

Rheology of Polyaniline Dispersions in Acrylic Resin

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Acrylic dispersions based on polyaniline were obtained and characterised. The polyaniline was obtained by chemical polymerisation of aniline in different organic acid containing phosphorous, in the presence of ammonium-peroxodisulphate as oxidant agent. The blends were obtained by mechanical dispersion of polyaniline in commercially available acrylic resin. The flow behaviour of these dispersions at different shear rates was studied. Furthermore, the resulting acrylic dispersions were analysed by IR spectroscopy, and were characterised in terms of their electrical resistance and rheological behaviour.

Introduction

Conducting polymers exhibit a wide range of novel electrochemical and chemical properties that has led to their use in a diverse array of applications. Among the conductive polymers, polyaniline (PANI) is one of the most promising candidates for industrial application due to its good conductivity, special doping mechanism, and excellent chemical stability^{1–3}. Its poor solubility in many solvents remains the main disadvantage.

One of the advantages of making the composite and blends of conducting polymer is to improve the lower processability and to obtain high performance of the former, which combines the desirable mechanical properties of the insulating host matrix together with the electrical and optical properties of the PANI guest. Some methods were used to obtain blends and composites^{4–12}. The reviewed data confirm that the properties of PANI composites and blends are determined by specific physical–chemical interactions among their components (PANI with a dopant, PANI with a host polymer, and the dopant with the host polymer), by the method and conditions of the material formation, by the quantitative ratio of the material components, by host polymer preconditions depending on a producer etc.^{4–5,13}. Numerous studies with formulations based on doped polyaniline have been carried out, with the intention of developing new applications as films^{14,15} and fibres¹⁴ and blending with thermoplastic polymers^{16,17}.

In the field of conducting polymers, one of the main problems is that intrinsically conducting polymers are semirigid, resulting in intractability due to its highly aromatic nature, interchain hydrogen bondings and charge delocalisation effects. The rigidity of PANI chains hinders the use of conventional processing methods,

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like extrusion or injection. To develop methods of processing 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. Some studies regarding rheological behaviour have been performed for doped and dedoped PANI form in solvents or in melted state^{18,19}.

In this paper we present studies about obtaining and characterising dispersed PANI in doped form (emeraldine salt) in commercially available acrylic resin with potential application in corrosion protection. The influence of the nature of the anion used in acrylic dispersions based on doped PANI upon the resistance and rheological behaviour of acrylic dispersions was evaluated. These anions are not mentioned in the literature as dopants for PANI acrylic dispersions. The anions from organic acid contain phosphorus-carbon (P-C) bonds, contrary to the phosphorus-oxygen (P-O) bonds in the common inorganic phosphate inhibitors. The P-C bonds are much more resistant to conversion into orthophosphates than P-O bonds in inorganic phosphates. It is known that inorganic phosphates present some disadvantages such as sensitivity to hydrolysis, temperature and pH fluctuations, as well as high residence time in industrial water²⁰. In all cases the pH, due to the organic acid used, was less than 1.5 and so the acidic medium where the aniline exists as an anilinium cation was achieved and an efficient oxidative polymerisation took place.

Experimental

Preparation of acrylic dispersion based on PANI

The PANI was obtained in the same conditions (aniline/oxidant molar ratio, aniline/acid molar ratio, temperature); only the nature of the acid differs.

PANI particles were synthesised using the conventional oxidation polymerisation of aniline to produce a fine emeraldine doped form. Aniline freshly distilled and cooled at $-4\text{ }^{\circ}\text{C}$ (monomer), phenylphosphinic acid ($\text{C}_6\text{H}_5\text{PH}(\text{O})\text{OH}$, APP, Aldrich), styrylphosphonic acid ($\text{C}_6\text{H}_5\text{CH}=\text{CHP}(\text{O})(\text{OH})_2$, ASP, prepared in our laboratory), 2-chloro-ethylphosphonic acid ($\text{Cl}-\text{C}_2\text{H}_5-\text{P}(\text{O})(\text{OH})_2$, ACIEP (Merck) as dopants, ammonium peroxydisulphate (Merck) as oxidant, and ammonium hydroxide, N,N dimethyl-formamide (DMF, Fluka) were used. A solution of aniline monomer in 2 mol L^{-1} organic acids containing phosphorous was cooled, and polymerisation was initiated at $0\text{ }^{\circ}\text{C}$ by a precooled solution of ammonium peroxydisulphate (molar ratio aniline/oxidant =1). The reaction was maintained for 24 h to complete the reaction and produce the emeraldine doped form. The doped PANI particles were washed with methanol to remove the oligomers and unreacted monomer. Products were subsequently dried for 24 h in vacuo. The product was converted to PANI-base form (dedoped PANI) with ammonium hydroxide.

