

The Rheological Behaviour of Some Polyaniline Dispersions Melamine-Formaldehyde Resin

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Abstract: 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, PANI is one of the most promising candidates for industrial application due to its good conductivity, special doping mechanism, and excellent chemical stability. Numerous studies with formulations based on doped polyaniline have been carried out, with the intention of developing new applications as films, fibbers and blending with thermoplastic polymers.

Keywords: polyaniline, melamine formaldehyde, rheological behaviour)

1. 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, PANI is one of the most promising candidates for industrial application due to its good conductivity, special doping mechanism, and excellent chemical stability¹⁻³. Its poor solubility in many solvents remains the main disadvantage.

One of the advantage 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 insulating host matrix together with the electrical and optical properties of PANI guest. Some methods were used to obtain blends and composites [1-5]. 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, 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. Numerous studies with formulations based on doped polyaniline have been carried out, with the intention of developing new applications as films, fibers and blending with thermoplastic polymers. In the field of conducting polymers, one of the main problems is that intrinsically conducting polymers are semirigid, resulting in intractability that is due to its highly aromatic nature, interchain hydrogen bondings and charge delocalization effects [1-3]. The rigidity of PANI chains hinders the use of conventional processing methods, like extrusion or injection [4,5]. To develop methods of processing PANI and its blends with other classic polymers, determination of the rheological parameters of this material is necessary [6-10]. These parameters are extremely helpful in the

designing of forming methods, choosing the type of processing equipment, extruder dies, or formers construction, etc. The influence of the nature of anion used in melamine formaldehyde dispersions based on doped PANI, upon the resistance and rheological behaviour of melamine formaldehyde dispersions was evaluated. To investigate the viscosity-shear rate dependency the Carreau model [11] was used, which has proven to be a useful model for fitting the non-Newtonian viscosity curve for the dispersions of polyaniline doped with anions with phosphor in commercially melamine formaldehyde resin.

2. Experimental

Melamine formaldehyde dispersions based on polyaniline (PANI) were obtained and characterised. The PANI was obtained by chemical polymerization of aniline in different organic acid containing phosphorous like phenylphosphinic acid (C₆H₅PH(O)OH, APP, Aldrich), styrylphosphonic acid (C₆H₅CH=CHP(O)(OH)₂, ASP, 2-chloro-ethylphosphonic acid (Cl-C₂H₅-P(O)(OH)₂, ACIEP Merk), in the presence of ammonium-peroxodisulfat as oxidant agent. The acid capacity of the polymer was determined from the quantity of natrium hydroxide (0.005 mol L⁻¹) required for the titration of the polymer samples. PANI powder was suspended in water and titrated by natrium hydroxide in a closed cell under nitrogen. The titration was performed very slowly, with incremental addition of 0.2-0.5 ml, and the delay between two consecutive additions required for pH stabilization, was 15 min. The pH measurements were determined with CG 841 SCHOTT, using a glass electrode type SCHOTT GERATEN N 2041A. Three determinations were performed for each sample. The acid capacity reported at 1 g of polymer, was determined from the neutralization curve. The inherent viscosities of doped PANI samples were determined with Ubbelohde viscosimeter in 97% sulfuric acid 0.01% solution. The density of PANI was

determined according to the picnometer method, in decaline.

Dispersions with different PANI contents in commercially melamine formaldehyde resin (AZAMIN M514 (SC Azur SA Timisoara) were prepared.

For the obtaining of dispersions based on PANI, doped PANI powder was dispersed onto a laboratory dispersing equipment (three rolls machine) until a particle size 40 μm . The resulted paste contains doped PANI (33.12 %), commercial melamine-formaldehyde resin AZAMIN M514 (9.55 %), toluene (47.50%), buthanol (3.83%) and dispersing additives (5.73 %). Melamine-formaldehyde dispersions with different content of doped PANI (5 until 25% PANI) were obtained by dispersing different amounts of prior prepared paste in melamine-formaldehyde resins.

The melamine formaldehyde resins characteristics were: $60\pm 3\%$ nonvolatile substances flow time (cup Φ 4mm) 180-230s, acidity index 2 mg KOH/g resin and Gardner color, max 3.

The behaviour of these dispersions to flow at different shear rates was studied. Also, the resulting melamine formaldehyde dispersions were analysed by IR spectroscopy and resistance. The dispersions resistance was measured with the Rezistest Cella (Hungary).

3. Results and discussion

The yield of the polyaniline (PANI) was about 57-62%. The density determined for polymer sample shows that the average density is $1,395 \text{ g cm}^{-3}$ for PANI-salt and $1,203 \text{ g cm}^{-3}$ for PANI-base. Acid capacity of PANI depends on synthesis parameters and maximum value was 15.02 mequiv./g polymer. The yield, conductivity, inherent viscosity of PANI and percent of hydrogen per gram polymer for polyaniline obtained in different organic acids containing phosphor is presented in table 1.

