

Modification of Non-Newtonian Flow Behavior of Aqueous Solution of Poly(vinyl alcohol) by Conducting Polypyrrole Prepared by *In Situ* Polymerization of Pyrrole

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ABSTRACT: The rheological behavior of an aqueous solution of poly(vinyl alcohol) (PVA) and polypyrrole (PPY) dispersions prepared by ferric chloride (FeCl_3)-catalyzed polymerization of pyrrole was investigated at 12°C using a coaxial rotational viscometer. The results show that the addition of a low dose of FeCl_3 to the PVA solution greatly influences its rheology. The prominent shear-thickening (dilatant) nature of PVA turns significantly pseudoplastic (shear thinning) in the presence of FeCl_3 . Polypyrrole-loaded PVA was obtained in a stable, optically clear dispersion by *in situ* polymerization of pyrrole in an aqueous PVA solution (5%) using FeCl_3 as the oxidative catalyst at 12°C . The PPY dispersions in aqueous PVA systems having a low loading of PPY and low Fe^{+3} content retain the dilatant

character of an aqueous PVA solution; however, for an aqueous PVA system having a relatively high PPY loading and also a high Fe^{+3} content, prominent pseudoplastic (shear thinning) behavior is exhibited. The odd novel rheological patterns exhibited by a PVA solution in the absence and presence of FeCl_3 and the PVA–PPY dispersions containing FeCl_3 under different sets of conditions are explained on the basis of the complexation of PVA by Fe^{+3} and related ions and also as a consequence of some degree of H-bonding and chemical grafting between the support polymer PVA and the PPY formed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3737–3741, 2004

Key words: rheology; polypyrroles; relaxation; shear

INTRODUCTION

Polymer-dispersion systems show a variety of intriguing rheological phenomena, which have been the subject of many investigations in the last few decades, mainly because of the need for relevant information across diverse industries, in addition to intellectual curiosity within the scientific community. Polymer dispersions cover the complete spectrum of rheological behavior from purely viscous to viscoelastic and elastic. Although the viscosity behavior of different polymer and polymer dispersions has been well researched, the generalization of the flow behavior of a dispersion and subsequent prediction of viscosity of that system were found to be difficult owing to many odd influencing parameters. The rheological behavior of a polymer solution holding dispersed particles depends mainly on the polymer matrix¹ and its concentration and on the type of dispersed particles including their particle size and particle-size distribution.² A fluid medium consisting of a polymer or containing a polymer in solution or dispersion is mostly non-Newtonian. Deviations from Newtonian behavior for a

dispersed system increase with an increasing concentration of the dispersed particles. For non-Newtonian polymeric dispersions, the relative viscosity is a function of the shear stress rather than of the shear rate and volume fraction of the dispersed particles. The relative viscosity normally decreases with an increasing shear rate.^{3–5}

Rheological studies of solutions or dispersions of conducting polymers such as polyaniline and polypyrrole are scanty.^{6–8} The present article reports the rheological patterns of an aqueous solution of poly(vinyl alcohol) (PVA) and its modification in the presence of a complexing metal salt such as FeCl_3 . Modifications of the rheology of a PVA solution also due to *in situ* formation of polypyrrole (PPY) as a consequence of oxidative polymerization of pyrrole in its presence under the influence of an FeCl_3 catalyst also constitute part of the subject matter of the present study.

EXPERIMENTAL

Materials

PVA (molecular weight 100,000, from Wilson Laboratories, India), ferric chloride (FeCl_3 ; S.D Fine-Chem. Ltd), and pyrrole, (S.R.L., India) were used without purification. The water used for polymerization was purified by distillation in a borosilicate glass distillation unit.