For the obtaining of dispersions based on PANI, doped PANI powder was dispersed onto laboratory dispersing equipment (3-roll machine) until particle size $40\text{ }\mu\text{m}$. The resulting paste contains doped PANI (33.12%), acrylic resin (9.55%), toluene (47.50%), butanol (3.83%) and dispersing additives (5.73%). From dispersed paste the dispersions with different content of doped PANI were obtained (10 until 50% PANI in acrylic resin). Acrylic resin SMP 62 (SC. AZUR SA. Timisoara) with the following characteristics, content in nonvolatile substances: $50 \pm 2\%$, flow time: 35-80 s (cup DIN Φ 4 mm, at $20\text{ }^{\circ}\text{C}$ sol. 50% in xylene), acidity index, max. 16 mg KOH/g resin, density at $20\text{ }^{\circ}\text{C}$: $0.960 \pm 0.015\text{ g cm}^{-3}$, was used.

Measurements

The IR spectra were recorded with a Specord 75 IR (Carl Zeiss) in KBr pellets. The spectra allowed the identification of the chemical structure of the particles and confirmation of their chemical reactions. The shape and the size of the particles were measured with the transmission optical microscope IOR type MCI.

The inherent viscosities of doped PANI samples doped with different organic acid containing anions with phosphorus were determined with an Ubbelohde viscosimeter in 97% sulphuric acid 0.01% solution. The electrical conductivity of the doped PANI samples was measured at ambient temperature using the 2-probe method on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The density of doped PANI was determined according to the picnometer method, in decaline.

The viscosity measurements of acrylic dispersion based on doped PANI were performed using a Brookfield RVT viscosimeter, at room temperature. The Ostwald-de Waele power model ²¹, describing apparent viscosity–shear rate dependency (equation 3), was used:

$$\eta_a = k \cdot \gamma^{n-1} \quad (1)$$

where k is the consistency coefficient, n the flow coefficient and γ the shear rate.

Equation (1), in the function of flow index n , indicates 3 different behaviours: Newtonian, for $n = 1$ the $\eta_a = k = \text{constant}$; pseudoplastic, for $n < 1$ the η_a decreases with the increase in γ ; and dilatant for $n > 1$ η_a increases with the increase in γ .

The dispersion resistance was measured with the Rezistest Cella (Hungary).

Results and Discussion

All the doped PANI samples were obtained in the same conditions (aniline/oxidant molar ratio, aniline/acid molar ratio, temperature); only the nature of the acid differed. The characteristics of the obtained doped PANIs used as dispersed particles are presented in Table 1.

Table 1. The conductivity, inherent viscosity and density of PANI in function of acid nature *A/O- aniline/oxidant; ** A/AH- aniline/acid *determined with Ubbelohde viscosimeter in sulphuric acid 97%.

PANI-AH	A/AH	A/O	Conductivity S cm ⁻¹	Inherent viscosity* dL g ⁻¹	Density g cm ⁻³
PANI-ASP	1/2	1/1	2.19	0.572	1.402
PANI-ACIEP			2.91	0.534	1.365
PANI-APP			1.10	0.523	1.396

Figure 1 shows the FT-IR spectra for a) PANI powder and b) dispersions of PANI-APP in acrylic resins. The all PANI samples (spectrum a) present peaks at 824, 1144 and 1309, at 1490, and at 1586 cm⁻¹, indicating aromatic C–H, aromatic amine and aromatic C–C stretching vibrations, respectively. Spectrum (b) is obtained from PANI-APP dispersed in acrylic resin and there is a strong peak at 1731 cm⁻¹ from carbonyl groups characteristic of the C=O stretching mode²².

