

Fibers from Urea–Formaldehyde Resins

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ABSTRACT: The preparation of fibers from aqueous urea–formaldehyde resins has been investigated; a dry spinning process has been developed based on the extrusion of catalyzed resin into a drying chamber at 180–220°C, producing a multifilament yarn at spinning speeds of up to 600 m/min. A range of UF filaments was produced with diameters between 10–70 μm ; the tenacities of spun filaments were 6–10 cN/tex, initial moduli were 220–340 cN/tex, and elongation at break was 4–10%. The best tensile properties resulted from conditions that produced the smallest diameter fibers. Postspin heat treatment improved the tenacity to 14 cN/tex and the elongation to 20%. Spinnability improved with increased viscosity of the spinning solution and increased cell temperature, while tenacity and elongation increased with increasing cell temperature and spinning stretch. A correlation was found between TGA weight loss (between 105 and 200°C) and fiber tenacity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 64–74, 2000

Key words: urea–formaldehyde resin; fibers; catalyst; spinning; tensile properties

INTRODUCTION

Almost all of the well-known fibers in general use are very flammable, with the exception of inorganic and carbon fibers and specialty flame-resistant fibers such as Nomex, the modacrylics (e.g., Kanekaron), and flame-resistant viscose and flame-resistant polyester fibers (e.g. Trevira). Thermosetting resins have disadvantages that prevent their general use in the textile field, such as poor spinnability, low flexibility, large thermal conductivity, low hygroscopicity, poor handling, and low dyeability. The inherently superior fire resistance of a cross-linked fiber is attractive to the textile industry, and cross-linked UF fibers offer the additional advantages of low cost and

dyeability (UF resins are among the cheapest of synthetic organic polymers).

Thermosetting polymers, however, do not possess the general requirements of linearity and orientability on which much of the art of fiber production is based. The extrusion stage in fiber production invariably requires the polymer to be a melt or in the form of a viscous solution if spinning is to be carried out, and such polymers should be able to undergo orientation during post-spin drawing in order that the mechanical properties of the fiber can be fully realized. Polymers such as urea formaldehyde (UF), melamine formaldehyde (MF), and phenol formaldehyde (PF) thus present considerable difficulties for processing into fibers because of their insolubility and infusibility once substantial polymerization has taken place. Hence, it is necessary to produce the fibers from a thermoplastic or soluble precursor and then to complete the polymerization in a final curing stage when the polymer is in the fiber form.

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Despite these difficulties, a few fibers have been made commercially from thermosetting resins such as phenol formaldehyde (Kynol) and melamine formaldehyde (Basofil). These fibers are attractive because they have inherently superior flammability characteristics. For example, the limiting oxygen index for Kynol is reported in the literature as 30–34%.

Although some industrial companies have evaluated the potential of UF resins as fiber-forming materials,^{1–9} very few publications (even in patent form) have appeared, and no commercial product has resulted. The present work was undertaken to examine the problems involved in developing a useful fiber-spinning process and to evaluate the properties of the resulting fibers.

EXPERIMENTAL

Materials

UF resins were synthesized from reagent-grade urea and formalin (35–37% formaldehyde) obtained from BDH Ltd. In addition, two commercial UF resins were used: Aerolite 300 (Ciba Geigy UK Ltd.), and Borden UL96 (Borden UK Ltd., Southampton), both of which are viscous aqueous resins containing 60–70% resin solids.

Resin Synthesis

The chemistry of the reaction between urea and formaldehyde has been described extensively in the literature,^{10–17} and the complexity of this reaction is well known. Several factors affect the reaction in a major way: U : F ratio, pH, temperature, concentration, time, and reaction sequence, which give rise to a variety of UF resin types. During the resin condensation stage, the pH, temperature, and reaction time have to be controlled to achieve the desired degree of polymerization. UF resins in the present report were synthesized using procedures that are employed in commercial resin manufacture,¹⁸ and the required degree of condensation of the resins was controlled by measuring the water tolerance of the resin. A typical resin synthesis procedure is as follows:

Formalin (36.8% HCHO), 2995 g (36.73 mol) was charged to a 5-L reaction vessel equipped with a stirrer, reflux condenser, thermometer, and pH probe. The pH of the formalin was adjusted to 8.0 with 10% aqueous sodium hydroxide, and then 1102 g (18.36 mol) of urea were added

with vigorous stirring. The pH of the solution was then adjusted to 7.0 with 2% formic acid to establish buffer conditions in the reaction mixture. The contents were heated to reflux at 98–101°C, and refluxing was continued for 30 min, keeping the pH of the solution above 6.5 by additions of 10% aqueous sodium hydroxide from a burette. After refluxing the mixture for 30 min (neutral reflux period), the pH was decreased and maintained at 5.2, using 2% aqueous formic acid, enabling the condensation reaction to proceed at a controllable rate.