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TABLE I
Composition of PVA Solutions and PPY-PVA-Fe⁺³ Systems

Composition	Sample code						
	S ₀	S ₁	S _a	S _b	S _c	S _d	S _e
PVA solution (10%; mL)	35	35	35	35	35	35	35
Water (mL)	35	35	35	35	35	35	35
FeCl ₃ (g)	0	1.17	0.58	1.16	2.33	3.49	4.67
Pyrrole (cm ³)	0	0	0.25	0.50	1.00	1.5	2.00

Methods

Synthesis of PPY in presence of PVA as the water-soluble support polymer

PPY was synthesized from the pyrrole monomer in the presence of an aqueous solution of PVA as the support polymer using ferric chloride as the catalyst for oxidative polymerization of pyrrole. In a typical experiment, 0.25–2.0 mL of purified pyrrole was added to 35 mL of a 10% aqueous solution of PVA and stirred for 1 h at 12°C, and the resulting solution was named solution A. In another container, 0.58–4.67 g of ferric chloride was dissolved in 35 mL of chilled (12°C) water (solution B) which was then added dropwise with constant stirring to solution A, maintaining a 1:1 mol ratio of pyrrole to ferric chloride in each case after the final addition. Oxidative polymerization of pyrrole was carried out for 3 h and the result was optically clear; fine dispersions containing different loadings of PPY nanoparticles stabilized by the support of the water-soluble polymer PVA were then studied for assessment of their rheological behavior.

Rheological studies of aqueous PVA solution and PPY-PVA-Fe⁺³ dispersions

The recipe of different dispersions used for the rheological studies are shown in Table I. The rheological behaviors of different solutions or dispersions (Table I) were studied using a coaxial rotational viscometer (Rheotron, Model 2744 E, from Brabender, Germany). The coaxial cylinder system with the inner fixed cylinder (8-cm diameter, 54-mm height) and the outer rotating cylinder (56-mm height) and about a 63–65 mL solution was used for the rheological studies in each case. Measurements in the Rheotron equipment were done at 12°C, employing shear rates of 1–20 s⁻¹.

The shear stress (τ) developed and shear viscosity (η) values corresponding to the different applied shear rates (D) were calculated from the data recorded or displayed using instrument constants. A time interval of 30 s was allowed between the application of successive shear rates. The relaxation time of a selected sample was obtained from the measured value of the maximum shear stress developed at a given shear rate (2–10 s⁻¹), and in each such case, the exponential

decay of the maximum stress on withdrawal of the shearing action was followed for obtaining the relaxation time (t_R).

RESULTS AND DISCUSSION

Shear viscosity versus shear rate data for PVA solutions

The shear responses of aqueous PVA solutions in the absence and presence of FeCl₃ are shown in Figure 1. In each case, viscosity changes with time with an increasing trend until it reaches a steady maximum value for a given shear rate and the maximum viscosity attained is considered in the plots. The viscosity of an aqueous PVA solution (5%) increases with increase in the shear rate and, finally, it nearly attains a steady-state value (38 MPa s) over a higher shear-rate zone (>4 s⁻¹; shear thickening or dilatant behavior). Over a very low shear-rate zone (to 0.5 s⁻¹), a hump or over-

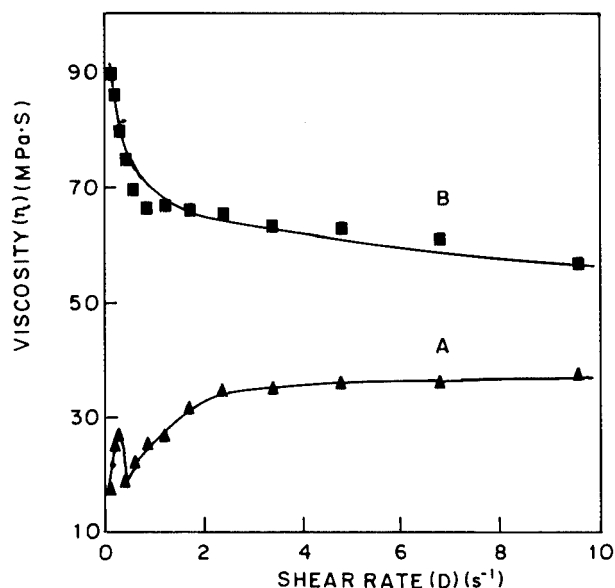


Figure 1 Plots of shear viscosity (η) versus shear rate (D) for PVA solutions: (A) PVA only; (B) PVA with FeCl₃ [spread of experimental data for η is covered by the height of triangles (for plot A) and squares (for plot B) in the figure].

