Rheology of Poly(Vinyl Pyrrolidone) in Aqueous and Organic Media

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Summary: The viscosity of moderately concentrated solution of Poly(vinyl pyrrolidone) (PVP) has been studied in water and ethanol at different shear rate conditions in the temperature range of 283-323 K and concentration range of 2-10g/dl. The study shows that PVP solutions are Newtonian at high shear rates and non Newtonian fluid in the low shear rate region.

Introduction

The rheological behaviour of concentrated polymer solution in low molecular weight solvent is important in polymer processing and considerable attention has been given to the determination of the temperature and molecular weight dependence of the zero shear viscosity of polymer solution and melts [1].

The rheological properties of PVP in selective solvents have been investigated either in very dilute or in concentrated solutions [2-5]. Similar data in the moderately concentrated region are not available. In this presentation a study on PVP in water and ethanol media has been undertaken for understanding the structure, shear viscosity-concentration and viscosity-temperature dependence.

Results and Discussion

Values of shear viscosity at different shear rates and concentrations in water and ethanol were determined and Figures 1 and 2 are representative plots of the same data. It can be seen that shear viscosity decreases rapidly upto shear rate 50 sec^{-1} and beyond this values it becomes independent of the shear rate. This means that PVP solutions are non-Newtonian in the shear rate range 7-50 sec^{-1}. Moreover, significant increase in the viscosity takes place with increasing PVP concentration as the system offers more resistance to flow. This behaviour can be explained by the hydrodynamic theory of rodshaped particles [6]. The PVP molecule is tightly coiled [7,8]. A decrease in shear viscosity with increasing shear rate is due to tendency of PVP molecule to orient more and more in the direction of shear. However at high shear rates the elastic forces of deformation of the molecules counter balance the effects of shear and thus the viscosity is independent of the shear rate (Newtonian region). This behaviour is observed for PVP solution in ethanol and water. The solution are Newtonian in the shear rate range 57.6-460.8 sec^{-1} while a rapid decrease in viscosity was observed at shear rate range 7.2-57.6 sec^{-1}. In this region the molecules start behaving like fully extended chains, shear stress open up the structure of PVP in solution.

The zero shear viscosity, η_o, which is a measure of the energy dissipation and complex function of several variables such as molecular weight, concentration, temperature, and nature of solvent, can be estimated from the graph of shear
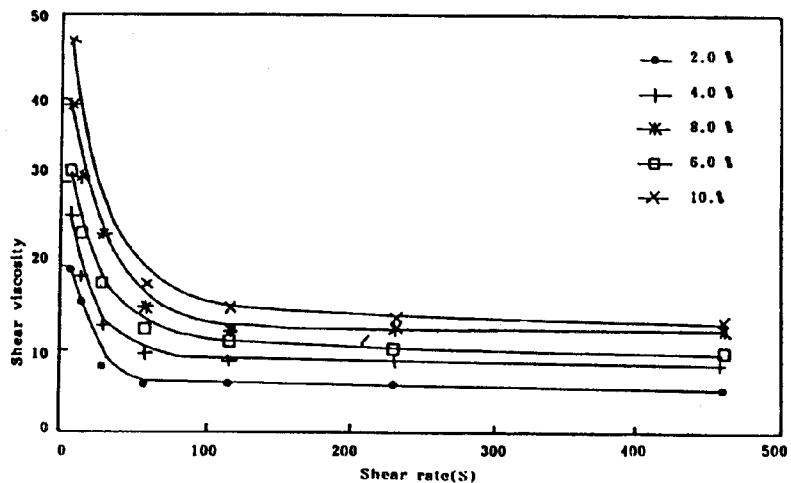
Fig. 1: Plot of shear viscosity vs shear rate for aqueous PVP solution at 303K.
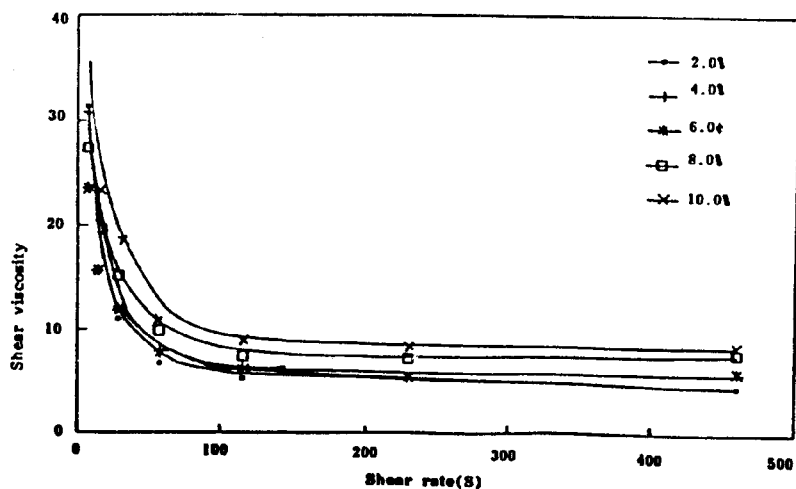

