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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 processabilty 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 MacDiarmids 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 propylene urea (DMPU) containing 20% w/w PANI is not sensitive to the normal shears 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 PANI solutions in NMP, NMP/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 ammonium persulfate as the oxidant (0.5M) in a 2M HCl aqueous solution at -2°C according to a method previously described by MacDiarmid et al [6]. The neutral emeraldene base form of PANI was obtained by dedoping the PANI salt in a 3 wt % NH_4OH 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 um) 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.

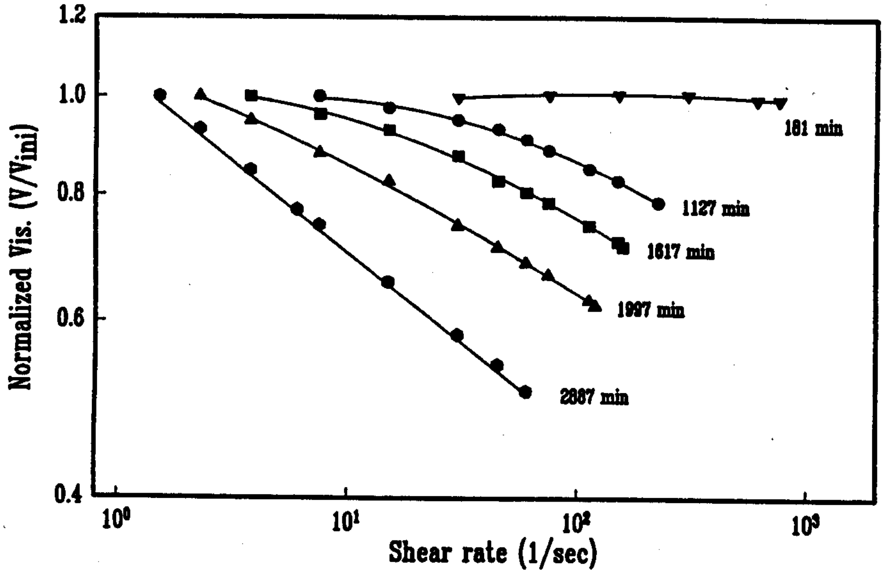

Fig. 1 Normalized viscosities vs. shear rates of a 6 wt% PANI/NMP solution at different aging times.

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

Eq. (1)

$$\tau_{y,x} = -\mu \frac{dU_x}{dy}$$

Where:

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

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)

$$\tau_{y,x} = -k\left(\frac{dU_{y,x}}{dy}\right)^n$$

Where:

$\tau_{y,x}$ = shear stress
$-k$ = proportionality constant relating shear stress to the n^{th} power of the shear rate
$dU_{y,x}/dy$ = gradient of velocity component in y direction

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.

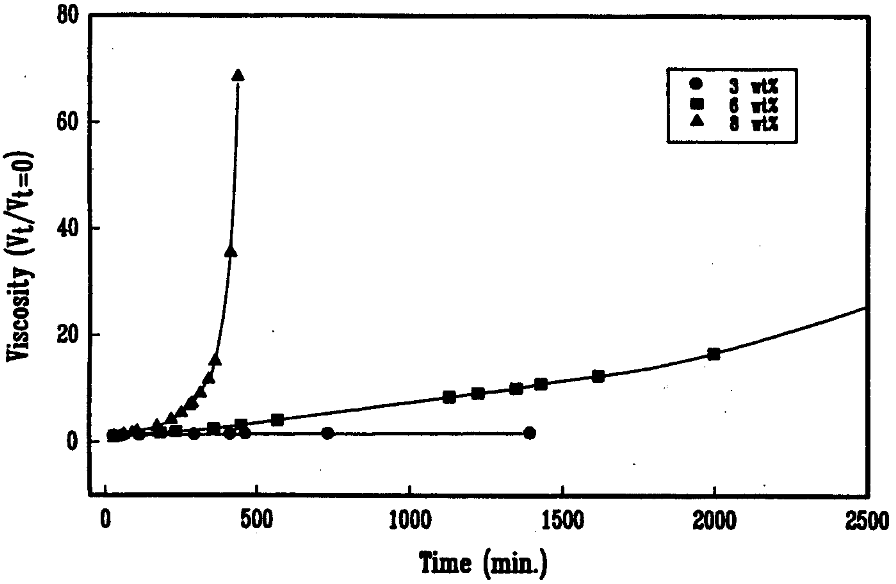

Fig. 2 Normalized viscosities vs time of PANI/NMP solutions at 3 wt%, 6 wt.%, and 8 wt.% at 25°C; $\eta_{t=0}$ is the viscosity at time equals 0.

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.

