

# Recycling Cotton from Cotton/ Polyester Fabrics

By Ioan I. Negulescu, Hyojung Kwon, Billie J. Collier, John R. Collier, and Ajit Pendse,  
Louisiana State University, Baton Rouge

Over four million tons of post-consumer textiles enter the waste stream annually, amounting to more than 5% of total municipal solid waste.<sup>1</sup> The disposal of such large volumes of waste is an increasing problem along with preconsumer cutting and sewing scrap fabric from the apparel industry. The rising cost of disposal operations, reduction in available space, and increasing environmental concern have made textile and apparel manufacturers pay attention to research and development of recycling technologies for textile wastes.<sup>2</sup>

A large percentage of the textile wastes produced from manufacturing

## ABSTRACT

**Recycling of cotton (or rayon) cellulose as lyocell fibers is proposed based on the selective solubility of cellulose in organic *N*-oxides and the selective hydrolysis of polyesters in NaOH solutions. In the first step, the cotton component of a fabric made of 50/50 cotton/polyethylene terephthalate was separated from the polyester by basic hydrolysis of the latter in NaOH solutions. In the second step, the cellulose component from another sample of the same fabric was selectively dissolved in *N*-methyl morpholine monohydrate to form a 1-2% cellulose solution. It was then concentrated to a spinnable 15-17% solution by dissolving the cotton separated in the first step. Lyocell fibers were subsequently spun at 85-90C using an advanced capillary extrusion rheometer system.**

## KEY TERMS

Cotton  
Lyocell  
*N*-Methyl Morpholine *N*-Oxide  
Mesomorphic Solutions  
Rayon  
Polyester  
Polyester Hydrolysis  
Recycling  
Spinning

clothing and other textile products is accounted for by fabrics such as polyester/cotton and polyester/rayon blends. Reuse of the blended materials is complicated because there are inherent differences in the chemical composition and physical properties of the two components. In addition, dyeing and finishing treatments make it nearly impossible to reuse these materials in a non-modified form.

Recovery of polyester waste scrap has been studied extensively.<sup>3</sup> The polyester (polyethylene terephthalate, PET) is either converted into starting polycondensation monomers; e.g., ethylene glycol and terephthalic acid or terephthalic acid esters, by alkaline hydrolysis<sup>4,5</sup> or transesterification,<sup>6</sup> or it is recovered from mixed collections of common fibers using highly selective solvents for polyesters.<sup>7</sup> The common fibers are acetate, acrylic, cotton, wool, nylons, polypropylene, and rayon, and the nature of solvents varies from chlorinated solvents/organic acids or phenols mixtures to aromatic polynuclear derivatives. Naphthalene has been found especially suitable for the separation process for dye stripping and as a primary dissolution solvent because the solubility of polyester in naphthalene is a strong function of temperature, ranging from zero solubility at 170C to about 55% polyester solubility at 218C (boiling point of naphthalene). In another method for polyester recovery and reuse, textile wastes formed from blended cellulose and polyester fibers are treated with a mineral acid, such as sulfuric acid, under conditions which serve to hydrolyze the cellulose and convert it to a form which is readily removed from polyester fibers while leaving the polyester fiber substantially unaffected.<sup>8</sup>

Some patented methods also consider the parallel recovery and recycling of cellulosic materials from different textile blends containing polyester and cellulosic fibers. A process for recycling polyester and cotton blend fabrics by separating the polyes-

ter from the cotton fabric is described in Ref. 9. The process includes charging the blend into a sulfone solvent, dissolving the polyester at 190C for a period of about 35 minutes or less, separating the dissolved polyester and sulfone solution from the cotton fabric, filtering the cotton to obtain isolated cotton fabric, releasing the dissolved polyester into a coagulation solution of a second sulfone solvent and water at which time the polyester precipitates out of solution, and filtering the polyester. A preliminary step is, however, necessary in which the fabric samples are dried at an appropriate temperature, pressure, and time interval to prevent degradation of the polyester during the process. Alternatively, textile wastes composed of blended polyester and cellulose fibers might be subjected to the action of glacial acetic acid and acetic anhydride in the presence of a catalyst under conditions which serve to convert the cellulose component of the waste to cellulose acetate. The acetate can be separated from the unreacted polyester component in the form of a solution adapted for production of cellulose derivatives, whereas the polyester is recovered in a form which may be converted to a staple fiber for reuse.<sup>10</sup>

The methods described above are considered by the authors of the present work to be neither environmentally safe nor economically feasible for recycling—particularly for recycling the cellulosic component. Therefore, the main concern of this paper is to investigate the possibility of complete recycling of the textile components of cotton/polyester blends in an environmentally safe manner.

