**Colloid & Polymer Science** Colloid Polym Sci 272:393–399 (1994)

# A novel orientation technique for semi-rigid polymers. 2. Mechanical properties of cellulose acetate and hydroxypropylcellulose films

J. E. Mark,[1] Yong Yang,[1] A. Kloczkowski,[1] B. Erman,[2] and I. Bahar[2]

[1] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, USA
[2] School of Engineering and the Polymer Research Center, Bogazici University, and TUBITAK Advanced Polymeric Materials Research Center, Bebek, Istanbul, Turkey

*Abstract*: The networks of cellulose acetate and hydroxypropylcellulose prepared in the first part of this investigation were studied with regard to their mechanical properties. The quantities of particular interest were increases in tensile modulus and tensile strength obtained by drying the swollen films under strain, both uniaxial and equi-biaxial. These increases or improvements in mechanical properties were determined as a function of polymer concentration during cross-linking, polymer molecular weight, degree of cross-linking, and elongation during drying. In all cases, the improvements increased with increase in elongation during drying, and the largest increases were obtained in the case of the highest molecular weight polymer which had been lightly cross-linked in dilute (isotropic) solutions. The extent of ordering in these systems was gauged approximately by measurements of birefringence, which were correlated with their tensile moduli and tensile strengths.

*Key words*: Cellulose acetate – hydroxypropylcellulose – cross-linking – liquid-crystalline state – anisotropic state – novel orientation technique – oriented films – mechanical properties – maximum extensibility – tensile modulus – tensile strength – birefringence

## Introduction

The cross-linked films of cellulose acetate (CA) and hydroxypropylcellulose (HPC) prepared in the first part [1] of this two-part investigation were now evaluated with regard to their mechanical properties in tension and in biaxial extension. The films were swollen, deformed, and then dried under the deformation, as described elsewhere [1–8]. The purpose of these procedures is to try to line up the anisotropic domains formed by these relatively rigid chains, thereby increasing the mechanical properties of the films. Of particular interest are their values of the tensile modulus and tensile strength, as a function of polymer concentration during cross linking, polymer molecular weight, degree of cross linking, and elongation during drying. Some preliminary information on the degree of ordering in the films will be obtained from birefringence measurements.

## Experimental

### Materials

The samples prepared in the first part [1] of this investigation are described in the first eight columns of Table 1. The first two films were cross-linked at sufficiently high polymer concentrations for the systems to be in the anisotropic state, and the others at sufficiently low concentrations to make them isotropic. The weight-averge molecular weights $M_w$ of the starting or "primary" chains was relatively low except for the last sample of HPC, which could be obtained and investigated at a much higher value.

Also of importance is the molecular weight $M_c$ between cross-links in the resulting networks, i.e., the molecular weights of the "network chains". Values of $M_c$ were estimated from swelling equilibrium measurements [9], in acetone for CA and

Table 1. Conditions used for cross-linking cellulose acetate (CA) and hydroxypropylcellulose (HPC) [1], and their characterization in swelling equilibrium

| Polymer | $M_w$ ($\mathrm{g\,mol^{-1}}$) | Wt polymer (g) | Solvent | Vol (ml) solvent | Vol formaldehyde[1] (ml) | Reaction temp (°C) | Reaction time (h) | $v_{2m}$ | $10^{-3}\,M_c$ ($\mathrm{g\,mol^{-1}}$) |
|---|---|---|---|---|---|---|---|---|---|
| CA[2] | 61000 | 6 | Acetone | 6 | 0.300 | 45 | 8 | – | – |
| HPC[2] | 80000 | 6 | MeOH | 6 | 0.300 | 60 | 12 | – | – |
| CA[3] | 61000 | 6 | Acetone | 60 | 0.200 | 56 | 2 | 0.176 | 12.3 |
| HPC[3] | 80000 | 6 | Acetone | 40 | 0.023 | 56 | 1 | 0.213 | 1.5 |
| HPC[3] | 370000 | 6 | Acetone | 120 | 0.023 | 56 | 1 | 0.064 | 20.3 |

