

Rheological study of polyaniline dispersions

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Abstract: In this work, polymer/polymer and polymer/solvent interactions of different PANi systems were investigated by rheometer, viscosimeter and scanning electron micrograph (SEM) techniques. Aggregation can be observed in the DMAc/DMF mixtures, through mixing a fixed amount of PANi at molecular weight =100 000. On application of steady shear micellar entanglements are ruptured and the system exhibits yield properties followed by shear thinning. From the frequency dependence of storage and loss modulus (G' and G'') it seems that the system behaves more like a viscous fluid rather than an elastic liquid. Physical network structures can also be formed by aggregation process with certain solvents.

Key words: Polymer; chemical synthesis; chemical techniques; elastic properties

Résumé: Dans notre travail, polymère/polymère et polymère/ solvant interactions de différents systèmes de PANi ont été étudiés par des différentes techniques ; le rhéomètre, le viscosimètre et le microscope électronique à balayage (SEM). On peut observer l'agrégation dans les mélanges de DMAc/DMF, en mélangeant une quantité déterminée de PANi au poids moléculaire =100000. Sur l'application du cisaillement régulier des enchevêtrements micellaires sont rompues et tout système manifeste de propriétés suivies de l'effet de rhéofluidication. A partir de la dépendance de fréquence du modulus de stockage et de perte (G' et G''), ces systèmes comportent plutôt un fluide visqueux qu'un liquide élastique. Des structures de réseau physique peuvent également formés par un processus d'agrégation à certaines compositions de solvants.

Mots clés: Polymère ; synthèse chimique ; techniques chimiques ; propriétés élastiques

INTRODUCTION

Inherently conducting polymers (ICP) in general, and polyaniline (PANI) in particular, are an attractive class of materials with potential applications in a number of devices such as electrode materials in rechargeable batteries [1-3], light-emitting diodes [4], electromagnetic shielding [5], and anticorrosive materials [6]. It is well known that insoluble and infusible nature of ICP have prevented the formation of their solution/melt using a soluble support polymer [7, 8] or inorganic nanoparticles/colloid [9]. Therefore, and despite their highly important physical properties and widespread application potential, rheology proper-

ties of these polymers are still rarely explored. Nandi et al. have studied the rheological properties of (PNCs) polyaniline-(\pm champhor-10-sulfonic acid) 0.5-m-cresol[PANI-CSA0.5-m-cresol] with Na-montmorillonite (intercalated tactoids) [10] and demonstrated that the storage modulus was increased with increasing clay concentration in composite and gel melting temperature was also increased. Some studies reported dynamic steady and flow properties of a series of PANi-based dispersions in which a water-soluble polymer polyvinyl pyrrolidone (PVP) and two anionic surfactants such as *p*-dodecylbenzenesulfonic acid (DBSA) and sodium dodecylsulfate (SDS) which

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were used as stabilizers along PANi backbones. In the PVP–PANi system [11], hydrogen bonding between these polymers are formed, and depending upon the concentration of PANi and extent of hydrogen bonding, a sol-to gel transition was observed. Alternatively, a gel-to sol transition was detected for PANi–DBSA system [12]. The rheological properties of these polymers have been investigated, revealing flocculation change in emulsions on which SDS adopts gel-like structure. The interaction between 2-acrylamido- 2-methyl propanesulphonic acid (AMPS) and PANi was studied by rheometer techniques by Yang et al. [13]. Garai et al have reported physical and mechanical properties of PANi-dinonylnaphtalene disulfonic acid (DNNSA) gel nanocomposites (GNCS) with organically modified (OM) montmorillonite clay [14] and concluded that the incorporation of clay tactoids causes a dramatic increase of (G') and the crossover frequency decreased with increase in clay concentration and it increased with increase in temperature for GNC gel. In brief, we have carried out rheological properties of PANi with surfactant like sodium dodecylsulphate (SDS) oligomers with different N,N dimethylacetamide (DMAc)-dimethylformamide (DMF) mixtures. The interactional behavior of systems has been examined using viscosimetry. Other techniques, such as rheometer and scanning electron micrograph have been used to understand the aggregation process toward polymer chain

EXPERIMENTAL

1. Materials

Before performing experiments, aniline monomer (C_6H_7N) was purified by vacuum distillation and stored in a refrigerator. ammonium persulfate (APS, $(NH_4)_2S_2O_8$) and ionic surfactant sodium dodecylsulphate ($NaC_{12}H_{25}SO_4$) were purchased from Sigma Aldrich. Dimethylacetamide (DMAc) and dimethylformamide (DMF) were obtained from Acros Organics. PANi has been synthesized and purified in our laboratory.