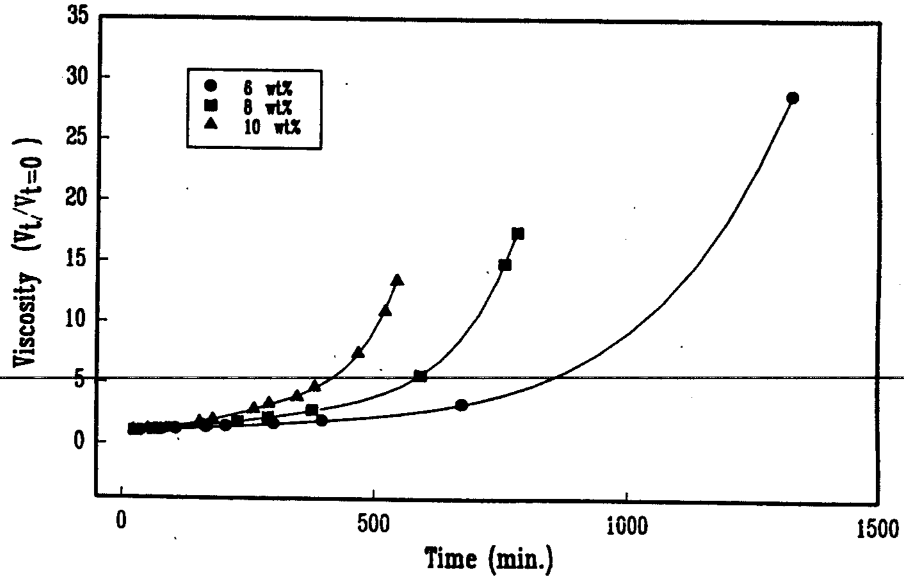

Fig. 3 Normalized viscosities vs time of PANI solutions in 0.5 wt% LiCl/NMP at concentrations of 6, 8, and 10 wt% at 25°C

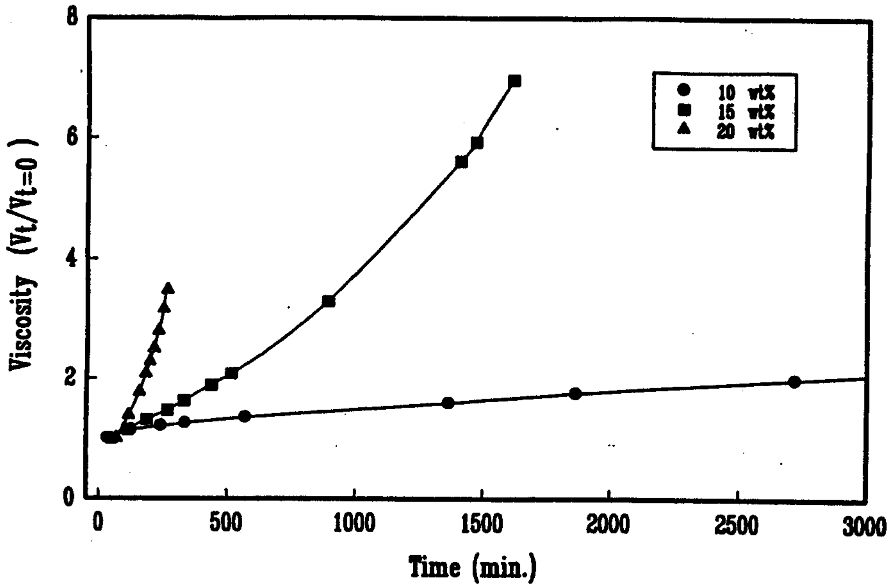

Fig. 4 Normalized viscosities vs time of PANI/DMPU solutions at concentrations of 10, 15, and 20 wt.% at 25°C.

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.

