Fibers Based on Cellulose-Chitin Blends

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ABSTRACT: Fibers made of cellulose (CE) and chitin (CH) in different proportion were wet spun from solutions in dimethylacetamide containing 5% LiCl (w/w). Polymer concentration was purposely maintained as low as possible ($\cong$2.4% w/w). Moreover, dope temperature was 60°C to have good spinability. Comparison of the elastic modulus (E) of fibers "as spun" at different CE/CH ratio showed a synergy between the components: at CE/CH $\cong$ 50/50, E is $\cong$15 GPa with respect to $\cong$9 and $\cong$11 GPa for neat CE and CH fibers, respectively. Application of a pull-off ratio during the coagulation allows the E value to increase further. These results, as well as the electronic microscopy of fibers section, agree with a complete miscibility of two polymers at the solid state, probably enhanced by the presence of LiCl. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1825–1831, 2002

Key words: fibers; cellulose; chitin

INTRODUCTION

Cellulose (CE) and chitin (CH) are two natural, biorenewable, and biodegradable polymers. Their chemical composition and molecular conformation allow some peculiar properties to be achieved: in particular, the presence of a few —OH groups in their repetition units promotes intramolecular hydrogen bonds that stiffen the chain, and at the same time, intermolecular hydrogen bonds can also be formed, giving interchain association phenomena. Moreover, OH groups easily react with various reagents, allowing the synthesis of derivatives; each of them shows specific behaviors and applications. A further interesting peculiarity of CE and CH, regarding chain semirigidity, is the capacity to assume cholesteric organization in solution and (or) at the solid state: this behavior was exploited to produce high performance fibers of CE by wet spinning of concentrated solutions.[1] Cholesteric organization of CH was at the moment observed only in swelled films[2] and in spontaneous organization of sedimented microfibers.[3]

The strong fibrogenic nature of CE and CH is probably the main reason why wet spinning processes of these polymers (melt spinning was impossible due to the decomposition temperature that occurs before the melting) were developed before a complete molecular characterization.

Nogushi et al.[4] first produced mixed CE/CH fibers by spinning a mixture of CE and CH viscose. Addition of amounts of CH up to 10% with respect to CE gave fibers with improved properties, especially dyeability when compared to regenerated CE. Very recently,[5] filaments containing CE/CH 41/59 (w/w) were produced from sodium chitin salt and sodium cellulose xanthate, but the high alkalinity (40% of NaOH) and temperature (100°C) of the coagulation bath caused a partial hydrolysis of polymers with negative effects on the fiber behavior.

Some years ago[6,7] we selected the mixture dimethylacetamide/LiCl (DMAc/LiCl), among the

several organic solvents useful to dissolve and to spin CE. Dopes of CE in this solvent are stable for a long time and may reach polymer concentration up to 15% (w/w). Considering that CH also dissolves in the same solvent, we were interested in studying the properties of dilute solutions of two polymers in different proportions.[10]

The trend of the second viral coefficient from light scattering measurements as a function of the polymer composition indicated complete miscibility between the components.[11] Moreover a single homogeneous phase at any polymer composition was evidenced up to polymer concentration C_p as high as 9% (w/w) (volume fraction about 0.06). A further increase of C_p gave a liquid–liquid demixing.[10] The presence of a miscibility gap is foreseen in the case of polymers having semirigid chains. According to the theory,[12] when the two polymers are miscible, the gap closes at high concentration, and, at the solid state, the components are mixed at molecular level. In our case, limits of solubility hampered a study of the phase diagram at high C_p values.

However, spectroscopic analysis of films revealed the existence of interactions between the components, which means there is a good miscibility of CE and CH also in absence of a diluent: in other terms, we believe it possible that CE/CH blends show similar behaviors at the solid state to those expected for single phase systems. This peculiarity together with the fibrogenic character of both polymers is the basis for studying fiber production from dopes containing both CE and CH. The best conditions for spinning experiments, as well as fiber characterization in terms of mechanical behavior and morphology, are the object of this paper.