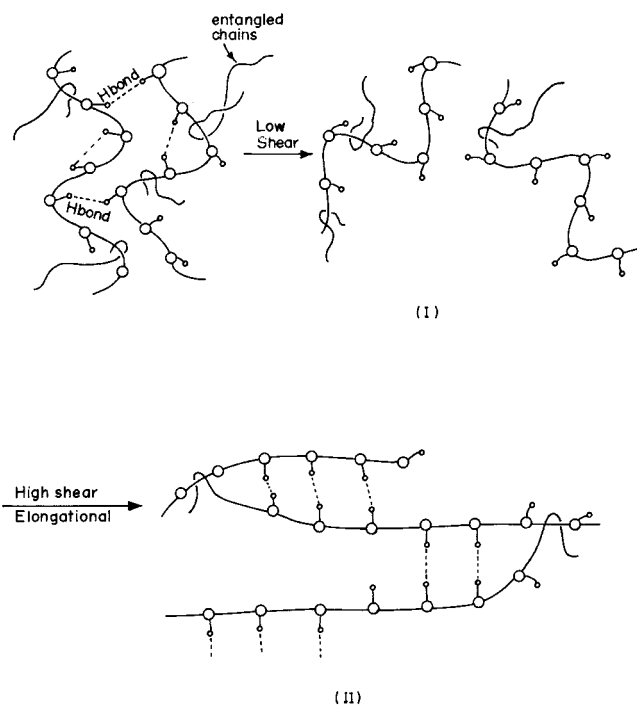


Figure 2 Schematic structural changes in PVA during shearing in solution.

shoot is (repeatedly) observed, and it apparently originates from the energetic association or clustering of chain segments of PVA and it is certainly not due to the spread of experimental values or other odd effects. Transient network theories^{9,10} are best suited to explain the odd perturbation or overshoot phenomenon over a very low shear-rate zone. The transient networks formed through H-bonding can be susceptible to breakage and reformation in the presence of a deformation field (shear action). The energy of a H-bonding interaction is an order of magnitude less than is the energy of a carbon-carbon covalent bond. Therefore, the static-state energetic interactions can be broken easily without disturbing the strong covalent bonds by separating the interacting sites to a distance greater than the minimum bonding distance (2–5 Å) simply by application of the shear action. Strong shear would have sufficient energy to easily break both intrachain as well as interchain H bonds [Fig. 2(I)]. The broken H bonds will try to reform due to a thermodynamic (free energy) driving force.

The reformation process would involve cooperative mobility of the network chains, which inherently have slow dynamics. Moreover, the probability of successful bonding depends on the proper orientation of the approaching donor-acceptor groups. On the other hand, the stretching of individual chain molecular coils caused by the shear-induced flow can also aid rapid association of the molecular chains primarily through interchain H-bonding. The chain entangle-

ments can favorably assist in the building up of the H-bonding [Fig. 2(II)], by keeping the close-by chains in a stretched state and the forming or reforming of staggered intermolecular structures as shown in Figure 2(II) by a cooperating zipping effect; the polar groups located next to an already-formed H bond then find it relatively easy (in an entropy sense) to form a similar bond. It is very clear that at high shear rates the formation of staggered ladderlike structures [Fig. 2(II)] are highly favored, so the viscosity increases with an increasing shearing action and it finally reaches a nearly steady value for use of a shear rate of $>4 \text{ s}^{-1}$ on attainment of equilibrium staggering of PVA chain molecules (plot A, Fig. 1).

So, due to the cooperative effects, the PVA solution initially shows a prominent dilatancy behavior although some odd perturbations in the initial stage, with an increasing shear rate that finally turns near-Newtonian over the high shear-rate zone ($>4 \text{ s}^{-1}$). We have also made another observation, that is, the viscosity of an aqueous PVA solution (5% w/v) tends to follow an increasing trend with a relatively long time of aging, but the rheological nature of the solution (dilatancy) in the low shear-rate zone remains much the same (data not shown).