## Experimental

### Materials

Plain weave cotton (CT), polyester (PET), and blends of cotton/polyester with no finishing treatment were used. *N*-methylmorpholine *N*-oxide (NMMO) solvent was purchased as a



monohydrate or as a 60% solution in water. Solutions of sodium hydroxide of various concentrations were prepared before use from NaOH pellets.

### Methods and Equipment

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) methods were used to determine the average content of polyester in samples. Seiko DSC 220C and Seiko TG/DTA 220 instruments were used. Known amounts of cotton and/or polyester fabrics were cut in small pieces or blended intimately in a coffee grinder, and samples of about 3-8 mg were weighed in aluminum pans and analyzed in an inert nitrogen atmosphere. An empty aluminum pan was used as a reference. The heating and cooling rates were controlled at 5C and the highest temperature limit was 300C. The breaking strength of cotton strips (6" x 1") was determined using an Instron 4301 tester. Rheological characteristics of 10-17% cellulose solutions in NMMO monohydrate (NMMO•H<sub>2</sub>O, m.p. 72C by DSC at 5C/min) were determined using a Seiko dynamo-mechanical spectrometer DMS-110. An advanced capillary extrusion rheometer (ACER) made by Polymer Laboratory was used as an extruder to spin lyocell fibers from 15-17% cellulose solution in NMMO•H<sub>2</sub>O (containing 87% NMMO and 13% H<sub>2</sub>O). A specially designed die was used as a 500- $\mu$ m one-hole spinneret.

### Components Separation

Samples (5 g) were used for separation of cotton and polyester from a 50/50 blended fabric. First the polyester component was subjected to alkaline hydrolysis in 3M NaOH solutions at 95-108C. Ethylene glycol (EG) was added as a wetting agent for PET. Terephthalic acid, TA, (DSC: m.p. 322C,  $\Delta H$  of 750 mJ/mg) was subsequently precipitated quantitatively by acidifying the solution after the removal of cotton fibers by filtration. The cotton fibers were washed with water and dried. The liquid part obtained after the filtration of terephthalic acid was further concentrated in a Buchi rotavapor at 100C and 15 mm Hg as an ethylene glycol aqueous solution. In the second step, the cellulose component from another sample of the same fabric (5 g) was selectively dissolved in NMMO•H<sub>2</sub>O to form a 1-2% cellulose solution at 85-90C. The polyester component was removed by filtration at 85C, washed with hot NMMO•H<sub>2</sub>O, then with water, and dried. Subsequently it was submitted to the first hydrolysis step together with a new fabric sample. The cellulose containing

filtrate was concentrated to a spinable 15-17% solution by dissolving the cotton separated in the first step. Rayon and wood pulp were also tested as additional cellulose sources for concentration of cotton solutions. A flow diagram for recycling the cotton component from cotton/polyester blends as lyocell fibers is shown in Fig. 1. Bleaching is optional, depending on the color of the fabric mixtures to be recycled.

### Polyester Hydrolysis

Four sets of seven mixtures of cotton and polyester fabric strips containing 0.40 g of cotton and 0.15 g of polyester (sets A and C) or 0.30 g of polyester (sets B and D) were subjected to the action of 100 mL of 1.0-5.0 M NaOH solutions at 95-108C. The time for complete disappearance of polyester fabrics was recorded. The cotton strips were then separated, washed with water, dried, and tested to determine the breaking strength.

### Cellulose Solution Preparation

The typical process used for preparing the cellulose solutions for fiber extrusion is as follows. To a 500-mL spherical flask containing 123 g of 60% aqueous NMMO, 61.5 g of water was added, the flask was immersed in a water bath, and the bath temperature increased to 70C. A slurry was then obtained by adding 15 g of cellulose (the amounts of NMMO, water, and cellulose were modified to the same concentrations as above if NMMO•H<sub>2</sub>O containing 1-2% cellulose separated as described before was used instead of 60% aqueous NMMO). The flask was hooked up for a couple of hours to a Buchi rotavapor operated at 70C and atmospheric pressure. The temperature of the bath was increased to 95C and the rotavapor was then connected to a water pump giving a vacuum of about 15 mm Hg. Within one to two hours of rapid rotation, a yellowish film of transparent cellulose solution was formed on the inner wall

