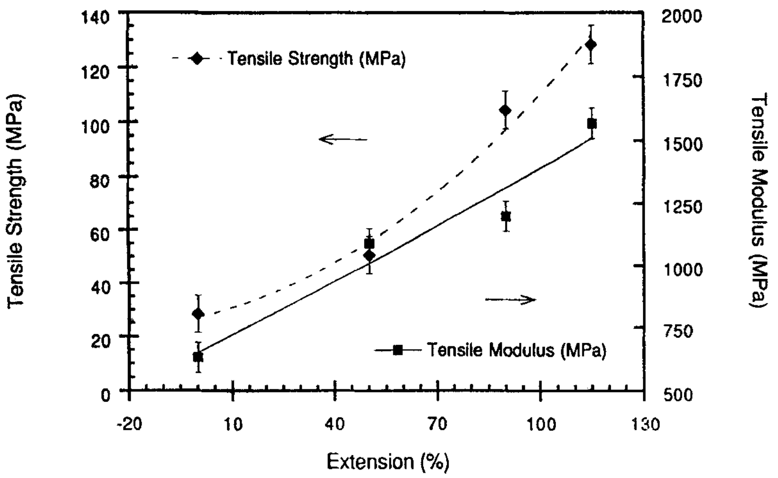


FIG. 8. Tensile strength (◆) and modulus (■) as a function of extension ratio during drying for biaxially oriented type A gelatin. Swelling solvent: water; v_2 at stretching: 0.2–0.25.

The preservation of orientation is demonstrated in Figure 2(b), which is a microphotograph of a piece of dried gelatin after orientation. It is seen to be highly birefringent under the cross-polarized microscope. The effectiveness of the orientation was further demonstrated by the following results from the birefringence measurements.

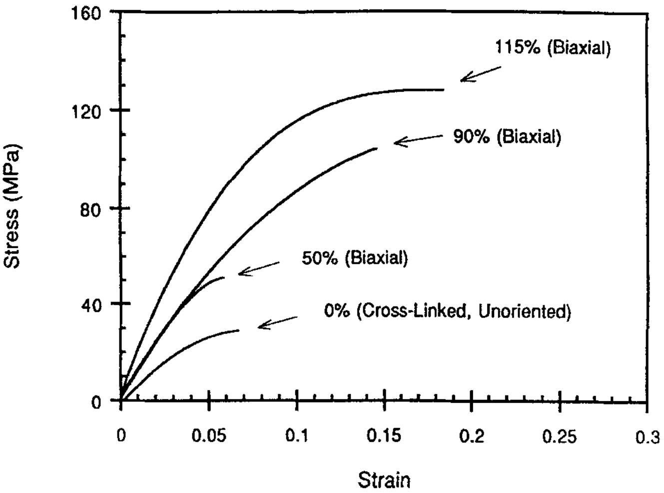


FIG. 9. Stress-strain behavior of biaxially oriented type A gelatin. Swelling solvent: water; v_2 at stretching: 0.2–0.25.

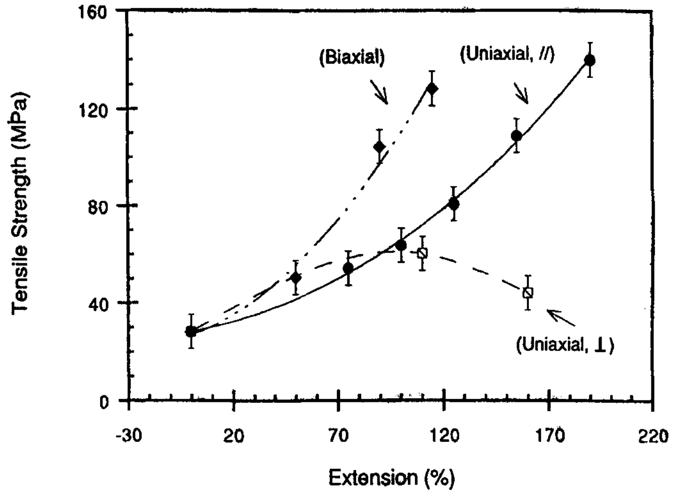


FIG. 10. Tensile strength as a function of extension ratio during drying for type A gelatin by different orientation methods. Uniaxial, // (●); uniaxial, ⊥ (▨); biaxial (◆).

