

Elastic Behavior of Concentrated Solutions of Acrylonitrile Copolymers. II. The Shear-Stress Dependence of the Shear Modulus of a Pseudo Network in Concentrated Solutions

TAKURO HAYAHARA and SEIJI TAKAO, *Saidaiji Plant, Research Division, Japan Exlan Co., Ltd., Okayama, Japan*

Synopsis

The shear-stress dependence of the shear modulus in concentrated solutions of acrylonitrile copolymer was investigated by the capillary end-correction method. The shear modulus decreases with an increase of shear stress above a critical polymer concentration at a higher shear rate than that at which the decrease of the viscosity begins to occur. The non-Hookian behavior of the concentrated solutions may be considered to arise from the breakdown of the tangled network structure, namely elastically deformable pseudo network.

Introduction

Molten polymers and concentrated solutions of polymers are very elastic fluids; i.e., the viscous flow of these fluids is associated with elastic deformations. Our previous^{1,2} studies of concentrated solutions of acrylonitrile copolymer indicated the existence of an elastically deformable tangled network which is different from that network which causes a rapid increase of viscosity above the critical molecular weight or concentration of polymer. It is generally observed that polymer solutions become less viscous at higher shear rates because of a transient preferred orientation of the molecules or a change in structure of the polymer solutions. The decrease of viscosity with increase of shear stress has been attributed to the breaking down of molecular interactions arising from chain entanglements or a slippage of molecules past each other at entanglement points. Therefore, it is easily predicted that such a change in structure of a polymer solution at the higher shear rates also influences the shear modulus of the pseudo network formed by chain entanglements in concentrated solutions of polymers.

In this paper the dependence of shear moduli of concentrated solutions of acrylonitrile copolymers on shear stress was investigated by using the procedure proposed by Bagley,³ who showed that the end correction on capillary extrusion could be separated into two components, the Couette correction and recoverable shear strain.

Experimental

Philippoff and Gaskins⁴ showed that the relationship between applied pressure P_T and die dimension L/R could be written as follows, considering the energy balance for the capillary extrusion;

$$P_T - m(\rho Q^2/\pi^2 R^4) = \tau_R(2L/R + 2n + S_R)$$

where τ_R is the shear stress at the wall, n is termed the Couette correction, S_R is the recoverable shear strain at radius R , and $m(\rho Q^2/\pi^2 R^4)$ is the kinetic energy correction which is less than 1.0% of P_T for this system, assuming $m \approx 1.0$. If we neglect the kinetic-energy correction, this equation shows that P_T is a linear function of L/R ; measuring P_T at a constant shear rate with capillaries having different ratios of L/R , we can calculate τ_R and $n + S_R/2$.

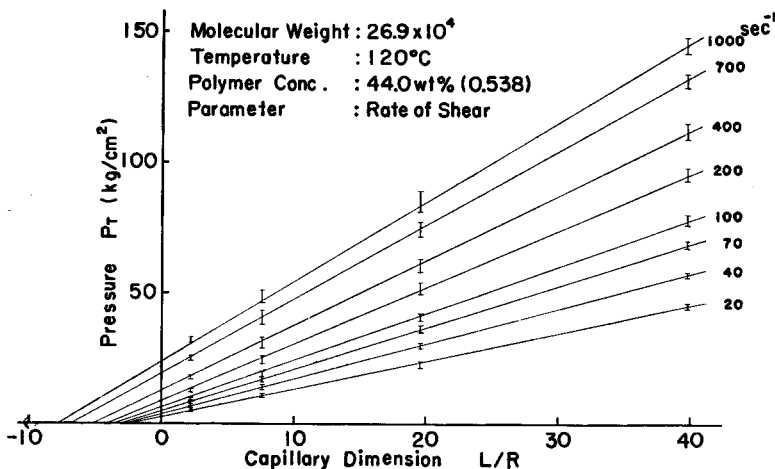


Fig. 1. Pressure P_T versus capillary dimension L/R in 44.0 wt.-% solutions of acrylonitrile copolymer of $M_w = 26.9 \times 10^4$ in aqueous NaSCN solution at 120°C .

