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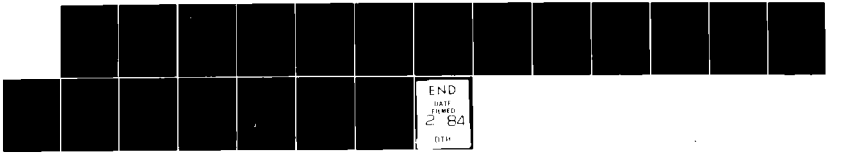

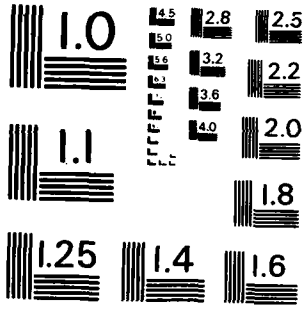

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TICA STUDY OF HIGH-TEMPERATURE THERMOPLASTICS

J. R. Fried and A. Letton
Department of Chemical and Nuclear Engineering
and the Polymer Research Center
The University of Cincinnati

Final Report, August 25, 1982-August 24, 1983

AFOSR-82-0301

Air Force Office of Scientific Research

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TICA	Annealing	Liquid-liquid transition
Dynamic mechanical	Impact	Glass transition
Polysulfone	Composites	Relaxation spectra
Filler interactions	Secondary relaxations	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Methods have been developed to obtain relaxation spectra for highly filled cloth composites by application of torsion impregnated cloth analysis (TICA) techniques. Comparison of spectra for filled and unfilled polysulfone samples suggest that polymer-filler interactions result in substantial broadening of the relaxation time distribution although there is little change in shift parameters, glass transition temperatures, or Arrhenius activation energies. In addition, TICA loss modulus measurements suggest the presence of a previously

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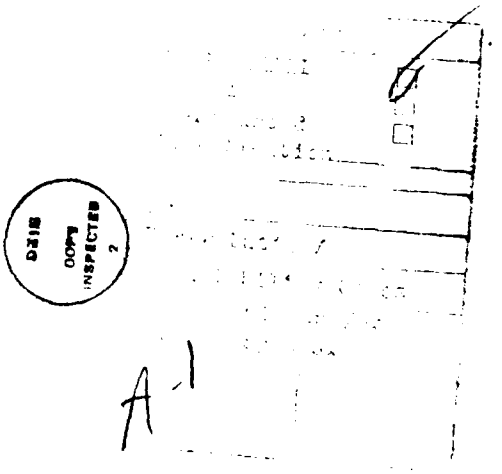
reported weak relaxational process (liquid-liquid transition) above the glass transition temperature.

Dynamic mechanical measurements of polysulfone torsion bars indicate the presence of two secondary relaxations below the glass transition temperature. These include a strong γ peak near -100°C and weak β peak near 60°C. Annealing or slow cooling results in a suppression of the β peak and intensifications of the high temperature side of the γ peak which appears to correlate with a small decrease in impact strength. Preliminary quantum mechanical calculations suggest that the γ relaxation may represent contributions from methyl group rotations and swivel motions of isopropylidene and diphenyl sulfone moieties while more energetic diphenyl ether swivels may be responsible for the β relaxation. No effect of thermal conditioning in the region of the liquid-liquid transition has been observed.



FOREWORD

This report was prepared at the Department of Chemical Engineering of the University of Cincinnati, under grant AFOSR-82-0301. The research described herein was administered under the direction of the Air Force Office of Scientific Research, Bolling Air Force Base, Washington, D.C. 20332.

The report covers work carried out between August 25, 1982, and August 24, 1983, and was prepared in December, 1983.