Synthesis of PANi nanoparticles: Aniline (2 g) and SDS (3.25 g) were dispersed in 50 mL of water. The mixture of aniline and SDS was magnetically stirred at room temperature for 1 h. The mixture was cooled in an ice bath for 30 min. This happens before oxidative polymerization which is carried out by slow addition of a solution of APS (6.5 g in 15 mL of water) to the reaction medium under

stirring in a cold bath (0-5° C). The precipitated product was collected by filtration, and subsequently washed with water and ethanol to remove unreacted chemicals, aniline oligomers and SDS. The recovered fine green powder was dried under vacuum at 60° C for 24 hours and kept in a dessicator until used.

Polymers and aggregates in solution: the concentration of the polymer in solutions was fixed at 4.5% (wt/vol) and varied the percentage of DMAc/DMF solvents. All studied systems were stirred for 12 h, and thereafter dispersed using an ultrasound disperser Sonics VibraCell, and then filtered through a 0.42 μm Millipore membrane filter. The average viscometric molecular weight (M_v) of PANi has been 100 000. (Using Mark-Houwink-Sakurada equation) [15]. Their characteristic is given in Table I.

2. Methods

Experiments in solutions: the viscosity of the solutions was measured with an automatic viscosimeter (AVMn, Anton Paar) at 25, 35 and 45° C. Dynamic rheology in solution were done with a dynamic shear TA 2000 equipped with cone-plate geometry (50 mm diameter, 1° cone angle). The measurements have been performed in a circulating water bath with an uncertainty of 0.01 K at a temperature range of (298.15-318.15) K. For each concentration, at least twice measurements were done and the strain amplitude was fixed at 10% followed by a strain sweep test on selected samples.

Experiments on thin films: the solutions were spin-coated onto silicon wafers which have been treated

Table I. Summary of solubility parameter of PANi, NMP, DMAc and DMF at 298.15K.

Chemical products	$\delta(J/cm^3)^{1/2}$	Réf
PANi EB	22.8	[16]
	22.2	[17]
NMP	23.1	[17]
DMAc	22.1	[17]
DMF	23.4	[17]



prior to the polymer deposition. Scanning electron microscopy experiments were made with Philips Field Effect Gun XL-30, at an accelerating voltage of 5 kV. Image treatments were performed using the digital instructions software.

RESULTS AND DISCUSSIONS

1. Intrinsic viscosity

From viscosimetry, the intrinsic viscosity of the PANi/DMAc/DMF solutions is measured at 25°C. The reduced viscosity (η_{sp}/c) of the solutions are observed in Figures 1-4 as a function of polymer concentrations in an interested range. In every plot, the studied systems exhibit linear dependence between (η_{sp}/c) and c in the whole range of concentrations. The extrapolation (η_{sp}/c) to zero concentration is allotted as the intrinsic viscosities $[\eta]$ [18,19]. The values of $[\eta]$ for PANi/DMAc/DMF solutions have been compared in Table II and have the order PANi/30 DMAc/70 DMF > PANi/NMP > PANi/DMAc > PANi/60/40 > PANi/50/50. Similar trends have been observed for PANi/DMPU and PANi/NMP solutions [20].

The intrinsic viscosity $[\eta]$ values have been found to be higher in 1, 3-Dimethyl-3, 4, 5, 6-tetrahydro-2(1H)-pyrimidinone (DMPU) than in N-Methyl-2-pyrrolidone (NMP). Mangaraj et al. demonstrated that the increase of the intrinsic viscosity of a polymer led to an expansion of the polymer chains due to polymer/solvent interactions [21]. From figures 1-4, it is clear that $[\eta]$ of the studied systems increases for some compositions of solvents. Among DMAc/DMF percentage, the $[\eta]$ value for PANi/30:70 (DMAc/DMF) ($[\eta] \sim 0.95$ dL/g) was higher than $[\eta]$ value for PANi /NMP ($[\eta] \sim 0.88$ dL/g), and PANi/DMAc ($[\eta] \sim 0.79$ dL/g) whereas in the case of PANi/60DMAc/40DMF, the $[\eta]$ value are equal to 0.21 dL/g. the results suggest that 60DMAc/40DMF solvents has least effect on the structure change toward PANi segments whereas 30 DMAc/70 DMF percentages

Table II. Summarizes the calculated intrinsic viscosities $[\eta]$ and Huggins constants, k_H for all polymer solutions.