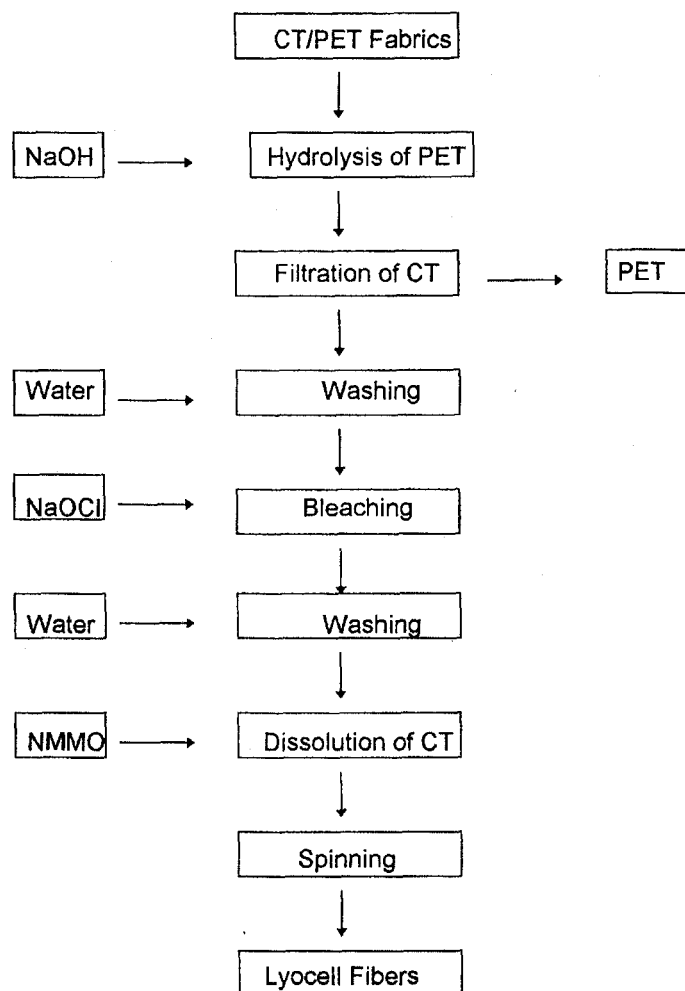


Fig. 1. Flow diagram for recycling cotton from cotton/polyester fabrics as a new lyocell fiber.

of the flask after 99.5 g of water was removed. The solution contained 15% cellulose, 73.8% NMMO, and 11.2% water; the last two components being in a 1:1 molar ratio. The film was bubble free and had a thickness of between 2.5 and 5 mm. The absence of bubbles and insoluble particles was checked by sampling a drop of solution and positioning it on a glass slide for observation with a polarizing optical microscope. The flask was then brought to atmospheric pressure, cooled down to room temperature, capped, and refrigerated until further use.

## Results and Discussion

### Manufacturing Cellulosic Fibers Comparative Trends

Reclaiming the cellulosic component from a mixture of textiles containing both cotton and rayon in various amounts is not an easy task. The molecular weight, the morphology, and all related properties of cotton and rayon cellulose are different. For example, cotton cellulose has a much higher molecular weight and is more crystalline than rayon, which is a regenerated cellulose, with a degree of polymerization much less than 1000. At the same time, the fineness and the length of cellulosic fibers in a mixture of fabrics containing both cotton and rayon blended or not with polyester vary tremendously. Therefore, due to these heterogeneities, one might consider obtaining a new fiber using the cellulosic components of to-be-recycled textiles as starting materials. The process to produce this fiber should be, however, in line with the present trends of manufacturing cellulose.

The most common commercial manufactured cellulosic fiber is produced by the viscose process. The essence of the process is the conversion by reaction with carbon disulfide of wood pulp cellulose to cellulose xanthate, which is then dissolved in caustic soda to yield the so-called viscose solution. Extrusion of the viscose solution into a coagulation bath containing sulfuric acid and mineral salts brings about regeneration of the cellulose. The entire process is complex and requires the control of by-products formed at different stages. As legislation imposes ever-tighter restrictions, the viscose process to produce rayon fibers becomes inevitably more and more costly and in some instances can limit its economic viability. A method for recycling regenerated cellulose scrap, such as rayon produced in the viscose process, has been proposed following the steps described above,<sup>11</sup> but its future is also limited by the same environ-

mental and economic shortcomings as that of the viscose process.

