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Production and Characterization of Textile Fibers Made from Intrinsically Conductive Polymers.

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General Introduction:

The development of a conductive fiber produced from an inherently conductive polymer (ICP) polyaniline (**PANI**) was accomplished during this the third year of our National Textile Center funding. This goal accomplished the stated mission of the research effort. The fiber produced has tensile properties approaching that of nylon 6 and a conductivity of around 350 S/cm. This achievement has led to worldwide recognition of our research efforts and has resulted in our being invited to several national and international conferences to present our work. Notable among these was the "International Conference on the Science and Technology of Synthetic Metals" ICSM 94 in Seoul Korea in July of 94 and the Symposia on Conductive and Conjugated Organic Solid State Polymers at the 201st national meeting of the American Chemical Society in San Diego in April of 94. We have also published six papers over the course of this year with regard to the production and characterization of conductive polymers. The research into these unique materials is continuing and technology transfer to interested industries is underway. Present industrial contacts include Hoechst Celanese, Granitville, Monsanto Fibers, Allied Signal, Milliken & Co., Walter Reed Army Hospital, Shaw Carpets, and several other fiber and textile producers. At the present time seven graduate students are pursuing degrees in the area of conductive polymers and fibers and two degrees (one **M.S.** & one Ph.D) have been awarded resulting from this area of work. As a direct result of the NTC effort collaborative efforts have been established with faculty from Ga. Tech, N.C. State, and other major universities around the country not associated directly with textiles and fiber science and engineering. Recently in recognition of our contributions our research group has been asked to contribute to the new addition of "The Handbook of Conductive Polymers". The **first** edition is one of the most cited references in the area of solid state organic and magnetic polymers and the second edition will be even more extensively quoted and contain our contribution on ICP fibers.

Year 3 Introduction:

One of the more, interesting conductive polymers from a processability standpoint is polyaniline (**PANI**) due to its solubility in its base form and the environmental stability of the conducting state once the base is doped. This ICP has seen commercial applications as electrodes in batteries as well as other novel applications such as biosensors, remote sensors, smart windows, etc.. While novel applications continue to grow, the notable exception is the feasible production **of** pure **PANI** fibers. Other **ICPs** have been produced that can be processed into fibers, such as the polythiophene derivatives, but the synthesis of the monomers is expensive and

may prove to be cost prohibitive to large scale production. The purpose of the research efforts in our applications laboratory is to develop a technique to process **PANI** into a filament form on a large scale using standard spinning technologies used in the production of textile fibers.

Originally, **PANI** was considered to be intractable from a processing point of view as most of the other environmentally stable **ICPs**. However, articles of films and fibers have recently been processed from PANI solutions since reports indicating that the **PANI** base form readily dissolves in N-methyl-2-pyrrolidinone (**NMP**) [1]. Recent studies carried out in this laboratory, and by **MacDiarmid** group at the University of Pennsylvania, demonstrate that a solution of **PANI** in NMP greater than 6% or so rapidly gels [2,3]. Further studies indicate that the application of thermal or mechanical stress accelerates this process. Since standard wet spinning of fiber usually requires a spin bath concentration of 15 to 20 percent the gelation process substantially limits the formation of fiber filaments. As reported recently the addition of lithium chloride (**LiCl**) reduces the formation of **coagulants** in the solution but does not effectively moderate the gelation process [3]. Recently Han and co-workers reported that some Lewis-base organic solvents have a better solvency than NMP for **PANI** [4]. Cohen and co-workers successfully spun fibers from concentrated solutions (20%) using basic solvents such as 1,4 diaminocyclohexane and 1,5 diazabicyclo(4.3.0)non-5-ene but the solution is very sensitive to the shear rates applied during the mixing process [5]. We have found that the solvent **N,N'-dimethyl (DMPU)w/wtPANI** 20% not sensitive to the nor encountered in wet spinning and is stable to the gelation process over a much greater length of time than NMP or for that matter **NMP/LiCl**, a solvent system often used to stabilize wet spin baths.

In this study the stabilities of concentrated **PANINMP/LiCl**, and **DMPU** are compared by monitoring the viscosity changes with time based on solution concentration. Spinnability of concentrated solutions are evaluated in terms of their rheologies and the results are used to predict spin bath parameters.