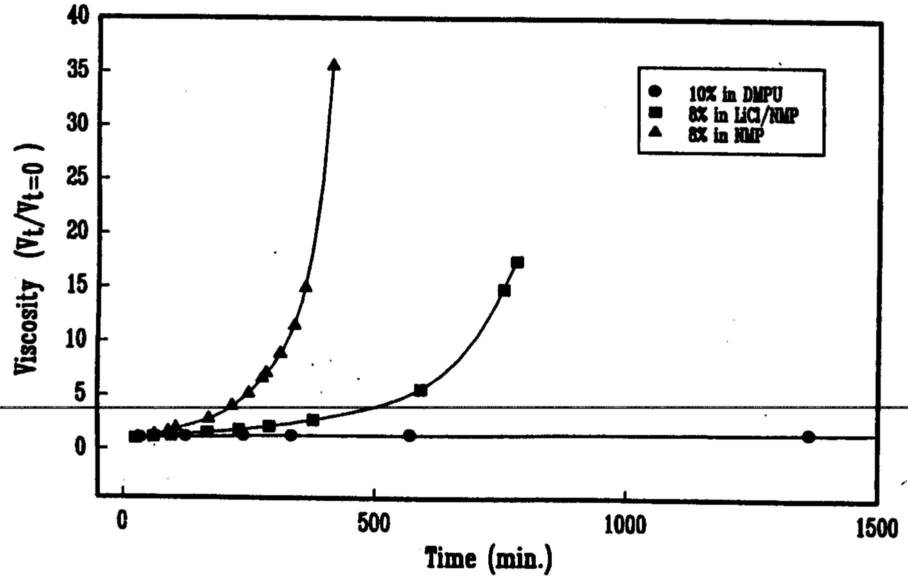

Fig.5 Normalized viscosities vs time of PANI solutions in NMP (8 wt.%), 0.5 wt% LiCl/NMP (8 wt.%), and DMPU (10 wt.%).

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 ($MESO_3$) 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 $MESO_3$ 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.

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

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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C93-8

TITLE: Chaos in Polymer Phase Transitions

PI(s): Michael S. Ellison, Clemson University
Maureen Campbell, Graduate Student

Introduction

As experimental work progresses, the goal often changes. So it has been with this project. While the underlying motivation for our activities remains an examination of the role that Chaos Theory may play in observed transition behavior of polymers, the focus of our work has shifted in the past few months. We were originally exploring the edges of Chaos for a deeper understanding of the origins of the glass transition. We began by using powerful numerical analysis programs which enabled us to perform a phase space analysis of the traditional non-linear mathematical models of viscoelastic behavior. Chaos was not found in these models. We then looked to applications of traditional thermal analysis instrumentation, with a phase space representation of the raw data. Commercial instruments generally are not easily amenable to this data analysis. With some assistance from contacts at ONR and the Ga Tech Physics department[1], software was obtained which enabled our analysis to proceed. We are presently finding that these data analysis and presentation tools, which are so powerful in many branches of the physical sciences, are providing us with potentially very rewarding insights into the interplay of polymer fine structure and thermal transition behavior. The potential for a chaotic underpinning to polymer thermal transitions remains elusive, albeit possible.

Experimental

The two analytical techniques chosen for our analyses were Thermally Stimulated Current (TSC) and Modulated Differential Scanning Calorimetry (M-DSC). In TSC experiments the sample is polarized by a high voltage, static electric field at an elevated temperature, for a specified time, after which the temperature is rapidly lowered. The electric field is then turned off. The temperature is subsequently raised at a controlled rate, and the relaxation of the induced polarization causes a current in the external circuit. The measurement of this current as a function of temperature, a "TSC plot", provides information about the molecular relaxations occurring in the material.[2]

Modulated-Differential Scanning Calorimetry utilizes an oscillating temperature ramp and measures the total heat flow associated with the system. It enables separation of the heat flow into its reversible and non-reversible components. Reversible heat flow is the work added to the system as the temperature increases and is directly related to the heat capacity. Nonreversible heat flow is the kinetic portion of the heat flow. The nonreversible portion is related to the magnitude of non-equilibrium thermal processes such as cold crystallization and thermo-oxidative reactions.[3] This technique will be discussed in the concluding work section.

Methods

Careful sample preparation is essential in TSC experiments. Since electrical conductivity of a material is comprised of surface as well as volume (bulk) contributions, we removed the residual surface contaminants from the polymer pellets, using Freon. When dry, the sample ends were leveled and copper wire electrodes were attached to each end of the pellet with silver paint. The conductivity of these samples should now be mostly dependent on the state of the material; the current should now course evenly through the polymer, instead of along the surface.

The testing parameters for the TSC experiments were chosen according to the glass transition temperature of the polymer. The sample was heated to a polarization temperature 5 °C above its nominal T_g. All the samples were subsequently cooled to 0 °C using either quench cooling, in the case of PAN, or a controlled cooling rate of 20 °C/min and the polarization field was removed. A five minute stabilization period was maintained. The samples were then heated at 7 °C/min to approximately 20 °C below their reported melting temperature or reported decomposition temperature. The current passing through the polymer was recorded for only the final heating period. Temperature and current data were obtained from this set of experiments.

Data Analysis

The data was analyzed using time delayed coordinate embedding techniques which often are used to examine data for chaotic behavior. This technique involves the displacement of the time series data by a shift factor larger than or equal to one and then replotting the shifted data against the original data set.[1,8] This method enables construction of an analog to the classical (two-dimensional) phase space in which one dynamical variable is plotted against its derivative. This forms a pseudo phase space portrait of the time series data that can allow hidden attractors to be detected.[6]

The concept of a phase space is best explained using the simple pendulum as a model.