It is reported that the recently developed *N*-methylmorpholine *N*-oxide solvent spinning process of cellulose has been successful in producing new fibers with many favorable properties.<sup>12,13</sup> As a matter of fact, the idea of spinning cellulose fibers from solvents was coined some 60 years ago,<sup>14</sup> but it was not until the late 1960s and early 1970s that patents began to be filed in this area.<sup>15-17</sup> By 1979 and the early 1980s, the use of amine oxide was attracting attention from manufacturers who had begun to look to new routes of cellulosic fiber production giving improved fiber properties and performance.<sup>18-21</sup> However, researchers gradually came to focus on the possibilities of using NMMO as the solvent. The NMMO solvent is a nonderivatizing system that dissolves the polymer by intermolecular interaction only by the formation of hydrogen bond complexes.<sup>15</sup> This cyclic amine morpholine compound results in no degradation of the cellulosic material, imparts no color to it, and leaves no potentially dangerous or unpleasant residue in the product.<sup>15,22</sup> Fibers of higher strength are readily produced without any modification of the spinning system as compared with rayon technology.<sup>23</sup> The process is simple: wood pulp and amine oxide, as a solution in water, are mixed and then passed to a continuous dissolving unit to yield a clear, viscous solution. The solution is then extruded into a dilute aqueous solution of amine oxide which precipitates the cellulose as fiber (called lyocell, as opposed to rayon, which is a regenerated cellulose fiber). NMMO is not an inexpensive solvent. Therefore, the diluted NMMO resulting from the process is purified on ion exchange columns and re-used after the removal of excess water. Since the

manufacturing process contains a closed circuit, virtually all of the solvent is recycled (i.e., more than 99.5%; the very low emissions left over are decomposed in adapted biological purification plants). The whole process utilizes materials that are environmentally clean and, since the solvent is recycled, the waste products are both minimal and non-hazardous.<sup>12</sup>

Taking into consideration the simplicity of producing lyocell fibers as compared with the viscose process, and because of environmental concerns as well, for this work it was decided to recycle the cellulosic component (cotton, rayon) from discarded textiles as a new fiber spun from NMMO solutions.

### Determination of Polyester Content in Blends

To proceed with separation of polyester and cellulosic components as described in the experimental section, it is necessary to know beforehand the bulk proportion of these components in the mixture of fabrics subjected to recycling. DSC yielded reliable quantitative data for determination of the polyester content in blended textiles. DSC thermograms of a polyester fabric sample and of a blend containing 50% cotton and 50% polyester are shown in Fig. 2. The average enthalpy change during the melting of polyester for a 100% polyester fabric sample ( $\Delta H_{PET}$ ) was 54 mJ/mg. The percent content of polyester in cotton/polyester blends was then assayed using the following equation:

$$\%PET = 100 \times (\Delta H_S / \Delta H_{PET}) \quad \text{Eq. 1}$$

where  $\Delta H_S$  is the melting enthalpy of polyester from the blended sample. The percent of dry cotton was calculated taking into account the water content of the sample:

$$\%cotton = 100 - (\%PET + \%W_{H_2O}) \quad \text{Eq. 2}$$

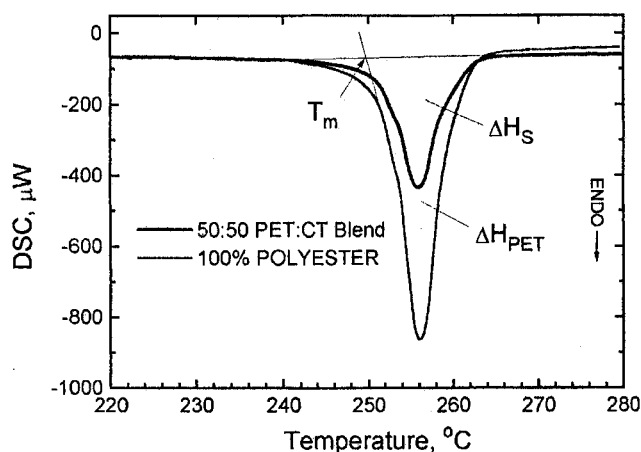


Fig. 2. DSC thermograms of poly(ethylene terephthalate) and of a blend containing 50% polyester and 50% cotton.