Different PANi	$[\eta]$ (dl/g) (± 0.03)	k_H (± 0.03)
PANi in NMP	0.88	0.8
PANi in DMAc	0.79	0.73
PANi in 30:70(%wt)(DMAc/DMF)	0.95	0.65
PANi in 40:60(%wt)(DMAc/DMF)	0.15	2.6
PANi in 50:50(%wt)(DMAc/DMF)	0.11	-4.42
PANi in 60:40(%wt)(DMAc/DMF)	0.21	-5.3
PANi in 70:30(%wt)(DMAc/DMF)	0.18	1.72
PANi in 90:10 (% wt) (DMAc/DMF)	0.2	1.032

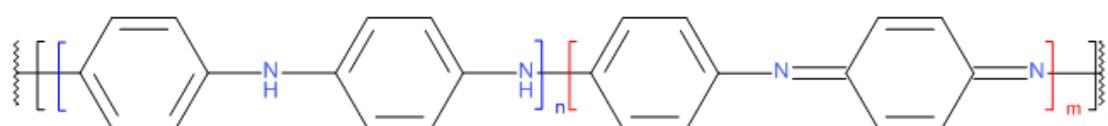
has more accessibility for hydrogen bonding with carbonyl groups of PANi side.

The arrangement of the side groups of polymer may then lead to differences in the accessibility of the DMAc/DMF molecules to the polar carbonyl groups. Therefore, Table II shows that Huggins coefficients can be obtained from the following equation [22, 23],

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 C \quad \text{Eq.1}$$

Where, k_H , and C are respectively the Huggins constant and solute concentration.

Extrapolation of the reduced viscosity to zero polymer concentration in the same figures (2-4) gives Huggins constant (k_H) of all PANi solutions. The Huggins constant of PANi/30:70 (DMAc/



Scheme 1. Main polyaniline structures $n+m = 1$, $x =$ half degree of polymerization. Leucoemeraldine with $n = 1$, $m = 0$ is the fully reduced state. Pernigraniline is the fully oxidized state ($n = 0$, $m = 1$) with imine links instead of amine links. Emeraldine base with ($n = m = 0.5$) is neutral.

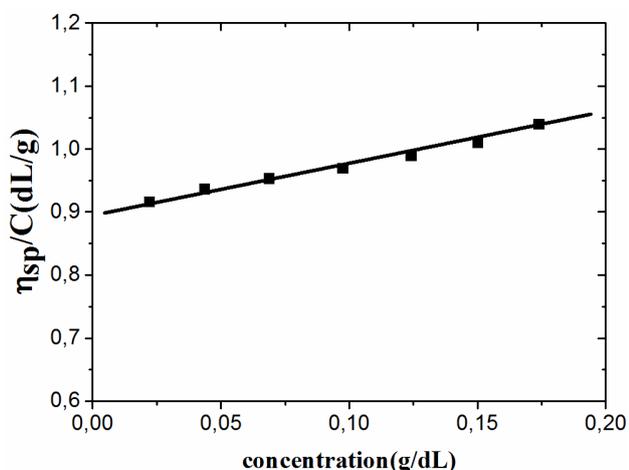


Figure 1. Plots between reduced viscosity and concentration for PANi emeraldine base in N-methylpyrrolidone (NMP) at 30°C.

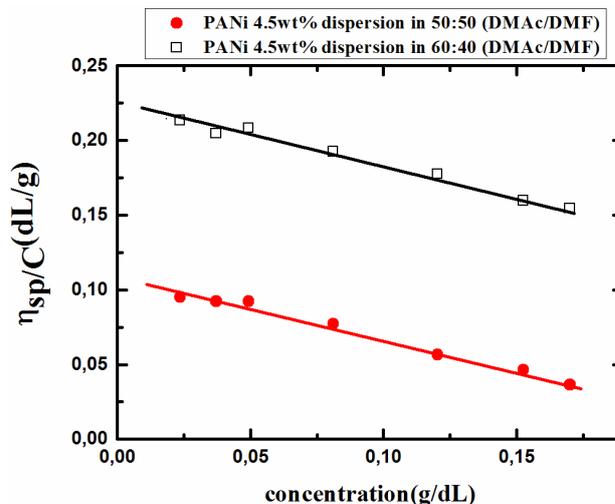


Figure 3. Huggins plots of polyaniiline dispersions in DMAc and DMF binary mixture at 25°C; ○ : PANi in 50:50 (DMAc/DMF) and □ : PANi in 60:40 (DMAc/DMF).