After refluxing for 30 min at pH 5.2, small samples of the reaction mixture were extracted with a pipette and added to a mixture of ice and water and examined for signs of turbidity. The procedure was repeated at intervals of 10 min until turbidity was observed, at which point aliquots of 3.3 mL were extracted at intervals and, after cooling, titrated with distilled water to an end point of faint but definite permanent turbidity. A water-tolerance number, Nw ,¹⁸ was calculated from the relation:

$$Nw = 1000/(A - 1.7)$$

where A is the titer (in mL) of water for the resin sample. A plot of Nw against time is invariably linear, allowing prediction of reaction time to the required degree of condensation. The condensation reaction can then be arrested by fast-cooling the resin—for example, by circulating it through a heat exchanger—and adjusting the pH to 7.5. The experimental amino resins in this work were condensed to a water tolerance number of 200. The method, although empirical, has been widely used in the resin-manufacturing industry and provides a simple way to prepare resins of consistent quality (continuous monitoring of viscosity is now used mostly to determine the reaction end-point). Subsequently, the resin was concentrated to 65–70 wt % solids by vacuum distillation (45°C, 70 mm Hg) and, after cooling, sealed in a container to prevent loss of moisture and formaldehyde.

Resin Characterization

Solids Content

A 2-g sample of resin was dried at 60°C for 3 h in a vacuum oven, cooled for 1 min in a desiccator, and then weighed.

Resin Viscosity

Viscosities were determined using a rotational viscometer (Haake Rotovisko) at 21°C and at shear rates from 1.3 to 216 s⁻¹.

Gel Time

A small sample (approximately 10 mL) of catalyzed resin was poured into a test tube 1 cm in diameter to a depth of 5 cm. A thermometer was inserted and the test tube was then fixed vertically in a water bath at the required temperature. The timer was started, and the thermometer was oscillated gently in a vertical plane until the viscosity of the resin suddenly increased to a level where oscillation was not possible (i.e., the resin gelled). This clearly observable point was noted as the gel time. Three measurements were carried out on samples from each batch to ensure reproducibility. This simple technique was shown to give reproducible (± 5 s) results and was more convenient to use than a measurement of the change in resin viscosity with time.

Fiber Spinning

The conditions used for spinning the fibers are given in the Results and Discussion section.

Fiber Characterization

Fiber Diameter and Linear Density

Fiber diameter was measured (10 specimens per sample) using a calibrated Zeiss optical microscope, and the mean was then calculated. Linear density was measured using a torsion balance and 10 m of yarn.

Specific Gravity

The specific gravity of fibers was determined using flotation measurements in mixtures of toluene and tetrachloroethylene; at the point where the fiber neither floats nor sinks, its specific gravity ρ_{fiber} is given by

$$\rho_{\text{fiber}} = (\rho_1 V_1 + \rho_2 V_2) / (V_1 + V_2)$$

where ρ_1 and V_1 are the specific gravity and volume of liquid 1, and ρ_2 and V_2 are the specific gravity and volume of liquid 2.

Mechanical Properties

The UF fibers were conditioned for 24 h at 65% relative humidity and 20°C. Individual filaments

were mounted on 2-cm test squares, and tensile properties were measured on an Instron Model 1122 Tensile Testing machine, using an extension rate of 10%/min. Batches of 10 samples were tested, and the mean breaking tenacity, elongation at break, and 2% secant modulus were determined.

Moisture Regain

The moisture regain of the fibers was determined by conditioning a sample of UF fiber for 24 h at 65% r.h./20°C, weighing, drying to constant weight at 105°C, and reweighing. The moisture regain is given by $(m_1 - m_2)/m_2 \times 100\%$, where m_1 and m_2 are the masses of undried and dried fibers, respectively.

Thermal Analysis

UF fibers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), using a DuPont 910 scanning calorimeter and 951 thermogravimetric analyzer. DSC runs were carried out at 10°C/min under a nitrogen flow rate of 50 mL/min. TGA runs were carried out at 10°C/min.

X-ray Diffraction

Wide-angle X-ray diffraction photographs were obtained from a Hilger and Watts Y90 constant output generator with a water-cooled copper target in a sealed tube.

Surface and Fracture Characteristics

Examination of filament surfaces and fractured ends was carried out using a Cambridge Stereoscan 150 MK2 and a CamScan 3/30 BM scanning electron microscope.

RESULTS AND DISCUSSION

Preliminary Spinning Trials

Fiber spinning was carried out using acrylic fiber dry-spinning equipment incorporating a 5-m-long drying cell. The main components of the spinning unit consisted of a stainless-steel reservoir pressurized to feed the catalyzed resin via line filters and a gear metering pump to a spinneret mounted inside the drying cell.

Preliminary spinning trials were unsuccessful. This was due mainly to the ease with which ge-

lation of catalyzed UF resins occurs, particularly at elevated temperatures. Using catalysts sufficiently active to cure the filaments in the drying cell resulted in significant gelation of the spinning solution, making the process unworkable. Even when using a cold spinning solution, conduction of heat from the spinneret to the feed lines led to gelation within the feed system in undesirably short times. It was found to be necessary to construct a water-cooled feed line in order to increase the gel time of the catalyzed resin in order to make spinning possible.

It was found that the catalysts normally used for UF resins, such as ammonium sulfate, were too rapid in their action, even at ambient conditions, and they also caused problems in degassing the catalyzed spinning solutions due to rapid increases in viscosity. Investigation of a range of alternative catalysts showed that zinc salts, particularly zinc nitrate, were relatively inactive when mixed with resin at room temperature but were highly active at elevated temperatures and caused gelation of the resins within a few seconds at 100°C (Fig. 1). For comparison, gel times are also shown for ammonium sulfate-catalyzed resins.