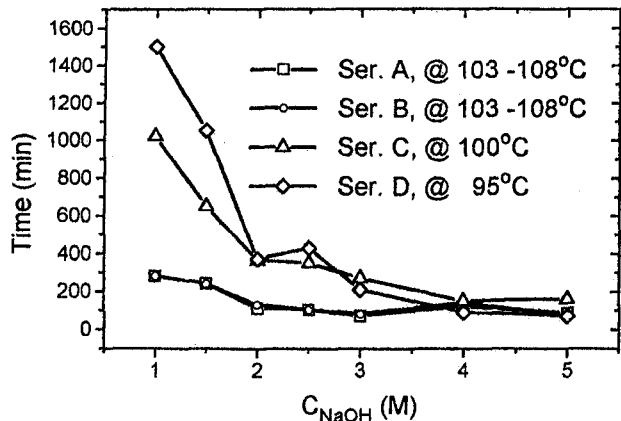


Fig. 3. The dependence of time for complete hydrolysis of polyester upon temperature and concentration of NaOH solutions.

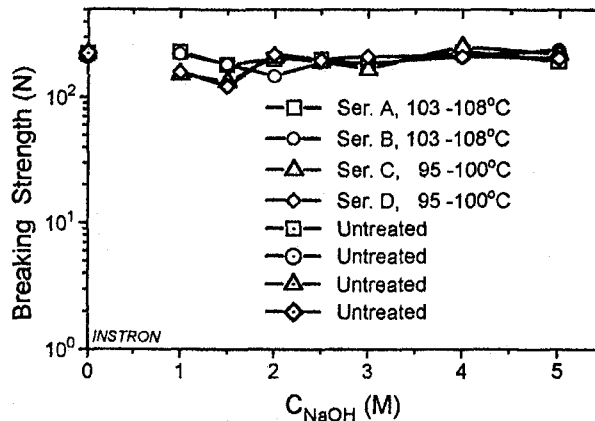


Fig. 4. Variation of cotton breaking strength with reaction conditions for hydrolysis of polyester.

where %  $W_{H_2O}$  is the water content of the sample determined from TG curves as the percent weight loss at 125°C. Using a large series of blends of known composition, it was confirmed that DSC and TG data provided accurate information regarding the blending ratio of two different textile materials containing cotton and polyester.<sup>24</sup>

#### Treatment of Mixtures with NaOH Solutions

The time required for the complete hydrolysis of polyester from cotton/polyester mixtures was plotted vs. the molarity of NaOH solution (Fig. 3). The lower the temperature of treatment, the longer the hydrolysis time of polyester. Sets A and B were treated at the boiling temperature of solutions, while sets C and D were treated at 95-100°C. The main concern was the degradation of cotton in conditions used for complete hydrolysis of polyester from cotton/polyester blends. An inspection of Fig. 4 shows, however, that no loss in cotton strength occurred when the hydrolysis was carried out, for example, for 280 minutes at 103°C and 1M concentration or for 70 minutes at 108°C

and 5M concentration. There is, therefore, a large window of NaOH concentration to be considered for economic optimization of reaction parameters. A slack mercerization effect was noticed occasionally for higher NaOH concentrations (e.g., 4M concentration at 100°C).

#### Rheology of Cellulose Solution and Spinning of Lyocell Fibers

The dilute solution viscosity ( $\eta$ ) of cellulose in many nonaqueous solvent systems is rather high due to the chain-stiffening effect of complex formation between cellulose and solvent. A steep viscosity increase is observed with increasing cellulose concentration.<sup>22</sup> At a high cellulose concentration ( $c$ ), a change in the course of  $\eta$  vs.  $c$  may occur due to the formation of a liquid crystalline system resulting in a viscosity drop. However, as the temperature rises, an increase of viscosity might be observed due to the isotropization of the system. For a certain  $c$ , it is advantageous to know the domain of temperatures in which the system is anisotropic because fibers of higher

modulus are spun from mesomorphic solutions and a lower translates in a lower energy demand for spinning. As shown in Fig. 5, for a cellulose (pulp) solution in NMMO•H<sub>2</sub>O with  $c$  of 15%, the critical temperature of isotropization,  $T^*$ , is about 85°C (determined as the temperature at which the dependence of versus temperature changed the trend). This temperature is dependent, however, both on  $c$  and the frequency of determination,  $f$ ; i. e., the higher the concentration or  $f$ , the higher the  $T^*$  (Fig. 6). Consequently, the spinning of lyocell fibers from the NMMO•H<sub>2</sub>O cellulose systems described above, with  $c$  of 15 and 17%, was accomplished with the ACER instrument having the barrel and the capillary at 85°C; i.e., below  $T^*$ . Fibers were spun using different strain rates. The elongational viscosity and pressure drop as a function of elongational strain rate are given in Fig. 7. As expected, the pressure drop increased with the ram speed (strain rate), while an inverse dependence was recorded for the corresponding elongational viscosity. Preliminary tests have pointed