I. Introduction

One objective of this research was to explore the usefulness of torsion impregnated cloth analysis or TICA (1) as a possible technique to study polymer-filler interactions in thermoplastic composite materials. Additional objectives were an investigation of the controversial liquid-liquid transition or $T_{\ell\ell}$ (2) which sometimes is reported to occur at temperatures above the glass transition (T_g) and an investigation of the effect of both high and low temperature thermal conditioning on the dynamic mechanical and impact properties of one important engineering thermoplastic, bisphenol-A polysulfone (PSF). TICA and dynamic torsion bar and melt measurements were made by use of a Rheometrics Dynamic Spectrometer (RDS-7700) at the Polymer Branch, Materials Laboratory, AFWAL, WPAFB, with the cooperation of Dr. Charles Lee. Impact strength was determined by means of an instrumented falling film impact tester developed in part with funds provided by AFOSR 82-0301 and described in detail in the grant proposal. Force-time data was recorded by means of a Nicolet 3091 digital oscilloscope and transmitted through its RS-232 serial port to a Digital MINC-23 microcomputer for which software has been written to integrate the force-time curve.

II. Results and Discussion

TICA Studies. Four cloths (S- and E-glass, Kevlar, and graphite) were used to prepare TICA samples of Udel P-3500 PSF from a 7.5 (w/v)% solution in (3/1) methylene chloride/chloroform by procedures described elsewhere (3). Cloth specifications are given in Table I. Solvent extraction of dried TICA samples (100°C for 24 hrs. in vacuum) indicated approximately 69-76 wt % cloth content.

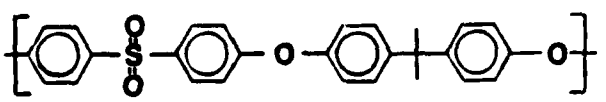
Comparison between loss modulus spectra of the TICA samples and a neat torsion bar is shown in Fig. 1. Differences in spectra between E- and S-glass were negligible and therefore only a single spectrum is shown. The bar sample exhibits a strong low temperature (γ) secondary relaxation peak with a maximum near -100°C, a weak secondary (β) peak near 60°C, and a glass transition (α) peak at 198°C. These results are in agreement with those of other studies (4). In contrast, no secondary relaxation peaks are apparent in the TICA spectra. The small peak centered near 100°C in the spectrum of the graphite TICA sample is attributed to phase separation of the phenoxy finish which has a reported T_g in this region. The presence of the cloth filler has little affect on the temperature location of the α peak (T_g) but appears to broaden the temperature range over which the transition occurs. In addition, there is evidence for a weak $T>T_g$ peak ($T_{\ell\ell}$) near 250°C which is more pronounced during the initial temperature scan of the TICA samples (not shown), particularly in the case of the glass TICA samples.

Master curves of loss modulus (Fig. 2) were obtained by shifting spectra obtained over a frequency range from 0.1 to 100 rad/sec. A Williams-Landel-Ferry (WLF) plot of the shift factors is shown in Fig. 3. Although data is scattered there is a strong suggestion that the presence of different cloth fillers has little affect on the shift factors. A computer program was developed to calculate relaxation spectra of the TICA as well as torsion bar and melt data from loss modulus data by use of a forth order finite element technique suggested by Tschoegl. Results are shown in Fig. 4. In comparison to the neat PSF results, the relaxation spectra for the TICA samples appear to be significantly broadened over a wide range of relaxation times. Broadening appears particularly pronounced for the graphite TICA sample. Although it is not possible at the present time to fully explain the trend in relaxation

behavior, the results suggest strong interactions at the filler-polymer interface.

Dynamic Mechanical/Thermal History Studies. The effect of thermal history on the dynamic mechanical spectra of neat PSF torsion bars is illustrated in Fig. 5. Quenching from above T_g or from above $T_{\ell\ell}$ does not significantly affect the loss modulus spectrum. In all cases, a weak β peak and strong γ peak is observed as previously discussed. In addition, there is a suggestion that the γ peak may consist of two or more overlapping relaxations. From the frequency dependence of these peaks, the apparent Arrhenius activation energies of the α, β, and γ peaks have been determined to be 220 ± 55, 67 ± 35, and 10.7 ± 1.1 kcal/mole. The apparent activation energy of the α peak observed in the TICA sample was (198 kcal/mole) in good agreement with the neat samples (220 ± 55 kcal/mole). The large error bars (95% confidence limits) determined for the activation energy of the β peak reflect the larger uncertainty in assigning peak temperatures for these very weak, broad relaxations. Annealing below T_g or slow cooling, decreases the β peak and appears to intensify the high temperature peak of the γ peak. These latter observations are in agreement with earlier conclusions (4).