Figure 1 shows the relationship between pressure P_T and capillary dimensions L/R for a 44.0 wt.-% solution of acrylonitrile copolymer of molecular weight 26.9×10^4 in NaSCN aqueous solution at 120°C . The Couette correction n can be obtained from a plot of pressure versus capillary dimension in sodium silicate solution at low shear stresses. In such case we found that sodium silicate solution shows Newtonian flow and has no recoverable shear strain S_R ; 2.03 was obtained as the value of n .¹ The Couette correction term $n = 2.03$ appears too large for a Newtonian fluid (n of 0.5 or 0.6). Large Couette correction terms ($n = 1.75$ and 1.95) are also reported by Bagley³ for polyethylene melt, by extrapolation of the plots of $2n + S_R$ versus τ_R to the limit of $\tau_R = 0$. In this paper 2.03 was used as the Couette correction term for the calculation of the recoverable shear strain S_R . The shear modulus G of a concentrated solution of

polymer can be calculated from the ratio of the shear stress to the recoverable shear strain.

The testing apparatus used in this work is a plunger extrusion rheometer (Shimazu Seisakusho Co., Ltd., Japan). The L/R ratios of the capillaries, which were drilled in cylinders of stainless steel, were from 2 to 30. All the capillaries reported here had 180° entry angles.

All samples were acrylonitrile-methyl acrylate copolymers (90:10) prepared in a continuous reactor with a redox system as catalyst. The molecular weights of the samples were 26.9×10^4 and 16.5×10^4 , calculated from the intrinsic viscosity at 30°C . in dimethylformamide.

Reagent-grade sodium thiocyanate and deionized water were supplied for the preparation of the polymer solutions. Polymer solutions were prepared by mixing dried polymer with 55% NaSCN aqueous solution as a solvent and then dissolving the polymer at 120°C . under pressure. The range of concentrations covered 25–55% solids.

Results and Discussion

Figures 2 and 3 are the plots of recoverable strain versus shear stress of concentrated solutions of acrylonitrile copolymers with molecular weights of 26.9×10^4 and 16.5×10^4 , respectively. The shear moduli at various shear stresses are obtained from ratios of the shear stresses to the recoverable shear strains in Figures 2 and 3.

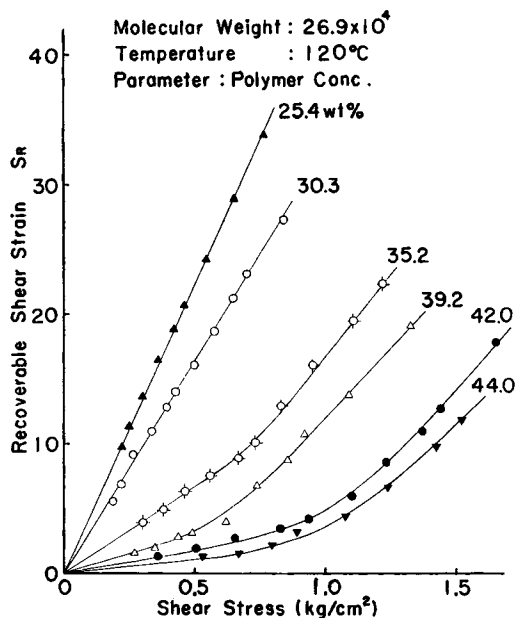


Fig. 2. Recoverable shear strain versus shear stress for solution of acrylonitrile copolymer of $M_w = 26.9 \times 10^4$ at various concentrations.