This property of zinc salts, in which it was inactive when mixed with resin at room temperature, allowed time to carry out efficient blending of the catalyst with the resin and also to degass the resin spinning solution at room temperature. This process was not possible when using ammonium sulfate. Degassing was essential to remove air bubbles entrapped in the dope, which would otherwise lead to spinning breakdowns and poor fiber properties from the resulting voids. Further investigation of optimum catalyst concentration showed (Fig. 2) that increasing the catalyst concentration markedly shortened the gel time at 100°C and that concentrations below 1% (wt catalyst/wt resin solids) were likely to be ineffectual in the short transit time of the filaments in the drying cell. A concentration of 2% was therefore used as standard in most of the experimental extrusions; the highest concentration used in this work was 3%. Although spinning was successful at this concentration, no obvious advantage in spinnability or fiber properties was observed over 2% catalyzed resins.

Mixing the UF resin with catalyst and carrying out a degassing procedure, which is necessary for successful dry spinning, creates an unacceptable time delay, during which gelation of the catalyzed resin can occur. Teijin³ circumvented this prob-

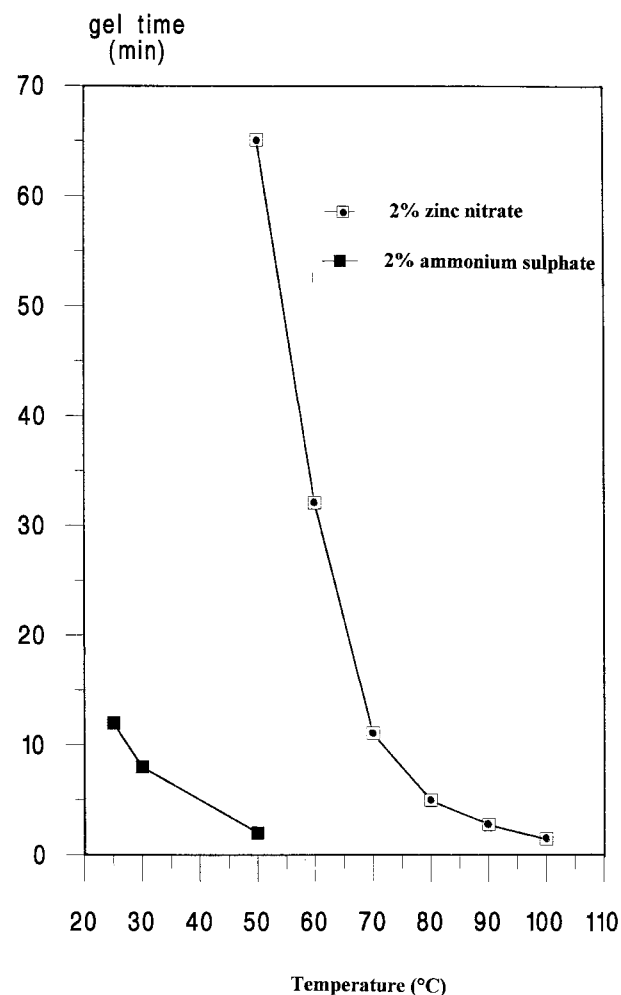


Figure 1 Gelation time versus temperature.

lem by concentrating the resin to a high viscosity and then using a screw extruder to feed the spinneret while injecting the catalyst simultaneously into the extruder. An alternative procedure, which was developed in the present work, is to premix the UF resin with a latent catalyst, degas the solution at low viscosity, and then allow the viscosity to increase to the required value for dry spinning before carrying out the extrusion.

Preparation of UF Spinning Solutions

The preparation of a UF spinning solution was a four-stage process consisting of (1) vacuum concentration of laboratory-synthesized or commercial aqueous resin to the required solids content and viscosity (generally 70–75% solids and 70–200 Pa · s), (2) addition of catalyst, (3) degassing the catalyzed solution, and (4) aging to the required viscosity for spinning.