In independent cooperation with this research, Professor James Mark and Dr. William Welsh of the Chemistry Department of UC have used CNDO/2 geometry optimized quantum mechanical calculations (5) to determine activation energies for different molecular group motions of the PSF whose structure is shown below.

PSF 

Preliminary results indicate activation energies for swivel motions at the diphenyl ether linkage to be 39.2 kcal/mole which is in the range observed for the β peak. In contrast, activation energies for methyl group rotation, isopropylidene group swivel, and diphenyl sulfone group swivel appear to be in the range of 10 kcal/mole observed for the strong broad γ peak.

Impact Studies. A typical force-time curve for dart impact of neat PSF films is shown in Fig. 6. Measurements of a number of similarly prepared samples indicate that the impact strength of quenched PSF films is 8.17 ± 41 ergs/inch thickness compared to 7.48 ± 45 ergs/inch for both slow cooled and annealed films. Although there is overlap in the error bounds (95% confidence limits) for these two numbers, the results seem to suggest a small decrease in impact strength upon annealing which may correlate with the observed decrease in the small β peak and enhancement of the high temperature side of the strong γ peak.

III. Continuing Studies

Several studies are being continued to aid in the interpretation of results. We are planning to perform dynamic mechanical measurements of TICA samples that have been irradiated by a Co^{60} source available in our Department and those which contain glass cloth treated with a PSF compatible amino silane coupling agent supplied to us by Union Carbide Corporation. Results of these measurements should help clarify the relation between polymer chain mobility on the filler surface and the relaxation time distribution. In addition we are taking additional impact data on long time annealed samples for which dynamic mechanical, density, and enthalpy measurements will be

available. Tensile impact data also will be obtained and compared with the instrumented dart results. Preliminary results with poly(dimethyl siloxane) show good correlation between the area under the stress-strain curve and impact strength as measured by the impact test.

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2. Boyer, R.F., Polym. Eng. Sci. 19, 732 (1979).

3. Fried, J.R. and Lee, C.Y.-C, AFWAL TR 83-4036.

4. Fried, J.R. and Kalkanoglu, H., J. Polym. Sci., Polym. Lett. Ed. 20, 381 (1982).

5. Kando, N., PhD Dissertation, University of Cincinnati, 1979.

PROFESSIONAL PERSONNEL

1. Dr. Joel R. Fried, principal investigator; Associate Professor of Chemical Engineering, University of Cincinnati.

2. Mr. Alan Letton, PhD candidate and NSF minority graduate fellow, Department of Chemical Engineering, University of Cincinnati.

INTERACTIONS

Portions of the above material have been presented by Mr. Letton at the annual meeting of the Society of Rheology in Knoxville, TN, October 20, 1983.

TABLE I

TICA Cloth Specifications

	E-glass	S-glass	Graphite	Kevlar
style	7268	15651	03100	181
weave	plain	plain	plain	plain
weight (oz/yd^2)	6.0	5.9	5.7	NA
thread count	44x32	44x32	NA	NA
finish/treatment	heat cleaned	heat cleaned	phenoxy	heat cleaned
supplier	Stevens	Stevens	Hercules AS4	Ferro Corp

FIGURE CAPTIONS

Fig. 1 Torsional shear loss modulus (G") of a PSF solid bar (quenched from 280°C) and three TICA samples (curves obtained after prior heating to 350°C and quenching in the RDS liquid nitrogen environmental chamber). Heating rate was 4°/min at a frequency of 10 rad/sec. Curves arbitrarily shifted for comparison.

Fig. 2 Loss modulus master curves (referenced to 218°C) for neat PSF (torsion bar and melt) and three TICA samples.

Fig. 3 WLF plot of shift factors for PSF melt and TICA samples.