Figures 4 and 5 are plots of the shear-stress dependence of the shear modulus in polymer solutions. From these figures one can see that all the shear moduli begin to decrease almost at the same shear stress, regardless of the concentration and the molecular weight of the polymer in solution. Furthermore, these figures show that the shear modulus of solutions with concentrations that are lower than the critical concentration keeps a

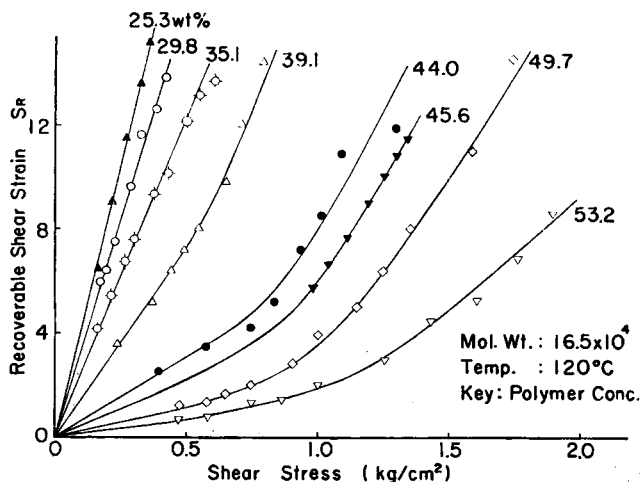


Fig. 3. Recoverable shear strain versus shear stress for solution of acrylonitrile copolymer of $M_w = 16.5 \times 10^4$ at various concentrations.

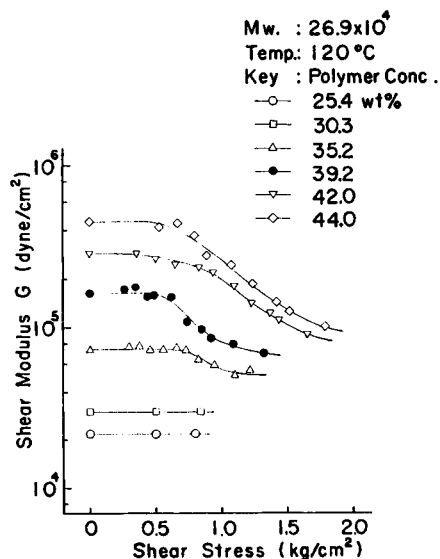


Fig. 4. Shear-stress dependence of shear modulus for solutions of acrylonitrile copolymer of $M_w = 26.9 \times 10^4$ at various concentrations.

constant value independently of the shear stress. The critical concentration depends on the molecular weight of the samples, and its meaning is described elsewhere.¹

Figures 6 and 7 show the dependence of the shear modulus on the shear stress. The increase in shear stress turns out to be a reduction in shear

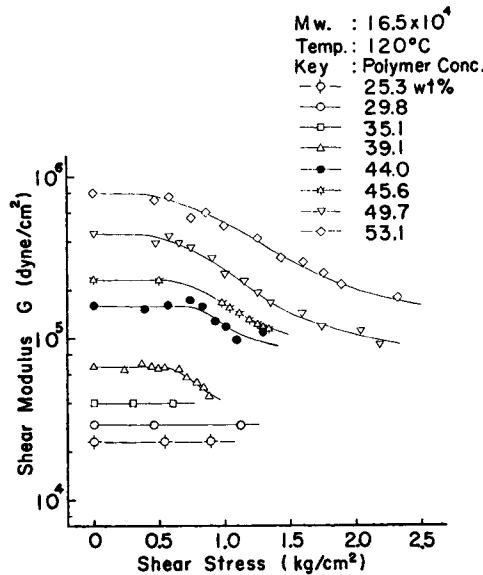


Fig. 5. Shear-stress dependence of shear modulus for solutions of acrylonitrile copolymer of $M_w = 16.5 \times 10^4$ at various concentrations.

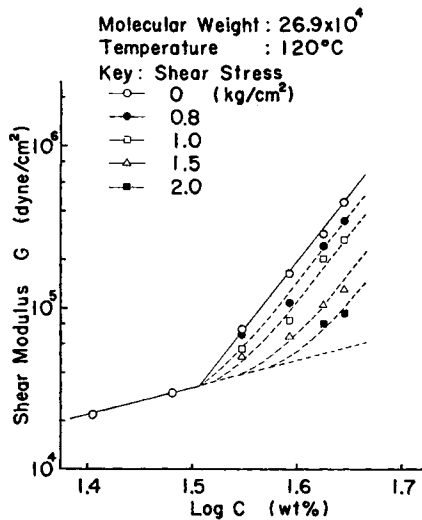


Fig. 6. Shear modulus versus polymer concentration for solutions of acrylonitrile copolymer of $M_w = 26.9 \times 10^4$ at various shear stresses.

modulus. It means a breakdown of the tangled network structure, namely, the elastically deformable pseudo network. Furthermore, these figures indicate that the critical concentrations, which are represented as inflection points of the plots of $\log G$ versus $\log C$ on the constant shear-stress basis, become higher with increasing shear stress.

