

Rheological Behavior of Plasticized Polyaniline

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SYNOPSIS

In this article, rheological properties of polyaniline (PANI) doped with diisooctyl phosphate (DIOHP) are described. Rheological properties of this material depend strongly on the content of the dopant. For low concentrations, the material is rather stiff but becomes a Bingham or St. Venant body for higher contents of the dopant. Rheological parameters for samples containing various molar ratios of PANI to DIOHP were determined. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymers containing conjugated π -electrons systems like polyaniline, polythiophene, polypyrrole, etc., have been well known for many years.¹ A significant increase in interest in these materials was observed at the end of the 1970s, i.e., after discovering that after doping they showed very high conductivity which could be compared to the conductivity of some metals.²

However, this important discovery did not involve technological applications of conducting polymers. Synthesized polymers like poly(*p*-phenylene vinylene), polypyrrole, and nonsubstituted polythiophene³⁻⁶ were insoluble in common organic solvents and did not melt. As a consequence, they could not be processed into technologically useful forms.

During the last 10 years, soluble conducting polymers were obtained which can be processed from solution.⁷⁻⁹ However, this method of processing is usually technologically difficult and thus is rarely applied in industry. The most common methods of industrial processing of polymers are thermal processes. Much research, then, has focused on preparing thermally processable conducting polymers. The first thermally processable conducting polymer was obtained by PronŃ et al.¹⁰ In testing the process of protonation of PANI with phosphoric acid dyes-

ters, these authors noticed that the dopants not only increased conductivity of PANI but also plasticized it.^{10,11}

Plasticized PANI can be easily processed using methods commonly applied for plasticized PVC or cellulose derivatives. Thus, to develop methods of processing plasticized PANI and its blends with other classic polymers, determination of the rheological parameters of this material is necessary. These parameters are extremely helpful in the designing of forming methods, choosing the type of processing equipment, extruder dies, or formers construction, etc.

Most classical polymer melts are qualified as nonlinear viscoelastic liquids, i.e., are rheostable, possess a yield point, and undergo large entrance pressure drops. Depending on the shear rate, they show variable apparent viscosity.¹²⁻¹⁶ The simplest model that correctly describes the rheological properties of nonlinear viscoelastic liquids in the extended range of shear rate is the Herschel-Bulkey model. Equation (1) refers to this model^{17,18}:

$$\tau = \tau_0 + k\dot{\gamma}^{1/m} \quad (1)$$

where τ is the shear stress; τ_0 , the flow limit; k , the consistency coefficient; m , the flow coefficient; and $\dot{\gamma}$, the shear rate. Most well-known polymer melts show k and m values greater than 1.¹⁹⁻²²

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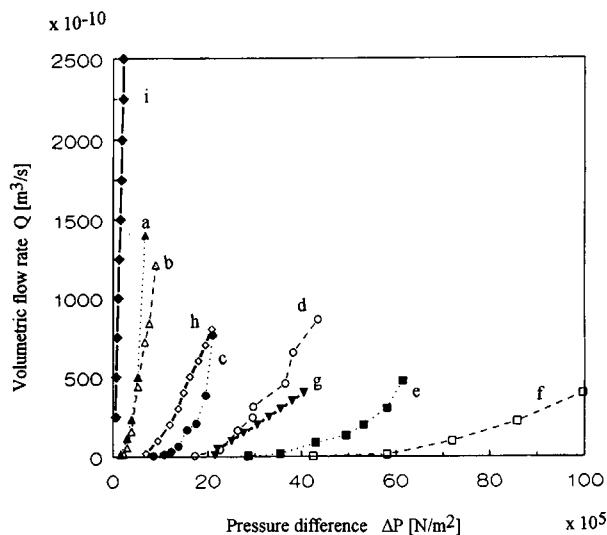


Figure 1 Volumetric flow rate vs. pressure difference for PANI(DIOHP)_y samples: (a) PANI(DIOHP)_{0.35}, capillary length 8 mm; (b) PANI(DIOHP)_{0.35}, capillary length 16 mm; (c) PANI(DIOHP)_{0.40}, capillary length 8 mm; (d) PANI(DIOHP)_{0.40}, capillary length 16 mm; (e) PANI(DIOHP)_{0.50}, capillary length 8 mm; (f) PANI(DIOHP)_{0.50}, capillary length 16 mm; (g–i) corrected flow curves for PANI(DIOHP)_{0.35}, PANI(DIOHP)_{0.40} and PANI(DIOHP)_{0.50}.

EXPERIMENTAL

Polyaniline was synthesized according to the method described previously.²³ Protonated polyaniline was obtained by extended mixing of PANI powder with neat liquid DIOHP in a mortar.

Rheological measurements were taken for the samples containing 0.35, 0.40, and 0.50 mol of DIOHP per 1 mol of PANI mers. Appropriate samples will be described in this article as PANI(DIOHP)_y, where $y = 0.35, 0.40,$ or 0.50 . All experiments were made at room temperature ($22 \pm 2^\circ\text{C}$) on a capillary rheometer (melt indexer).