Fig. 4 Calculated relaxation spectra of neat PSF and three TICA samples.

Fig. 5 Loss modulus of PSF torsion bars which have been given different thermal treatments.

Fig. 6 Representative force-time traces from which impact energy is calculated. Sample is a PSF disk (1.5" in diameter and 0.05" in thickness) that was quenched from 320°C in an ice-water bath.

Figure 1

Loss Modulus Curve

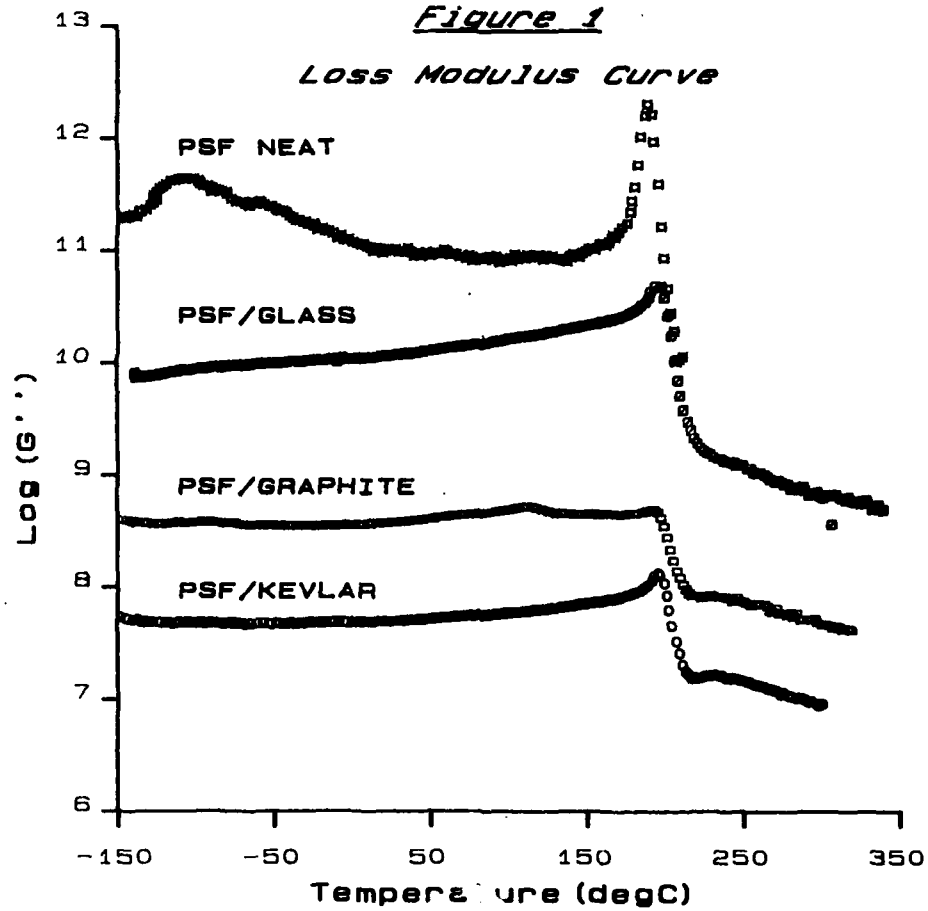