Schreiber⁵ has shown that there are at least three ways in which the dependence of viscosity-molecular weight functions on shear stress could

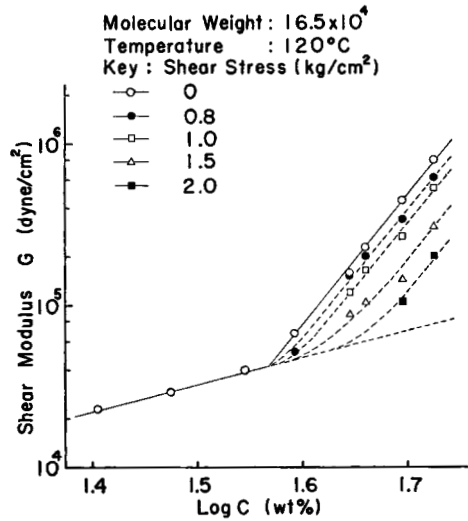


Fig. 7. Shear modulus versus polymer concentration for solutions of acrylonitrile copolymer of $M_w = 16.5 \times 10^4$ at various shear stresses.

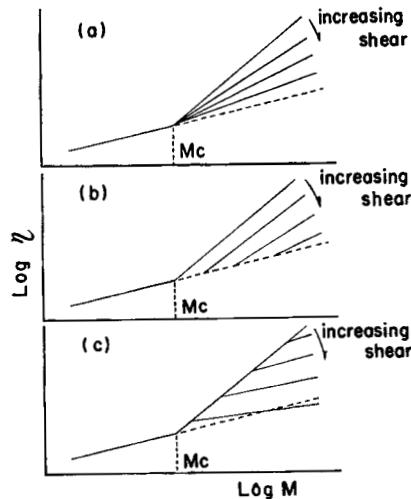


Fig. 8. Possible shear dependence of viscosity-molecular weight function of polymers.

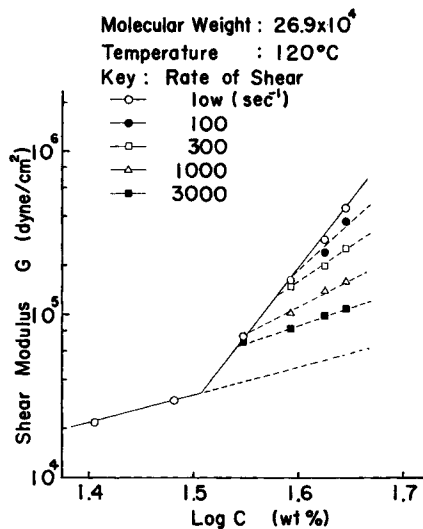


Fig. 9. Shear modulus versus polymer concentration for solutions of acrylonitrile copolymer of $M_w = 26.9 \times 10^4$ at various shear rates.

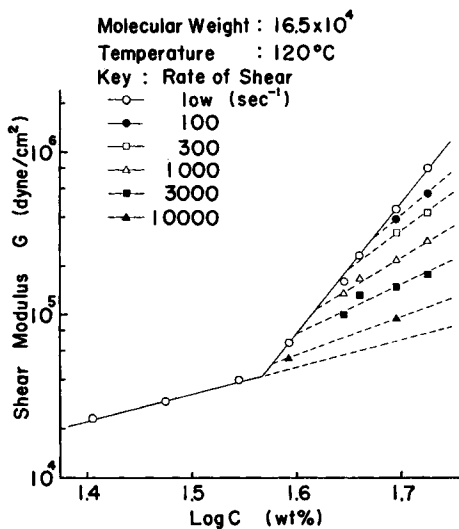


Fig. 10. Shear modulus versus polymer concentration for solutions of acrylonitrile copolymer of $M_w = 16.5 \times 10^4$ at various shear rates.