However, the addition of FeCl_3 to the initially dilatant PVA solution (system S_0 , Table I, and plot A, Fig. 1) turns the system prominently pseudoplastic (as shown for system S_1 , Table I, and plot B, Fig. 1). The low initial shear viscosity of the PVA solution undergoes a big jump from nearly 15–90 MPa s on addition of FeCl_3 , mainly as a consequence of the complexing of Fe^{+3} ions with the —OH groups of the surrounding PVA chain segments. At high shear rates, the two curves A and B in Figure 1 approach each other with a tendency to reach a viscosity level that apparently corresponds to the limiting solution viscosity of the PVA chains corresponding to attainment of equilibrium clustering or staggering of the said chain molecules.

Shear response of aqueous PVA and PVA-PPY- Fe^{+3} system

Shear stress (τ) versus shear rate (D) plots (not shown) for aqueous PVA in the absence and presence of FeCl_3 [system S_0 and S_1 are, respectively, concave upward (dilatant) and concave downward (pseudoplastic)]; such curves for a PVA solution loaded with increasing proportions of PPY (systems S_a , S_b , S_c , S_d , and S_e) formed *in situ* in solution or a dispersion formed under the catalytic action of FeCl_3 as in Table I were also obtained for the assessment (data not shown) of rheological trends. Figure 1 clearly shows how the initial dilatant nature of the PVA solution (S_0) turns pseudoplastic on addition of a low dose of FeCl_3 (S_1) due to Fe^{+3} ion-PVA complexation. For use of a low dose of

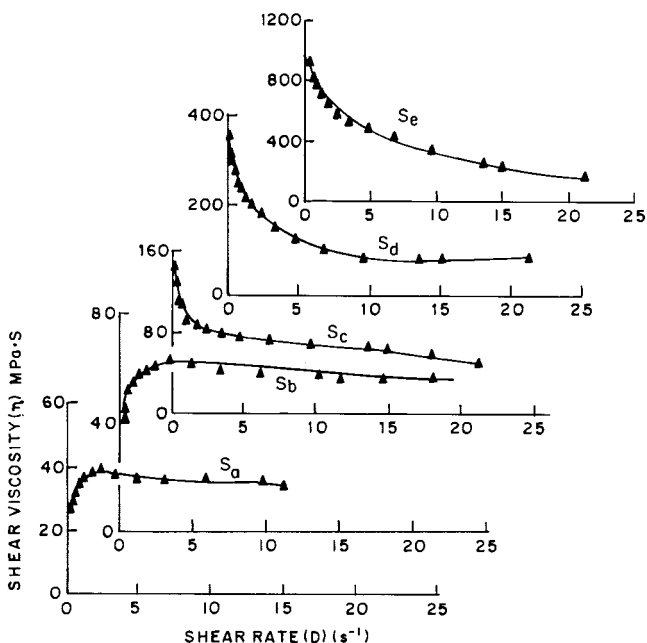


Figure 3 Plots of shear viscosity (η) versus shear rate (D) for PPY-PVA-Fe⁺³ dispersions, S_a , S_b , S_c , S_d , and S_e .

FeCl₃ and a corresponding lower loading of PVA with PPY (systems S_a and S_b) found *in situ*, the dilatant nature of the initial PVA solution is still retained, apparently because the dual presence of a low proportion of added Fe⁺³ and of PPY formed *in situ* could not effectively perturb the structure of PVA in solution. However, for the use of much higher doses of FeCl₃ and relatively high doses of the pyrrole monomer causing much higher loading of PVA with PPY formed *in situ*, the PVA structure suffers an effective perturbation due to much more meaningful complexation with the excess Fe⁺³ and related ions along with possible doping and networking of substantial proportions of the PPY formed, and, as a consequence, systems S_c , S_d , and S_e assume a prominent pseudoplastic character as for the system S_1 .