Experimental

Synthesis of Polyaniline

Polyaniline salt was synthesized by the polymerization of aniline monomer (.5M) with **MacDiarmid et al** [6]. **PANIPANI** salt in a 3NH₄OH solution for 8 hours. The recovered product was washed in acetone and dried under vacuum for 8 hrs. at 60°C. No effort was made to control the final oxidation state or the molecular weight distribution of the PANI base. The polydispersity of the PANI base was not measured in this initial study.

Rheological measurements

Solutions for the determination of viscosities were prepared by dissolving known amount of PANI base in NMP, .5wt% LiCl in NMP, and in DMPU. The mixtures were stirred for thirty

minutes under low shear and then passed through a **25-mm** glass fiber filter (pore size 2.7 μm) by syringe prior to transferring to a rheometer cell. Viscosities were recorded using a Brookfield HADV-III cone/plate rheometer with controlled cell temperature. A cone spindle with a cone angle of 0.8" was employed for the measurements.

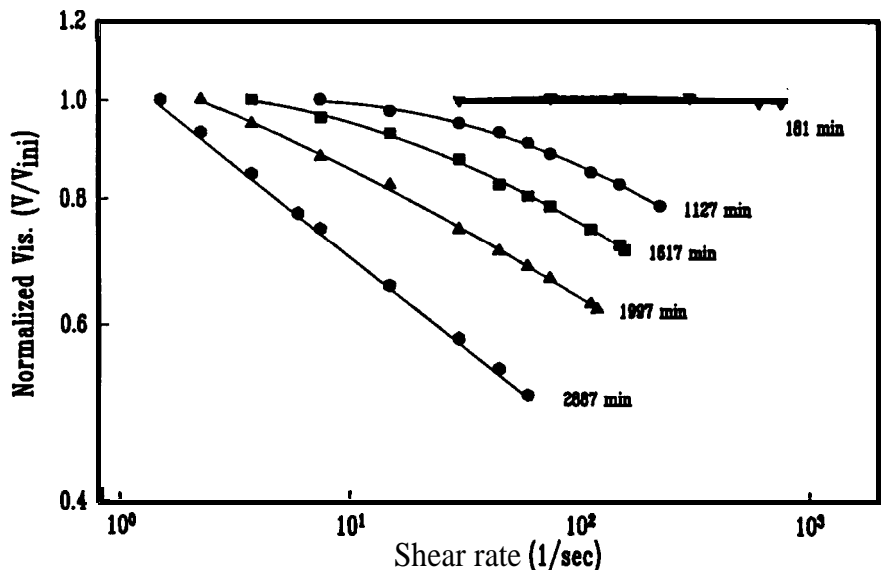
Fiber spinning

Fiber was spun through a stainless steel spin cell (30ml) driven by a HPLC grade pump. The spinnerette used in the fiber spinning produced 3 filaments using a hole diameter of **.004"** with a L/D ratio of **2/1**. No compensator was used in the spinnerette.

Results and Discussion

Stabilities of concentrated PANI solutions

In order to determine the behavior of a 6% **PANI** base solution in NMP, and to investigate the differing **rheological** behavior of aged solutions, the normalized shear viscosities versus shear rate was determined using a cone/plate rheometer. The results are shown in Fig. 1.



PANI/NMP normalized viscosities vs. shear rates of a 6 wt%

6 % PANI/NMP solution aged for 181 min. behaves as a Newtonian fluid and follows the general Newtonian relation in equation 1.

Eq. (1)

$$\tau_{yx} = \mu \frac{dU_x}{dy}$$

Where:

$$\begin{aligned} \tau_{x,y} &= \text{shear stress} \\ \mu &= \text{fluid viscosity} \\ dU_x/dy &= \text{gradient of the x component of velocity in the y direction} \end{aligned}$$

We observe however that ageing for a longer period of time results in a deviation from Newtonian behavior and finally in the solution aged for 2887 min. we **find** the **PANI/NMP** solution having the **rheological** behavior of a power law fluid obeying the general power law form as shown in equation 2.

