

NOTES

Rheological Properties of a Phenyl Substituted Siloxane Polymer

INTRODUCTION

Detectors of high-energy radiation employ phenyl-substituted polymers in scintillating fiber materials to measure the energy of radioactive particles. Such particles excite π electrons in the phenyl rings. Relaxation to the ground state involves the emission of photons. These photons are detected to record the energy and position of particles in the detector.

Commercially available scintillators made from polystyrene or polyvinyl toluene yellow upon exposure to high-energy radiation. This results in the unwanted absorption of photons produced in the scintillation process.

We have determined that siloxane polymers and copolymers have superior resistance to yellowing when exposed to ionizing radiation.¹⁻⁴ Phenyl-substituted siloxanes are therefore potential materials for use as scintillating fibers in detectors of high-energy radiation.

Linear noncrystalline siloxane polymers, however, have glass transition temperatures below room temperature. They do not, therefore form self-supporting one-component fibers. Such viscous liquids can be spun into fibers by a bicomponent spinning process wherein the siloxane core is surrounded by a rigid thermoplastic cladding material.

Here, we report a study of the rheological properties of a polymethylphenyldiphenylsiloxane copolymer. The purpose is to predict whether or not the viscous siloxane will remain inside the cladding material and not flow out of the cladding "tube" when the fiber is placed in a vertical position. The stability of the fiber is important since there will be a period of time during which the fiber has a liquid core before it is crosslinked to form a solid elastomer at which point the stability of the fiber is guaranteed.

EXPERIMENTAL

Polymer

Polymethylphenyldiphenylsiloxane was obtained from Hüls Petrarch Systems. The copolymer is 50 wt % meth-

ylphenyl siloxane. The molecular weight of the sample is quite low, 2000 as determined by GPC. A DuPont 910 differential scanning calorimeter characterized the glass transition temperature of 7°C.

Viscosity Measurements

The viscosity was measured at 30, 45, 60, 90, and 110°C on a Rheometrics Mechanical Spectrometer Model 800. A parallel plate geometry was used, and all measurements were made under steady-state conditions. The revolutions per minute (rpm) were regulated to ± 0.001 rpm and the temperature was regulated to ± 0.001 °C.

RESULTS AND DISCUSSION

The siloxane copolymer is a viscous liquid at room temperature. To ensure the stability of a clad fiber, a simple calculation was performed. The shear stress on the core material due to gravity is independent of the length of the fiber and for a vertically located fiber is

$$\tau = \frac{\rho g r}{2}$$

where ρ = density, g = acceleration due to gravity, r = radius, and τ = shear stress. With $\rho = 1.15$ g/cm³, for a 1-mm fiber τ is 28 dyn/cm² and for a 100- μ m fiber τ is 2.8 dyn/cm². If the yield stress of the material is greater than τ , the material will not flow out of the cladding.

The apparent yield stress was determined experimentally from a plot of shear stress versus shear rate. As the shear rate approaches zero, the shear stress approaches a limiting value, the apparent yield stress. This yield stress is determined from the y intercept of a plot of shear stress versus shear rate (Fig. 1).

The apparent yield stress of the polymer at 30°C is 671 dyn/cm². At 30°C the polymer will form stable 1-mm and 100- μ m clad fibers. As the test temperature was raised to 60°C, the yield stress dropped to 23 dyn/cm². This is depicted in Figure 1. At 60°C, 1-mm fibers are unstable, whereas 100- μ m fibers are still stable. Figure 2 summarizes yield stress data for the temperatures investigated.