The polymer was placed in a reservoir and then extruded out of the 8 or 16 mm-long capillary by means of a piston carrying varied dead weights. The quantities of the polymer coming from the capillary per unit of time were determined with 1 mg accuracy.

RESULTS AND DISCUSSION

The interpretation of the obtained results is based on the Rabinowitsch–Mooney equation¹⁶ describing the dependence of a volumetric flow rate on a pressure drop along the capillary caused by internal friction in the liquid. The capillary rheometer has a number of advantages. One of them is that the shear rates and flow geometry are similar to the conditions found in extrusion and in injection molding. However, the main disadvantage is that rate of shear is not constant but varies across the capillary and a sizable amount of the potential energy in the system must be used to accelerate the sample to the flow speed at the exit and to overcome turbulence at the entrance to the capillary. The measured pressure difference is strongly affected by entrance effects, nonlaminar flow in the entrance region, and non-steady-state flow conditions when the polymer is accelerated to flow through the capillary.

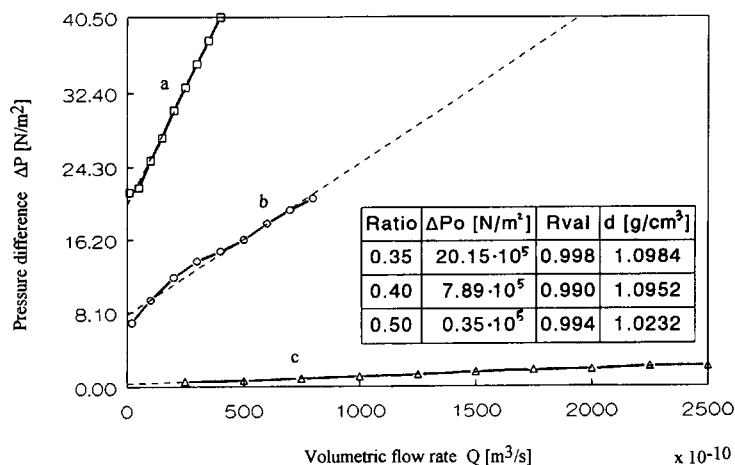


Figure 2 Graphical determination of yield points for (a) PANI(DIOHP)_{0.35}, (b) PANI(DIOHP)_{0.40}, and (c) PANI(DIOHP)_{0.50}.

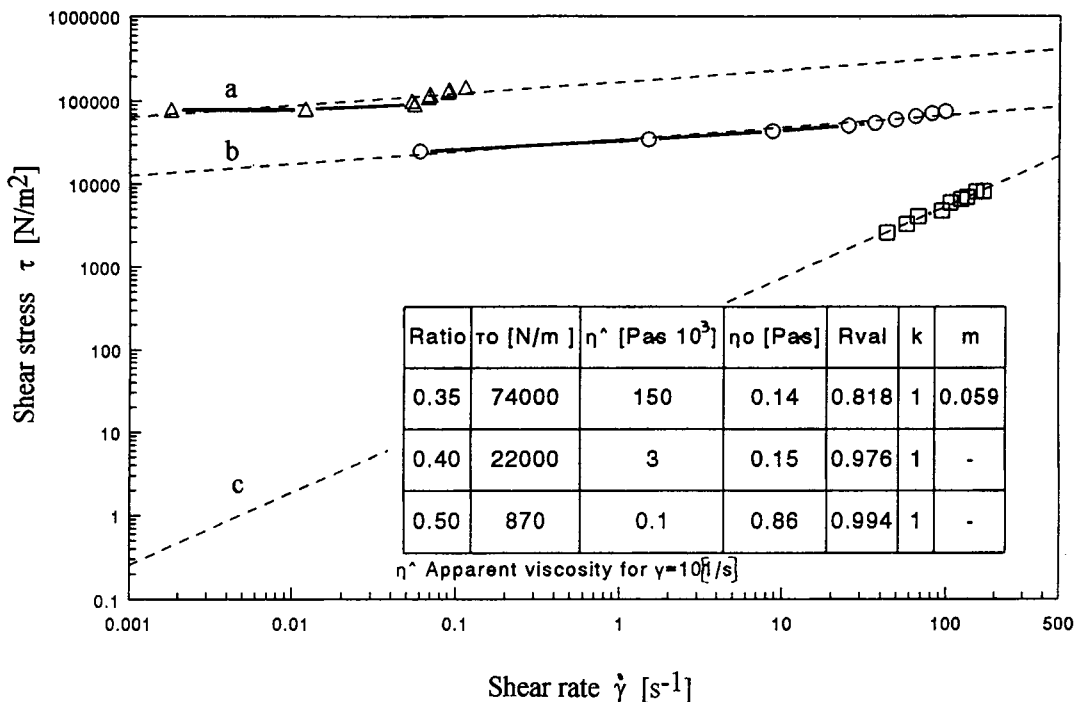


Figure 3 Flow curves of (a) PANI(DIOHP)_{0.35}, (b) PANI(DIOHP)_{0.40}, and (c) PANI(DIOHP)_{0.50}.