Eq. (2)

$$\tau_{yx} = k \left(\frac{dU_{yx}}{dy} \right)^n$$

$$\begin{aligned} \tau_{yx} &= \\ -k &= \text{proportionality constant relating shear stress} \\ & \text{to the } n^{\text{th}} \text{ power of the shear rate} \\ dU_{yx}/dy &= \text{gradient of velocity component in y direction} \end{aligned}$$

This behavior indicates that these solutions will behave initially as a Newtonian fluid when fresh but deviate to a non-Newtonian fluid with the passage of time. Since the fluid is in a state of flux, spinning a fiber with consistency over an extended period of time would prove difficult.

Observing the viscosity changes over a period of time is a useful way study the solution stabilities and determine which solvents provide a “window of opportunity” from which to spin fiber. Fig. 2 shows the plots of the normalized viscosities vs. time for a **6%, 8%**, and a **10% wt/wt** solution of **PANI** in NMP.

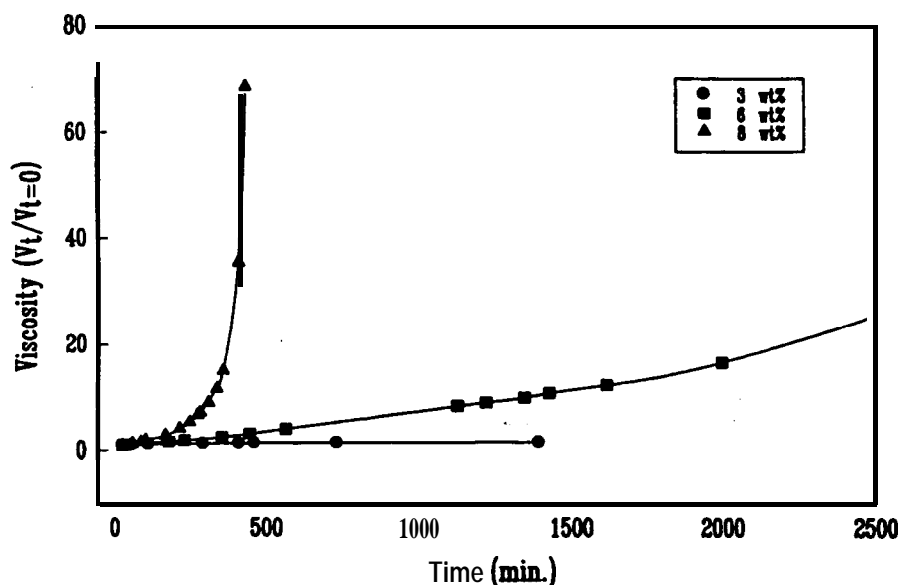


Fig. 2 Normalized viscosities vs time of **PANI/NMP** solutions at 3 wt%, 6 wt.%, and 8 wt.% at 25°C; $\eta_{t=0}$ is the viscosity at time equals 0.

At a concentration of 6% the viscosity does not significantly change with time. However at higher concentrations the viscosities change dramatically. Fig. 3 shows similar concentrations of **PANI** in NMP but in this case **.5% wt/wt LiCl** has been added to the NMP solution. It clearly shows that the increase in viscosity is slowed but is still unacceptable for spin purposes at a concentration of 10%. In Fig. 4 a similar plot as Figs. 2 & 3, but at higher concentrations and using DMPU as the solvent, demonstrates a much higher solution stability and in fact a 10% solution is stable to viscosity and gelation for over 2500 minutes.