Simple Pendulum

The normal mathematical description of the simple pendulum is linearized so as to enable an analytical solution to the equation. The result is then the concept of simple harmonic motion (SHM) which is then exploited for understanding phenomena ranging from sound to quantum wave functions. The same approach lends itself to understanding chaotic dynamics[10].

In the small-amplitude approximation to the simple pendulum, the restoring force term dependence is linearized to q. With time measured in units of the inverse of the natural frequency, the equation of motion is

$$\frac{d^2q}{dt^2} + q = 0 \qquad (2)$$

Incorporating the angular velocity variable

$$w = \frac{dq}{dt} \qquad (3)$$

the second order equation reduces to two first order equations

$$\frac{dw}{dt} = -q$$

and (4)

$$\frac{dq}{dt} = w$$

With appropriate initial conditions, the solution becomes

$$q = a_i\cos(wt)$$

and (5)

$$w = a_i\sin(wt)$$

These equations provide the parametric curves for w and q. Eliminating t gives the phase space diagram for the SHM of the linearized pendulum (Figure 1).

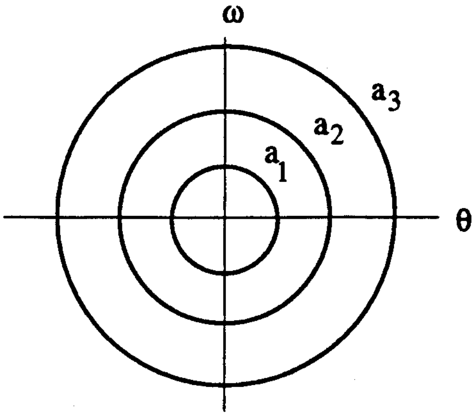


Figure 1. Periodic Phase Space Trajectories

Several features of phase space may be gleaned from this simple example. The concentric circles, the trajectories in the phase space, correspond to different energies of the system. The fact that they are closed loops follows from the periodicity of the motion: fully closed trajectories occur only when the system returns to a particular state. Two trajectories never cross, for if they did, the time evolution of the system would be indeterminate. For conservative systems, area in phase space is preserved as the system evolves.

There are three classic types of dynamical motion that can be found in the phase space of a system: equilibrium, periodic and quasiperiodic.[4] The system is in equilibrium when the phase space shows one stable point in the system toward which all other points tend. This point is referred to as a fixed point.[4]

Fixed points are important when studying dynamic systems because they represent persistent behavior. But when characterizing the long-term behavior of chaotic systems, it is necessary to find and account for those points which form an attracting set. This type of recurrent behavior is termed nonwandering behavior. Transient behavior is characterized by wandering points (Figure 2).

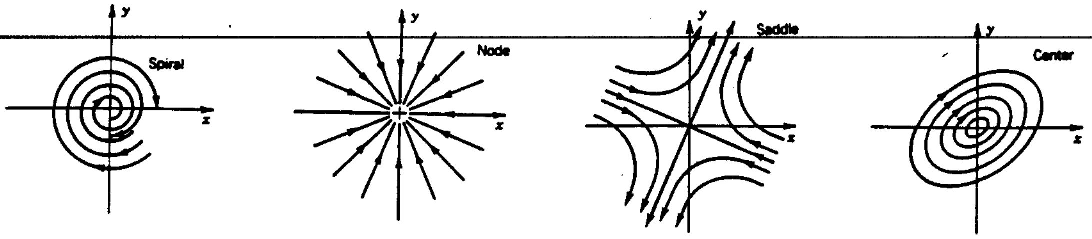


Figure 2.· Classical phase plane portraits near four different types of equilibrium[4]

Periodic motion in real systems is represented in the form of limit cycles. Truly periodic motion occurs when the motion of the system is found to circle a point in a phase space (Figure 3).

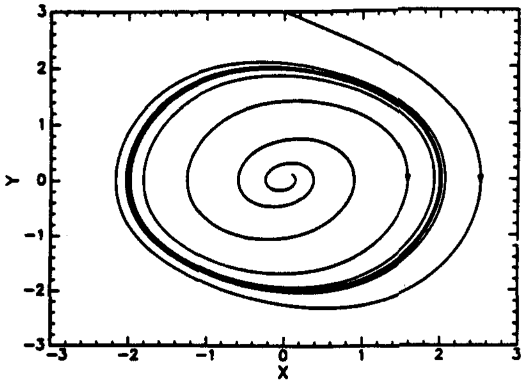


Figure 3. Limit Cycle[4]

Quasiperiodic motion, when the motion is almost periodic, results in complex phase space plots.

