

THE RHEOLOGICAL PROPERTIES OF POLYANILINE SOLUTION

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ABSTRACT

This paper presents our work on the rheological properties of the solution of polyaniline (PAn) in N-methyl-2-pyrrolidone (NMP). The results indicate that the solution's non-Newtonian property becomes more prominent with the increase in solution-concentration, exhibiting the behavior of pseudo-plastic fluid. Besides, there is a critical concentration C_c (around 0.06 g/ml), beyond which the viscosity of the PAn/NMP solution takes a sudden increase. With temperature rising, both the viscosity and the thixotropy of the solution decrease, implying that there exist physical cross-linking interactions between the molecular chains in the solution.

INTRODUCTION

As a novel conductive polymeric material, polyaniline has attracted much attention because of its high electrical conductivity, air stability and potential of practical application^[1-3]. At present, research in this field has been very active. Since polyaniline is not possible for melt processing, processing with its solution becomes more and more important, but its insolubility in most organic solvents has hindered the study of its structure, processing and application^[4,5]. However, rapid development has been made for the synthesis of soluble polyaniline recently^[6,7]. In our laboratory too, two soluble polyanilines, poly-(o-methylaniline) and poly-(m-methylaniline), have been successfully synthesized^[8]. And studies on synthesis, relationship between structure and properties, and application of these soluble polyanilines have been carried out^[9-11], especially on the rheological

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properties of the solution, as solution processing is the only way to realize its application, while not much work on this subject has been reported in literature. This paper presents our work on the rheological properties of the solution of polyaniline in *N*-methyl-2-pyrrolidone.

EXPERIMENTAL

The polyaniline (PAn) used in this work was the powder without doping, synthesized by a chemical method^[8] in our laboratory. Chemically pure *N*-methyl-2-pyrrolidone (NMP) was used as solvent. PAn/NMP solutions of different concentrations were prepared under the same conditions. RPX-705 multi-function rheometer was used to determine the viscosity of concentrated PAn/NMP solution at room temperature (21.5°C). A cone viscometer with diameter of 6 cm and angle of 1.5° was used.

RESULTS AND DISCUSSION

Shown in Fig. 1 are the curves of relationship between the shear stress τ and the shear rate $\dot{\gamma}$ of three solutions of different concentrations, i. e., 0.05, 0.07 and 0.09 g/ml for curves 1, 2 and 3, respectively. It can be seen that curve 1 is linear which typifies the behavior of Newtonian fluid. However, with the increase in concentration, behavior of pseudo-plasticity of PAn/NMP solutions becomes more and more obvious, as shown by curves 2 and 3. It should be pointed out that for curve 2, when the $\dot{\gamma}$ is over 1000s^{-1} , the relation between τ and $\dot{\gamma}$ is linear, implying that the rheological behavior depends on shear rate as well. This result is in agreement with that shown in Fig. 2.

Fig. 2 shows the dependence of viscosity on shear rate for PAn/NMP solutions of different concentrations. η_0 is the viscosity of solution, η_s is the viscosity of solvent. It can be seen that at lower solution concentration, i. e., curves 1 and 2, the viscosity of PAn/NMP solution almost remains unchanged with respect to the shear rate, which indicates the behavior of Newtonian fluid. However, with the increase in concentration, the viscosity deviates from the behavior of Newtonian fluid gradually and exhibits the property of pseudo-plasticity. This means that the chance of interchain contact increases with

solution concentration which in turn strengthens the interchain force, resulting in the formation of interchain cross-links. But this kind of cross-linkages can be disrupted easily by a strong shear stress, which makes the viscosity decrease. The higher the shear rate is, the more quickly the viscosity decreases, especially, at higher solution concentration, the higher the rate of decrease in viscosity is, as shown by that the distance between curves 1, 2 and curves 3, 4 and 5, is getting nearer and nearer with increasing shear rate.

