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Development of Unique Fibers Using Renewable Resources via Environmentally Friendly Technology

-- Cellulose --

Principal Investigator: Dr. John A. Cuculo
Contributing Student: Norman Aminuddin

During the past year, we have improved the physical properties of the cellulose fibers. Figure 1, the cellulose molecular structure is given for reference. We have used a highly concentrated, spinnable anisotropic solution of cellulose/NH_3/NH_4SCN as the precursor to high performance cellulosic fibers. These solutions were spun with the appropriate coagulant, to provide a high jet-stretch ratio and to produce a fine denier of a dense and highly oriented fiber. The spinning process was the dry jet-wet spinning method, using recently installed improved equipment. It includes new godet rolls, the coagulant bath and a precision lab winder. In continuing work on fiber spinning, we have obtained fibers with tenacities as high as 5 grams/denier. Although this is a breakthrough for us, it must be reproduced. We have consistently produced fibers with linear density ca. 3-5 denier/filament and modulus greater than 150 grams/denier. The scanning electron microscope (SEM) results show well formed fibrils of cellulose fiber, see figure 2.

Presently, continuous efforts to improve the fiber physical properties and fiber characterization are in progress. The inconsistent results, especially in tenacity of the fiber, have been attributed to the uneven fiber diameter. Several appropriate steps have been taken to provide smooth delivery of the spinning solutions. These steps include repairing and adjusting the pump and redesigning of the piston in the extrusion unit. We are also studying the microstructures of the fiber, such as the density, morphology, polymorph, orientation, birefringence, etc.

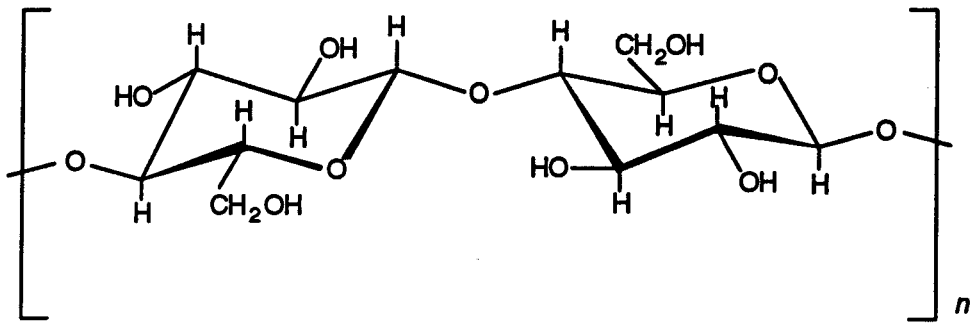


Figure 1. The molecular structure of cellulose.

Figure 2. The SEM photograph of cellulose fiber showing well formed, but short fibrils.

One of our major efforts will be reproduction of fibers with tenacity greater than 5 gram/denier. Analysis of the processing conditions and implementation of these findings combined with theory of mesophase solution should influence the properties further. Remember that the technology of processing mesophase polymeric solutions is not as mature as that associated with the usual isotropic systems.

An additional potential point of improvement resides in the detailed structure of the anisotropic cellulose solution itself. For example, one observes generally a well defined anisotropic solution of nematic type, composed of individually ordered but randomly positioned domains. Attempts will be made to reorganize the overall arrangement of the precursor solution to render it more amenable to coagulating as a dense and highly aligned fibrillar structure. Simultaneously, characterization of the fibers, as mentioned above, will continue.

--- Chitosan ---

Principle Investigator: Dr. Samuel M. Hudson
Contributing Student: Monika Mac Manus

The primary focus of the chitosan project is to chemically modify fibers to produce desirable properties such as high wet and dry strength and increased crystallinity. This will be accomplished by devising an improved method of spinning fibers from these polymers. Maximum spinnable polymer concentration and tensile properties of the fibers produced still place limits on current systems.