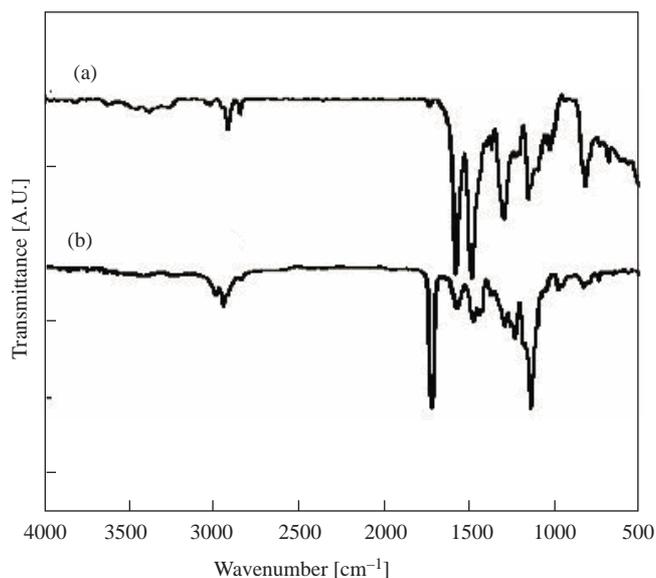


Figure 1. The IR spectra of (a) dedoped PANI and (b) 10% PANI –APP dispersed in acrylic resin.

The obtained doped PANI was dispersed in the acrylic resins. Its surface was wetted with the acrylic resins (Figure 2). The particle size was measured using an optic microscope with a grid.

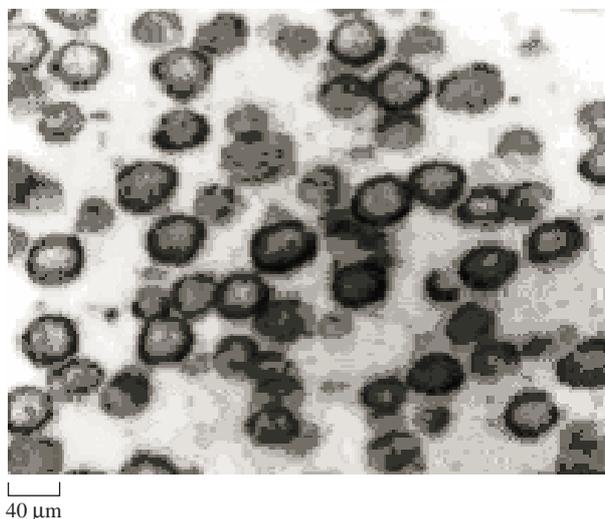


Figure 2. The morphology of 30% PANI-APP dispersed in acrylic resin.

The time required for dispersing the doped PANI samples in acrylic resins until a particle size of 40 μm decreases in the order PANI-ASP; PANI-ACIEP; PANI-APP (Figure 3).

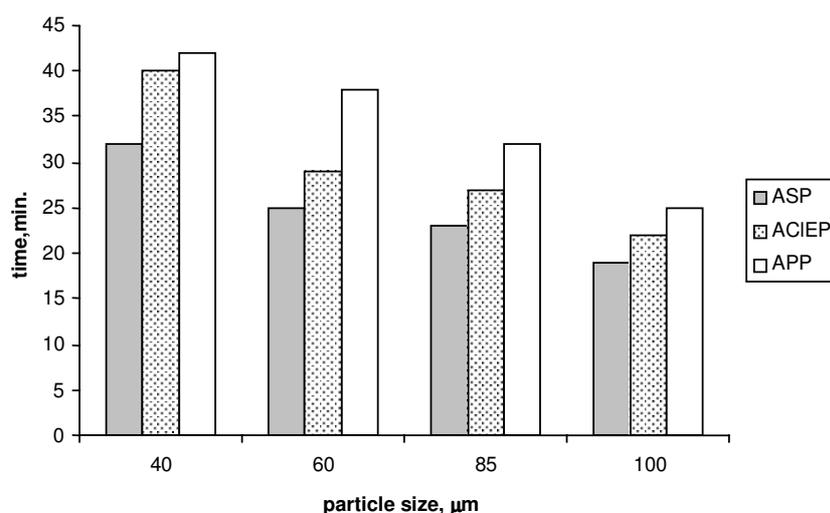


Figure 3. Variation of dispersed PANI-particle size in acrylic resin in time (50% PANI content).