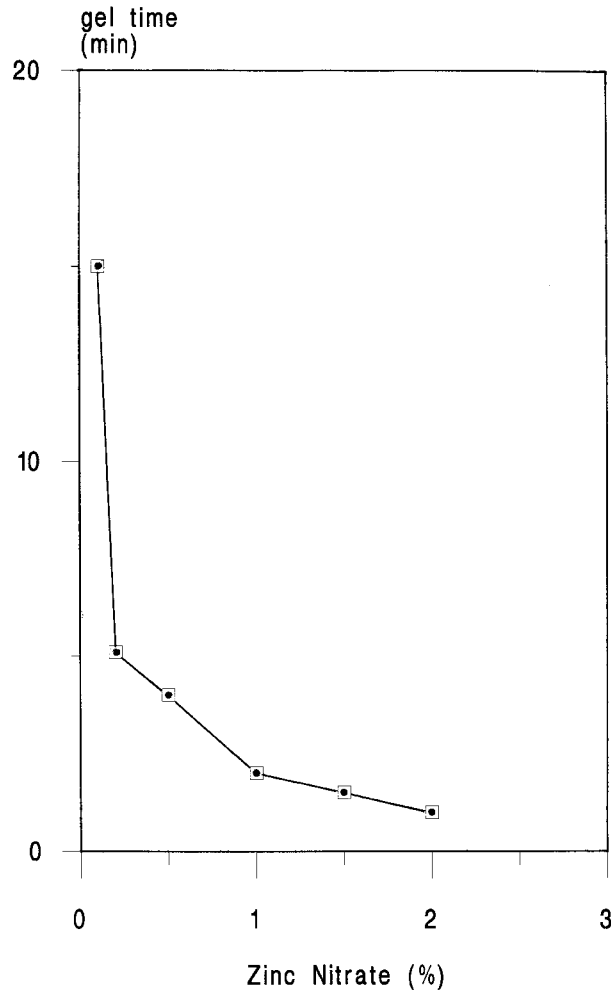


Figure 2 Gelation time at 100°C versus concentration of zinc nitrate in resin.

Vacuum Concentration

The initial viscosities of UF precondensates were usually in the range 10–20 Pa · s at 25°C. Typically, 5000 g resin was charged to a 5-L reaction kettle equipped for vacuum distillation and heated on a water bath to 70°C. Stirring and heating was then stopped, and distillation under vacuum was carried out until 200–250 mL distillate was collected (including distillate in CO₂-isopropanol cold traps). The solids content and viscosity of the resin at this point were generally 68–75 wt % and 70–200 Pa · s, respectively.

Catalyst Addition

Typically, 13.9 mL of a 40% w/v aqueous solution of zinc nitrate (62.8 g zinc nitrate hexahydrate in 100 mL distilled water) was added to 398.5 g resin

(69.7% solids) with high shear stirring to produce a spinning solution containing 2% (wt/wt resin solids) catalyst.

Degassing

The spinning solution was degassed by applying a vacuum for 30 min and then left to stand overnight in the spinning reservoir.

Resin Ageing

Catalyzed UF resins increase in viscosity with time (Fig. 3). Depending on the initial viscosity of the resin prior to addition of catalyst, this aging time is short or long. The viscosity just after addition of the catalyst is usually within the range 15–25 Pa · s. Within 30–60 h at room temperature the catalyzed resin reached a viscosity of 70–130 Pa · s, and spinning can be commenced when viscosities are at least 50 Pa · s. At viscos-

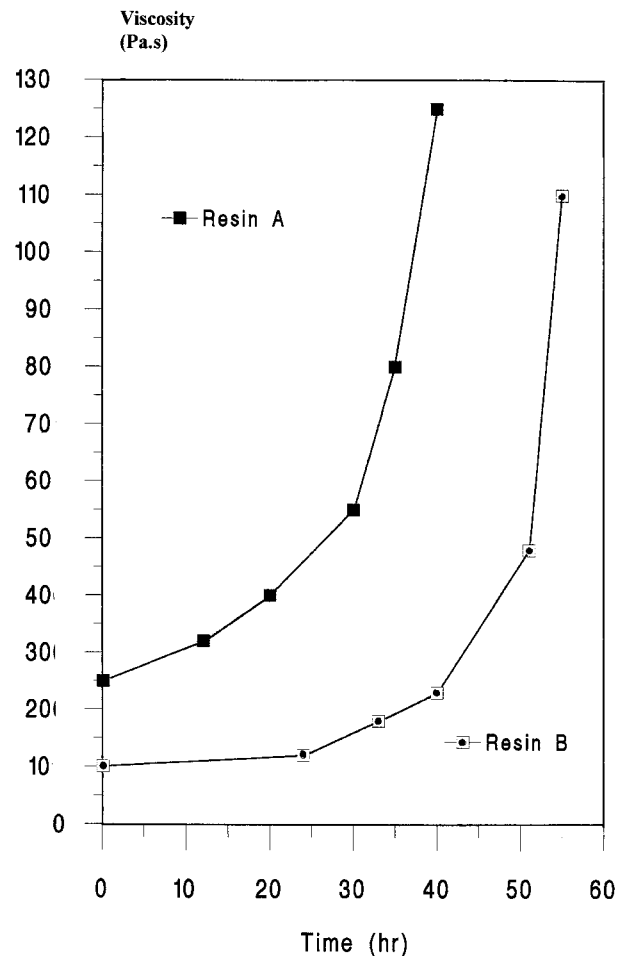


Figure 3 Aging of catalyzed resins at 21°C.

Table I Limits of Spinning Conditions for Production of Dry-Spun UF Fibers

Variable	Operation Range ^a	Optimum Range ^a
Spinning solution viscosity (21°C, 1.3 s ⁻¹ shear rate)	40–130 Pa · s	70–100 Pa · s
Linear extrusion rate	10–40 m/min	15–30 m/min
Cell temperature	130–250°C	180–200°C
Windup speed	100–600 m/min	250–600 m/min

^a Based on 10-hole 150- μm spinneret.

ities below 50 Pa · s, frequent spinning breakdowns are likely to occur.

Fiber Spinning

UF fibers were successfully spun using 10-hole spinnerets with hole diameters of either 90 μm or 150 μm . The viscosity of useful catalyzed and aged spinning solutions ranged from 40 to 130 Pa · s at 21°C. Viscosities outside this range caused spinning difficulties, and the optimum viscosity range (at which the lowest number of spinning breaks occurred and which gave the longest continuous spinning) was 70–100 Pa · s.