In the past year, chitosan control fibers were spun and characterized. They had deniers ranging from 5 to 10 dpf and tenacities up to 2 gpd. We are continuing to work on the chitosan derivative which is made using an aqueous Michael addition reaction. Characterization methods including NMR and birefringence patterns have been used to learn more about these fibers. We would also like to produce and analyze some fibers using sodium dodecyl sulfate as the coagulation bath. We have also prepared some chitosan film samples to be characterized by Dr. Samuels' group at Georgia Tech.

Another interesting study just getting started is the microfibrillation of chitosan. By applying this process to cellulose, useful end products can be made. We are hoping to produce a chitosan product with similar characteristics.

The literature search topic has been narrowed down to articles dealing with the graft copolymerization of chitosan with vinyl compounds. This will provide a basic background for the subject of the research.

GEORGIA TECH : CONVERSION OF WASTE CHITIN TO NONLINEAR OPTICAL FIBERS

PRINCIPLE INVESTIGATORS: M. B. Polk and R. J. Samuels

SUMMARY OF MAJOR ACCOMPLISHMENTS:

A nonlinear optical (NLO) mesogen has been synthesized and reacted with chitosan to form the NLO graft copolymer. The three dimensional refractive indices, optical dispersion, infrared spectra and x-ray diffraction of chitosan films produced by different wash treatments has been measured. The effect of deformation on the three dimensional refractive indices, birefringences, and infrared dichroism has also been investigated. Wet stretching produces higher molecular orientation than dry stretching. A linear correlation has been obtained between the birefringence and the infrared dichroism of oriented chitosan films.

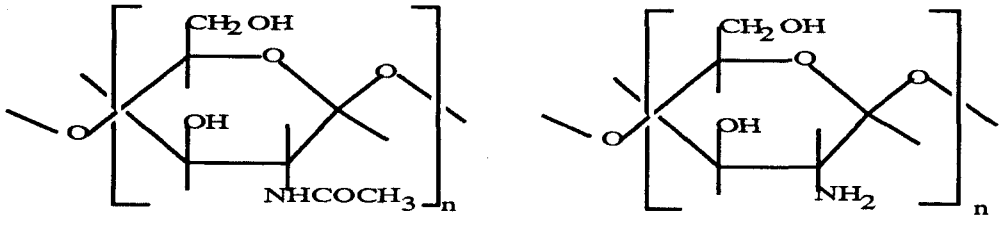
GOAL:

The objective of this study is to establish new applications for chitosan and its derivatives through chemical modification, conversion to fibers and film, structural studies, and property studies; with special emphasis on nonlinear optical behavior.

INTRODUCTION:

This project is designed to utilize Chitosan, a derivative of the second most abundant organic material in the world, Chitin, for the development and manufacturing of new, natural polymer, liquid crystalline non-linear optical fibers.. By using Chitin as as our source we are utilizing, for fiber processing, a waste product from other industries. The project is designed to develop new materials and manufacturing processes, provide trained personnel, and strengthen the nations textile research and educational efforts by uniting diverse experts and resources in a unique collaborative effort.

Organic structures may be attached to polymer chains to obtain films and fibers with good mechanical properties as well as the required optical performance. Liquid crystallinity has been shown to lead to the enhancement of orientation under certain poling conditions. Predicted applications include second harmonic generation, optical modulation, optical switching and memories. In order to achieve these properties, highly ordered systems, incorporating these structures must be fabricated. This project incorporates the following steps to achieve this goal.
1) Characterization of the host liquid crystalline polymer chitosan (Figure 1).
2) Synthesis and characterization of the NLO mesogen (Figure2).
3) Graft copolymerization of the mesogen onto chitosan (Figure 3).
4) Characterization of the copolymer system.