be represented. They are schematically shown in Figure 8. The two types shown in the diagrams (a) and (c) have been reported by several workers, but the other type (b) has not been reported with any experimental evidence to substantiate its existence. Figures 6 and 7 have the intermediate properties of the type (a) and (b) on the constant shear stress basis, although viscosity and molecular weight must be replaced by shear

modulus and polymer concentration, respectively. However, Figures 9 and 10, which are plotted on the constant shear rate basis for the same data, resemble the type (c) of Figure 8. The same phenomena have been observed in the plots of viscosity versus molecular weight, as suggested by Schreiber.

To compare the shear-rate dependence of viscosity with the shear-rate dependence of the shear modulus, Figure 11 is shown for a 44.0 wt.-% solution of acrylonitrile copolymer of molecular weight 26.9×10^4 . This figure shows that the decrease of the shear modulus occurs at higher shear rates than those at which the decrease of the viscosity occurs and that the viscosity still decreases in the shear-rate region where the shear modulus becomes constant. A similar tendency has been reported by Jobling and Roberts⁶ for Al-laurate in petrol peptized with an ethoxyethyl system.

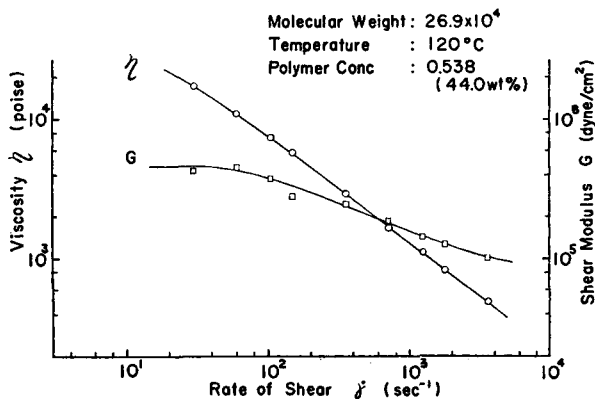


Fig. 11. Viscosity and shear modulus as functions of rate of shear in 44.0 wt.-% concentrated solutions of acrylonitrile copolymer of $M_w = 26.9 \times 10^4$.

In conclusion, the shear modulus of the concentrated solution of acrylonitrile copolymer exhibits non-Hookian behavior, just as the viscosity of this solution exhibits non-Newtonian characteristics. However, when a stress is applied to the system, there are two kinds of response which are caused by a breakdown of the network structure of the chain entanglements. The first is shown to be a late change in shear modulus caused by the bulk deformation of the network as the shear rate increases; the second, an early change in viscosity caused by the local disappearance of network points, which might contribute slightly to the first-type, considering the shear-stress dependence of viscosity and shear modulus.

The authors wish to thank Masao Sone for his advice in the preparation of this manuscript and Japan Exlan Co. Ltd., for permission to publish this work. We are indebted to Hiroshi Inagaki and Tadao Kotaka of Kyoto University for their valuable discussion of the problems. Some of the measurements were performed with the assistance of Toshio Suda, for whose help we also express sincere thanks.

References

1. T. Hayahara and S. Takao, *J. Appl. Polymer Sci.*, **11**, 735 (1967).
2. T. Hayahara and S. Takao, *Kobunshi Kagaku*, **23**, 181 (1966).
3. E. B. Bagley, *Trans. Soc. Rheol.*, **5**, 355 (1961).
4. W. Philippoff and F. H. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
5. H. P. Schreiber, *Polymer*, **4**, 365 (1963).
6. A. Jobling and J. E. Roberts, in F. Eirigh, Ed., *Rheology*, Vol. II, Academic Press, New York, 1958, Ch. 13.

Received December 11, 1967