[1] 37 wt% aqueous solution
[2] Cross-linked in the anisotropic state
[3] Cross-linked in the isotropic state

in distilled water for HPC [1, 10]. The thermodynamic interaction parameter $\chi$ [9] at 25 °C was taken to be 0.43 for CA in acetone, and 0.47 for HPC in water [11]. The densities for the polymers was taken to be 1.30 and 1.17 $\mathrm{g\,ml^{-1}}$ for CA and HPC, respectively, and for the diluents acetone and water to be 0.79 and 1.0 $\mathrm{g\,ml^{-1}}$, respectively. Column nine of Table 1 gives the values obtained for the volume fraction $v_{2m}$ of polymer present at maximum (equilibrium) swelling, and the final column lists the values obtained for $M_c$ from interpretation of these data using standard swelling theory [1, 9, 10]. The last sample is seen to have a large value of $M_c$ (low degree of cross-linking), as well as a large value of $M_w$.

### Deformation and drying procedures

The CA and HPC films were swollen in trifluoroethanol and methanol, respectively, for several days, and each of the swollen films was mounted between two movable clamps. Each film was then uniaxially deformed to the desired elongation or extension ratio by moving the clamps apart, and then holding them at fixed separation. Biaxial orientation was similarly performed by stretching the films in two perpendicular directions, simultaneously and to equal extents ("equi-biaxial extension"). Some of the HPC networks were oriented using a range of polymer/solvent ratios, specifically 30/70, 40/60, and 50/50 by weight. From the polarized microscopy results, it was known that a swollen network having 30 wt% HPC was isotropic, and one having 50 wt% was anisotropic; thus, one having 40 wt% HPC was near the phase-transition region.

After either type of deformation, the films were dried under vacuum at constant strain, first at room temperature for about 2 weeks, and then at 50 °C for 1 day. The extension ratio prevailing during drying was defined as

$$\text{Extension (\%)} = 100\,(L - L_o)/L_o\,, \qquad (1)$$

where $L$ was the length of stretched sample and $L_o$ was the length of the original (dried and unstretched) sample. The films were kept in a desiccator until used in the mechanical property and birefringence measurements.

### Mechanical property measurements

The oriented and dried films were cut into strips having dimensions of approximately $50 \times 5 \times 0.5\ \mathrm{mm^3}$. In the case of the uniaxially-oriented films, the long dimension of the strip generally lay along the direction in which the film had been drawn prior to drying. The tensile modulus and tensile strength of the strips were measured with an Instron mechanical tester (Model 1122) at room temperature. The cross-head speed (rate of extension) was 0.1 in $\mathrm{min^{-1}}$, and the force and deformation were recorded with an x–y recorder. At least five strips from each film were studied, and the results averaged.

### Birefringence measurements

The birefringence of some of the oriented films was measured using a compensation method [12], with a Babinet-Soleil compensator (Karl Lambert Corp.). The light source was a He-Ne laser beam with a wavelength of 632.8 nm.

## Results on networks prepared in the anisotropic state

Typical values of the mechanical properties obtained on the networks cross-linked in relatively concentrated solutions are shown in Figs. 1 and 2, specifically for films of HPC. The corresponding results for the CA films were very similar, and are given elsewhere [10]. Figure 1 shows the tensile modulus as a function of the uniaxial extension maintained during drying, and Fig. 2 shows the corresponding dependence for the tensile strength. Both the tensile modulus and tensile strength are seen to increase monotonically and substantially with increase of extension during drying. The increases are approximately two-fold for an extension of only 25%!

Mechanical properties were also measured on the HPC networks which had been oriented using a range of polymer/solvent ratios. Figures 3 and 4 show that both tensile modulus and tensile strength exhibit higher values for networks deformed at the lowest polymer concentration, when comparisons are made at the same extension ratio. This suggests that higher orientations are achieved in the case of networks stretched at higher dilutions. Under these conditions, liquid-crystalline phase separation will occur in the strained material only during drying, and this would increase the chances of forming domains

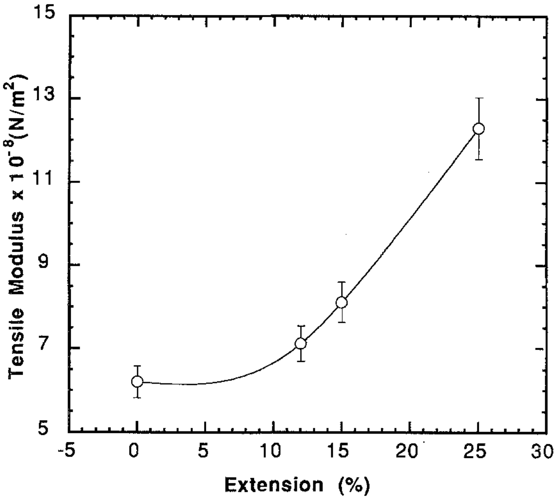

Fig. 1. Tensile modulus as a function of the extension ratio during drying for oriented films of hydroxypropylcellulose (HPC). The swollen networks had been extended to the amounts shown on the abscissa while their composition corresponded to a HPC/methanol ratio of 1/1 by weight. They were then dried while under this deformation. Standard deviations are shown by the error bars.