Figure 2

MASTER CURVES

PSF and PSF Composites

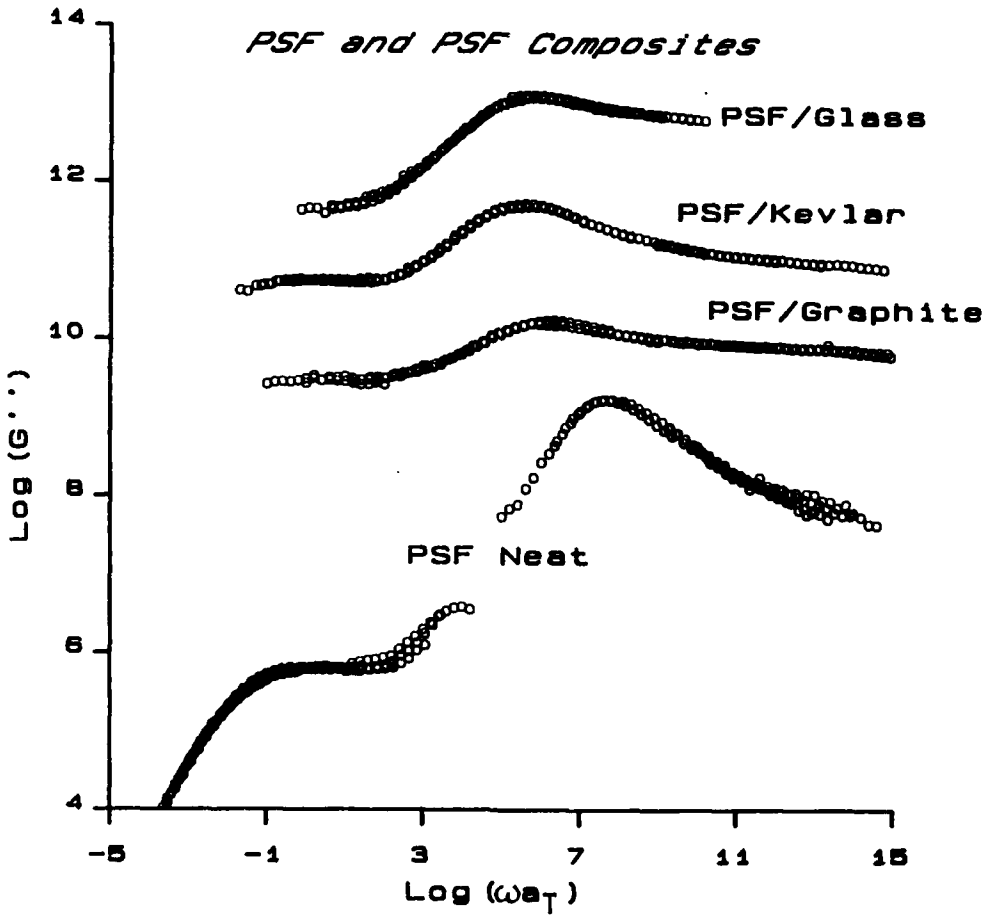


Figure 3

Shift Factors

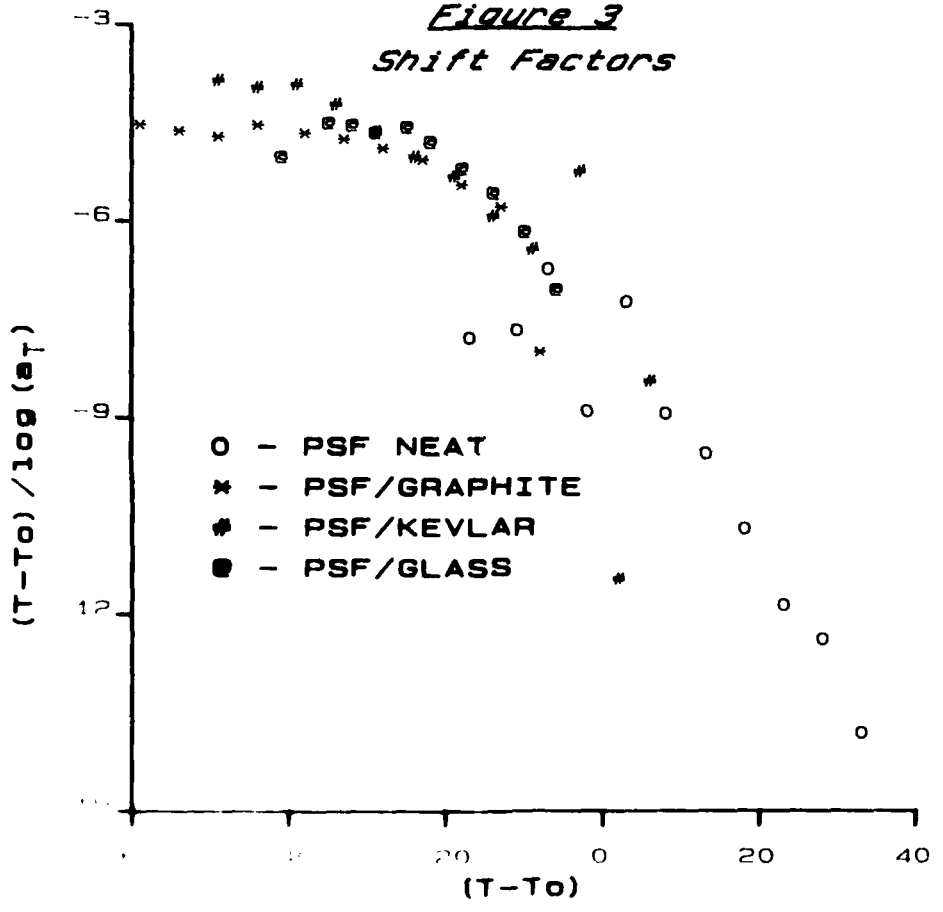
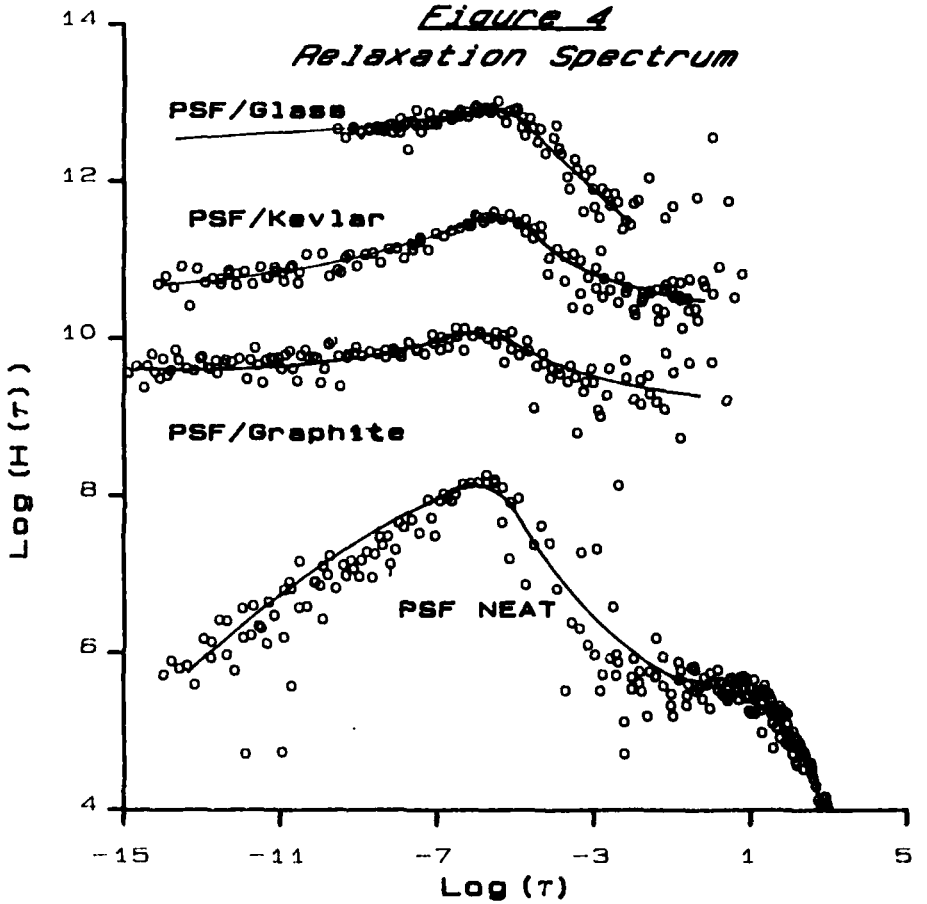