The birefringence of some of the films prepared from gelatin (type A, swelling solvent: water) after uniaxial orientation is shown in Fig. 12. There is a monotonic and substantial increase in birefringence with an increase in extension ratio during drying. A dramatic 50-fold increase in birefringence in the oriented direction was observed at an extension ratio of only 165%. The increases of birefringence as a

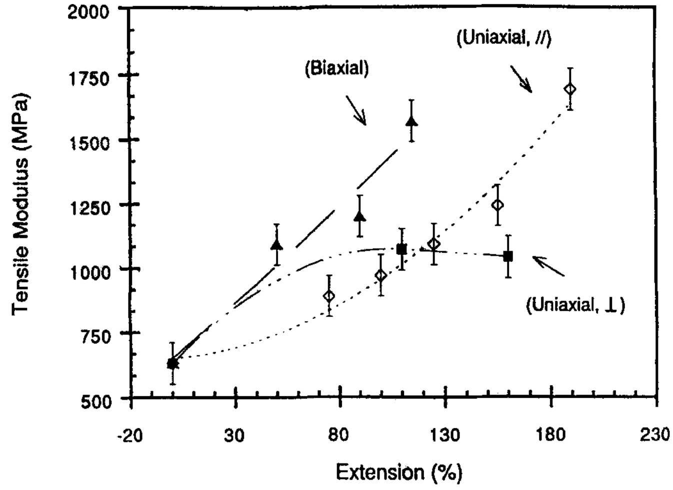


FIG. 11. Tensile modulus as a function of extension ratio during drying for type A gelatin by different orientation methods. Uniaxial, // (◆); uniaxial, ⊥ (■); biaxial (▲).

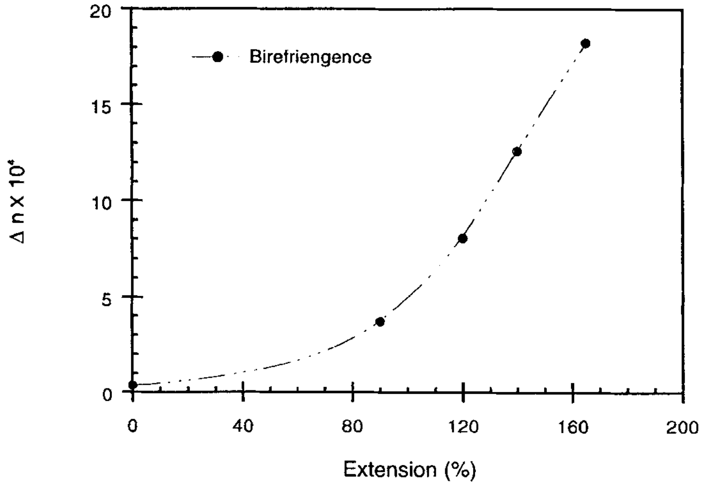


FIG. 12. Birefringence (●) as a function of extension ratio during drying for uniaxially-oriented type A gelatin.

function of extension ratio are consistent with the observed improvements in mechanical properties.

Table 2 summarizes the above discussed mechanical properties. The type B gelatin produced tough plastics with tensile strengths ranging from 65 to 84 MPa and tensile moduli of 900 to 1300 MPa, depending on the orientation conditions. For type A gelatin, tough plastics with tensile strengths ranging from 128 to 140 MPa and tensile moduli of 1570 to 1690 MPa were obtained. The higher values for the mechanical properties of the type A gelatin are attributed to its higher molecular weight. The oriented gelatin films are still water-swellable, but would obviously

TABLE 2. Maximum Values of Mechanical Properties Obtained after Orientation

	Tensile strength,[a] MPa	Tensile modulus,[a] MPa	Toughness,[a] MPa	Elongation at break,[a] %
Type B in water	84.3	1300	4.10	8.24
(uniaxial)	(25.6)	(470)	(1.24)	(7.65)
Type B in	65.3	900	8.74	16.57
CF$_3$CH$_2$OH	(25.6)	(470)	(1.24)	(7.65)
Type A in water	140.0	1690	23.68	22.54
(uniaxial)	(28.4)	(630)	(1.20)	(6.67)
Type A in water	128.4	1570	17.45	18.39
(biaxial)	(28.4)	(630)	(1.20)	(6.67)

[a] The data within parentheses are reference values obtained before orientation.

swell anisotropically. The sensitivity to water remains a drawback in some applications, but would be a great advantage for biodegradation.