Equilibrium, periodic and quasiperiodic motion are all forms of attractors the reason being that when the transients decay, the system is attracted to these states.[6] There is also another class of motion that can occur: chaos. The attractor that corresponds to this state is called a strange attractor.[6]

Materials

Several polymers were chosen for the study. We found, upon examination of the TSC phase space portraits for these polymers, that the materials used in these experiments fell into two distinct categories. The polymers were grouped into these categories because of topological differences in their phase space. The polymers in category 1 generally produced a wholly open circle in the phase space, while category 2 polymers had only a small circular portion in the phase space with two straight lines emanating from the circle.

Category 1 contained polymers with pendant groups that were prepared from vinyl polymers. This category contains four polymers: polyacrylonitrile (PAN), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVC).

The polymers in category 2 have no side groups attached and have backbones which contain large aromatic repeat units. The polymers in this group are poly(ethylene terephthalate) (PET), polycarbonate (PC), poly(ether sulfone) (PES), and Nomex. We have not yet obtained data for the Nomex and the PES. They were placed in this group because they contain at least one aromatic ring in their backbone, and we presume that the aromaticity of the PES and Nomex will produce a topology in the phase space similar to that of the other polymers in this group.

Results and Discussion

Category 1 Polymers

PAN

The polyacrylonitrile samples that were tested displayed a very interesting transitional behavior on the original TSC plot. The polymer appeared to undergo several transitions as it was heated to below its recorded degradation point. The phase space for PAN pellet 1 exhibited a possible period doubling or possibly even tripling behavior. (Figure 4)

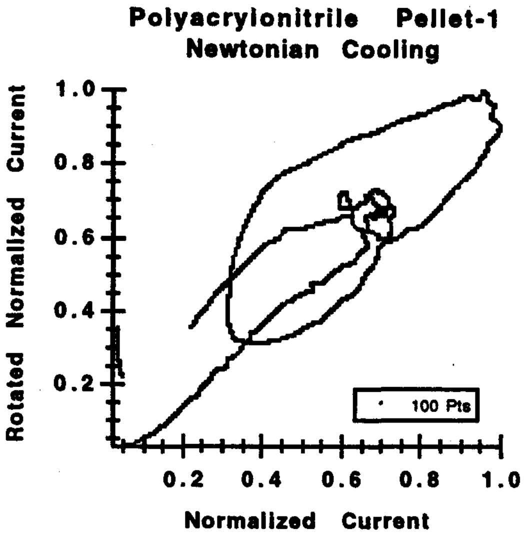


Figure 4a) Phase space portrait of PAN Pellet 1.

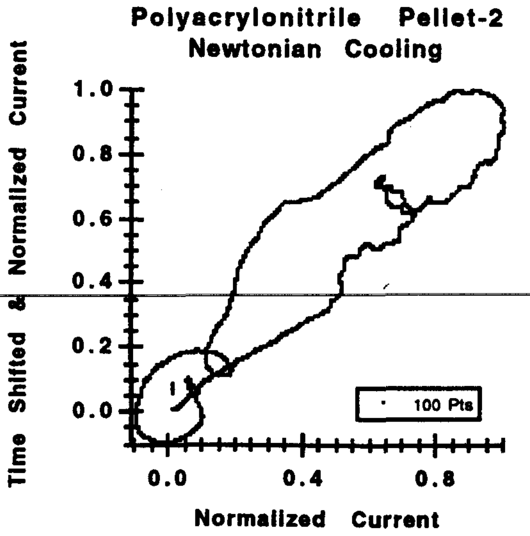


Figure 4b) Phase space portrait of PAN Pellet 2.

The TSC plots of each PAN sample were essentially the same. However, the phase space data of PAN pellet 2 resulted in a much more interesting portrait. In Figure 4b, there appears to be three separate sections that show a period doubling, or even a higher level of periodicity. The use of phase space representations in thermal analysis is such a new technique, that any interpretation of the phase space plots would be pure conjecture. However, these results do seem to imply that there may be subtle differences in the underlying dynamics between these two PAN samples.

PS

Much like the PAN phase space plots, the PS plots also generated a nearly closed loop in the phase space (Figure 5). However, there was only a single loop present.

As seen below, the data obtained for the PS is more consistent than that of the PAN, perhaps because PS is a much more stable compound than PAN.

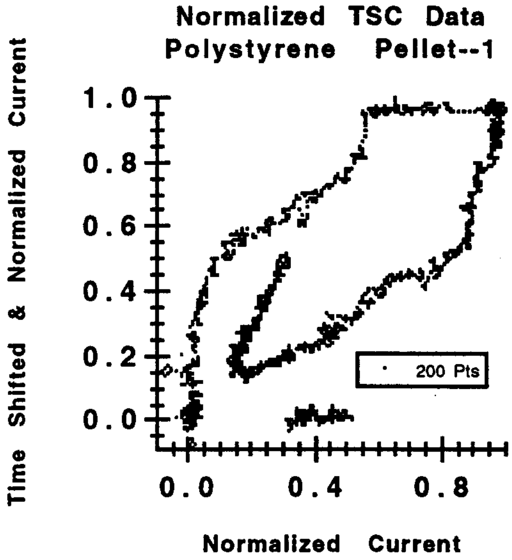


Figure 5a) Phase space portrait of PS Pellet 1.