CHITIN CHITOSAN

FIGURE 1

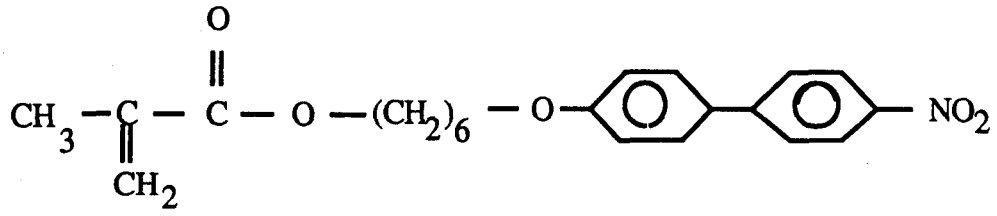


FIGURE 2: MESOGEN I

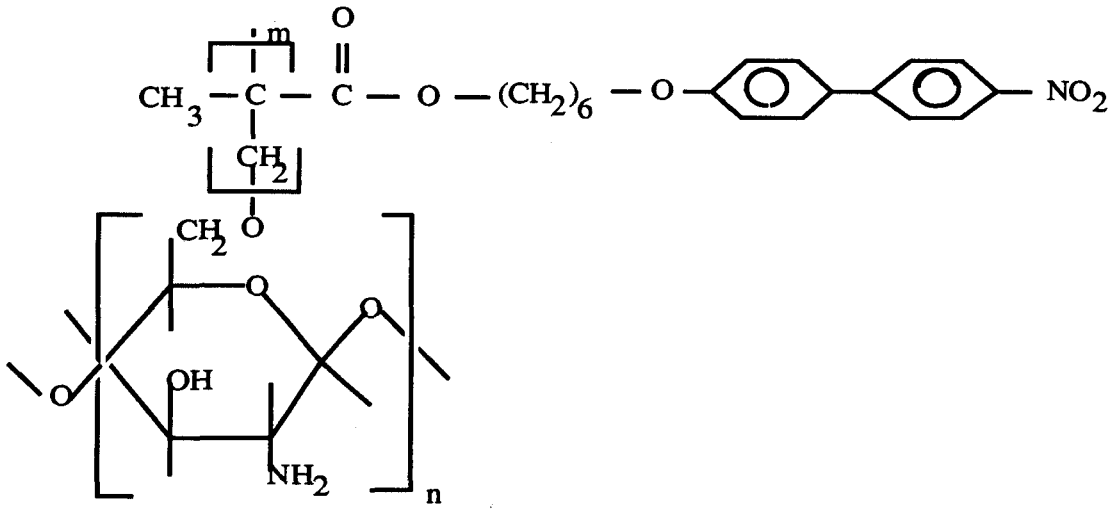


FIGURE 3: GRAFT COPOLYMER

ACCOMPLISHMENTS (THIS YEAR)

1) Characterization of the host liquid crystalline polymer chitosan :

a) Film Casting and Wash Systems :

1) The effect of film casting and nonsolvent wash systems on structure was studied (some films were prepared at NCSU by Dr. Hudson).
2) The three dimensional refractive indices and birefringences of the differently prepared films were determined using prism wave guide coupling techniques (see for example table below).
3) The optical relative dispersion of Chitosan (0.017) was determined using variable wavelength prism wave guide coupling techniques.
4) The infrared spectra of the differently prepared films was determined using FTIR techniques

Table 1: Refractive Indices of Chitosan Films

Description:	N(z):	N(y):	N(x):	N(avg):
AS CAST	1.5367	1.5367	1.5239	1.5324
1N NaOCH3/MeOH (washed)	1.5360	1.5360	1.5234	1.5318
1N NaOH/MeOH (washed)	1.5320	1.5320	1.5202	1.5281
10% NH4OH/MeOH (washed)	1.5372	1.5372	1.5261	1.5335

b) Deformation optimization studies :

In order to optimize the second order nonlinear optical properties of the copolymer the molecular orientation of the host polymer must be at a maximum. It therefore becomes necessary to determine (a) methods for quantitatively measuring the orientation of the host chitosan; and (b) the optimum experimental conditions for achieving very high orientation. The achievements to date include:
1) Films have been deformed both dry and immersed in water with subsequent restraint during drying.
2) The three dimensional refractive indices and birefringences of the differently deformed films were determined using prism wave guide coupling techniques.
3) The Dichroic Ratio and Dichroic Function (a measure of orientation) of the differently deformed films were determined for several absoption frequencies using polarized FTIR spectoscopy.
4) The in-plane birefringence has been correlated with the infrared Dichroic Function for these deformed films (see Figure 4).