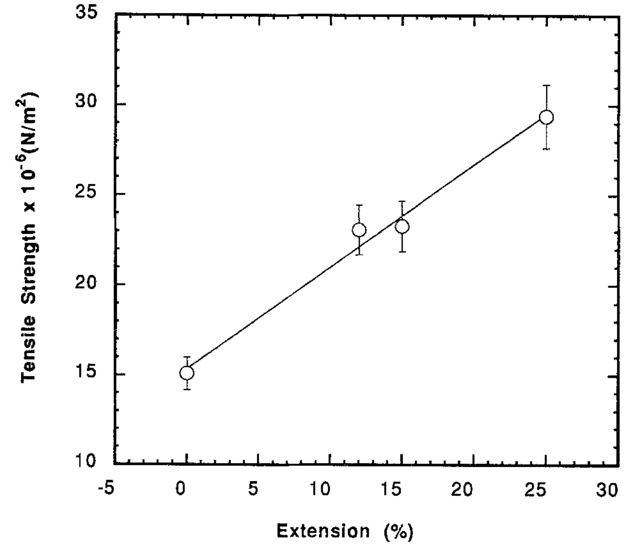

Fig. 2. Tensile strength as a function of extension ratio during drying for the same samples described in Fig. 1.

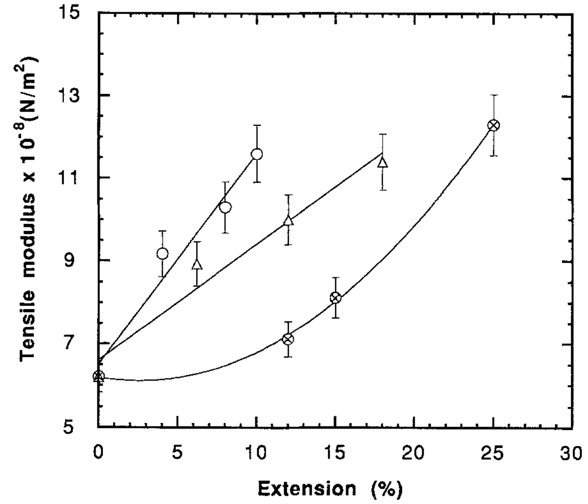

Fig. 3. Tensile modulus as a function of extension ratio during drying for HPC films which had HPC/methanol ratios of 30/70 (○), 40/60 (△), and 50/50 (⊗) by weight during the orientation process.

with their directors preferentially oriented in the drawing direction, possibly even forming a structure approaching a "monodomain". In contrast, stretching gels already in the anisotropic phase involves more of a reorienting of the already-formed domains of liquid-crystalline mesophases, and such a transition from polydomains to a monodomain is probably less likely. Also, these gels have relatively low extensibility (possibly due to inhomogeneous cross-linking), and there are difficulties in handling solutions at high polymer concentrations which discouraged use of high molecular weight polymers to increase extensibility. Finally, cross-linking in dilute solutions could have the advantage of reduced chain entangling [13]. In any case, the results do suggest that it may be possible to increase the improvements in mechanical properties by cross-linking in the dilute, isotropic state.

## Results on networks prepared in the isotropic state

### *Short primary chains and relatively short network chains*

The networks in this category had small values of $M_w$ and relatively small values of $M_c$. Some of the results [10] obtained on these materials are summarized in Table 2. It can be seen that cross-linking in solutions that are dilute rather than concentrated does further improve the mechanical properties of the films.