DMF) has the value 0.65 ± 0.03 , as a good solvent conditions for PANi at $M_v=100\ 000$. In the good solvent, the polymer chains should expand and form as many contact as possible with solvent molecules whereas polymer-solvent contacts are less favorable compared with the polymer-polymer and solvent-solvent contacts in poor solvent [24]. The 30/70 (DMAc/DMF) ratio solvents solubilize the PANi side groups and SDS oligomers rather than PANi segments and do not allow the PANi segments to aggregate in solution. The compa-

ratively larger values of k_H for PANi/40/60, PANi/70/30 and PANi/90DMAc/10 DMF solutions regarding PANi/DMAc indicates that polymers are in poor solvents, caused by contractions of the polymer chains due to intramolecular association (attractive forces). PANi/ 50:50 (DMAc/DMF) and PANi/60:40 (DMAc/DMF) solutions show negative values of k_H . The Huggins coefficient which was observed to be negative seems there exist attractive interactions occurring between the hydrophobic groups within

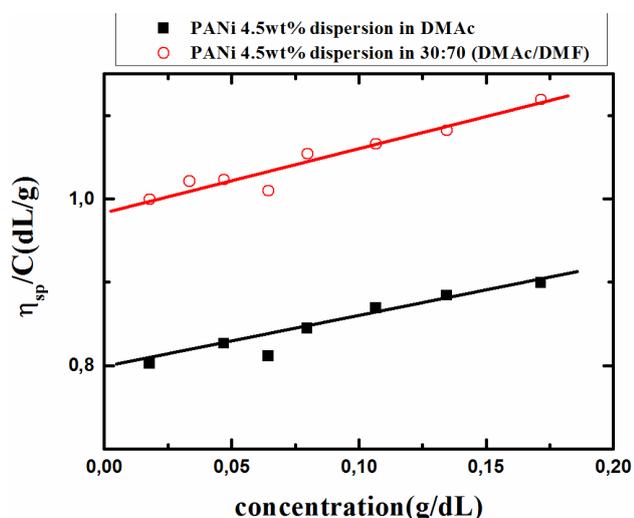


Figure 2. Huggins plots of polyaniiline dispersions in DMAc and DMF binary mixture at 25°C; ○ : PANi in 30:70 (DMAc/DMF) and □ : PANi in DMAc.

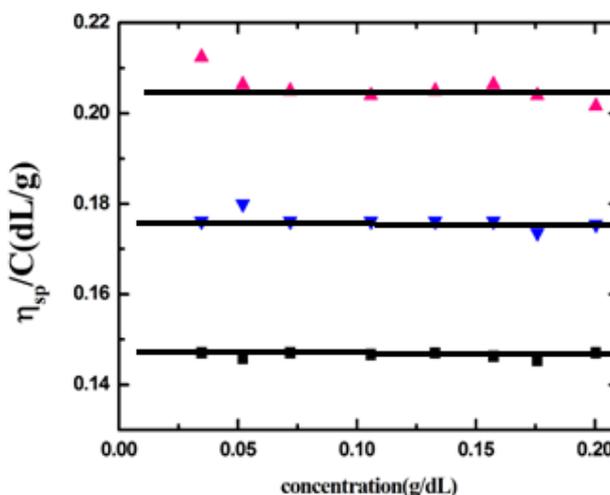


Figure 4. Huggins plots of polyaniiline dispersions in DMAc and DMF binary mixture at 25°C; □ : (40 :60) (DMAc/DMF) ; ▽ : (70 :30) (DMAc/DMF) and ▲ :90 :10 (DMAc/DMF).

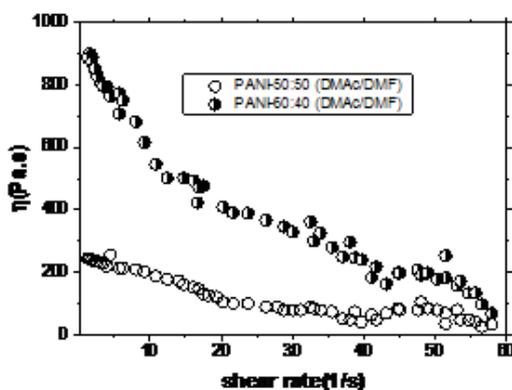


Figure 5. Viscosity versus shear rates plot for PANi dispersions in 50:50 (DMAc/DMF) and 60:40 (DMAc/DMF) at 25° C.