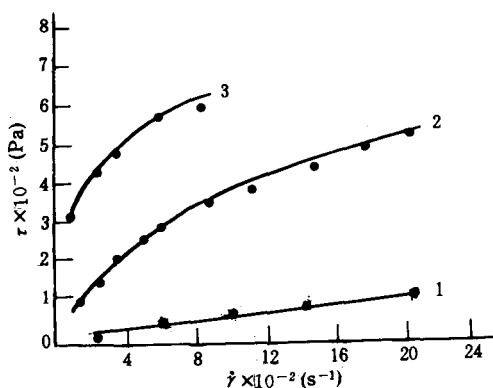


Fig. 1 Shear rate dependence of shear stress for PAN/NMP solution. The concentrations of the solutions are (1) 0.05 g/ml, (2) 0.07 g/ml, (3) 0.09 g/ml, respectively

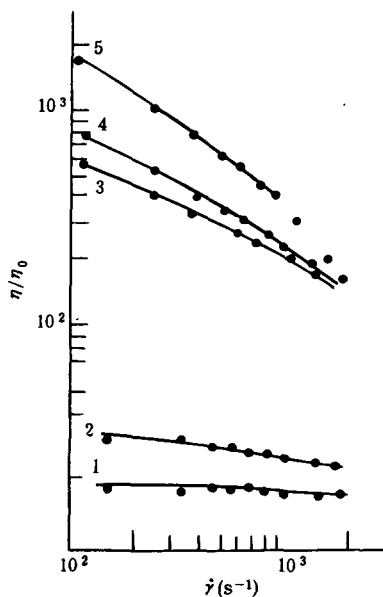


Fig. 2 Shear rate dependence of the viscosity for PAN/NMP solution at the concentration of (1) 0.04, (2) 0.05, (3) 0.07, (4) 0.08, (5) 0.09 g/ml, respectively

The rheological behaviors of samples 1 and 2 are quite different from that of samples 3, 4 and 5, (see Fig. 2). This fact indicates that there exists an obvious change of the rheological property of PAN/NMP solution within the concentration range of 0.05–0.07 g/ml. The relation between viscosity and concentration for PAN/NMP solution is shown in Fig. 3. The viscosity of PAN/NMP solution increases with the increase in solution concentration in the same manner even under different shear rates until solution concentration is 0.06 g/ml. After that the viscosity increases sharply, but with different rates for the three different samples, i. e., it separates into three curves. Therefore, the solution concentra-

tion of 0.06 g/ml could be considered as the critical concentration C_v , over which the concentration dependence of viscosity is very strong. This is because when concentration is higher than C_v , the near enough distance between PAn molecular chains and the strong solvation action of NMP make the interchain force abruptly increase, which results in the formation of network system of the chains. This makes the volume of fluid mechanics increase and hence the viscosity rises rapidly. Such kind of interchain action may be the main cause for the formation of gel of PAn/NMP concentrated solution. The gelation behavior of this solution will be reported in another paper.

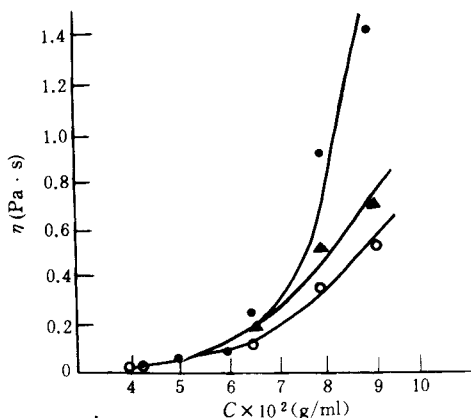


Fig. 3 The relation between viscosity and concentration for PAn/NMP solution at different shear rates: (○) 1000s^{-1} (▲) 600s^{-1} (●) 200s^{-1}

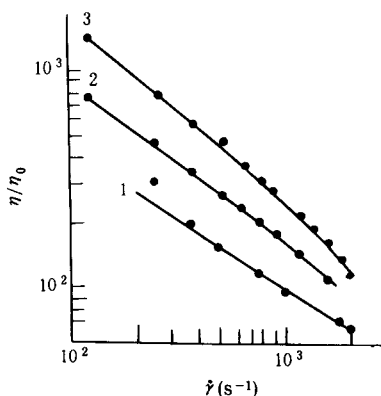


Fig. 4 The change of the viscosity of PAn/NMP solution with the shear rate at different temperatures: (1) 43.0°C (2) 33.1°C (3) 23.1°C

From Fig. 2, it is known that the shear rate dependence of viscosity is very strong when $C=0.09$ g/ml. This dependence is also affected by temperature as shown by the curves in Fig. 4, i. e., the lower the temperature, the greater the effect. It is reasonable that at lower temperature, molecular thermal motion is weak, the physical crosslinks are slightly destroyed by thermal motion but strongly affected by shear stress. The temperature dependence of viscosity for PAn/NMP solution is shown in Fig. 5. The viscosity decreases rapidly at near room temperature but when the temperature is raised above 30°C , the viscosity decreases rather slowly.