The birefringence of some of the films prepared from HPC ($M_c = 1{,}500\ \mathrm{g\,mol^{-1}}$) is shown as a function of extension during drying in Fig. 5. There is seen to be a monotonic and substantial increase in birefringence with extension, which is

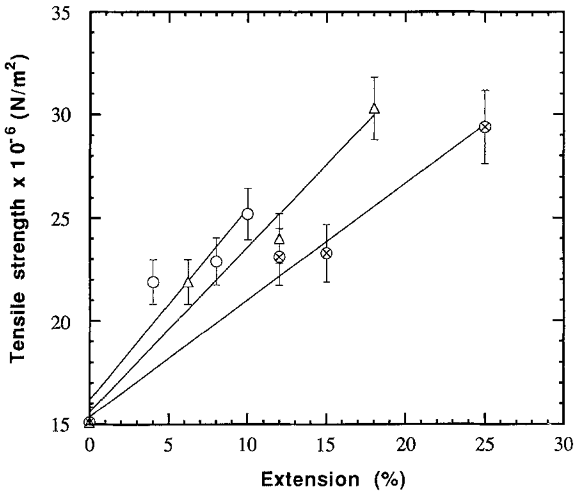

Fig. 4. Tensile strength as a function of extension ratio during drying for the same samples described in Fig. 3.

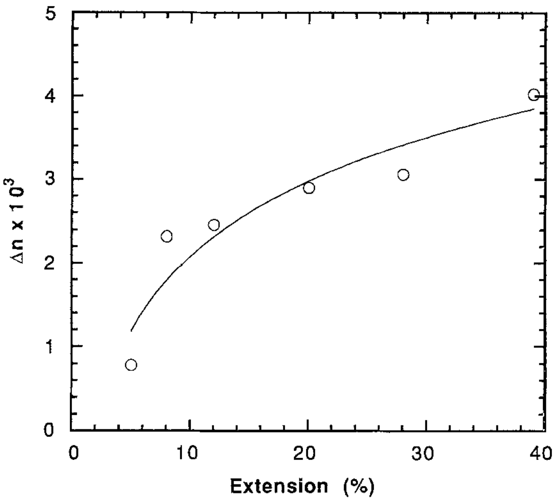

Fig. 5. Birefringence of films prepared from HPC ($M_c = 1{,}500\ \mathrm{g\,mol^{-1}}$) as a function of extension ratio during drying. The networks were deformed while swollen, with a HPC/methanol ratio of 70/30 by weight.

Table 2. Mechanical properties of the films prepared from the CA and HPC chains of relatively low $M_w$

| | CA | | | HPC | | |
|---|---|---|---|---|---|---|
| | Unoriented | Conc soln | Dilute soln[1]) | Unoriented | Conc soln | Dilute soln[2]) |
| Max extensibility (%) | – | 20 | 25 | – | 25 | 40 |
| Tensile Strength × $10^{-6}$ ($\mathrm{N\,m^{-2}}$) | 10 | 15 | 17 | 16 | 28 | 39 |
| Tensile Modulus × $10^{-8}$ ($\mathrm{N\,m^{-2}}$) | 23 | 40 | 57 | 6.3 | 12 | 16 |

[1]) $M_c = 12.3 \times 10^3\ \mathrm{g\,mol^{-1}}$
[2]) $M_c = 1.50 \times 10^3\ \mathrm{g\,mol^{-1}}$

consistent with considerable chain orientation. The values of the birefringence are correlated with the mechanical properties in Fig. 6. The leveling off of the tensile modulus and tensile strength while the birefringence is still increasing suggests that after a point, the orientation process has a larger effect on the birefringence than it has on the mechanical properties.

HPC gels prepared at different polymer/solvent ratios which were all in the dilute region had almost the same values of the tensile modulus, tensile strength, and birefringence [10]. This is consistent with the conclusion that changes in this ratio are very important only when they change the system from anisotropic to isotropic, or vice-versa.