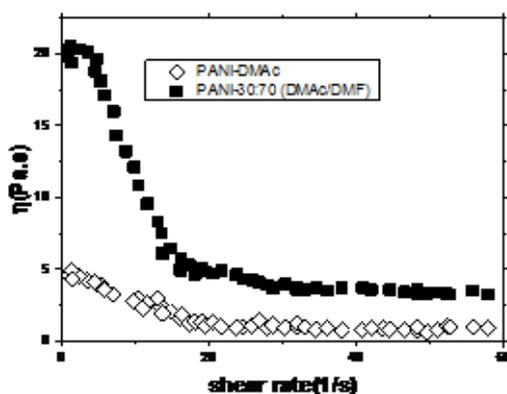


Figure 6. Viscosity versus shear rates plot for PANi dispersions in DMAc and in 30:70 (DMAc/DMF) mixtures at 25° C.

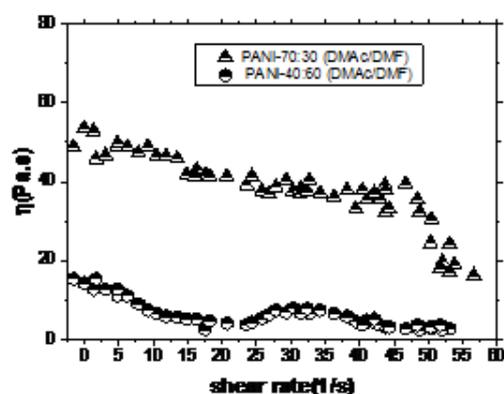


Figure 7. Viscosity versus shear rates plot for PANi dispersions in: 40:60 (DMAc/DMF) and 70:30 (DMAc/DMF) mixtures at 25° C.

the macromolecule, which makes the polymer less soluble in the solvent.

2. Rheological studies

2.1. Steady rheology

Steady viscosity profiles: The steady viscosity profiles of both the studied PANi/DMAc/DMF systems as function of steady shear rates is shown in Figures 5-7.

It was observed that PANi/DMAc and PANi/30 DMAc/70DMF solution exhibits Newtonian behavior at high shear rates while shear thinning (non-Newtonian) is observed at the low shear rates. However the thinning is most evident at shear rates ($5s^{-1}$) and gradually diminishes at higher shear rates. Similar type of behavior for some polymers was also observed by other researchers [25-26]. It is observed that PANi/50DMAc/50DMF and PANi/60DMAc/40DMF exhibits shear thinning at over the whole range of shear rates whereas PANi/40/60 and PANi70/30 exhibits shear thinning behavior at higher shear rates. In addition of this, the increase in zero shear viscosity (η_0) of both PANi/50/50 and PANi/60/40 solutions may be due to structural changes towards this polymer. Nandi et al. demonstrated that the higher η_0 value of PANi gel might be due to the presence of three dimensional network structures in the gel and in the GNCs and also due to the very rigid nature of PANi chains [10]. The increase in (η_0) of the PANi/60:40 and PANi/50/50 solutions with that of PANi/DMAc may be due to this proposing effect: firstly, DMAc and 30:70 (DMAc/DMF) solvents penetrate easily in the aggregate and solubilize them. Secondly, 50 DMAc/50 DMF and 60 DMAc/40 DMF mixture has less effect, PANi segments with SDS molecules come close together, preventing the formation of secondary structure with possible growth of such clusters [28-29].

Arrhenius behavior: Figure 8 shows the logarithm of shear viscosity $\ln(\eta)$ plot at each composition of DMAc/DMF mixtures. By using Andrade–Eyring model, which is valid over a wide temperature range for viscous flows, the activation energy E_a in various mixed systems has been calculated by using the following [30,31]:

$$\eta = A \cdot e^{\frac{-E_a}{RT}} \quad \text{Eq.2}$$

Where η is the viscosity of a solution at a low shear rate, A is a pre-exponential term, and E_a is the activation energy for the viscous flow.

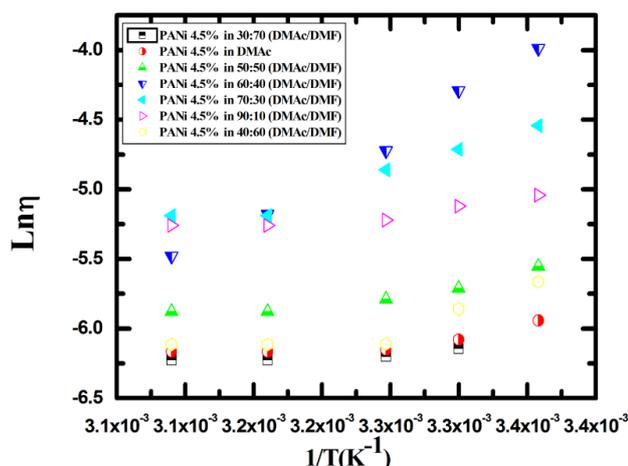


Figure 8. Activation energy determination for the viscous flow of all the PANi dispersions.