Fig. 2:   Plot of shear viscosity vs shear rate for PVP-ethanol system at 303K.
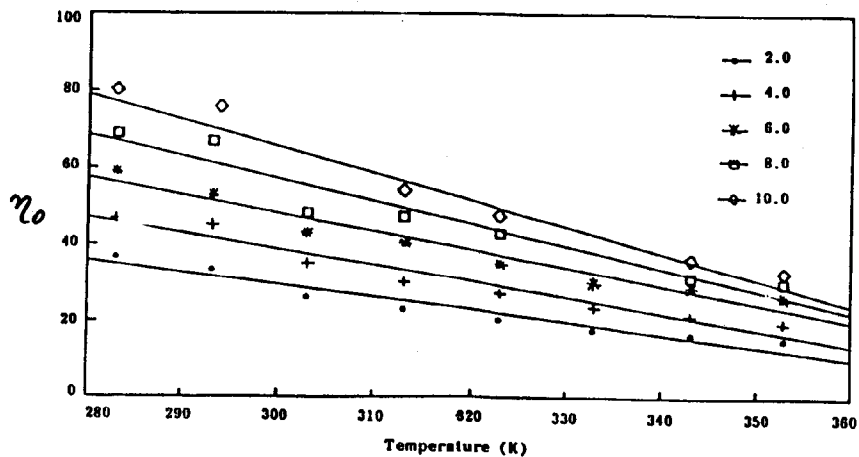

Fig. 3: Plot of zero shear viscosity versus temperature for aqueous PVP solutions at different concentrations.
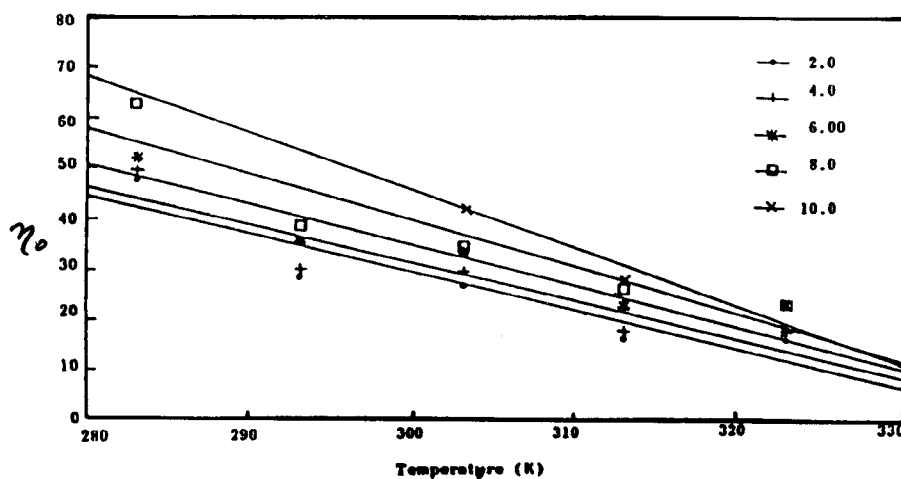
Fig.4:   Zero shear viscosity versus temperature for PVP-ethanol system at different concentrations.
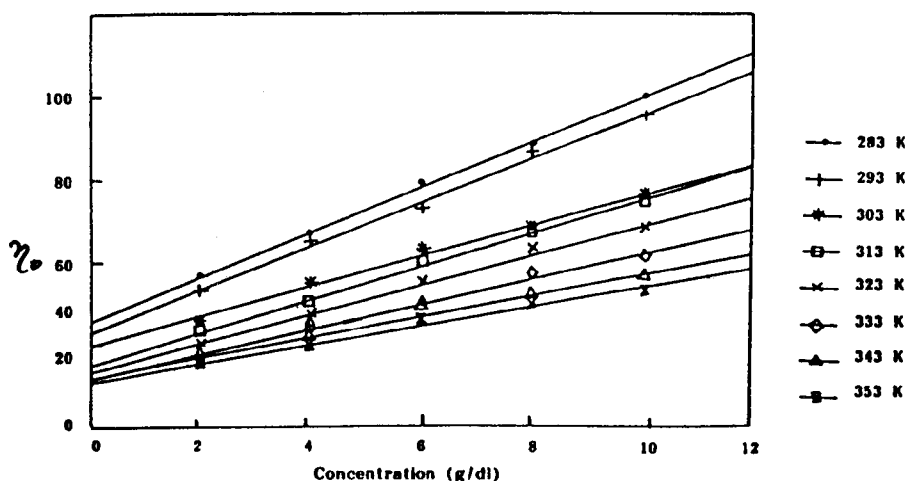