### *Long primary chains and long network chains*

Since these experiments pertain to polymers cross-linked in solutions that were dilute, it was possible to include the very high molecular weight HPC ($M_w = 370 \times 10^3$ g mol$^{-1}$) [10]. The networks prepared from it were lightly cross-linked, with a value of $M_c$ of $20.3 \times 10^3$ g mol$^{-1}$, as can be seen from Table 1. They exhibited exceptional extensibility in the orientation and drying process, with values as high as 200%. A typical plot of stress versus strain is shown in Fig. 7, with labels

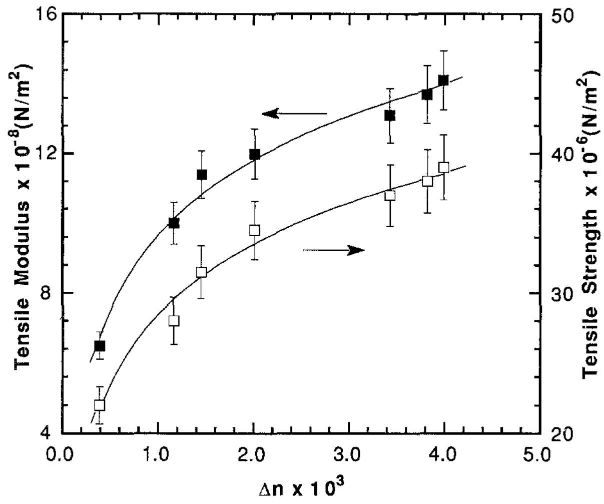

Fig. 6. Correlation between the tensile modulus (■) and tensile strength (□) and the birefringence of oriented films prepared from HPC ($M_c$ = 1,500 g mol$^{-1}$). The networks were deformed while swollen, with a HPC/methanol ratio of 70/30 by weight.

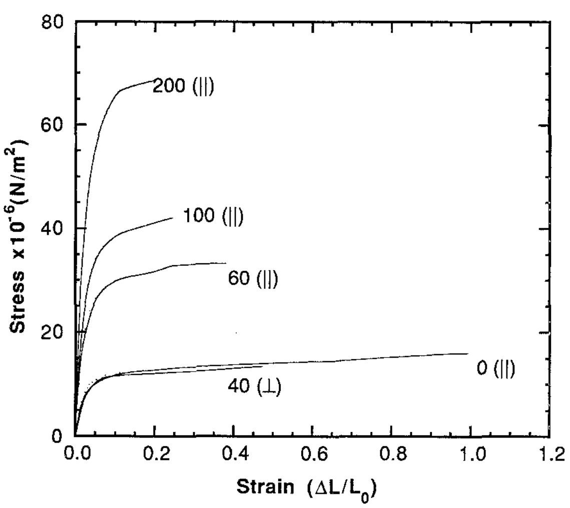

Fig. 7. Stress-strain behavior of oriented films prepared from HPC ($M_c = 20.3 \times 10^3$ g mol$^{-1}$). Labels on the curves are the values of the extension ratio during drying. The mechanical testing was carried out either parallel (∥) or perpendicular (⊥) to the orientation axis of the sample.

Table 3. Mechanical properties and birefringence of the films prepared in dilute solutions by lightly cross-linking the HPC chains of high $M_w$

| | Unoriented 2) | Uniaxially oriented 1) Testing direction 3) | | Equi-biaxially oriented 1) |
|---|---|---|---|---|
| | | ∥ | ⊥ | |
| Max extensibility (%) | – | 200 | 40 | 70 |
| Tensile modulus × 10$^{-8}$ (N m$^{-2}$) | 6.3 | 33 | 4.1 | 3 |
| Tensile strength × 10$^{-6}$ (N m$^{-2}$) | 16 | 68 | 13 | 33 |
| Birefringence × 10$^{-2}$ | – | 1.1 | – | – |

1) $M_w = 370 \times 10^3$ g mol$^{-1}$ and $M_c = 20.3 \times 10^3$ g mol$^{-1}$
2) Reference, unoriented material with $M_c = 1.50 \times 10^3$ g mol$^{-1}$
3) Testing direction parallel (∥) and perpendicular (⊥) to orientation axis

on the curves indicating extension ratios prevailing during drying. Measurements were performed both along the orientation direction (||), and perpendicular to it (⊥). The tensile modulus (determined as the initial slope of stress-strain curve), and the tensile strength (measured as the stress at break) are seen to exhibit enormous increases in the direction parallel to the orientation. The sample with 40% extension which had been cut in the transverse direction showed decreases in tensile strength and extensibility (during the mechanical testing), as would be expected in highly-oriented materials. These results [10] are summarized in the first four columns of Table 3.