The obtained values of E_a in all studied systems are reported in Table III. E_a is related to the molecular weight, chain branching, chain rigidity, and intermolecular force of attraction [32]. For molecular liquids, E_a is 10–30 kJ/mol, and for most polymer melts, E_a ranges from 25 to 85 kJ/mol [33,34].

Table III. Arrhenius activation energy E_a (kJ/mol) for these polyaniline solutions as a function of molar fraction of DMAC(x_1) over the temperature range from 25°C to 45°C

{DMAC(1)-DMF(2)} mixtures	
x_1	E_a (kJ/mol)
0.3	9.30
0.5	9.44
0.6	9.51
0.7	9.58
0.9	9.7
PANi 4.5%(w:v) in DMAC(1)/DMF(2)	
0.3	52.87
0.5	50.43
0.6	45.6
0.7	43.52
0.9	43.76

The values of Arrhenius activation energy are deduced from Arrhenius plots (the slope in Fig.8) for different concentrations of solutions. Then, the activation energy (E_a) represents a maximum (~ 53 kJ/mol) at DMAC percentages (30%) but it decreases with increasing DMAC compositions in solutions. This suggests that there could be as many as hydrogen bonds formed between PANi chains, and this implies very strong Interchain and intrachain interactions during the complexation [35]. Therefore, we find that a minimum of E_a has value 45 kJ/mol at 60DMAC/40DMF mixtures, here this energy is used only to reorient chains during the aggregation with Interchain contacts.

3. Dynamic Rheology: frequency sweep

Frequency dependent variation of elastic and storage modulus of solutions is compared in Figures 9-12.

In these solutions, the loss modulus (G'') is greater than the storage modulus (G'), indicating that the viscous contribution is greater than elastic contribution [36-39]. In the case of PANi/DMAC and PANi/30DMAC/70DMF solutions, (G') and (G'') remains parallel initially, followed by an increase with frequency to reach a crossover point around 60 rad/s. The crossover frequency is the characteristic of the viscoelastic behavior of the material and indicates that the system becomes more elastic than viscous [40]. Similar results have been reported by Gangopadhyay et al. In that work, they demonstrated that regular increase of (G') and (G'') with increasing frequency is indicative of regular disentanglement and reorientation of the micelles with development of solution anisotropy for PANi-SDS solutions [12]. Frequency dependent of storage and loss modulus of PANi/50/50 and PANi/60/40 (DMAC/DMF) solutions is shown in Figure 10 (A' and B'); the behavior is very different from that of PANi/DMAC mixture. There are slight increase in the storage modulus but the loss modulus is practically constant (independent of frequency), preventing the formation of physical network structure as a consequence of chain interactions resulting in the increased elasticity.

The loss tangent is the ratio of energy lost to energy stored in a cyclic deformation and is a measure of the fluidity of the solution ($\tan\delta=G''/G'$). The loss tangent for the different PANi dispersions is presented in Figures 13-15. The loss tangent reveals several characteristics. As shown in

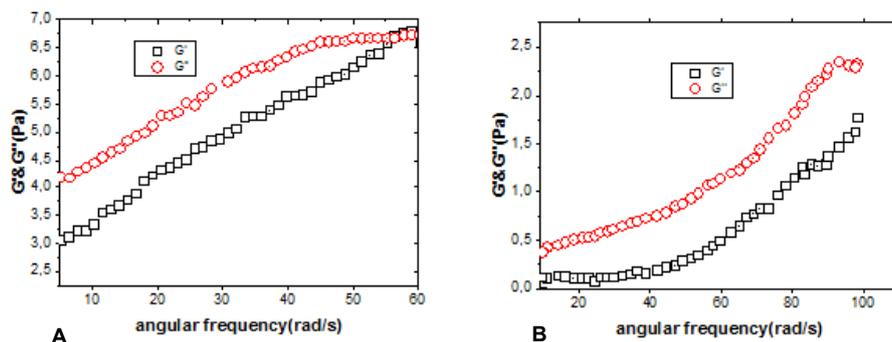


Figure 9. Variation of loss and storage modulus with frequency of 4.5wt% of PANi dispersions in: (A): 30:70 and (B): DMAc at 25° C.