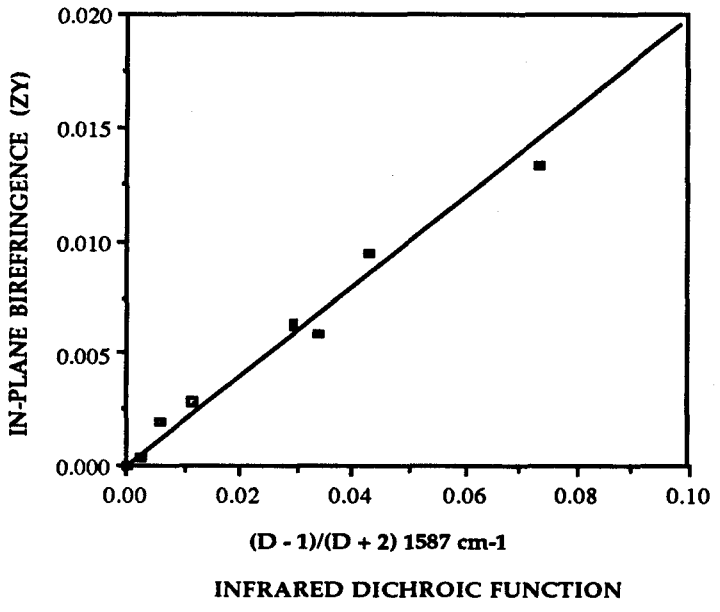


FIGURE 4: BIREFRINGENCE-IR DICHROIC FUNCTION CORRELATION OF WET-STRETCHED CHITOSAN

2) Synthesis and characterization of NLO mesogen I :

4-(6-Hydroxyhexyloxy)-4'-nitrobiphenyl was reacted with methacroyl chloride to form the mesogen, 4-(6-methacryloxyhexyloxy)-4'-nitrobiphenyl **I** (Figure 2). The infrared spectrum showed peaks at 1596 and 1343 cm^{-1} which are characteristic of the nitro group, a peak at 1718 cm^{-1} which is characteristic of the conjugated ester carbonyl, and absorptions in the range 1667-1640 cm^{-1} which represent the carbon-carbon double bond. The melting point was 58-60 C (the literature melting point was 53-56 C). The elemental analysis was as follows: found, C; 67.28%, H; 6.58%, N; 3.50%. theoretical, C, 68.90%, H; 6.57%,N; 3.65%.

3) Graft copoymerization of the mesogen onto chitosan :

4-(6-Methacryloxyhexyloxy)-4'-nitrobiphenyl was graft copolymerized onto chitosan under

heterogeneous conditions in water by using azobisisobutyronitrile in a minimum amount of acetone as the initiator (Figure 3). The infrared spectrum showed a new peak at 1734 cm^{-1} which is characteristic of the ester bond formed between the macromonomer and chitosan. The product isolated was a mixture of chitosan, graft copolymer, and homopolymer.

4) Characterization of the copolymer system :
That mixture isolated above could be cast into transparent films; however, when the chitosan was removed with 10% acetic acid solution, the resulting yellow solid was found to be only partially soluble in nitrobenzene. We will prepare more graft copolymer and attempt to cast a film from $AlCl_3$ /nitrobenzene solution.