Linear extrusion rates used for the 10-hole, 150- μm spinneret were between 15 and 30 m/min and allowed continuous spinning for up to 4 h without any yarn breaks. At extrusion rates below this range, spinning breakdowns became frequent, and filaments were porous and weak.

Two complex processes take place in the heated drying cell: a dehydration process involving volatilization of water and unreacted formaldehyde and a gelation process that involves crosslinking (curing) reactions. Since these processes can be considered a first approximation of a practically simultaneous occurrence within the short dwell time of the extrudate in the heated cell (prior to windup), ideally both processes will be relatively complete within this period of time. For a given cell temperature, if the dwell time is too short, for example, as a result of a high solution extrusion rate, a coherent thread line may not be established because the extent of dehydration will be too low, and only discontinuous filaments will form. At low extrusion rates, a high drawdown will cause finer filaments to form, which dehydrate more rapidly before sufficient curing has taken place, and weak (and often porous) filaments are the result. The aim is to establish a careful balance of dehydration and curing processes, which will lead to continuous filament production of sufficient strength to allow winding and to carry out postspin curing treatments.

Spinning was attempted in the drying cell at cell temperatures between 130 and 250°C, keeping the cocurrent air flow rate between 7 and 12 liters (the air flow rate was kept low and relatively constant to avoid turbulence in the extrudate). At cell temperatures below 150°C, the filaments produced were wet to the touch and had low strengths and extensibilities so that they could not be wound up, while at cell temperatures above 210–220°C, the dehydration of filaments became too abrupt, the sudden “flashing off” of the solvent causing brittle and foamlike filaments.

The fibers were wound up directly below the drying cell on a bobbin winder. Fibers were produced using a range of spinning parameters, and it was found that production could be carried out only within certain limits of spinning conditions (Table I). Spinning solution viscosities below 38 Pa · s caused capillary breakdown of the extrudate, and viscosities in excess of 130 Pa · s produced excessive spinning pressures. The drying cell temperature was also critical, with the optimum temperature between 180 and 220°C. Outside this range there was an increased tendency for filaments to be insufficiently cured at lower temperatures, or foaming of filaments occurred because of too abrupt a dehydration at high temperatures; in both cases fibers could not be wound up. Within the optimum temperature range fibers could be wound up at speeds up to 600 m/min.

At the highest winding speeds, using a hole diameter of 90 μm , filaments of 10 μm in diameter could be obtained. The spin stretch (ratio of windup speed to linear extrusion rate) attained a maximum value of 30.

Heat Treatment of Fibers

Preliminary experiments showed that the mechanical properties of as-spun UF fibers could be significantly improved by further heat treatment. Fibers were loosely mounted on cards and heated

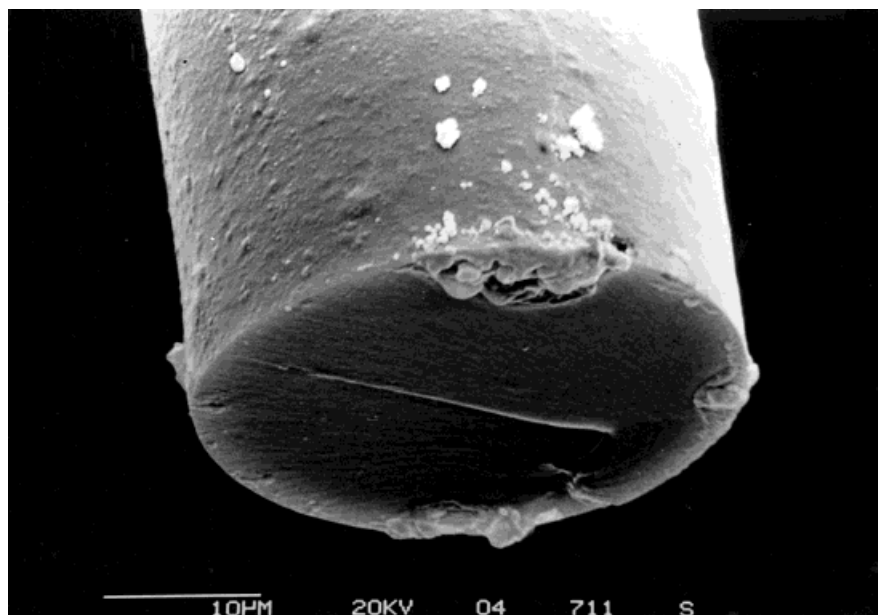


Figure 4 Transverse section of UF filaments.

in a relaxed state in a conventional oven for various combinations of temperature and time. Tensile testing was carried out after the cooling and conditioning the fibers.

Fiber Properties

General

The UF fibers produced were extremely lustrous in appearance and had a soft handle. Depending on the extrusion rate, spinneret hole diameter, and windup speed, UF fibers could be produced having diameters between 70 and 10 μm . Cross sections were circular (Fig. 4), which usually indicates that the surface evaporation rate is equal to or less than the diffusion rate of solvent from the centre of the filament to its surface. The situation here is rather more complex in that, apart from the process of solvent mass transfer, there is also a catalyzed crosslinking reaction occurring, which liberates formaldehyde and water. On application of a flame to a UF yarn, the filaments charred but then quickly self-extinguished on removal of the flame, leaving a white residue. The heat-treated fibers self-extinguished more quickly than the as-spun fibers.