EXPERIMENTAL

Materials

A regenerated CE II sample having $DP = 440$ ($M_v = 71,000$) and a CH sample having $DP = 2500$ ($M_v = 5.1 \times 10^5$) were supplied by "Stazione Sperimentale Cellulosa e Fibre Tessili, Milano Italy," and used for spinning experiments of neat polymers and their blends.

The polymers were successively treated with deionized water, acetone, and petroleum ether, then dried in vacuum oven at 40°C and maintained under dry conditions.

DMAc (Fluka) was distilled under vacuum before use and stored over Riedel type 4A molecular sieves. LiCl was dried in an oven at 200°C.

Dope Preparation

CE was dissolved at $C_p = 6\%$ (w/w), stock solution, in DMAc/5% LiCl following the method proposed by Turbak et al.[13,14]

CH was directly dissolved in CE solutions according to the selected polymer composition. A suitable amount of solvent was added to adjust the C_p value and the system was left under stirring for at least one month in nitrogen atmosphere.

Dopes at $C_p = 2.4$ and 6% (w/w) were obtained according to the previous method: optical observations checked absence of undissolved parts.

Spinning

Fibers were obtained by using the spinning line described in a previous work.[15] Extrusion rate at the spinneret, with die 100 μm, was $V_o = 7.9$ m/min corresponding to a shear rate 10500 s^{-1}. Dope temperature inside the extrusion cylinder was 25 or 60°C. Fibers were collected using "as spun" conditions (no stretch applied after coagulation, $V_1/V_f = 1$) and under stretching ratio $V_1/V_f \cong 2$, where V_f is the fiber velocity at the spinneret hole and V_1 is the take-up speed. When possible, V_1/V_f was raised up to 5. Water at room temperature was used as coagulation and washing solvent. The fibers were further washed for about 48 h to extract all the LiCl salt.

Fiber Characterization

Stress–strain measurements were made with an Instron dynamometer mod. 5500. Elastic modulus (E), strength (σ_b) and elongation (ϵ_b) at break are averages of at least 20 determinations, using monofilaments. The error on E values was estimated $\pm$1GPa, while it is $\pm$15% on ϵ_b and $\pm$0.02 GPa on σ_b. Deformation rate of 5 mm/min for samples with $\epsilon_b < 8\%$ and 10 mm/min for higher ϵ_b were used (BISFA 1983).

Morphology

Fiber morphology was investigated with a scanning electron microscope, Cambridge Stereoscan model 440 at 20 kV acceleration voltage.

Samples, cut from the same fibers used for tensile test, were cryogenically fractured and the

Table I   Mechanical Behaviors of CE/CH Fibers, C_p = 2.4%, T = 60°C

Sample	Fiber Composition (w/w, g) CE—CH		V_l/V_f	E (GPa)	σ_b (GPa)	ϵ_b (%)
1	100	0	1.0	8.8	0.21	9.9
2	80	20	1.0	10.9	0.16	7.0
3	60	40	1.0	14.6	0.23	6.5
4a	40	60	1.0	14.2	0.18	5.0
4b	40	60	2.0	18.2	0.22	4.4
5a	20	80	1.0	12.3	0.20	7.1
5b	20	80	2.0	16.0	0.23	4.3
6a	0	100	1.0	11.6	0.21	5.1
6b	0	100	2.0	14.8	0.24	7.5

surface gold coated with a sputtering coating unit, model Agar Aid PS3.

RESULTS AND DISCUSSION

Selection of dope concentration of CE, CH, and their mixtures as well as spinning temperature, was the first problem to be faced. In fact, while solutions of CE may be easily spun up to concentration over 13% (w/w), solutions of chitin are very viscous and need low C_p and high temperature to be spun by our apparatus. After some attempts, we selected the conditions C_p = 2.4% and T = 60°C. In fact when different values of polymer concentration and/or temperature were used, fibers of neat chitin or high chitin content were too irregular and showed at the optical microscope some sequences of thin parts and others thick: in these cases fiber diameter is meaningless and the mechanical properties vary from one filament to another. Therefore, it becomes doubtful whether a full spectrum of mechanical properties can be obtained when the fiber composition varies from 100% CE to 100% CH.

The data in Table I will be discussed separately for CE, CH, and their mixture, also referring to results in literature.