Figure 4

Relaxation Spectrum



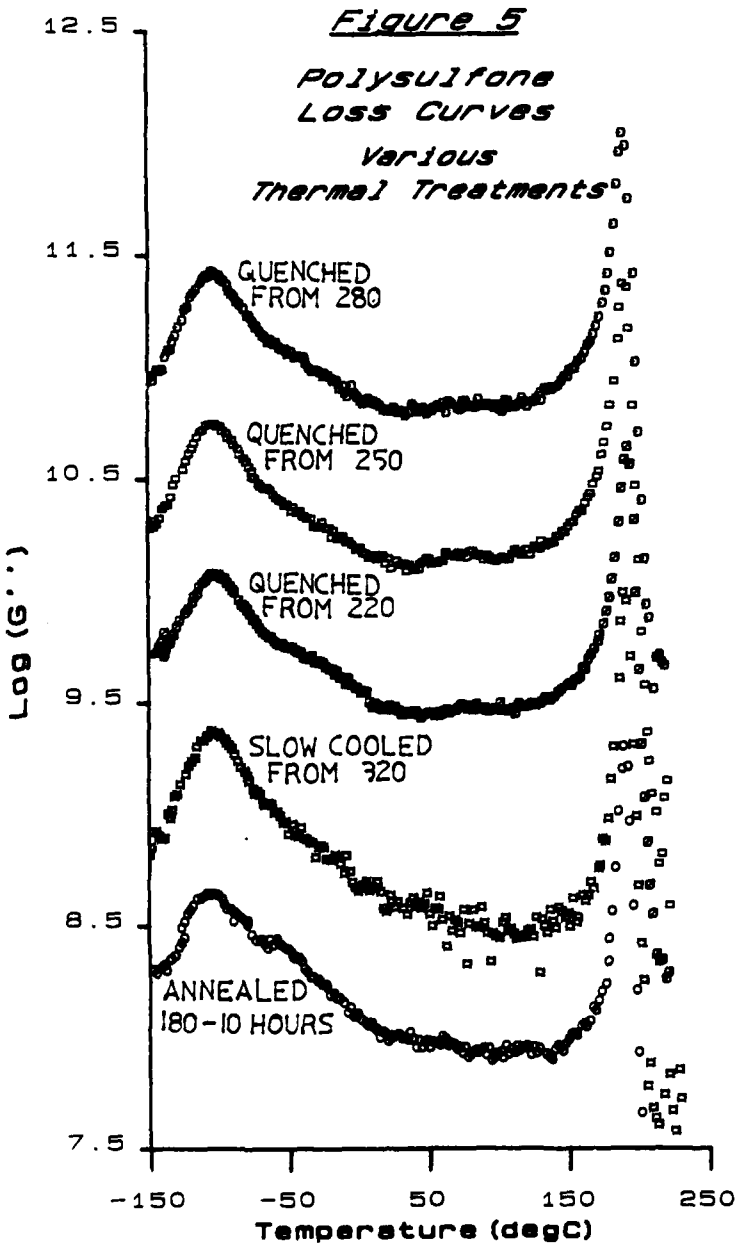


Figure 5
Polysulfone
Loss Curves
Various
Thermal Treatments
12.5
11.5
10.5
9.5
8.5
7.5
Log (G'')
QUENCHED FROM 280
QUENCHED FROM 250
QUENCHED FROM 220
SLOW COOLED FROM 320
ANNEALED 180-10 HOURS
-150
-50
50
150
250
Temperature (degC)