Mechanical Properties

The tenacity of as-spun UF fibers was generally in the range 6–10.5 cN/tex, with elongation at

break of 5–6% and a modulus of 220–340 cN/tex. Postspin heat treatment of fibers improved tenacity and modulus, and the highest mean

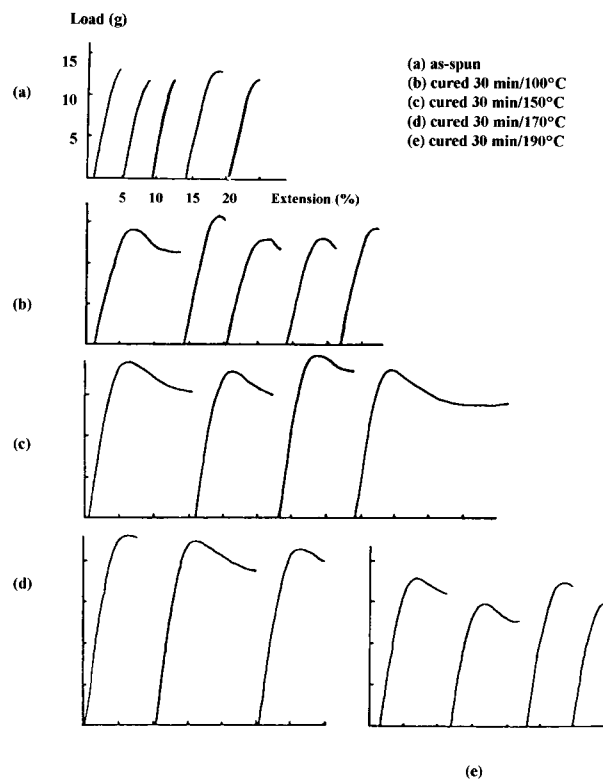


Figure 5 Typical load-extension curves for UF fibers.

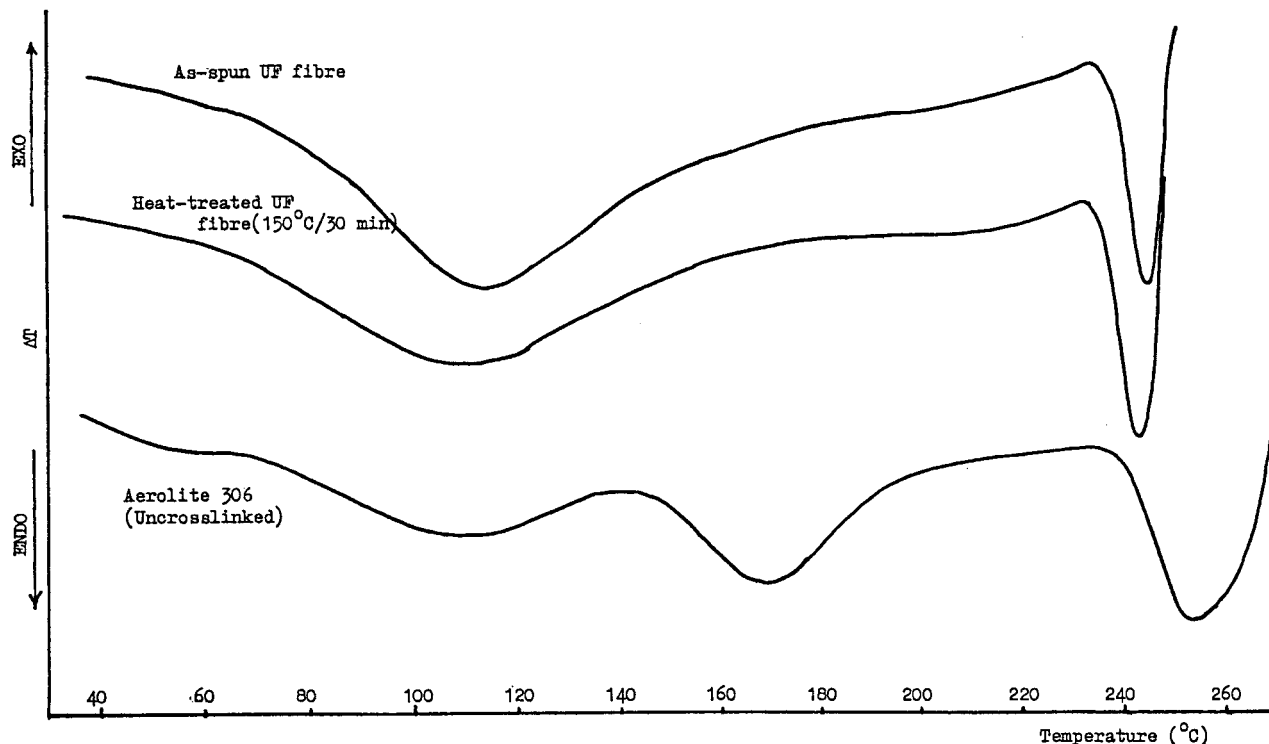


Figure 6 Typical DSC curves for UF fibers.

values of tenacity (14 cN/tex) and modulus (400 cN/tex) were achieved in fibers cured 15 min at 170–180°C. The overall improvement in properties, particularly extensibility, is illustrated in Figure 5.