It was observed that the nature of anions influences the time necessary to achieve the desired degree of dispersion and shows that the energy necessary to obtain a particle size of 40 μm was lower in the case of ASP dopant (the short time indicates lower energy in dispersing the PANI on the roll machine). Therefore, the explanation for the improving of the processability of doped polymer (the time and energy necessary for obtaining the required degree fraction decrease) was attributed to the presence of organic voluminous anion, which was able to perform the polymer-solvent interaction much stronger than the polymer-polymer one.

Due to the extremely high surface tension²³ PANI shows a high tendency to agglomerate, much stronger than any pigment. Therefore, individual molecules cluster to form primary particles (organic metals), which then form primary aggregates. Primary aggregates cluster to form secondary particles (Figure 4).

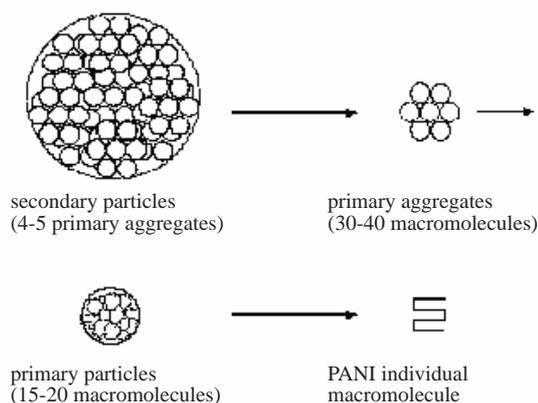


Figure 4. Morphological hierarchy of polyaniline particles and aggregates²⁰.

The surface tension is an expression of intramolecular forces. A voluminous anion can act as a spacer between the PANI chains and the dispersing media fill the space between the particles and can therefore reduce the attraction forces and improve the processability.

Viscosity measurements were performed only for the dispersion based on a doped PANI sample with a particle size of 40 μm and they indicate that the viscosity of PANI acrylic dispersions increases with the increase in PANI content in dispersion. The power law model is widely used among many engineers. It is simple since it contains only 2 parameters and analytical solutions to many problems in simple and defined flow fields can be found. It is known that if the onset of the power law region is at low share rates, then the power law model is probably safe to use. Therefore, we used this model for our experimental data.

Figure 5 shows plots of apparent viscosity versus shear rate for PANI doped samples with different organic anions containing phosphorus. Viscosity curves can be fitted to a power regression type ($y = a.x^b$), which is characteristic of an Ostwald-de Waele model. The decreasing apparent viscosity coupled with the increasing shear rate suggests that textural changes in the samples may be induced by the shear rate.

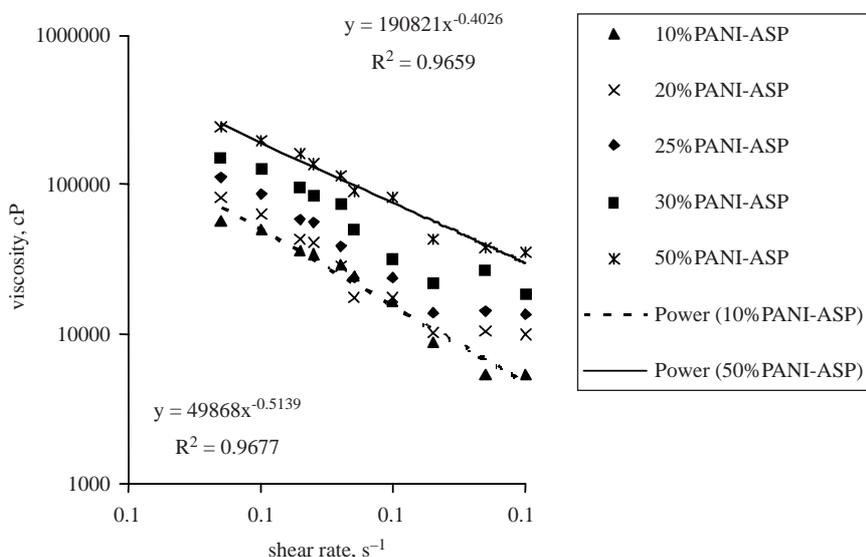


Figure 5. The variation of viscosity with the shear rate for different PANI-ASP concentrations in the dispersion.