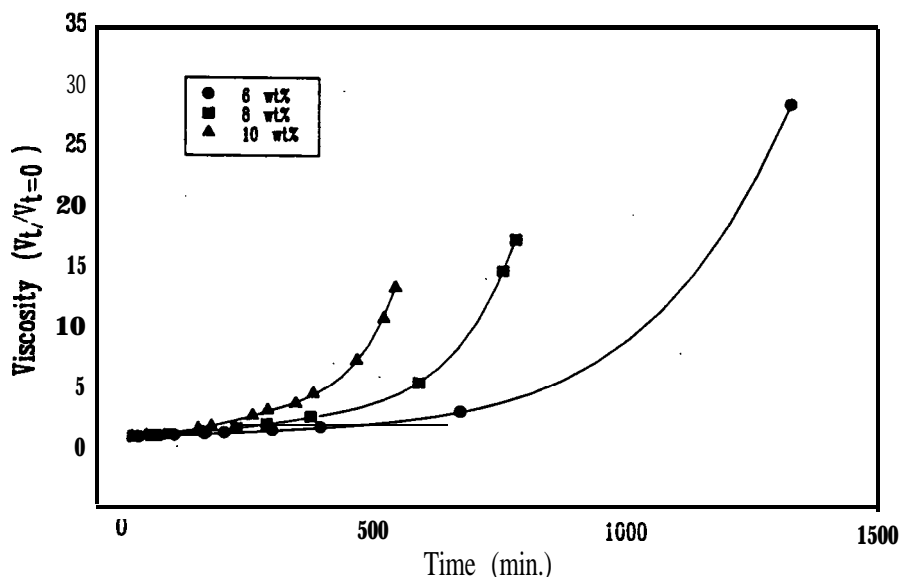


Fig. 3 Normalized viscosities vs time of **PANI** solutions in 0.5 wt% **LiCl/NMP** at concentrations of 6, 8, and 10 wt% at 25°C

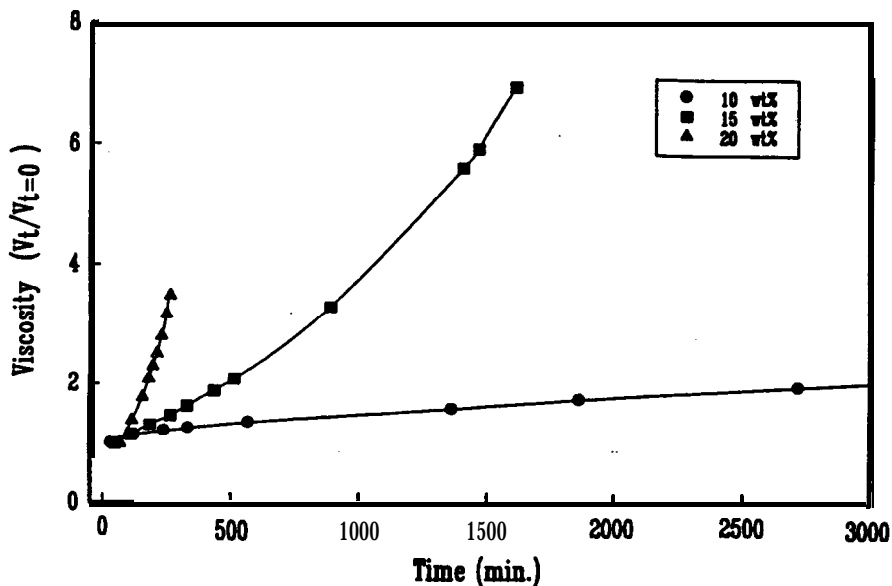


Fig. 4 Normalized viscosities vs time of PANI/DMPU solutions at concentrations of 10, 15, and 20 wt.% at 25°C.

Even at the higher concentration of 20 % the viscosity has only increased by a factor of four whereas a 10% PANI/NMP solution has increased by a factor of 75 as shown in Fig.2. Fig. 5 compares solutions of 8% PANI/NMP, 8% PANI/NMP/LiCl, and 10% PANI/DMPU. It clearly shows that the PANI/NMP solution is not as stable as the PANI/NMP/LiCl solution but neither of these is comparable to the PANI/DMPU solution. A 10% solution is essentially the lower limit for solution spinning of fiber with 15% to 20% being the norm. As can be seen DMPU provides a suitable spin bath for the production of PANI fibers.