Cellulose

The elastic modulus of CE fibers as spun is $\cong 9$ GPa (Table I). Spinning conditions were not optimal to apply any stretch, as the filament easily breaks. On the other hand, previous experience performed on a different sample at $C_p > 6\%$ and T = 25°C[1] gave a slightly higher modulus (12 GPa) and did not show any influence of the stretching

ratio. The σ_b was of the same order (0.2 GPa) for every isotropic solution, slightly increasing close to the isotropic $\rightarrow$ anisotropic transition and substantially coincident with the medium value found in the present experiments. On the other hand, ϵ_b is about 10% with respect to a medium value 12% of previous experiments. In general it could be acceptable to consider the mechanical behavior of present CE fibers consistent with that reported in Ref. 1, taking into account that the two samples have a different average degree of polymerization and probably different molecular weight distribution.

Chitin

Mechanical behaviors of CH fibers spun from solution in DMAc/5%LiCl at 60°C and coagulated in water at room temperature are quite relevant. Applying a stretching ratio equal to 2 allows a modulus E $\cong$ 15 GPa (Table I) to be obtained. When CH dopes were spun at room temperature, not only was E of the fibers as spun low (less than 7 GPa), but also its value did not change and it worsened in some experiments when a stretch was applied during the spinning.

These results may be due to several phenomena. First of all, it may be interesting to remember that aprotic solvents, based on amide/LiCl mixtures, are the last class of solvents of CH found in the last few years and used by different authors thanks to the good stability of CH dopes. However the results, reported in literature and well summarized in Ref. 16, are quite far from those presented in this paper: typical mechanical behavior quoted in Ref.16 for fibers as spun were $E \cong 1$–2 GPa , $\sigma_b \cong 0.01$–0.1 GPa , $\epsilon_b \cong$ up to 75%. A curious aspect is that the coagulants in the
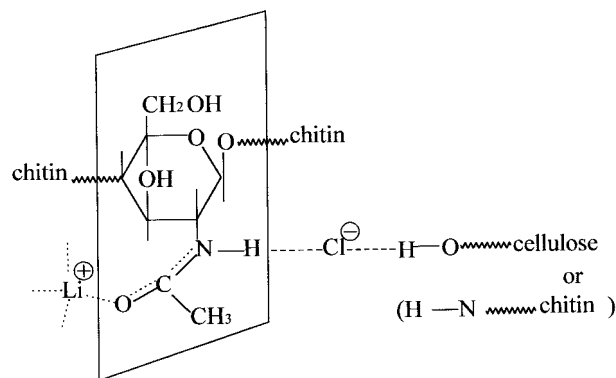
Scheme 1

spinning line were acetone, ethylacetate, ethanol, etc., while water was seldom used. So, the use of mixture DMAc/5% LiCl as solvent and water as coagulant, together with the other spinning conditions, seems particularly useful to exploit CH potentiality as fibrogenic material. Of course, the characteristics of CH chain cannot be forgotten: CH belongs to the class of semirigid polymers, having a persistence length (q) of about 214 Å,[8] higher than that of CE ($q \cong 125$ Å),[7] both calculated from the radius of gyration and by using Benoit–Doty treatment,[9] and these behaviors are relevant to obtain strong fibers. Unfortunately, anisotropic phases in solution have not been observed until now, probably due to the strong tendency of CH to give molecular aggregation, even at low C_p. However, some years ago cholesteric organization in swollen films was obtained by some of us,[2] confirming the mesogenic character of the polymer.

Finally, we must consider the peculiar characteristics of LiCl salt. It is well known that LiCl can interact with systems containing amide groups,[17,18] giving rise to physically crosslinked polymers. Crosslinks derive from ion–dipole interactions between lithium ion and the principal donor site in the amide, which is the oxygen of the amide group. As a consequence, an enhanced delocalization of the nonbonding electron pair of the nitrogen is produced, which weakens the N—H bond and allows the hydrogen atom to interact with chlorine anion. According to the findings on Nylon 6 /LiCl systems,[18] the coordination number of LiCl is 4 and then it acts as a tetrafunctional crosslinking agent. Such interactions will be active in the solution of CH/DMAc–LiCl too, because of the presence of amide groups in chitin molecules. A schematic representation is shown in Scheme 1.