According to the selected model, Weissenberg-Rabinowitsch-corrected flow curves^{24,25} were used for the analysis. The dependence of the flow rate on the pressure difference for different capillary lengths and appropriate corrected flow curves are shown in Figure 1.

Yield points for all samples were counted using eq. (2):

$$\tau_0 = \frac{\Delta P_{\tau_0} \cdot R}{2L} \tag{2}$$

where R is the capillary radius, and L , the capillary length. ΔP_{τ_0} values were determined by extrapolation of the corrected curves to the ordinate (Fig. 2).

Figure 3 gives flow curves for PANI(DIOHP)_y samples. These curves allow us to determine the two

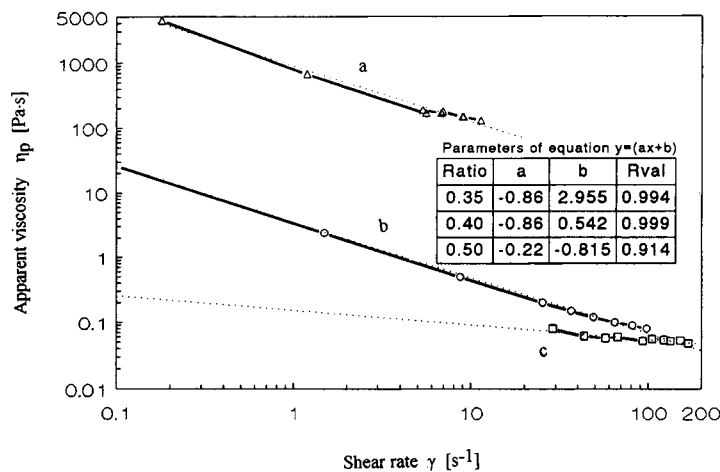


Figure 4 Viscosity curves for (a) PANI(DIOHP)_{0.35}, (b) PANI(DIOHP)_{0.40}, and (c) PANI(DIOHP)_{0.50}.

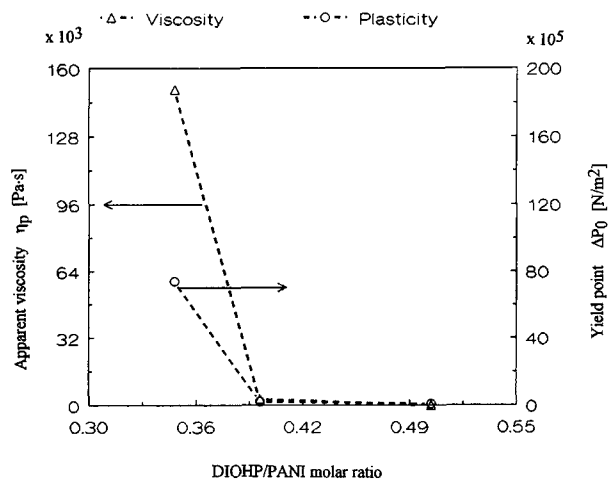


Figure 5 Apparent viscosity and yield points vs. DIOHP/PANI molar ratio. Shear rate: 10 s^{-1} .

constants k and m in the model defined by eq. (1). Having flow curves constructed, one can calculate apparent viscosities η_p from the definition:

$$\eta_p = \tau / \dot{\gamma} \quad (3)$$

Figure 4 shows plots of viscosity vs. shear rate for PANI(DIOHP)_y samples. Both flow and viscosity curves can be fitted to a straight line, which is characteristic of a Bingham-type body. Simultaneously, the decreasing of the apparent viscosity coupled with the increasing of the shear rate suggests that textural changes in the samples may be induced by shear. It is known that chain-type molecules can disentangle, stretch, and orient themselves parallel to the driving force. Figure 5 shows apparent viscosity and yield points vs. molar ratio of DIOHP to PANI at the same shear rate (10 s^{-1}). For PANI/DIOHP molar ratios lower than 0.4, a drastic apparent viscosity increase is observed. Similar changes are observed for yield point values. It indicates that the content of DIOHP in polyaniline samples has a significant influence on the rheological properties of the polymer.

The following explanation of an abrupt decrease of viscosity at ca. $y = 0.4$ can be proposed: Spectroscopic studies show²⁶ that for low values of y essentially all ester molecules participate in the protonation process. For $y > 0.3$, two types of ester molecules can be spectroscopically distinguished: those which protonate polyaniline and those which solvate the protonating species via hydrogen bonding. The plastification threshold occurs with the spectro-

scopic appearance of the solvating molecules. Moreover, even if a large excess of DiOHP is used, the protonation level of PANI(HCl)_{0.4} is never achieved, i.e., the solvation process is of crucial importance for the plasticization of polyaniline.

CONCLUSIONS

Aliphatic and aromatic diesters of phosphoric acid protonate polyaniline inducing its conductivity and simultaneously plasticizing it. Increasing the content of the diester in the material causes a significant decrease in its viscosity and lowers its yield point as well. Samples containing more than 0.35 mol of diester per 1 mol of polyaniline mers behave like Bingham bodies.

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