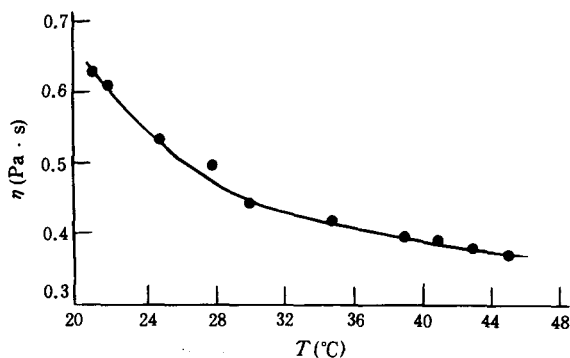


Fig. 5 The effect of temperature on the viscosity of PAn/NMP solution ($\dot{\gamma} = 582\text{s}^{-1}$, $C = 0.09\text{ g/ml}$)

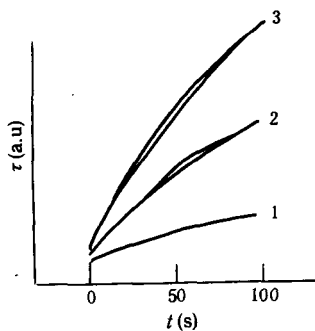


Fig. 6 The thixotropic behavior of the PAn/NMP solution at different concentrations: (1) $C = 0.055$ (2) 0.065 and (3) 0.09 g/ml , respectively, $\dot{\gamma} = 968\text{s}^{-1}$, $T = 30^\circ\text{C}$

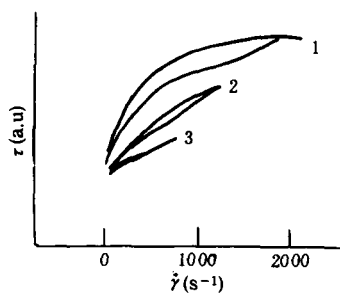


Fig. 7 The thixotropic behavior of the PAn/NMP solution at different $\dot{\gamma}_{\text{max}}$: (1) 1990s^{-1} (2) 1325s^{-1} (3) 698s^{-1}

The thixotropic behavior of concentrated PAn/NMP solution was determined in a "triangle" shear field. In this method the increase in shear rate is kept linear first to a predetermined maximum, then it decreases linearly. During this time, the value of the corresponding shear stress is determined and the rheometer automatically gives a hysteresis loop, as shown in Fig. 6–8.

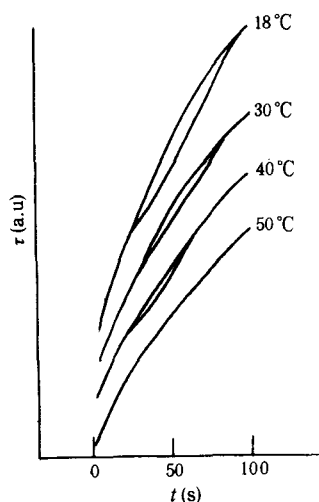


Fig. 8 The thixotropic behavior of the PAN/NMP solution at different temperatures as shown in the figure
 $C = 0.09 \text{ g/ml}$, $\dot{\gamma}_{\max} = 968 \text{ s}^{-1}$

As known, the bigger the enveloping area in the hysteresis loop is, the stronger the thixotropy of the solution is. Then, from the figures, it is seen that the thixotropic behavior of PAN/NMP solution becomes more and more obvious with increasing concentration (Fig. 6) and shear rate (Fig. 7), but reverse is true for temperature (Fig. 8). Right after the completion of the first hysteresis loop, the second one was recorded. It is noticed that the second one is below the first one and its area is smaller than that of the first one.

Keywords:

Polyaniline solution; Viscosity; Rheological property; Thixotropy

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