In the case of solutions, these interactions give a macromolecular fluctuating network and then more viscous solutions. This could be the reason for the experimental difficulty of spinning fibers at room temperature, even at low polymer concentration ($C_p = 2.4\%$).

Moreover, during the fibers' coagulation in water, part of the salt is extracted and part of it remains dissolved in fiber, as crosslinking agent. Therefore, LiCl would permit a higher extent of molecular orientation to be realized and stabilized during the spinning and stretching. This orientation does not practically change during the extraction of salt by washing fibers with water at room temperature. As a consequence, we observe that the modulus increases from 11.6 up to 14.8 MPa when the stretching ratio increases from 1 up to 2.

CE/CH Mixtures

Figure 1 shows the trend of E as a function of the composition at two values of V_1/V_f (Table I). The relevant increase of the modulus with respect to a linear trend with the composition [the maximum of the curve may be located around 50% of chitin (w/w)] is typical of this system. While σ_b does not depend on the composition and stretching ratio, ϵ_b shows a trend opposite to E, hardly decreasing as a function of chitin content, as a consequence of increased rigidity.

Theoretical treatment of a general property as a function of the composition for homogeneous and heterogeneous systems was proposed by Furukawa[19] in the case of mixtures of conventional
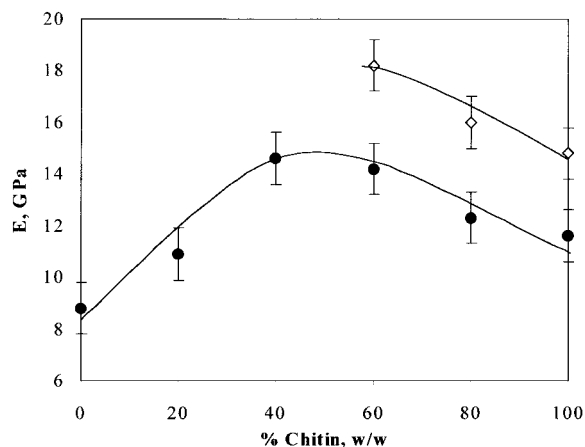

Figure 1 Modulus of CE/CH fibers "as spun" (●) and at $V_1/V_f = 2$ (◇).

Table II   Effect of Pull-Off Ratio on Fibers from Dopes at C_p = 6%, T = 60°C

Sample	Fiber Composition (w/w, g) CE—CH		V_l/V_f	E (GPa)	σ_b (GPa)	ϵ_b (%)
7a	100	0	1.0	8.0	0.14	20.5
7b	100	0	1.7	8.3	0.16	16.9
7c	100	0	2.5	9.1	0.18	16.0
7d	100	0	3.2	10.2	0.17	12.8
8a	80	20	1.0	10.8	0.19	16.8
8b	80	20	1.7	10.9	0.20	15.9
8c	80	20	2.5	11.2	0.22	15.6
8d	80	20	3.2	10.9	0.18	11.9
9a	60	40	1.0	12.8	0.20	12.6
9b	60	40	1.7	12.4	0.21	10.4
9c	60	40	2.5	13.2	0.23	8.7
9d	60	40	3.2	13.3	0.21	7.2

polymers. Unfortunately no extension to semi-rigid systems, the class to which cellulose and chitin belongs, was considered. So, at the moment, we have to accept the experimental results which are reasonably linked to the miscibility of the components and to the presence of salt during the spinning.

As mentioned in the introduction the problem of miscibility between CH and CE has been considered by us in last years.[10] Besides the good miscibility in solution, IR spectra of films containing CE and CH in any proportion evidenced the increase in the number of —C=O–HO— links by increasing the amount of CE at the solid state: this suggests that the two polymers strongly interact with each other and supported the conclusion of a total miscibility.