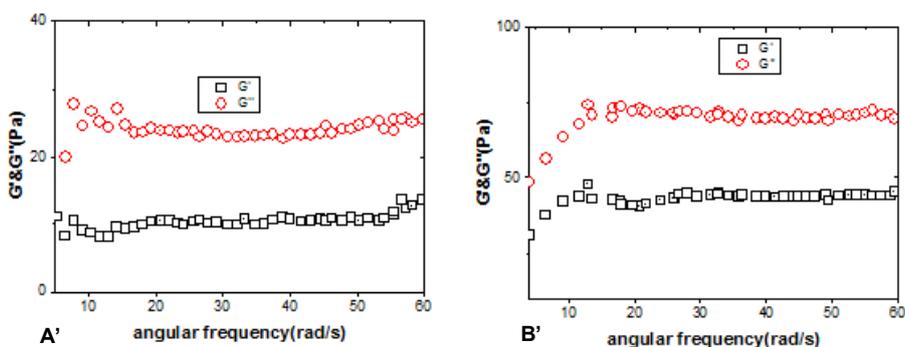


Figure 10. Variation of loss and storage modulus with frequency of 4.5wt% of PANi dispersions in (A'): 50:50 and (B'): 60:40 (DMAc/DMF) at 25° C.

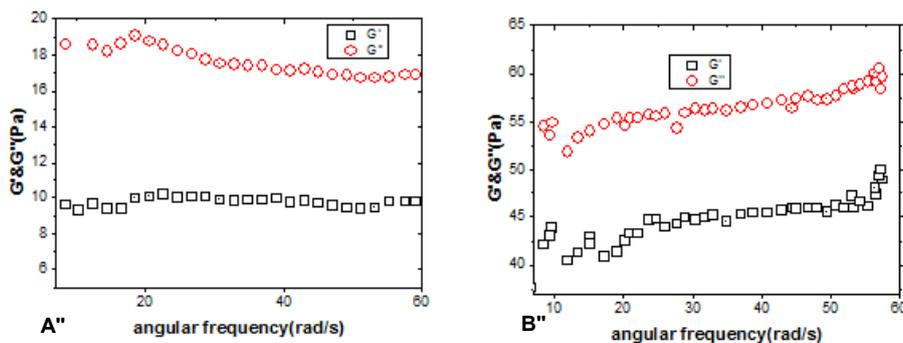


Figure 11. Variation of loss and storage modulus with frequency of 4.5wt% of PANi dispersions in (A''): 40:60 and (B''): 70:30 (DMAc/DMF) at 25° C

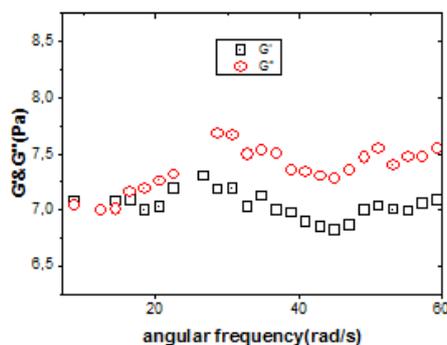


Figure 12. Variation of loss and storage modulus with frequency of 4.5wt% of PANi in 90:10 (DMAc/DMF) mixtures at 25° C

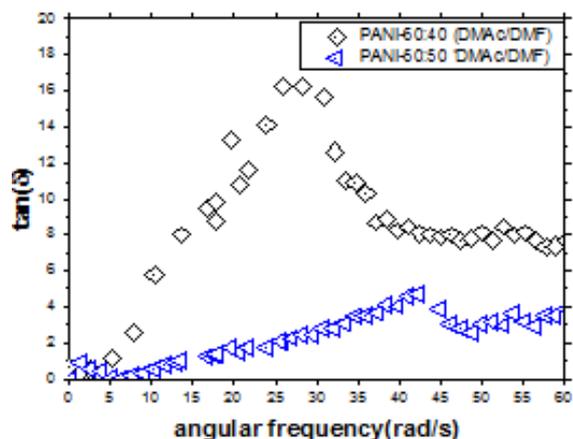


Figure 13. tangent delta curves of both PANi-50:50 and PANi-60:40(DMAc/DMF) dispersions with different oscillation frequencies

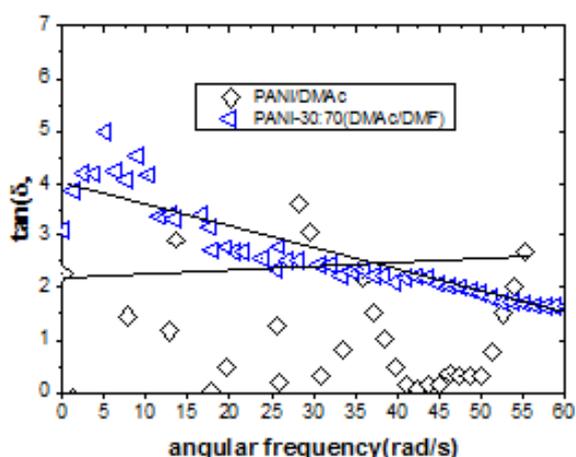


Figure 14. tangent delta curves of PANi-30:70 and PANi/DMAc dispersions with different oscillation frequencies.