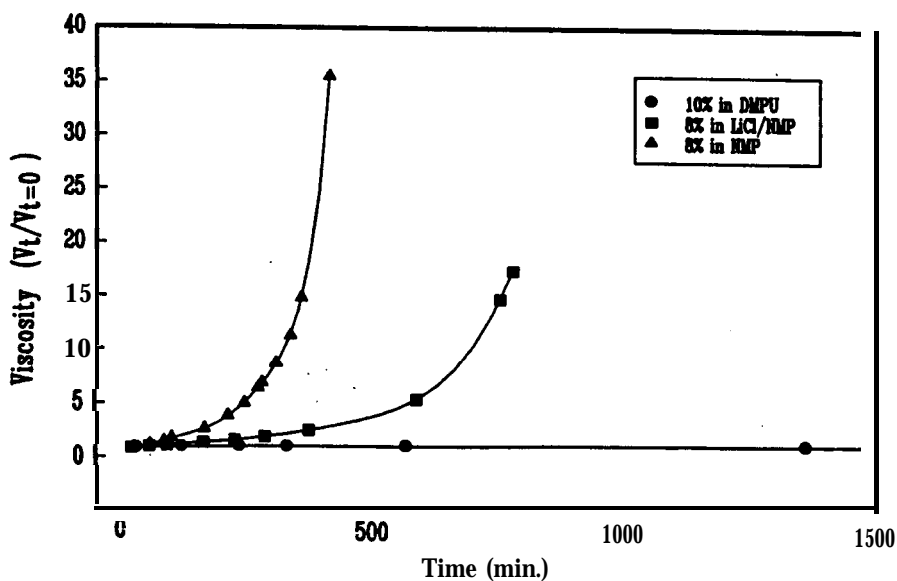


Fig.5 Normalized viscosities vs time of PANI solutions in NMP (8 wt.%), 0.5 wt% LiCl/NMP (8 wt.%), and DMPU (10 wt.%).

PANI filaments spun into a coagulation bath containing 50% DMPU and 50% water are drawn and doped in a separate hot draw bath. Residence time in the coagulation bath is of critical importance in order to minimize void spaces and subsequent mechanical stresses in the filament. The high boiling point of DMPU (146°C @ 44mm/Hg) presents a problem regarding solvent removal. We find however little evidence of remaining spin solvent in the fiber after the hot draw and dope bath indicating that most of the solvent is removed during the orientation and doping process.

A similar solvent, tetra methyl urea (TMU), with a boiling point of 177°C at ambient temperature may eventually replace DMPU as the spin bath solvent due to easier solvent removal and recovery. As in the case of Nylon, initial studies indicate that water may in fact be acting as a plasticizer for PANI gels doped with methane sulfonic acid. We have found that methane sulfonic acid (MESO₃) used as a dopant in the draw bath provides a good level of conductivity approaching 350 S/cm. This dopant was discussed in a previously reported paper from our laboratory concerning PANI gels as was the effect of water as a plasticizer [2,7]. Substantially higher levels of conductance have also been achieved using TMU and MESO₃ and will be reported once all studies are complete on the draw and dope bath using this solvent.

Conclusion

DMPU seems to be a good candidate for a spin bath solvent for the production of PANI fibers. It is significantly better than the commonly used NMP or NMP/LiCl solvents with regard to solution stability. The solution viscosities of PANI/NMP, PANI/NMP/LiCl, and DMPU all have a tendency to increase with time. However PANI/DMPU solution is the most stable with a significant spin window. Rheological properties of these solutions also change with time deviating from Newtonian behavior at low concentrations to power law fluids at higher concentrations demonstrating typical shear dependency. PANI/DMPU provides a window for spinning of PANI fiber which when doped has the mechanical properties approaching that of Nylon 6. Exact configuration of the spin line and bath parameters is currently being investigated along with morphological studies of PANI fibers produced under different thermodynamic conditions. Threadline mechanics is an active area of study and the effect of drawing, take up speed, Godet heating, etc. is presently being studied and the results will be reported in a timely manner. Additionally we are presently developing a set of constitutive equations concerning mass balance and momentum considerations for the production of PANI filaments employing wet spinning methods. Fibers spun from DMPU, according to the previously described method, are presently being aged by both accelerated aging methods commonly used in testing textile fibers and also by simply allowing the fiber to experience changing conditions (temperature, relative humidity, etc.) day to day on the bench top. These fibers will be examined for morphological changes and electrical stability over extended periods of time.

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Although **PANI** fibers may not prove as versatile as some of the other conductive filaments their low cost and relative ease of production due primarily to the availability of the starting monomer, will certainly lead to immediate industrial applications. We believe that existing spin technologies developed primarily for the production of Acrylics and other generic filaments, as well as those more sophisticated methods utilized to spin PAN fibers etc., can be adapted to the large scale production of **PANI** fibers once proper solvents and spin parameters are determined.

Our initial works leads us to believe that we have only begun to **find** the necessary conditions for the production of true “plastic wires”. Experimental results by our laboratory as well as those of others suggest that levels of conductivity approaching or even surpassing copper metal might be possible. With continued work in the area of processing coupled with a fundamental understanding of conduction mechanisms highly conductive filaments with unique electronic and optical signatures will be commercialized using existing textile fiber technologies.

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