CONCLUSIONS

Highly oriented gelatin films were obtained after drying swollen gelatin networks in the deformed state. It was found that values of the tensile strength, modulus, and toughness were all greatly increased for both type A and type B gelatin networks. The improvements increased monotonically with an increase in elongation during drying for both uniaxial and equi-biaxial strains. In addition, equibiaxial orientation gave almost twice the improvements in terms of strength and modulus obtained in the simpler uniaxial orientations (at essentially the same extension ratio). The dramatical improvements in mechanical properties clearly demonstrate the effectiveness of the novel orientation technique. A 50-fold increase in birefringence was obtained for type A gelatin films after uniaxial orientation.

In summary, the usual extreme brittleness of gelatin has been greatly reduced in this approach, resulting in the production of tough plastics with tensile strengths of 65 to 140 MPa and moduli of 900 to 1690 MPa.

ACKNOWLEDGMENTS

It is a pleaure to acknowledge the financial support provided by the Procter & Gamble Company through their "University Exploratory Research Program" and by the National Science Foundation through Grant DMR-9422223 (Polymers Program, Division of Materials Research). In addition, we acknowledge helpful discussions with Professor S. Fakirov (Sofia University), who also recognized the importance of suppressing the physical crosslink structure in gelatins to be treated by these orientation procedures.

REFERENCES

[1] P. J. Koepff, *J. Photogr. Sci., 40*, 198 (1992).

[2] P. I. Rose, in *Encyclopedia of Polymer Science and Engineering*, Vol. 7 (H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds.), Wiley, New York, 1987, p. 488.

[3] F. H. Silver and R. L. Trelsad, *Biopolymers, 20*, 359 (1981).

[4] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, *Macromolecules, 23*, 5335 (1990).

[5] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, *Ibid., 23*, 5341 (1990).

[6] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, in *Elastomeric Polymer Networks* (J. E. Mark and B. Erman, Eds.), Prentice-Hall, Englewood Cliffs, New Jersey, 1992, p. 142.

[7] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, in *Polymer Solutions, Blends and Interfaces* (I. Noda and P. N. Rubingh, Eds.), Elsevier Science, Amsterdam, 1992, p. 221.

[8] B. Erman, I. Bahar, Y. Yang, A. Kloczkowski, and J. E. Mark, in *Polymer Solutions, Blends and Interfaces* (I. Noda and P. N. Rubingh, Eds.), Elsevier Science, Amsterdam, 1992, p. 209.

[9] B. Erman, I. Bahar, A. Kloczkowski, and J. E. Mark, in *Synthesis, Characterization, and Theory of Polymeric Networks and Gels* (S. M. Aharoni, Ed.), Plenum, New York, 1992, p. 113.

[10] Y. Yang, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *Colloid Polym. Sci., 272*, 284 (1994).

[11] J. E. Mark, Y. Yang, A. Kloczowski, B. Erman, and I. Bahar, *Ibid., 272*, 393 (1994).

[12] Y. Yang, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *Macromolecules, 28*, 4927 (1995).

[13] W. Zhao, H. Zimmer, and J. E. Mark, *Prepr., PMSE Div. Am. Chem. Soc., 71*, 399 (1994).

[14] W. Zhao, unpublished work.

[15] W. Zhao, A. Kloczkowski, J. E. Mark, B. Erman, and I. Bahar, *Prepr., PMSE Div. Am. Chem. Soc., 72*, 86 (1995).

[16] S. Fakirov and coworkers, manuscript in preparation.

[17] B. E. Tabor, R. Owers, and J. W. Janus, *J. Photogr. Sci., 40*, 205 (1992).

[18] A. Ciferri and I. M. Ward, *Ultra-High Modulus Polymers*, Applied Science Publishers, London, 1979.

[19] A. E. Zachariades and R. S. Porter, *High Modulus Polymers*, Dekker, New York, 1988.