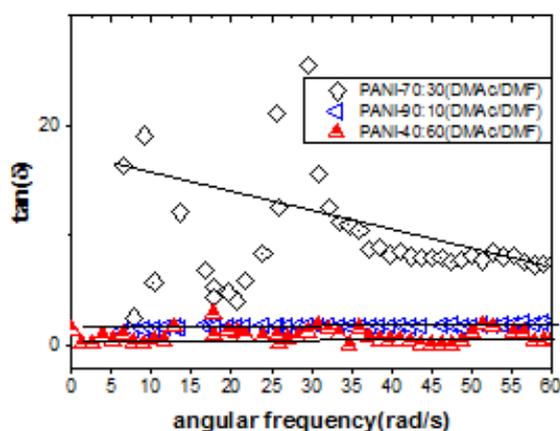


Figure 15. tangent delta curves of other PANi samples with different oscillation frequencies.

Figure 13, the maximum peaks of tangent delta curves decrease obviously. The low value of loss tangent for the PANi/60/40 (DMAc/DMF) indicates the formation of elastic cross links toward this polymer.

4. Investigation of the morphology of PANi Dispersions by SEM

The morphology results of the PANi solutions are observed in Figures 16-18. It is obvious from this observation that all the studied systems show typical features. These results can be correlated with the structure of the aggregation in solution, also discussed in earlier paragraphs. Compact aggregation of particles occurs at surface from the 60:40 and 50:50 (DMAc/DMF) percentages. This suggests that the aggregation process is slow where the cluster-cluster sticking is low and provides more compact structure. Both PANi/40DMAc/60

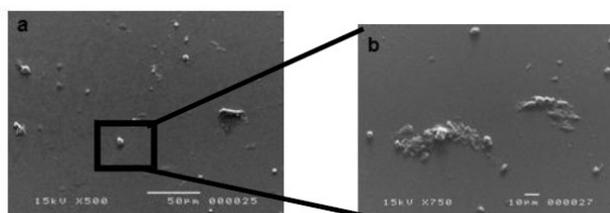


Figure 16. Scanning electronic image of polyaniline dispersions: in 30:70 (DMAc/DMF) and DMAc.

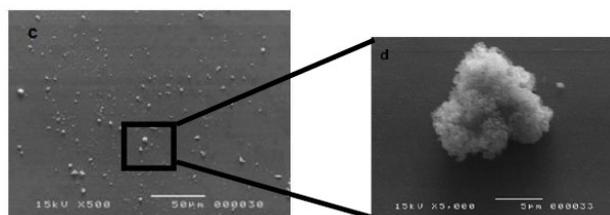


Figure 17. Scanning electronic image of polyaniline dispersions in 50:50 and 60: 40 (DMAc/DMF).

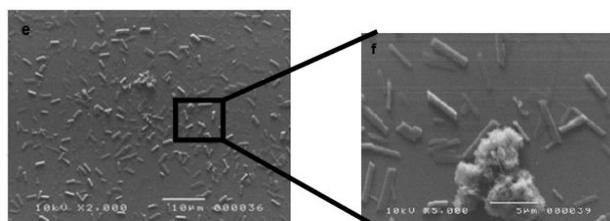


Figure 18. Scanning electronic image of polyaniline dispersions in 40:60 and 70:30 (DMAc/DMF).



DMF and PANi/70DMAc/30DMF (as seen in Fig.16) are be found to be gathered along the length of the aggregates. However, it can be observed that PANi/30DMAc/70DMF exhibits regulated morphology, preventing fast aggregative process with high cluster-cluster sticking.

CONCLUSION

The objective of the present paper was to perform the rheological characterizations of PANi solutions in different DMAc/DMF mixture ratios. First, we reported and discussed the steady viscosities as a function of shear rates. We investigated the dynamic rheological behaviors of dispersions. As the viscous fluid are the dominant ones. In PANi/30:70(DMAc/DMF), two phenomenon aggregation/clustering can be discerned by rheology. However, In the case of PANi solutions in 50:50(DMAc/DMF) and 60:40(DMAc/DMF), only the re-aggregation/flocculation was observed. In this context, both polymer-polymer interactions and dispersive interactions are to be considered for the aggregation in a physical network.

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