It would be reasonable to expect that UF fibers would have a three dimensionally crosslinked structure, albeit imperfect, and that their mechanical properties would be substantially different from typical textile fibers. However, their relatively high extensibility (10–15% after heat treatment) suggests a behavior closer to that of natural and synthetic fibers rather than that of cured bulk resins. Typical load-extension curves of heat-treated fibers (Fig. 5) show, prior to rupture of the filament, a reversible elastic region up to about 3–4% elongation, followed by a yield point, an increased elongation with decreasing stress, and a period of elongation at constant stress without any sign of the onset of strain hardening. Birefringence values, although low (0.003–0.004), do indicate a low level of molecular orientation along the fiber axis. The observed increase in tenacity and elongation after heat treatment and the relatively high tensile strengths of UF fibers compared to UF-molded plastics suggest that the crosslink density of the UF fiber is low enough to permit plasticity in the network.

If heat treatment is considered to result in increased mobility of reactive groups, that is, primary and secondary amide and methylol groups, to sterically favored positions for further condensation reactions, an increase in tenacity could be expected. It is more difficult to account for the observed increase in elongation with postspin heat treatment, but if heat treatment reduces the extent of structural flaws and defects in the fiber by a process of annealing, an increase in elongation would be expected as a result of allowing the UF structure allowing restricted mobility between partly crosslinked molecules. Indeed, there may be room for inducing further molecular orientation and improving UF fiber properties.

Moisture Regain

Moisture regain was found to be in the range of 10–11%.

Thermal Properties

Typical DSC curves are shown in Figure 6. Although three main endotherms (112°C, 170°C, and 255°C) were present in uncrosslinked resin, every UF fiber sample showed only two distinct regions: the first at 100–110°C, which can be at-

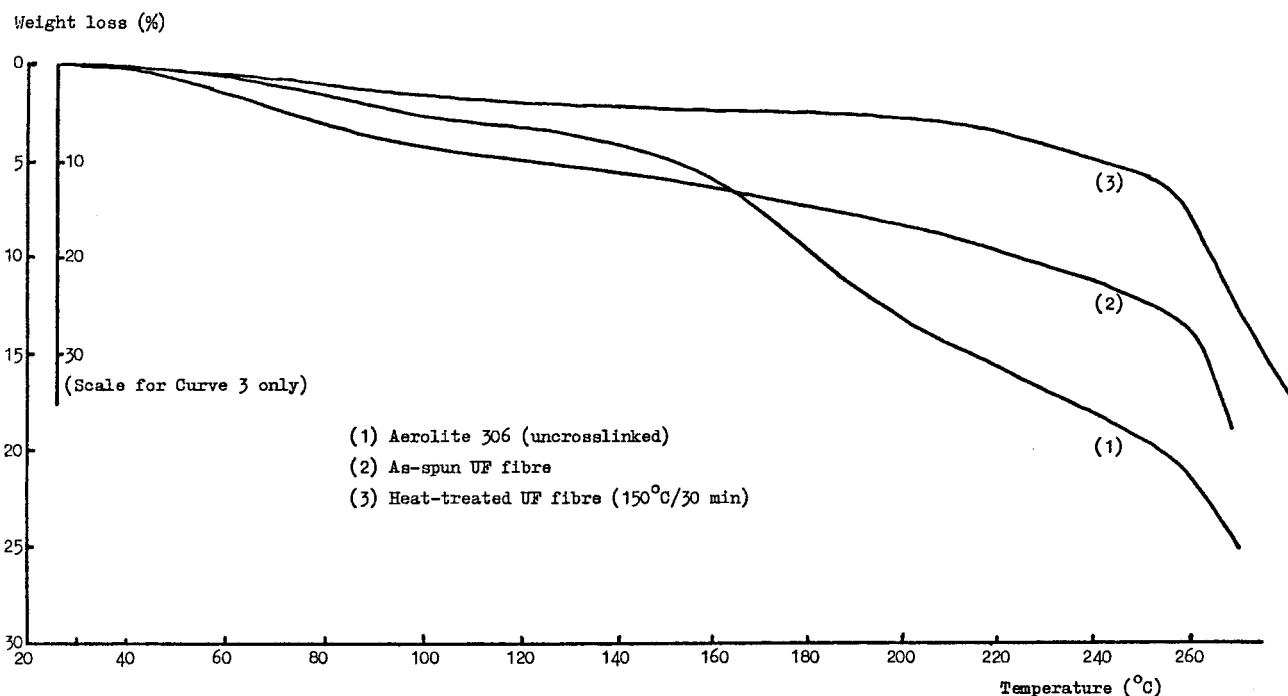


Figure 7 Typical TGA curves for UF fibers.

tributed to loss of volatiles, mostly water; and the second at 230–240°C, as a result of degradation reactions. However, it does not appear that DSC is particularly suitable for investigating UF fibers except in determining gross features, that is, whether the fiber was crosslinked or uncrosslinked.