With the increase in stress parameters the PANI aggregates (Figure 4) were destroyed and became orientated with the flow direction. The non-Newtonian fluids suffer slow structure modification and the behaviour depends on the history of stress. The hysteresis in the flow curve was also observed in a complete cycle of the shear rate measurements and plotted in Figure 6. In the hysteresis experiments the shear rate increases from 1 s^{-1} to 10² s^{-1} held for 1000 s and then linearly decreases from 10² to 1 s^{-1} . A hysteresis was observed for turn and return, due to the fact that reformed structures are not as complete as those before.

The hysteresis loop areas, which are the areas enclosed by the increasing and decreasing loops, increase with PANI content. The experimental data indicated at the high share rate after 1000 s^{-1} on return that the system can achieve the viscosity value on turn. However, at sufficiently high shear rate all the values overlap and the deformation and rearrangements are more homogeneous and continuous, as in a simple viscous liquid. This is probably due to the individual PANI molecules present in dispersion at high shear rate even on return. With the decreases in shear rate on return the PANI molecules cluster again to form primary particles, which then form primary aggregates and finally cluster to form secondary particles and as a result the viscosity increases but the value differs comparatively with the value on turn.

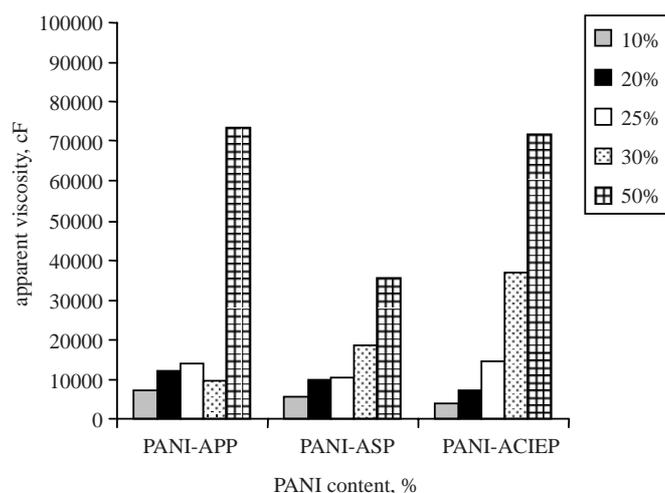


Figure 6. Variation of viscosity with shear rate for 50% PANI-APP dispersion for turn and return.

According to the selected model based on equation 1, the material coefficients k and n were determined (Figure 5) and are presented in Table 2.

Table 2. The parameters k and n for PANI acrylic dispersion.

PANI	PANI % content, %	a	k $N.s^n m^{-2}$	b	n	R^2
PANI-APP	10%	65703	65.703	-0.5139	0.4861	0.9677
	20%	66285	66.285	-0.4431	0.5569	0.9085
	25%	109246	109.246	-0.6495	0.3505	0.8713
	30%	119584	119.584	-0.5336	0.4664	0.8147
	50%	327734	327.734	-0.3394	0.6606	0.9583
PANI-ASP	10%	49868	49.868	-0.5139	0.4861	0.9677
	20%	54420	54.42	-0.4431	0.5569	0.9085
	25%	74011	74.011	-0.4431	0.5569	0.9085
	30%	115905	115.905	-0.434	0.566	0.9281
	50%	190821	190.821	-0.4026	0.5974	0.9659
PANI-ACIEP	10%	42069	42.069	-0.5139	0.4861	0.9677
	20%	54970	54.97	-0.5066	0.4934	0.8757
	25%	113428	113.428	-0.5705	0.4295	0.8107
	30%	228721	228.721	-0.434	0.566	0.9281
	50%	385341	385.341	-0.4026	0.5974	0.9659

From Table 2 it can be observed that with the increase in PANI content in dispersion the consistency factor k and flow index n increase too. The R-square values indicate good correlation for all PANI-ASP acrylic dispersion samples and only in acrylic dispersion at low (10%) and high (50%) PANI content based on doped PANI with APP and ACIEP. For acrylic samples with PANI doped with APP and ACIEP with 20%, 30% and 35% PANI content the correlation was lower than 0.9.