Fig.5:   Plot of zero shear viscosity versus concentration for aqueous PVP solutions at different temperatures.

viscosity versus shear rate by extrapolation to zero shear rate. To minimize the error, linear least square method was applied. The η_o values are sensitive to change in concentration [7]. Figs 3,4 represent graphically, this variation in both solvents. The low values of η_o at lower concentration may be due to the retardation of rotation in PVP molecules. When there is a lower retardation of rotation, the molecules are usually flexible and so the η_o is lower. Increase in concentration can cause a decrease in flexibility, more retardation of rotation will be occurring and there by the internal resistance to flow increase, eventually increasing the η_o [9]. Interaction among

polymer molecules at increased concentration results in overlapping of segments causing an increase in viscosity [10].

The zero shear viscosity is plotted against temperature for both solvents (Figs. 5,6). A gradual decrease in η_o with increase in temperature has been observed. This is expected as the fluidity is an increasing function of temperature.

Experimental

The polymer (PVP) used was obtained from General Aniline and Film Corporation Wayne, N.J.
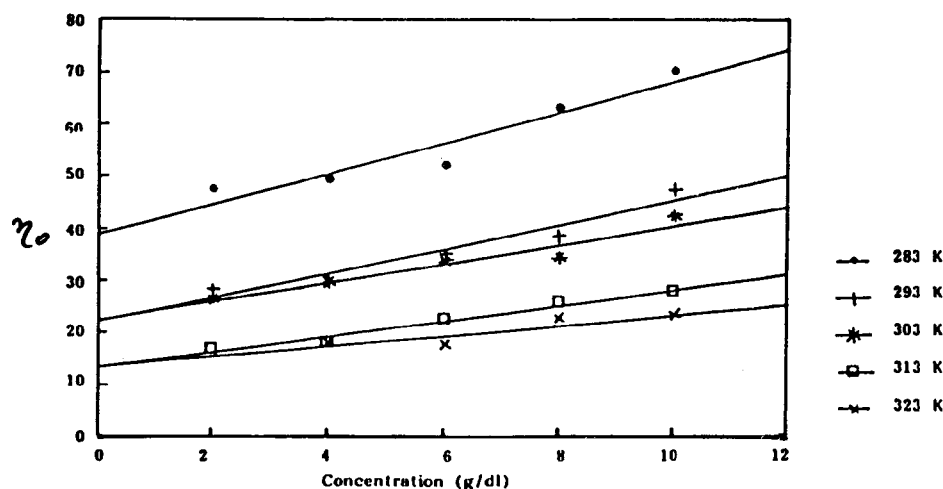
Fig.6:   Plot of zero shear viscosity versus concen-tration for PVP-ethanol system at different temperatures.

USA. The sample being hygroscopic, crystalline powder was heated in an oven for an hour at 50°C before use. Doubly distilled water and ethanol (analytical grade, Merck) were used as solvents.

Moderately concentrated solutions of PVP in the range 2.0-10.0g/dl were prepared. Shear viscosity of each sample was measured with a HAAKE rotary viscometer (Germany) using the system "MV II". The resultant torque(s) were obtained at different temperature ranging from 283-323 K for ethanol and 283-353 K for water with an interval of 10 K at known rotor speed. The shear viscosity was calculated using the relations, γ = M x n; τ = A x S and η = G x S/n, where M. A. and G are instrumental constants, for the MV II sensor system, having values M=0.9, A=3.76 and G = 4147. The shear rate (γ) has a unit sec^{-1}. Shear stress Pa (Pascal)= 1 N/m^2 and viscosity (η) = m. Pa. sec. Where 1mPa. sec=10^{-3}N.s/m^2.

Acknowledgement

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