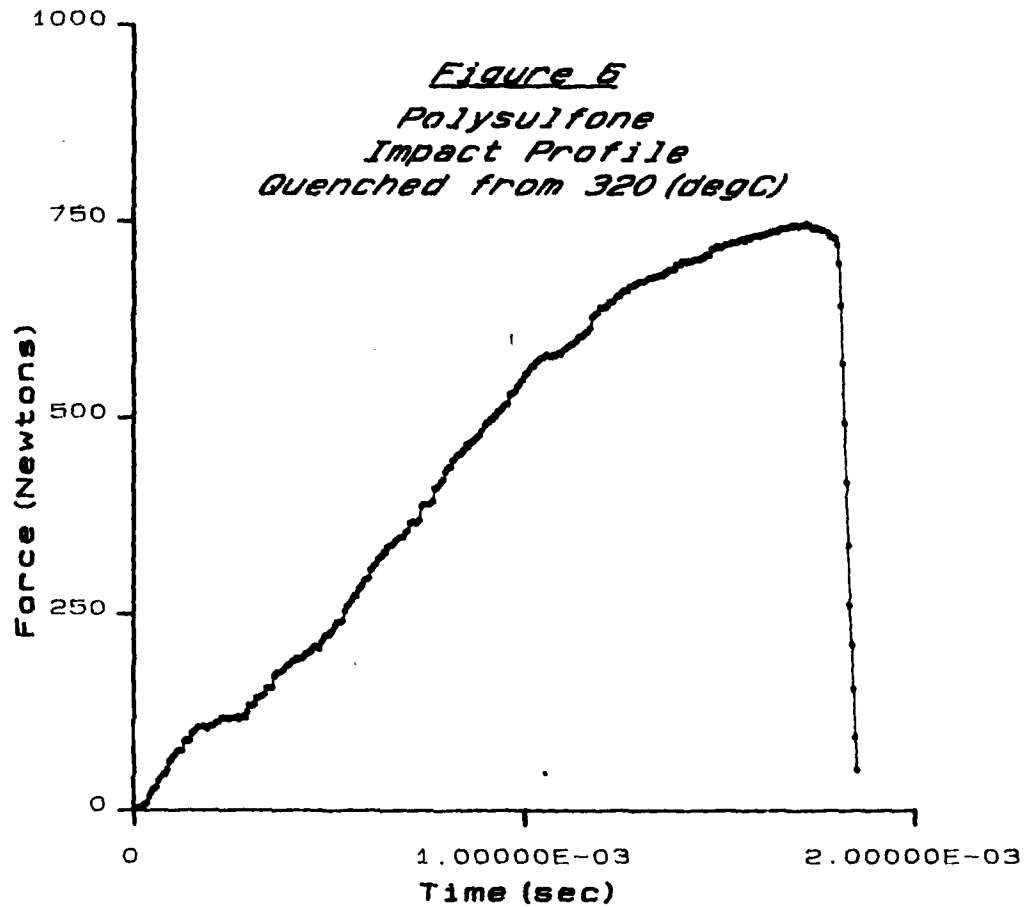
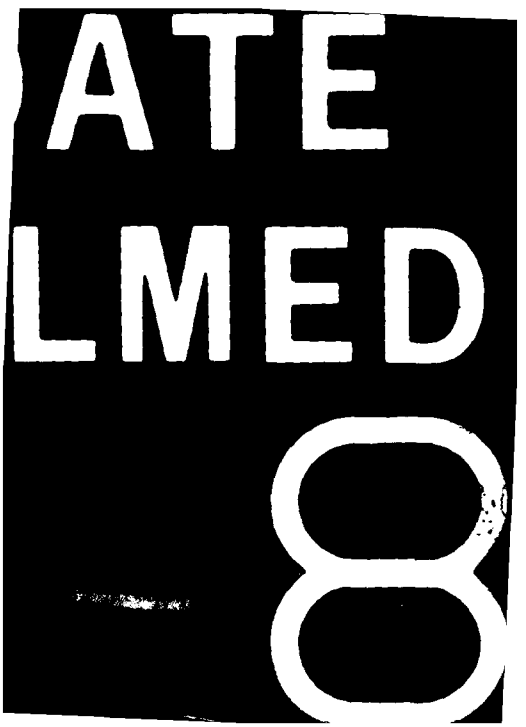


Figure 6
Polysulfone
Impact Profile
Quenched from 320 (degC)
1000
750
500
250
0
Force (Newtons)
0
1.00000E-03
2.00000E-03
Time (sec)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