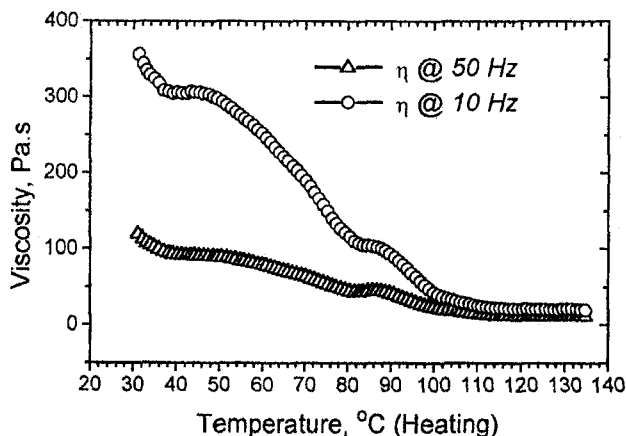


Fig. 5. Rheology of 15% cellulose (pulp) solution in NMMO•H<sub>2</sub>O.

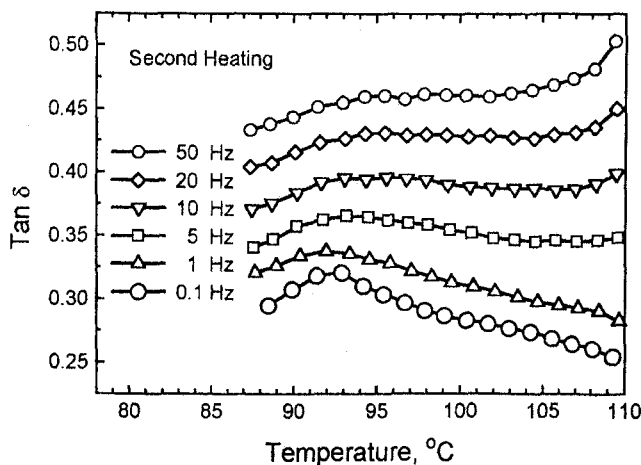


Fig. 6. Variation of  $\tan \delta$  with temperature and frequency for a 17% cellulose solution (recycled cotton) in NMMO•H<sub>2</sub>O.

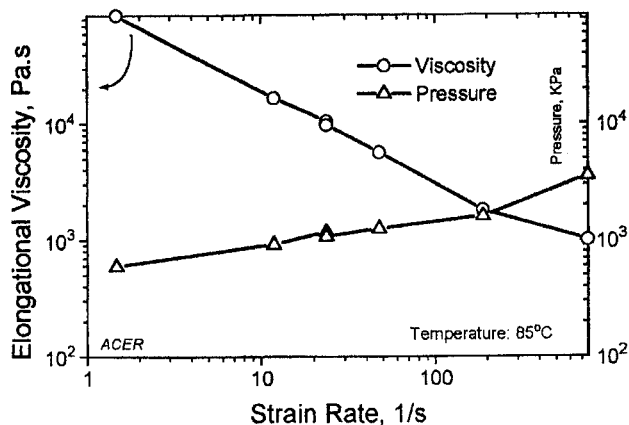


Fig. 7. Dependence of elongational viscosity and pressure on the strain rate for spinning lyocell fibers at 85°C from a 15% cellulose (pulp) solution in NMMO•H<sub>2</sub>O.

to a strong dependence between the tenacity of fibers and spinning conditions. These data are important for choosing the optimum parameters to spin lyocell fibers of high quality.