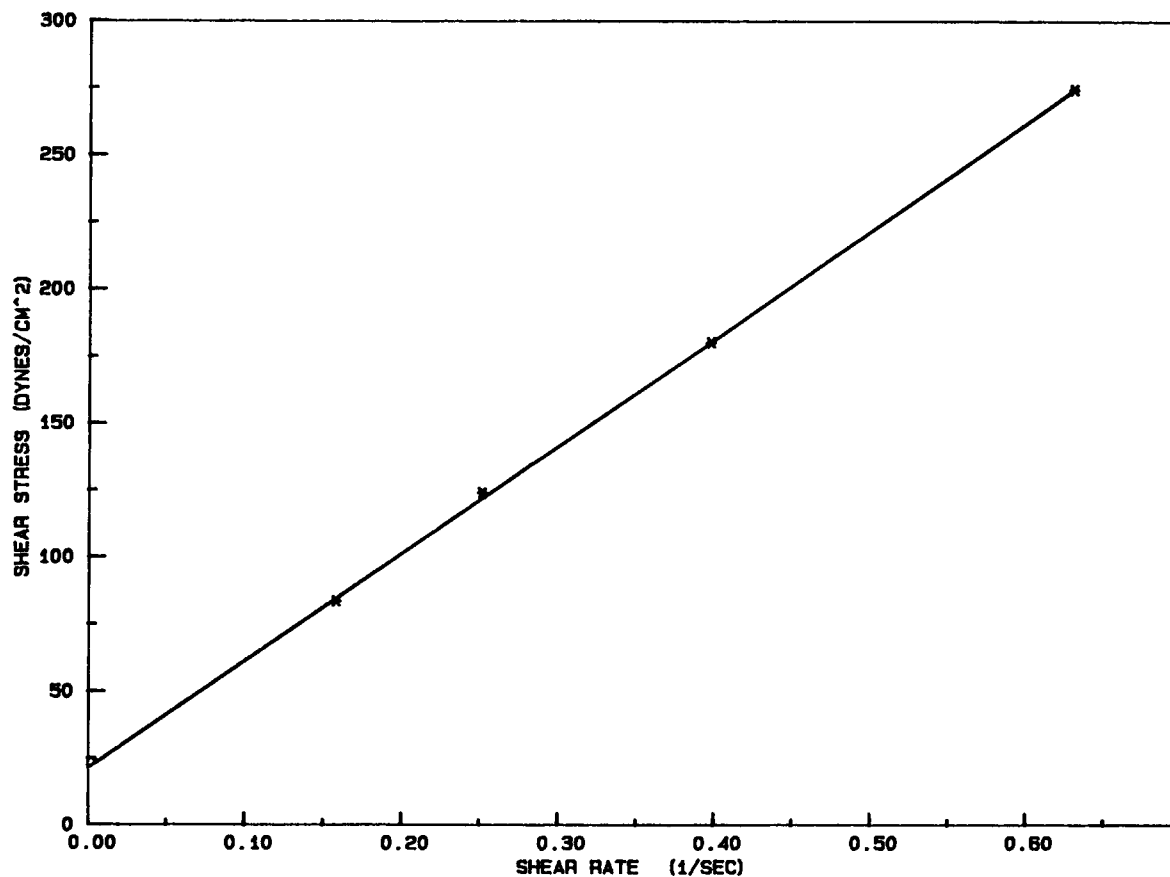


Figure 1 Shear stress versus shear rate for polymethylphenyldiphenylsiloxane at 60°C. The yield stress, y intercept, is 21.4 dyn/cm².

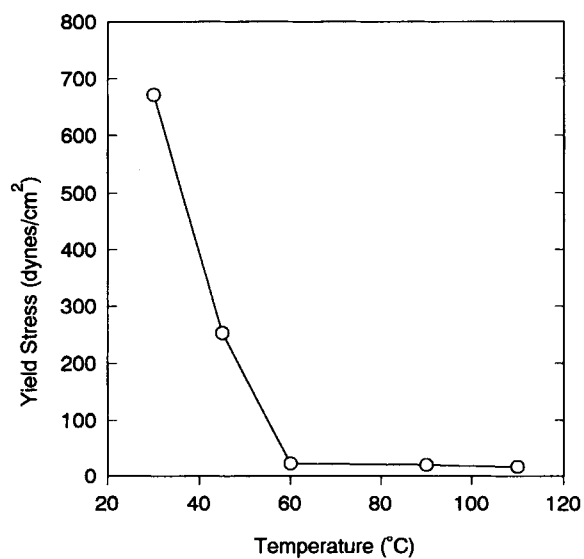


Figure 2 Plot of yield stress versus temperature for the siloxane copolymer.

