

UNPUBLISHED PRELIMINARY DATA

N 65 12623

Seventh Semi-Annual Report for the Period Ended 31 October 1964on the Program "Viscoelastic Behavior of Polymers at Long Times"Supported by NASA Grant No. NsG-147-61 at Mellon InstituteCode 1
CR-59761

During the past grant period progress was made in three areas of investigation: 1) the nature of the dispersion in crosslinked systems in the rubbery region of behavior, 2) the character of the response of linear amorphous polymers, and 3) the viscoelastic response of a nonpolar small molecule compound in the neighborhood of its glass temperature.

Pg-4
Cat. 18

1) It has become quite clear from our measurements along with those of Thirion, Ferry, and Kraus that the amount of dispersion in a crosslinked rubber at long times is principally related to the rearrangements which are possible within the entanglement network. The greater the concentration of chemical cross links the more the entanglement network is restricted. The molecular weights between entanglement points, M_e , and between primary chemical crosslinks, M_c , appear to be the pertinent characterizing parameters. It is our opinion that M_e is reflected in the Andrade creep intercept at zero time, J_A . To obtain values of M_e for Hevea and polybutadiene rubbers it was necessary to carry out creep measurements on high molecular weight uncrosslinked samples of these materials. The response of both high cis content polybutadiene and synthetic isoprene samples are well represented by the Andrade creep equation, $J(t) = J_A + \beta t^{1/3} + t/\eta$. The values of M_e obtained were 2600 and 6400 respectively. Comparison of the behavior of the crosslinked cis isoprene samples with the uncrosslinked material

GPO PRICE \$ _____

OTS PRICE(S) \$ _____

Hard copy (HC) 1.00Microfiche (MF) .50

appears to show a systematic pattern of deviation between the two as a function of M_c . At short times the compliance curves of all the crosslinked materials converge to that of the uncrosslinked. It is hoped that the manner in which the compliance curves separate can be used to help deduce better values for M_c . The creep behavior is compatible with the hypothesis that M_c obtained by conventional methods such as swelling are in error by a factor of 2 or 3. The more limited measurements on the polybutadiene system did not yield the same pattern of relative behavior, but the results became understandable when it was determined that the cis-trans ratio of the samples varied. It is therefore essential that the Andrade creep parameters be determined as a function of the cis-trans ratio. The influence of molecular weight will also be investigated.

2) At present we are concentrating on two features exhibited by the behavior of polyvinylacetate, PVAc. The data obtained earlier have been augmented by more extensive and accurate measurements in the levitation torsional creep apparatus. It has been deduced that the lack of simple time-temperature superposition of the creep compliance curves, mentioned in our last report, reflects significantly different temperature dependences for the viscoelastic mechanisms giving rise to the glass to rubber transition and those responsible for dispersion in the rubberlike plateau and beyond. The additional information makes it clear that the discrepancy was actually a time and not an amplitude shift. In addition an M_e value of 8600 remains temperature independent. Except

for the methacrylate series of polymers, where a reduction anomaly has been attributed to a rather large temperature dependence of M_e , the temperature dependences of the glass to rubber transition and that of the entanglement plateau for all examined linear amorphous polymers have been assumed to be identical. We expect our finding on PVAc will prove to be the general case and that predictions based upon extrapolation by means of reduced master curves in the literature will be significantly in error.

Comparison of the behavior of two PVAc samples which were addition polymerized at different temperatures, -20° and $+60^\circ\text{C}$, has revealed their position on the time scale to be different by 0.6 of a logarithmic unit at 40°C . This would reflect a difference in glass temperatures of about 2°C . At present we believe this reflects a difference in stereoregularity in the samples arising from their different temperatures of polymerization and not from the presence of residual solvent or differences in molecular weight. This hypothesis will be checked shortly with measurements on available samples which were polymerized at -70° and $+30^\circ\text{C}$. Samples of branched PVAc have also been obtained for investigation.