#### Economic Considerations

Lyocell is the Federal Trade Commission approved generic name for solvent spun cellulose. Lyocell fibers, the first "green" manufactured fibers, are already produced by the British Courtaulds Fibres Inc. under the brand name Tencel. In 1994 Courtaulds opened a manufacturing plant in Axis, Ala., capable of producing over 18,000 tons a year and plans to increase the production to 150,000 tons by the end of the decade. The first European large-scale lyocell plant was planned by Lenzing AG to begin operation late in 1997 in Burgenland, Austria. It will produce 24,000 tons of fibers per year under the brand name Lenzing Lyocell. Because of their limited availability and exceptional characteristics (e.g., in dry state lyocell fibers are significantly stronger than other cellulose fibers including cotton, approaching the strength of some polyesters, and are the only manufactured cellulose fibers to exceed the strength of cotton in a wet state),

lyocell fibers are not cheap. For example, the initial cost of Tencel was about 60% more than standard cotton, 50% more than rayon, and almost twice as much as polyester, and will remain in a high price niche of under 100,000 tons/year.<sup>25</sup> It is thought that by substituting cotton for pulp or by using a blend of cotton and pulp as starting materials for lyocell fibers, some characteristics of the fibers will be augmented. Therefore, making a new lyocell fiber based on recycled cotton is a feasible approach, even if it is assumed that the cost of recycled cotton will not be less than that of the pulp used to obtain lyocell fibers. And the recycled polyester will be a bonus to this approach!

#### Conclusions

An environmentally friendly method for separation and recycling of textile components from blends containing cotton or rayon and poly(ethylene terephthalate) has been discussed. The polyester component was hydrolyzed to initial monomeric materials in basic conditions which did not affect the strength of the accompanying cellulosic part (cotton). The cellulosic component was spun as a new fiber (lyocell)

from mesomorphic *N*-methyl morpholine *N*-oxide solutions.

#### References

- Javlonowski, E., *Waste Age*, January 1995, p83.
- Rudie, R., *Bobbins*, Vol. 35, No. 6, June 1994, p16.
- Ehrig, R. J., *Plastics Recycling: Products and Processes*, Hanser Publishers, New York, N.Y., 1994.
- Alfred, M. T., *U.S. Patent No. 3,801,273*, 1974.
- Schwartz Jr., J. A., *U.S. Patent No. 5,395,858*, 1995.
- Brossard, L. D. and V. P. G. Lasalle, *U.S. Patent No. 5,319,128*, 1994.
- Sidebotham, N. C., et al., *U.S. Patent No. 4,003,880*, 1977.
- Gruntfest, I. and R. Turner, *U.S. Patent No. 3,937,675*, 1976.
- Serad, S. L., *U.S. Patent No. 5,342,854*, 1994.
- Gruntfest, I., et al., *U.S. Patent No. 3,937,671*, 1976.
- Farrall, D. L., *U.S. Patent No. 4,145,533*, 1979.
- Cole, D. J., *Advances in Fibre Science*, edited by S. K. Mukhopadhyay, Textile Institute, Manchester, U.K., 1992, p.25.
- Lennox-Kerr, P., *Technical Textiles International*, Vol. 3, No. 6, December 1994, p18.
- Graenacher, C. and R. Sallmann, *U.S. Patent No. 2,179,181*, 1939.
- Johnson, D. L., *U.S. Patent No. 3,447,939*, 1969.
- Johnson, D. L., *U.S. Patent No. 3,447,956*, 1969.
- Johnson, D. L., *U.S. Patent No. 3,508,941*, 1970.
- McCorsley III, C. C. and J. K. Varga, *U.S. Patent No. 4,142,913*, 1979.
- Franks, N. E. and J. K. Varga, *U.S. Patent No. 4,145,532*, 1979.
- Franks, N. E. and J. K. Varga, *U.S. Patent No. 4,196,282*, 1980.
- McCorsley III, C. C. and J. K. Varga, *U.S. Patent No. 4,211,574*, 1980.
- Phillip, B., *Journal of Macromolecular Science-Pure Applied Chemistry*, Vol. A30, No. 9&10, 1993, p703.
- Chanzy, H., et al, *Polymer*, 1990, p400.
- Negulescu, I. I., et al, *Textile Chemist and Colorist*, Vol. 30, No. 6, June 1998, p21.
- Mileana, Dana, *The Wall Street Journal*, January 9, 1995.

#### Author's Address

Ioan I. Negulescu, Louisiana State University, School of Human Ecology, Human Ecology Bldg., Baton Rouge, La. 70803-4300; telephone 504-388-1684; fax 504-388-2697; e-mail inegule@unix1.sncc.lsu.edu.

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