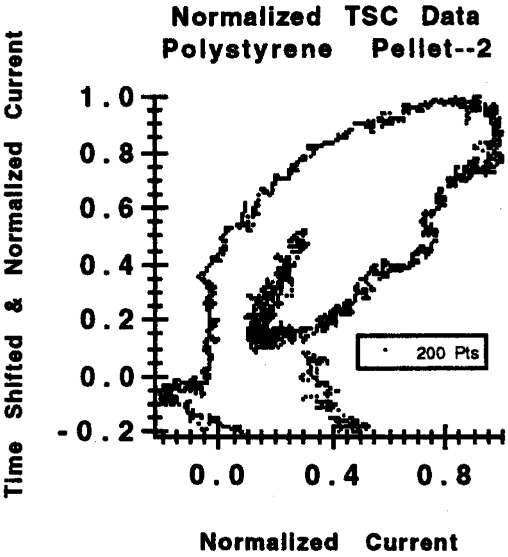


Figure 5b) Phase space portrait of PS Pellet 2.

PMMA

The phase space portraits obtained from the PMMA data were quite similar to that of the PS. This is not surprising considering the similarities present in the backbone of both polymers (Figure 6).

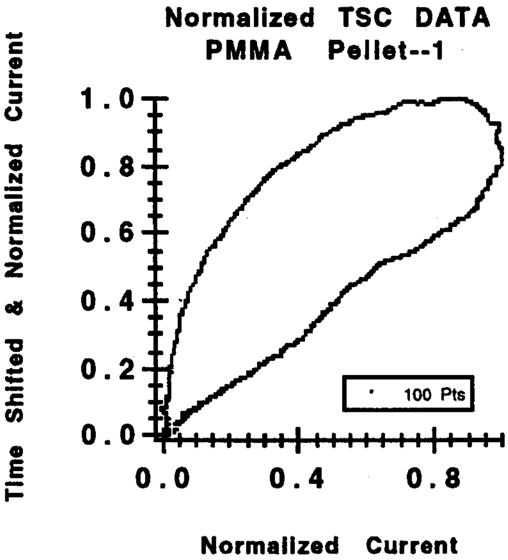


Figure 6a) Phase space portrait of PMMA pellet 1.

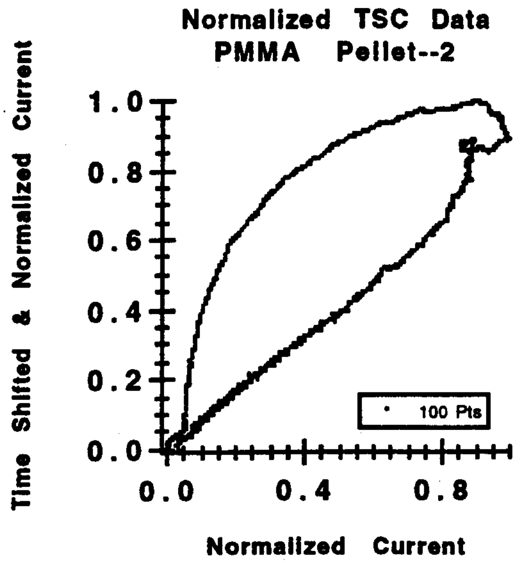


Figure 6b) Phase space portrait of PMMA pellet 2.

Category 2 Polymers

PET

The data from the PET TSC experiments yielded partially periodic phase space portraits. (Figure 7) The periodicity of the category 2 polymers is restricted to a small region in their phase space, as compared to that of category 1 which was wholly periodic.

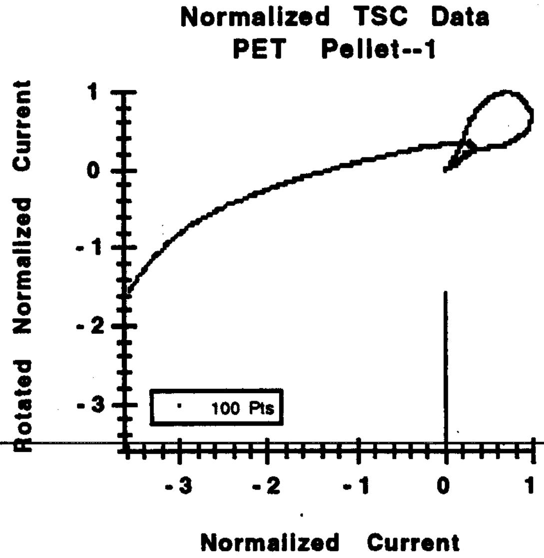


Figure 7a) Phase space portrait of PET Pellet 1.