FUTURE GOALS

The objective is to fabricate highly oriented chitosan and mesogen in the copolymer so as to obtain optimum NLO properties. To follow the orientation of each component seperately during fabrication their individual molecular characteristics must be known. Therefore the properties of the reference homopolymers must be quantitatively characterized.
CHITOSAN (reference polymer)
Study other cast and wash systems; determine the infrared transition moment angles, intrinsic birefringence and refractive indices of chitosan from experimental data and molecular modelling; measure the real-time molecular deformation of chitosan films (simultaneous stress-strain-molecular orientation).
PNOM POLYMER (reference polymer)
Polymerize the PNOM polymer; study the solubility and cast films; determine the three dimensional optical, infrared and x-ray characteristics of the polymer; study the effect of deformation on the properties.
CHITOSAN- PNOM GRAFT COPOLYMER FILMS
Polymerize chitosan-PNOM copolymer series; study their solubility and cast films; determine the three dimensional optical, infrared and x-ray characteristics of the polymer; measure in real-time simultaneously the stress-strain-molecular orientation of both the chitosan backbone and the PNOM mesogen during deformation; determine best system for film deformation to high orientation and optimum NLO properties
SYNTHESIZE SECOND NONLINEAR OPTICAL SYSTEM
Synthesize a second NLO mesogen; study the system in a manner similar to the Chitosan-PNOM system above.

EDUCATION

1) Students
a) Graduate Students : Vivan Thammongkol and Wen Ding, Chul Y. Cha and Qing Lian
b) Undergraduate Students: Peter Kim and Bridgette Gomillion

2) Relevant Presentations :
Kim, P., Cha,C. and Samuels, R.J., "Quantitative Characterization of the Optical Properties of Chitosan Films", MAKROAKRON'94 (35th IUPAC International Symposium on Macromolecules), Akron, Ohio, 7/94.

3) Awards :
Undergraduate Student Paper Award : "Optical Characterization of Molecular Orientation in Chitosan Films", 1994 AIChE Southern Regional Conference, Technical Paper Contest, Auburn University, Auburn, Alabama, 5/94.

Environmentally Friendly Fibers

Synthetic Polypeptides

May want to use as bullet

Fabrication of certain repetitive synthetic polypeptides into fibers and other shaped structures may provide biochemical sensors as well as biologically compatible materials.

One of our team members holds numerous patents for work in the area of synthetic polypeptides, specifically synthetic analogues of elastin. Dilute solutions of certain repetitive polypeptides have been shown to exhibit a spontaneous separation into polymer-rich and water-rich phase in response to environmental changes. The polymer-rich phase can flow, but also may be stabilized into a shaped gel by crosslinking with ionizing radiation. After crosslinking, the polymer exhibits large reversible dimension changes in response to environmental changes in temperature, pH etc. Previously this has required a mold to hold the polymer solution during the crosslinking process. While molding technology is acceptable for some shapes, the requirement of a mold to hold the liquid in a fiber shape while it is crosslinked is difficult to envision as a commercially viable fiber production method. The task of this research is to develop a process for accomplishing the crosslinking of the polymer solution during fiber manufacture.

Progress:

The first year of the project was occupied in producing a sufficient quantity of the polymer to attempt extrusion. About 5 g of the elastic polypeptide poly(GVGVP) - glycine valine glycine valine proline - have been produced for experimental spinning trials. A small length of fiber was produced inside of a glass capillary; however, forcing the crosslinked fiber from the capillary caused it to break into short lengths. Cellulose acetate dialysis tubing and PVC microtubing were also tried as molds for producing lengths of fiber. The cellulose acetate appeared to be too porous, thus preventing the maintenance of proper water content for crosslinking. The PVC tubing appears to be an adequate mold, but the ease of dissolution of the cellulose acetate mold is lost.

During the second year, several chemical and photochemical crosslinking techniques (which work on other polymer types) have been tried. To date, none of these have been successful. We are continuing to modify reaction conditions in an effort to find a suitable crosslinking process. We are also continuing to look at the irradiation process and to study the properties of materials produced in this way.

A high pressure piston pump with precise low output was evaluated for the wet extrusion of fibers. A small (< 100 micron) single acrylic filament was extruded from DMAC and coagulated in a water spin bath. The fiber appeared to have reasonable diameter uniformity unless a large draw-down was attempted in the spin bath. The extruder has been ordered.

Investigators: Roy M. Broughton, David Hall, Ian Hardin (UGA), Dan Urry (UAB)

Visiting Scholar: Liming Wang (AU)
Graduate Students: Paul Brady (AU), Chi-Xiang Luan (UAB)
Undergraduate Students: Mark Moe (now graduated)