The synergic effect observed for tensile modulus of CE/CH fibers, on increasing CH content and stretching ratio, could be attributed to the miscibility of two polymers as well as to the crosslinking action of LiCl: the two polymers interact in solution and during the spinning through direct –C=O–H—O links of carbonyl groups and hydroxyl groups of chitin and cellulose, respectively, but also by chlorine anion, which links N–H of chitin with H–O of cellulose, as sketched in Scheme 1. These interactions should induce higher molecular orientation during the fibers' formation and then higher modulus and brittleness with respect to fiber obtainable from LiCl-free solutions.

The significant positive influence of V_l/V_f, which allows us to reach modulus as high as 18 GPa at CE/CH 40/60, suggests that further improvement is predictable by using a more power-ful spinning apparatus. The previously mentioned results by Noguchi et al.[4] substantially agree with our findings, even if they added only a limited amount of CH to CE.

Returning to our results, when the CH percent does not goes over 40% (samples 1–3 of Table I) an attempt to improve the behaviors could consist of increasing dope concentration up to 6% and to spin at two temperatures, respectively 60 and 25°C. Tables II and III show the results obtained in the two cases.

Referring to dopes at 6% spun at T = 60°C (Table II), the main conclusions are as follows:

- Sample 7 of pure cellulose shows an increase of E with V_l/V_f, but the $\Delta<I>E$ value is too small considering the error of measurement ($\pm$1GPa) to infer the influence of V_l/V_f, at least in the used range. As previously mentioned, similar results were obtained by some of us[1] by spinning various dopes of CE (DP = 290) in the field of stability of isotropic solutions. As in that case, σ_b does not depend on V_l/V_f, while ϵ_b clearly decreases as V_l/V_f increases.

- Similar conclusions are also valid for samples 8 and 9. So it seems that V_l/V_f improves the mechanical behaviors only for fibers, which are richer in CH with respect to CE (CE/CH < 1) (Table I).

- Comparison among moduli of the tree samples at V_l/V_f = constant indicates a reliable effect of the CH content. For example, at V_l/V_f = 2.5, E is 9.1, 11.2 ,and 13.2 GPa, at 100, 80, and 60% CE (samples 7c, 8c, and 9c, respectively).

Table III   Mechanical Behaviors of Fibers from Dopes at $C_p = 6\%$, $T = 25°C$

Sample	Fiber Composition (w/w, g) CE—CH		V_l/V_f	E (GPa)	σ_b (GPa)	ϵ_b (%)
10a	100	0	1.0	9.5	0.19	23.5
10b	100	0	1.7	10.5	0.20	20.0
10c	100	0	2.5	11.5	0.19	15.6
10d	100	0	3.2	12.4	0.17	13.2
10e	100	0	4.0	13.4	0.19	11.3
10f	100	0	5.2	14.5	0.20	8.0
11a	80	20	1.0	11.2	0.24	14.9
11b	80	20	1.7	10.9	0.23	12.9
11c	80	20	2.5	12.8	0.24	10.0
11d	80	20	3.2	12.4	0.22	12.2
11e	80	20	4.0	12.0	0.20	10.6
12a	60	40	1.0	9.8	0.17	6.2
12b	60	40	1.7	9.7	0.20	6.6

A comparison between data from Tables I and II highlights that fibers prepared at the same temperature from the solutions with lower C_p are clearly more brittle (smaller ϵ_b); as a consequence, there is a higher degree of molecular orientation despite no affect on the corresponding E and σ_b values.

Finally, referring to dopes at $C_p = 6\%$ spun at $T=25°C$ (Table III), the following is evident:

- Spinning of CE dopes is noticeably favored, considering that V_l/V_f may be increased up to 5.2. In that condition, the E value is 14.5 GPa. Considering that $E > 14$ GPa was obtained in our previous work[1] only when the anisotropic phase of CE became stable (biphasic gap), we must conclude that the kind of CE sample in terms of molecular weight and molecular weight distribution is determining with respect to mechanical behavior.