The above-mentioned rheological trends of the aqueous PVA-PPY-Fe⁺³ system can be well appreciated by comparing their viscosity data as a function of the shear rate as in Figure 3. Perturbation of the PVA structure in the aqueous medium as a result of PVA-Fe⁺³ complexation and also a template or networking effect between the support polymer PVA and the conducting polymer PPY combine together to turn the dilatant character of aqueous PVA to a pseudoplastic character for use of high doses (>2.00 g) of FeCl₃ and high doses of the monomer pyrrole (>0.50 cm³), as in Table I.

It is interesting to note the enhancements in the low (zero) shear viscosity of the pseudoplastic PVA-PPY-Fe⁺³ system (Fig. 3) when we consider the systems S_c , S_d , and S_e , as described in Table I. As we increase the FeCl₃ catalyst dose (>1.20 g) and the monomer (pyrrole) dose (>0.5 cm³), the resulting PVA-PPY-Fe⁺³ system exhibits a progressively higher degree of modification of the base polymer PVA by extensive complexation with the excess Fe⁺³ and relevant ions and also as a consequence on the basis of a progressively enhanced scope for H-bonding and chemical grafting between the support polymer PVA and the increasing amounts of the conducting polymer PPY being formed *in situ*. The net outcome may manifest, to a good degree, a template effect.

Relaxation time (t_R)

The instantaneous maximum shear stress developed on an aqueous solution of PVA (S_0), the PVA-Fe⁺³ system (S_1), and the PPY-PVA-Fe⁺³ system in dispersions (S_a , S_b , S_c , S_d) on application of different low shear rates at 12°C was allowed to decay on withdrawal of the shearing action. The time (t) required for the stress to decay to 37% of the corresponding maximum stress¹¹ was taken as the relaxation time (t_R) according to the following relationship:

$$\tau = \tau_0 e^{-t/\lambda} \quad (1)$$

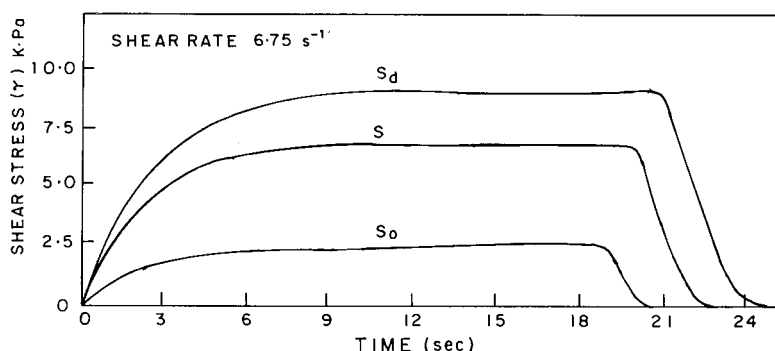


Figure 4 Plots of shear stress (τ) versus time (t) for different systems: S_0 , aqueous PVA only; S_1 , aqueous PVA containing FeCl₃, and S_d , aqueous dispersion of PVA-PPY-Fe⁺³ system. Exponential decay of the maximum shear stress with the time indicates a relaxation effect.

TABLE II
Relaxation Time of Different PVA Solutions
and PPY-PVA-Fe⁺³ Systems

Sample code	Relaxation time (t_R ; s)				
	t_{R1}	t_{R2}	t_{R3}	t_{R4}	t_{R5}
S ₀	0.2	0.37	0.47	0.75	1.05
S ₁	0.55	0.57	0.62	1.27	1.56
S _a	0.33	0.40	0.465	0.60	1.05
S _b	0.46	0.50	0.55	1.20	1.50
S _c	0.50	0.60	1.35	1.44	1.65
S _d	0.55	0.65	1.20	1.39	1.50

Suffixes 1, 2, 3, 4, and 5 attached to relaxation time (t_R) correspond to shear rates 2.39, 3.37, 4.48, 6.75, and 9.55 s⁻¹, respectively.