The tensile modulus and tensile strength of these materials are presented as a function of the extension ratio during drying in Fig. 8. The results show a *5-fold to 7-fold* increase in tensile strength and tensile modulus for the HPC film dried at 200% extension. These dramatic improvements in mechanical properties are the result of high degrees of segmental orientation which, in turn, are due to the high extensions attained prior to the drying step. Such high extensions are apparently achievable only from networks which are i) prepared from long primary chains (resulting in few dangling-chain irregularities [13]) and ii) have low cross-link densities. Part of the changes in properties obtained by cross-linking in the isotropic state could result from the fact that the presence of large amounts of diluent could change the relative amounts of the chiral nematic structures present, which would be distorted or destroyed by the applied shearing forces.

As illustrated in Fig. 9, the degree of orientation in these materials (as gauged by the birefringence) is extremely high. The birefringence is correlated with the tensile modulus and tensile strength in Fig. 10. In this case, it appears that the rate of increase in the birefringence is decreasing with increased orientation, with the tensile

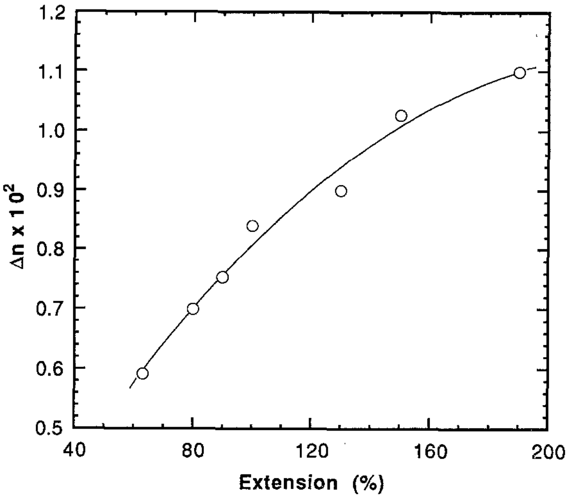

Fig. 9. Birefringence of the same films described in Fig. 8.

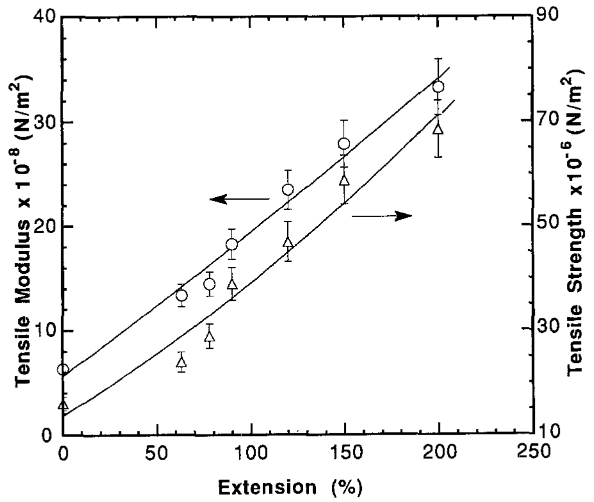

Fig. 8. Tensile modulus (○) and tensile strength (△) versus extension ratio during drying for films prepared from HPC ($M_c = 20.3 \times 10^3$ g mol$^{-1}$).

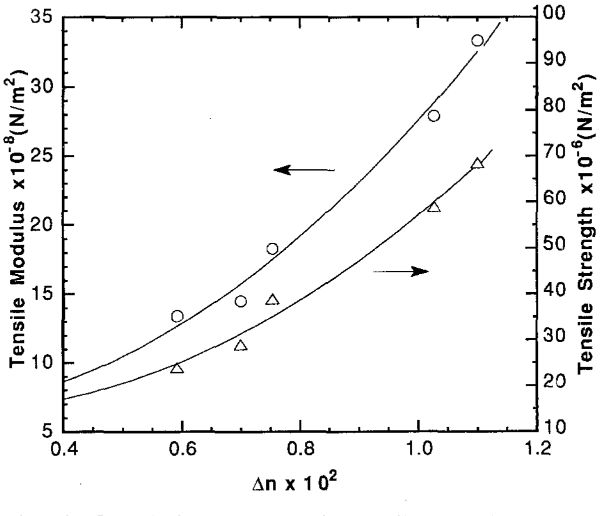

Fig. 10. Correlation between the tensile modulus (○) and tensile strength (△) and the birefringence of oriented films prepared from HPC ($M_c = 20.3 \times 10^3$ g mol$^{-1}$).