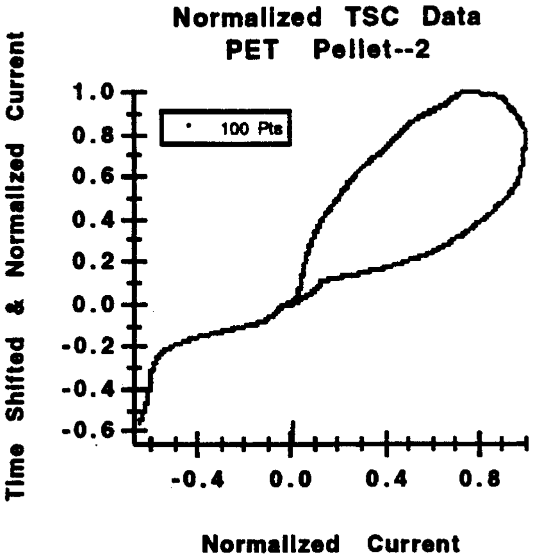


Figure 7b) Phase space portrait of PET Pellet 2.

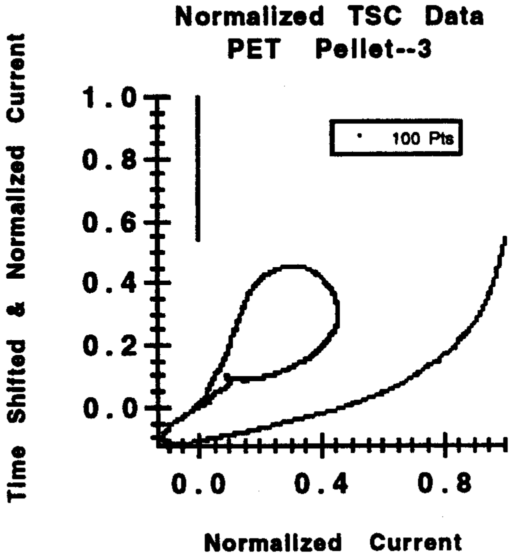


Figure 7c) Phase space portrait of PET Pellet 3.

The PET pellets seem to be quite similar in their appearance and all show possible periodic behavior.

As seen in Figure 8, the phase space portraits of the PC are quite similar to that of the PET. We conjecture that the phase behavior of the PET and PC would be different from that of the PS, PAN, and PMMA because of the structural differences in the polymers. PS, PAN, and PMMA all have relatively small repeat units and pendant groups on their backbone, while the PC and PET are basically linear polymers with large repeat units. Even though the PC contains two CH_3 groups that are suspended from either side of the polymer backbone, we speculate that it will behave more like the linear polymers simply because of its large repeat unit.

On comparison of the PC plots (Figure 8) to the PET plots (Figure 7) strong similarities can be observed. However, when comparing the PC and PET plots with those of the PMMA, PAN and PS portraits, a significant difference in the shape of the portraits is seen.

Polymers in Category 1 are wholly periodic, while the PC and PET plots are linear and then deviate into a circular/periodic behavior. It is possible that this phenomena could possibly be due to the scenario of pendant side groups present vs. no pendant groups present.