Figure 7 shows the apparent viscosity versus the dopant nature at different concentrations in the dispersions and for the same shear rate ($100 s^{-1}$).

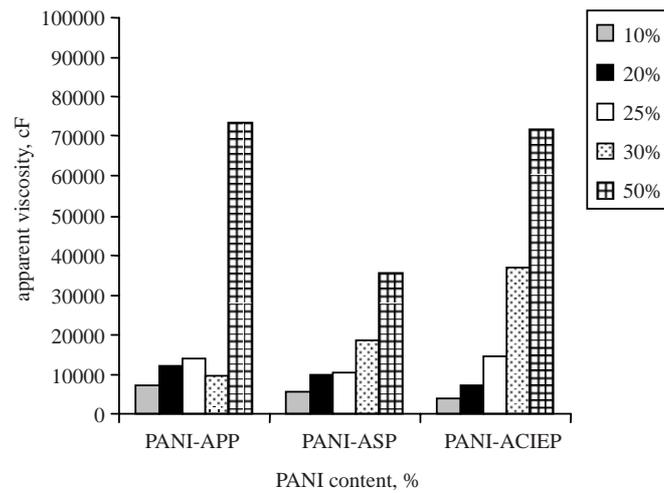


Figure 7. Apparent viscosity versus PANI content for different anions.

The apparent viscosity of dispersion is a function of PANI content and dopant nature. A low apparent viscosity was obtained for dispersion with high PANI content doped with ASP. At lower PANI content the ACIEP dopant shows only a slight decrease in apparent viscosity compared to ASP.

As a result of the resistance value obtained for dispersions samples the semiconductive acrylic dispersions were obtained (Figure 8).

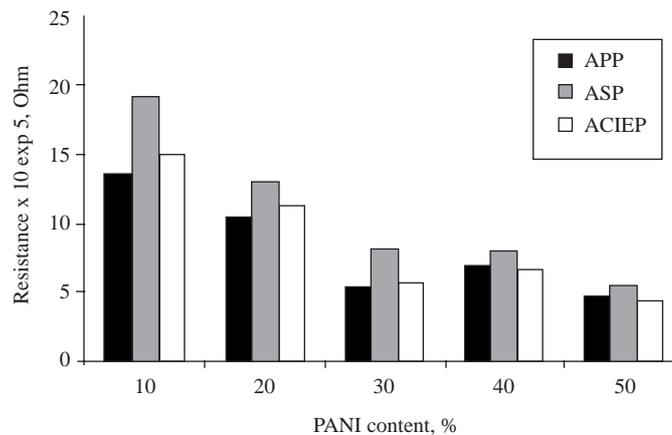


Figure 8. Resistance of acrylic dispersion based on PANI.

With the increase in the PANI content the resistance of dispersion decreases and high resistance was obtained in the case of PANI doped with ASP. Because the obtained value for all dispersions is situated in the domain of about 10^{-5} Ohm a semiconductive dispersion was obtained.

Conclusions

A series of PANI commercially available acrylic resin type SMP62 dispersions with different PANI contents were prepared. The viscosity of dispersion decreases with the increase in rotation speed and decreases with PANI content. The rheological behaviour of dispersions depends on the anion nature of PANI.

The electrical conductivity of the composites was improved with increasing amounts of PANI and the resistance of acrylic dispersion decreases. The dispersions of PANI powder in acrylic resins allowed

semiconductive dispersions to be obtained because the resistance is situated in the domain of about 10^{-5}Ohm . Therefore, a low value of resistance indicates a semiconductive dispersion, which allowed the use of dispersion like semiconductive coatings with a large application domain in modern industry and it can be used to remove electrostatic charges, and for shielding effects (i.e. Faraday screen, protective coat for the high voltage cables, etc.).

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