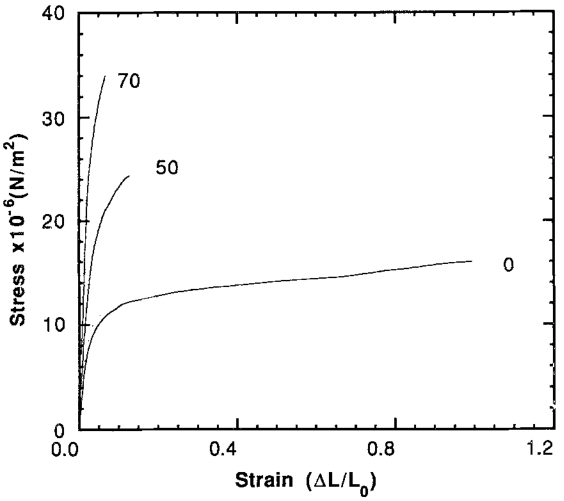

Fig. 11. Stress-strain behavior of films prepared from HPC ($M_c = 20.3 \times 10^3$ g mol$^{-1}$) which had been equi-biaxially oriented. Labels on the curves are the values of the extension ratio during drying.

modulus and tensile strength both still increasing substantially over the entire range of deformations studied.

Figure 11 shows some results [10] on the samples which had been under equi-biaxial orientation during drying. The labels on the curves correspond to values of the extension ratio during drying. Both the tensile modulus and tensile strength are increased by two-fold to three-fold, at extensions in the range from 50 to 70%. The corresponding values are listed in the final column of Table 3, and are seen to fall between the || and ⊥ values obtained on the same material using uniaxial extension. This type of orientation would, of course, be most important in applications requiring mechanical strengths that were relatively isotropic in the plane of the film.

## Concluding remarks

The present two-part investigation has demonstrated the utility of the described novel orientation technique for rigid-chain polymers. The next step is to develop more quantitative techniques, presumably spectroscopic, for characterizing the orientation in these materials. It would also be extremely interesting to extend these methods to some relatively rigid starchlike polymers, in particular because of their biodegradability.

### *Acknowledgements*

It is a pleasure to acknowledge the financial support provided by the Procter & Gamble Company through its University Exploratory Research Program, and by the National Science Foundation through Grant DMR 89-18002 (Polymers Program, Division of Materials Research).

## References

1. Yang Y, Mark JE, Kloczkowski A, Erman B, Bahar I, (1994) Colloid Polym Sci 272:284–292
2. Erman B, Bahar I, Kloczkowski A, Mark JE (1991) Macromolecules 23:5335
3. Bahar I, Erman B, Kloczkowski A, Mark JE (1991) Macromolecules 23:5341
4. Erman B, Bahar I, Kloczkowski A, Mark JE (1992) in: Mark JE, Erman B (eds) Elastomeric polymer networks, Prentice Hall, Englewood Cliffs, New Jersey
5. Erman B, Haliloglu T, Bahar I, Mark JE (1991) Macromolecules 24:901
6. Erman B, Bahar I, Yang Y, Kloczkowski A, Mark JE (1992) in: Noda I, Rubingh DN (eds) Polymer solutions, blends, and interfaces. Elsevier Sci. Pub., Amsterdam
7. Kloczkowski A, Mark JE, Erman B, Bahar I (1992) in: Noda I, Rubingh DN (eds) Polymer solutions, blends, and interfaces. Elsevier Sci. Pub., Amsterdam
8. Erman B, Bahar I, Kloczkowski A, Mark JE (1992) in: Aharoni SM (ed) Synthesis, characterization, and theory of polymeric networks and gels. Plenum, New York
9. Flory PJ (1953) Principles of polymer chemistry. Cornell Univ. Press. Ithaca, New York
10. Yang Y (1993) Ph.D. Thesis in Chemistry, The University of Cincinnati
11. Barton AFM (1991) Handbook of solubility parameters and other cohesion parameters. 2nd Ed. CRC Press, Boca Raton, Florida
12. Hay IL (1980) in: Fava RA (ed) Methods of experimental physics. Vol 2, Pt C, Academic Press, New York
13. Mark JE, Erman B (1988) Rubberlike elasticity. A molecular primer. Wiley-Interscience, New York

Received June 10, 1993;
accepted October 21, 1993

Author's address:

Prof. J. E. Mark
Department of Chemistry
University of Cincinnati
Cincinnati, OH 45221-0172, USA