TGA curves are shown in Figure 7. The curves appear to have four relatively distinct regions: (1)

an initial loss of volatiles at up to 100–105°C; (2) a relatively linear region of decreasing sample weight, which happens between 105 and 200°C; (3) an accelerating rate of weight loss occurring between 200 and 230°C; and (4) a steep degradative region, occurring above 230°C. In contrast to DSC measurements, TGA offers a potential for determining, albeit in an empirical and relatively simple way, the degree of cure or crosslinking of

Table II Percentage Weight Loss, Relative Weight Loss, and Tenacity of UF Fibers

Sample	Weight Loss (%) at 105–200°C	Relative Weight Loss (%)	Tenacity (cN/tex)
UF resin powder (uncrosslinked)	10.5	0	—
Gravity-spun UF filaments (no windup) at low temperature (130°C)	7.5	29	3.0
As above, given additional heat treatment (130°C)	5.4	49	6.8
Fiber spun at 190°C wound at 250 m/min 250 m/min winding speed + heat treatment (30 min/170°C)	3.6	66	7.5
As above, +90 min 170°C heat treatment	1.4	87	11
Fiber spun at 190°C heat treatment and 400 m/min winding speed	0.9	91	13
400 m/min winding speed + heat treatment 30 min/170°C	3.4	68	8.7
	1.5	86	11

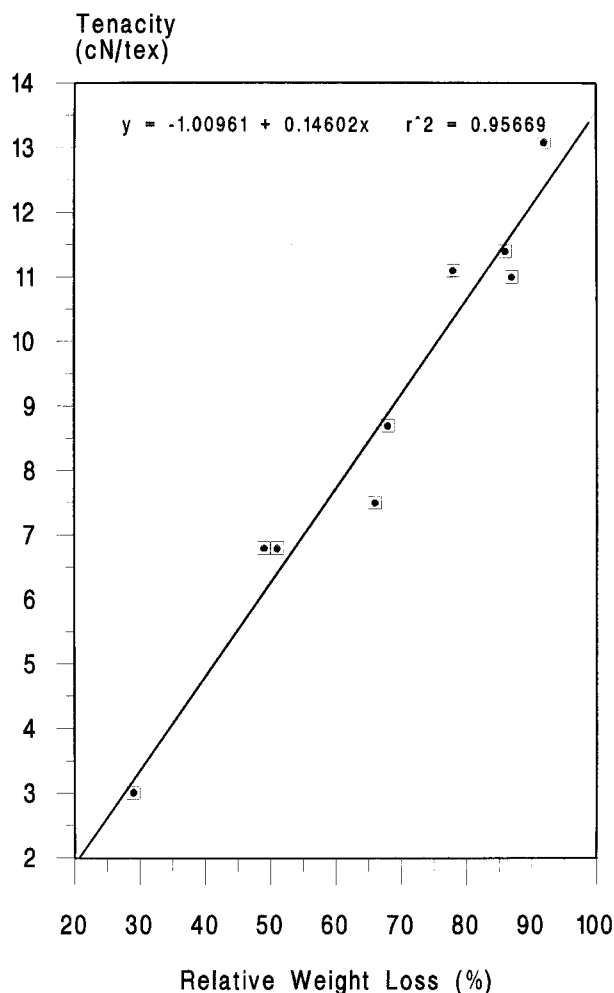


Figure 8 Tenacity versus relative weight loss at 105–200°C.

the fiber. Thus Table II shows the percentage weight loss between 105 and 200°C for a range of samples selected from uncrosslinked UF resin (0% cure) to heat-treated fibers at various degrees of cure. The calculation of relative weight loss, defined as [(weight loss of uncrosslinked resin-weight loss of sample)/weight loss uncrosslinked sample] \times 100%, can be used as a measure of degree of cure and was found to be related to the fiber tenacity (Fig. 8).

X-ray Diffraction and Fiber Surface Characteristics

Examination of as-spun fiber samples indicated typically amorphous structures, and differences between samples produced at different stretch ratios could not be detected from the X-ray diffraction patterns. SEM pictures of the fiber surfaces showed no sign of microcracks such as com-

monly occur in cured bulk UF resins due to repeated absorption and desorption of water, but they did reveal minor surface inhomogeneities that could possibly have arisen from submicron gel particles present in the solutions of the resins employed.

The fibers fractured in typical brittle fashion; occasionally, particles or voids were present at the fracture surface, which no doubt acted as a location for points of initiation, since such samples exhibited much lower extension at break. Examination of the fracture faces by energy dispersive X-ray microanalysis showed that the zinc content was similar across the fracture surface and in particulate inclusions, so deposits arising from the catalyst were not responsible for fracture initiation.

CONCLUSIONS

- Continuous filament UF yarns can be produced by dry-spinning a catalyzed aqueous UF precondensate into a heated cell at 180–200°C, producing filament diameters down to 10 μm (1.2 dtex) at wind-up speeds of up to 600 m/min.
- Zinc nitrate is a useful catalyst, possessing low activity at ambient conditions yet high activity at cell and curing temperatures.
- Postspin curing of the yarns at 170–180°C increases fiber tenacity and elongation at break.
- The best single-filament properties obtained by this process are a tenacity of 14 cN/tex, a modulus of 400 cN/tex, and an elongation of 20%.
- The tenacity of fibers can be correlated with the degree of cure, measured thermogravimetrically.

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