The effect of adding CH to the dopes is more complex: when the CH percent is about 20, an increase in brittleness and strength is observed, while the modulus does not vary considering the experimental error. When the CH percent is about 40, it causes a light decrease in all tensile properties (sample 12 a,b). This result agrees with our previous observation concerning the difficulty of spinning dopes when the overall polymer concentration and the CH content increase. Similar considerations can explain the effect of spinning temperature. If we compare mechanical properties of CE/CH 60/40 fibers (9a, 9b and 12a, 12b), the decrease in temperature causes an in-

creasing viscosity, the dope concentration being constant, which is too high with respect to our spinning apparatus.

As a conclusion, we believe that the illustrated effect of dope concentration, temperature, and CH content on the tensile properties should be referred to the dope viscosity, and this should enable the more useful spinning condition to be favored.

Morphology

As seen, previous results suggest a good miscibility of the cellulose with chitin for every composition. This finding is supported by morphological observations carried out on fracture surfaces of fibers. Figures 2 and 3 show the morphology of
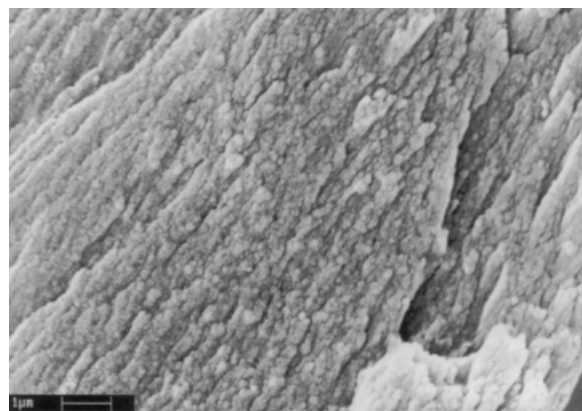
Figure 2 SEM microphotograph of fiber obtained from a CE/CH 60/40 mixture—sample 9a, Table II.
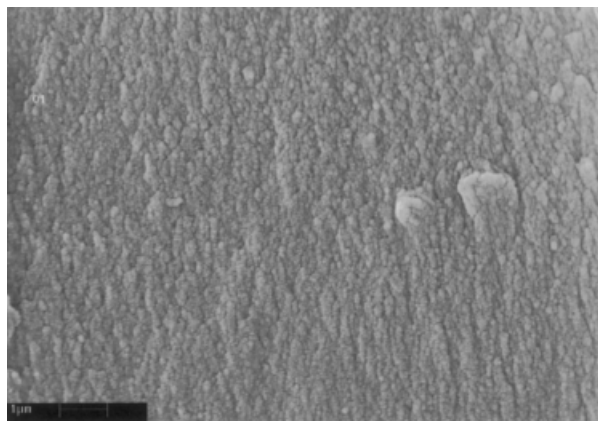
Figure 3 SEM microphotograph of fiber obtained from a CE/CH 20/80 mixture—sample 5a, Table I.

unstretched fibers of 60/40 and 20/80 CE/CH blends, obtained from solutions with $C_p = 6\%$, $C_s = 5\%$, and $C_p = 2.4\%$, $C_s = 5\%$ at 60°C, respectively. As we can see, independent of preparation conditions and solution concentration, no phase segregation is observed, but both blends exhibit morphology typical of the single phase of pure cellulose or chitin.

Conclusions

It was demonstrated that cellulose and chitin are two polymers showing miscibility at the solid state. In fact, morphology of the fibers does not reveal any phase segregation; moreover, the mechanical behaviors of blends highlight a synergic interaction between the components: elastic modulus of fibers increases when CH is added to CE dope and vice versa, reaching the maximum value at about CE/CH = 1/1 w/w. Considering our spinning conditions, characterized from relatively high T (60°C) of the dope inside the cylinder and the very low overall polymer concentration (2.4% w/w), the maximum value of the elastic modulus ($E = 18$ GPa) is, in our opinion, a promising result. We believe our DMAc/LiCl system to be an interesting solvent to induce a high degree of interaction between CH and CE and a consequent physical network able to be stretched and to realize a high molecular orientation level inside the CE/CH fibers. Furthermore, the crosslinking ac-

tion of LiCl permits solutions with low polymer concentration to be spun.

In this respect, and based on results for CE previously obtained by us, it would be interesting to spin dopes with a polymer concentration closer to the iso-aniso transition, obviously at an appropriate temperature.

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