3) At temperatures near and below its glass transition the mechanical response of a material, reflecting the enormously enhanced molecular friction coefficient, is greatly hindered; i.e., its retardation spectrum is shifted on the time scale toward long times. Very few investigations of the viscoelastic behavior of organic glasses

either polymeric or non-polymeric have been made and the various kinds of behavior present have yet to be enumerated. To provide a model for future studies on polymers and to provide pertinent data to probe some features of free volume theory, an intensive physical property study of 1,3,5-tri- α -naphthyl benzene was made in collaboration with Dr. Joseph Magill.

Andrade creep was observed as one of the viscoelastic mechanisms; however, the recoverable creep compliance was found to deviate from the Andrade form and attained a limiting steady state value, $J_e = 2.58 \times 10^{-10}$ cm²/dyne at 64.2°C. This behavior answers one of the questions originally posed in this program of investigation, whether or not a display of Andrade creep by a material precluded the existence of a true steady state compliance. A similar result for polymeric systems should be forthcoming. The results of this work were presented at the 35th Annual Meeting of the Society of Rheology. An abstract of the presentation appears below. Papers on this work are presently being prepared for publication.

ABSTRACT

Rheological Properties of 1,3,5-Tri- α -Naphthyl Benzene

D. J. Plazek and J. H. Magill

The viscous and viscoelastic torsional creep properties of 1,3,5-tri- α -naphthyl benzene (T α NB) have been studied at temperatures between 14° and 200°C. T α NB is a nonpolar small molecule that can be supercooled, with relative ease, through the freezing point, 198°C, to

form a glass at $T_g = 69^\circ\text{C}$. The measurements were made with a recently developed creep apparatus which employs a magnetically levitated rotor and a drag cup motor for the production of accurate torques. Recoverable deformation was detected between one and ten seconds at 79°C . Measurements at equilibrium densities were made down to a temperature ten degrees below the conventionally measured glass temperature. Between 14° and 49°C creep and recovery compliances were measured with the sample's density falling along a single glassy volume-temperature curve.

Temperature reduction to a single master curve of all of the above data was achieved. The logarithm of the recoverable compliance at the reference temperature of 64.2°C varied from -10.09 to a steady state value of -9.59 . The calculated retardation function, L_2 , indicates that two viscoelastic mechanisms in addition to simple viscous flow are present. Within experimental error all three observed processes exhibit the same time-temperature, a_T , shift factors. Just preceding the region of steady state behavior the dominating viscoelastic response has the form of Andrade creep, i.e. deformation linear with regard to the cube root of time.

Time independent viscosities from 4.0×10^{-1} poises at 473.0°K to 3.0×10^{13} poises at 332.5°K were measured to extend the higher temperature capillary results of Magill and Ubbelohde. Between 332° and 400°K the viscosity-temperature dependence is described by

$$\log \eta = -17.46 + 4.10 \times 10^3 (T-200)^{-1},$$

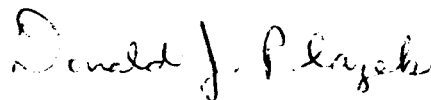
where T is the temperature, °K. The application of free volume theory concepts leads to a fractional free volume at T_g , f_g , of 0.067. It is also concluded that the expansion coefficient of the occupied volume α_0 is much smaller than that of the glass α_g : $\alpha_0 \ll \alpha_g$.

Creep compliance curves were determined during isothermal volume contraction below T_g . Dilatometric measurements of the isothermal volume contraction were also measured slightly below T_g . The temperature dependence of the crystal growth rate was studied. A maximum growth rate of 60 microns per minute (calculated from the crystal half length) was found at 176°C.

Instrumentation

A new temperature bath has been constructed for the levitation creep apparatus. It has been fitted with a pair of double windows which allows for precision optical measurements of the sample height which were not possible while the original lath was being used.

The accuracy of the float torsional creep apparatus was also increased by greatly reducing the dependence of the drag cup motor torque on axial displacements of the rotor.



Donald J. Plazek
Principal Investigator

10 November 1964