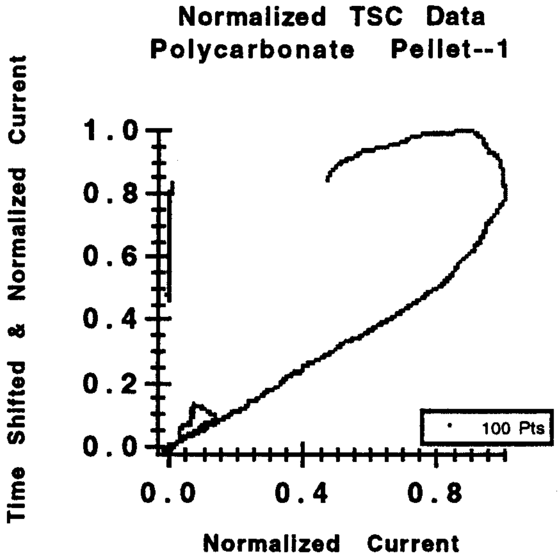
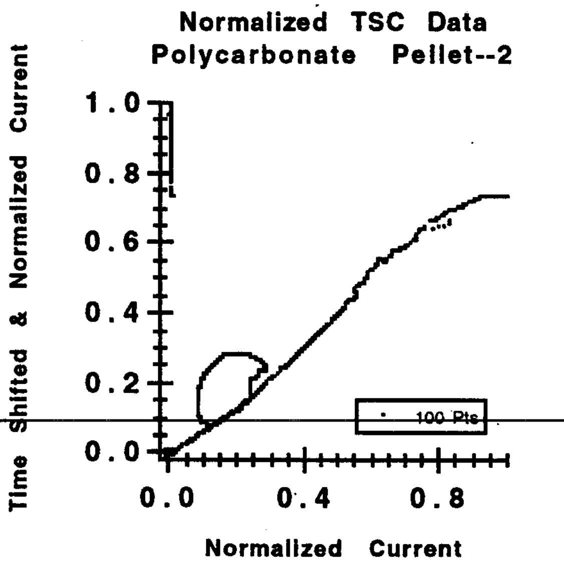
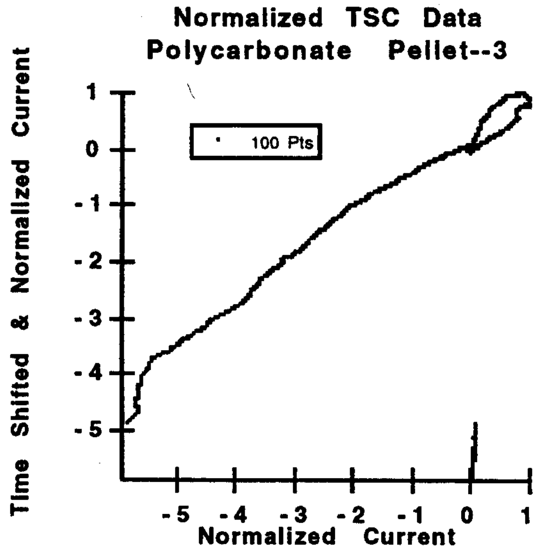


Figure 8a) Phase space portrait of PC Pellet 1.



8b) Phase space portrait of PC Pellet 2.



8c) Phase space portrait of PC Pellet 3.

The Category 1 polymers, PMMA, PAN, and PS, have phase space portraits which are reminiscent of the phase space of a simply periodic dynamic system. The phase space for Category 2 polymers is periodic only over a limited temperature range.

Conclusion

On comparison of the preliminary experimental results, we have observed a possible correlation between the polymers in each of their respective categories. From the plots presented in the previous section one can observe that the vinyl polymers produce a circular shape in the total phase space. The presence of an attractor such as this could be an indicator of underlying chaos. The polymers that have been tested from category 2 also appear to form consistent shapes in the phase space. However, the shape formed in the phase space of the polymers in the second category was rather different than that of the polymers in the first category. We are undecided as to whether the phase space portraits of the category 2 polymers could be indicative of chaos.

It is our hypothesis that the phase behavior of the PET and PC would be different from that of the PS, PAN, and PMMA because of the structural differences in the polymers. The PS, PAN, and PMMA all have relatively small repeat units and pendant groups on their backbone, while the PC and PET are basically linear polymers with large repeat units. Even though the PC contains two CH_3 groups suspended from either side of the polymer backbone, it behaves in the same manner as the linear polymers, possibly because of the large, aromatic repeat unit.

We believe that these differences are due to variations in the molecular structure of the polymer backbone. For instance, the flexible, aliphatic backbone versus the stiff, aromatic backbone; or possibly something as simple as the presence of the pendant groups in the first category.

Concluding Work

We will substantiate our TSC observations using Nylon 6, Nylon 6, 6 and polyethylene (PE). The two nylons are being used as a check to determine whether the amine group will affect the TSC response of the polymer injection differently in the Nomex than in the other polymers in the second category. Since the nylons have large repeat units and contain no pendent groups, we conjecture that they will fall in with the category 2 polymers. Our check for the category 1 polymers will involve the testing of polyethylene. Its significance to this group is that it has no pendant groups and is a vinyl polymer. These checks are being performed in order to determine the reason for the differences in the phase space portraits of the two different polymers categories.

Technical difficulties resulted in the delay of the M-DSC experiments. In addition, it was discovered that care must be taken in the manufacture of the samples for this experiment as well. Our preliminary work showed that the thickness and continuity of the sample should be our main concern in this case. It was decided that it would be necessary to use a microtome to slice the sample into a thin, flat disc, in order to allow the heat flow through the sample to be evenly distributed.

For the M-DSC experiment, the heating rate is to be set at the maximum allowable rate of 5 °C/min with an imposed oscillation frequency of ±2 °C/min. In order to be consistent with the TSC protocol, the samples will be heated to approximately 20 °C below their reported melting temperature or in the case of PAN, 20 °C below its reported decomposition temperature. These experiments will provide us with the overall heat flow as well as its reversible and nonreversible components.

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