The term λ gives the relaxation time (t_R) at which $\tau = \tau_0/e$. Figure 4 shows exponential decay of the maximum shear stress with time for S₀, S₁, and S_d on withdrawal of the shearing action. Table II gives the observed relaxation times for different PVA solutions and PVA-PPY-Fe⁺³ dispersions at 12°C. It was observed that the t_R values of different PVA solutions are in the order S₀ < S₁, indicating that, in the absence of FeCl₃, PVA solutions relax faster, but they relax at a slower rate in the presence of added ferric chloride. PVA in water exists in the form of a tightly held helix through intermolecular/intramolecular H-bonding. Ferric chloride or its hydrolyzed forms in water are expected to form complexes with PVA through its —OH groups. The t_R values of PPY-PVA-Fe⁺³ nanodispersions are notably higher than those of PVA and PVA-Fe⁺³ solutions. For the different optically clear PPY-PVA-Fe⁺³ nanodispersions, the t_R values are mostly in the order S_a < S_b < S_c ≤ S_d, that is, on a progressive increase in Fe⁺³ content and PPY fractions in the PPY-PVA-Fe⁺³ dispersions, the t_R values follow, by and large, an increasing trend. As we move from dispersion S_a to S_d, the additional physical hindrance to the mobility of the support polymer PVA due to the enhanced Fe⁺³ dose and successively enhanced dose of PPY particles being formed *in situ* causes progressive clustering of the supporting PVA chain molecules into nanoparticles of a higher size. The mobility of PVA in a solution/dispersion thus becomes notably restricted due possibly to a template effect and some degree of enhanced anchorage of segments of the PPY polymer chains formed on the chain

segments of the support polymer PVA through H-bonding, through chemical grafting, or simply by adsorption. All these together lead to the formation of polymer clusters of a bigger particle size that render the system much enhanced viscosity and relax at a relatively slow rate.

CONCLUSIONS

Rheological studies indicated that a net dilatant or shear-thickening character of a relatively low viscous aqueous solution of PVA prominently turns pseudoplastic (shear thinning) with a manifold enhancement in the shear viscosity at a low (zero) shear rate in the presence of FeCl₃. With FeCl₃-catalyzed polymerization of pyrrole in the presence of aqueous PVA, the rheological behavior of the initial PVA solution remains more or less unchanged as long as the PPY loading and FeCl₃ catalyst content are kept at a low level. However, as the FeCl₃ dose and PPY loading become much higher, the rheological character of the initial PVA solution suffers a sharp change and the initial dilatant system then becomes prominently pseudoplastic; large-scale complexation of PVA with excess Fe⁺³ and related ions remaining in the aqueous system and interchain interactions involving the support polymer PVA and the PPY formed *in situ* via widespread H-bonding and some degree of chemical grafting are considered important to explain the novel changes in the rheological behavior. The PVA-supported PPY dispersions as studied here may find special use as prospective conducting/semiconducting coatings.

References

1. Schoff, C. K. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1985; Vol. 14, p 454.
2. Mayadunne, A.; Bhattacharya, S. N.; Kosior, E. *Plast Rubb Comp Process Appl* 1996, 25(3), 126.
3. Krieger, I. M. *Adv Colloid Interf Sci* 1972, 3, 111.
4. Wildemuth, C. R.; Williams, M. C. *Rheol Acta* 1985, 24, 75.
5. Pal, R.; Bhattacharya, S. W.; Rhodes, E. *Can J Chem Eng* 1986, 64, 3.
6. Jain, R.; Gregory, R. V. *Synth Met* 1995, 74, 263.
7. Ghosh, P.; Chakraborti, A.; Siddhanta, S. K., unpublished work.
8. Tzou, K. T.; Gregory, R. V. *Synth Met* 1995, 69, 109.
9. Tanaka, F.; Edwards, S. F. *Macromolecules* 1992, 25, 1516.
10. Maruci, G.; Bhargava, S.; Cooper, S. L. *Macromolecules* 1993, 26, 6483.
11. Ghosh, P.; Dev, D.; Chakraborti, A. *Polymer* 1997, 38, 6175.