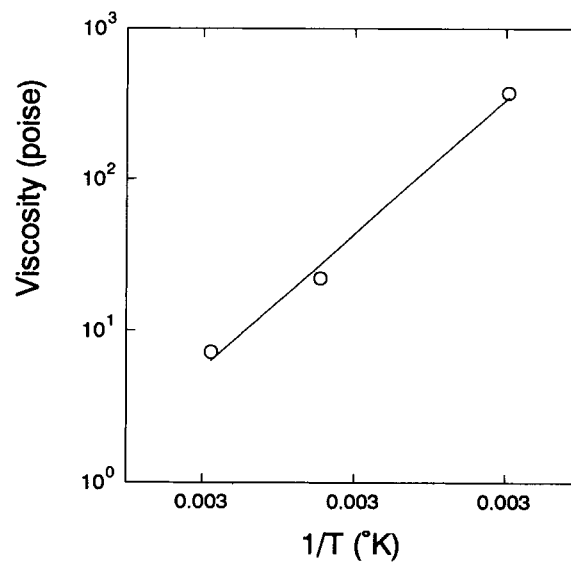


Figure 3 Plot of log viscosity versus 1/T for the siloxane copolymer at a shear rate of 25.12 s⁻¹.

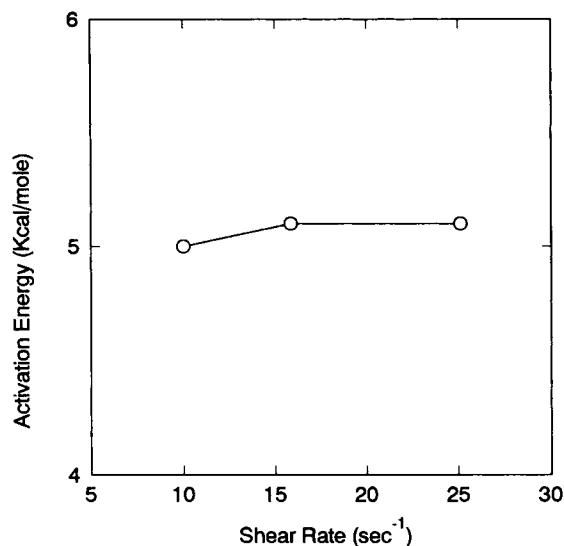


Figure 4 Plot of activation energy versus shear rate for the siloxane copolymer.

A 1-mm fiber clad with PMMA was heated in a glass box enclosed in an air bath. The temperature was increased by 2°C increments and held at each temperature for 10 min. At 58°C, the siloxane flowed out of the cladding material. A 20-cm-long 300-μm-diameter clad fiber was held vertically for 1 month and no siloxane flowed from the fiber. These latter measurements are seen to be in accord with the rheological data.

The viscosity of the siloxane material is dependent on the temperature.⁵

$$\eta = \eta_0 e^{-[E/R][1/T - 1/T_0]}$$

where E is the activation energy, R the gas constant, T is temperature in K, and η_0 and T_0 are constants. Plots of $\log \eta$ versus $1/T$ at constant shear rates were plotted for shear rates of 25.12, 15.85, and 10.00 s⁻¹. Figure 3 shows such a plot for a shear rate of 25.12 s⁻¹. The activation

energies obtained from the slope of the plot, E/R , are shown as Figure 4.

This data spans a temperature range of 80°C. E is often a constant over such a narrow temperature range. Values for most polymers range from 8 to 15 Kcal/mol.⁶ The low value of 5 Kcal/mol obtained here is likely due to the low molecular weight of the siloxane.

We conclude that the viscous siloxane liquid can be used as core material to form stable clad fiber over a temperature range with upper limits at about 50°C for 1-mm fibers. Higher molecular weight polymers are being investigated at this time. As stated earlier, the siloxane fiber core is crosslinked after the co-extrusion process is complete and forms a totally stable fiber.

References

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