TABLE 1. The yield, conductivity, inherent viscosity of PANI and percent of hydrogen per gram polymer in function of nature of dopant

No.	Acid	Yield, %	Inherent viscosity, dL g^{-1}	%H/g dry polymer
1	ASP	60.18	0.603	0.567
2	ACIEP	59.19	0.625	0.589
3	APP	57.78	0.523	0.562

The physical properties of PANI-melamine films are presented in table 2.

The decrease of the elasticity and increase of the hardness of resulting films were attributed to the presence of rigid phenyl ring in the anion structure of doping acid. The hardness of coatings also increases with the increase of polyaniline content. The value of the hardness is a measure of the solidity and firmness of the coating. So, the hardness of samples shows a good resistance of obtained coatings under a static load or to scratching and a good cohesion of the particles on the substrate.

TABLE 2. Physical properties of films based on melamine-formaldehyde dispersion of doped PANI with anions containing phosphorus

Sample type	PANI content %	Hardness, s^*	Elasticity, mm	Resistance, ohm^{**}
PANI-APP	5.0	183	1.9	$3.35 \cdot 10^{-5}$
	10.0	188	1.7	$2.15 \cdot 10^{-5}$
	20.0	192	1.5	$1.52 \cdot 10^{-5}$
PANI-ASP	5.0	186	2.1	$1.22 \cdot 10^{-5}$
	10.0	194	1.8	$1.13 \cdot 10^{-5}$
	20.0	201	1.7	$0.89 \cdot 10^{-5}$
PANI-ACIEP	5.0	178	2.7	$0.87 \cdot 10^{-5}$
	10.0	189	2.5	$0.63 \cdot 10^{-5}$
	20.0	197	2.6	$0.48 \cdot 10^{-5}$

* the pellicle presented drying type E,

** for dispersion

The time required for dispersing the doped PANI samples in melamine formaldehyde resins until a particle size of 40 μm , is presented in figure 1. This time decrease in order PANI-ASP < PANI-ACIEP < PANI-APP.

It was observed that the nature of anions influences the time necessary to achieved the wanted 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).

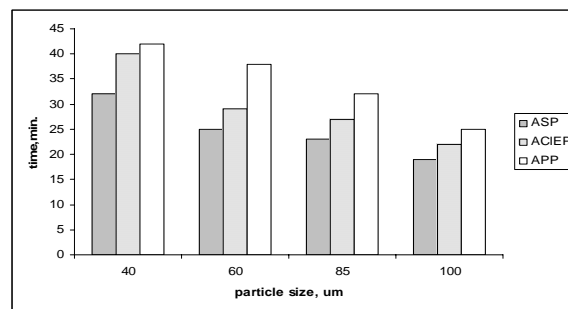


Figure 1. The time required for dispersing the doped PANI samples in melamine formaldehyde resins

Due to the surface tension extremely high [12] PANI shows a high tendency to agglomerate, much stronger than any pigment. So, individual molecules cluster to form primary particles (organic metals), which then form primary aggregates. Primary aggregates cluster to form secondary particles. 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.

Only for the dispersion based on doped PANI sample with a particle size of 40 μm the viscosity measurements were performed and indicate that the viscosity of PANI dispersions increases with the increase of PANI content in dispersion.

The viscosity measurements of melamine formaldehyde dispersion based on doped PANI were performed using Brookfield RVT viscosimeter, at room

temperature. The decreasing of apparent viscosity coupled with the increasing of the shear rate suggests that textural changes in the samples may be induced by the shear rate. With the increase of stress parameters the PANI aggregates (Figure 4) were destroyed and became orientated with the flow direction. The non-Newtonian fluids suffer slow structure modification. To investigate the dependence of the η on γ , we employed the Carreau model, which has proven to be a useful model for fitting the non-Newtonian viscosity curve for various polymeric systems:

$$\eta = \frac{\eta_0}{[1 + (\dot{\gamma} t_1)^2]^{(1-n)/2}}$$

Here η_0 is the zero shear rate viscosity, t_1 is the characteristic time, and n is dimensionless parameter.

The experimental data are presented in table 3 and figure 2.

TABLE 3. The parameters η_0 , t_1 and n for PANI melamine formaldehyde dispersions

PANI	PANI content %	η_0 Pa.s	t_1 s	n
PANI-APP	0%	6562	5.37	0.51
	5%	40500	3.10	0.47
	10%	82000	2.12	0.42
	15%	95000	1.60	0.38
	20%	110000	0.52	0.24
PANI-ASP	0%	6562	5.37	0.51
	5%	38000	3.37	0.49
	10%	75000	1.84	0.36
	15%	85000	1.54	0.38
	20%	100000	0.13	0.16
PANI-ACIEP	0%	6562	5.37	0.51
	5%	43000	4.20	0.50
	10%	68000	3.56	0.49
	15%	83500	2.60	0.35
	20%	90000	0.62	0.24

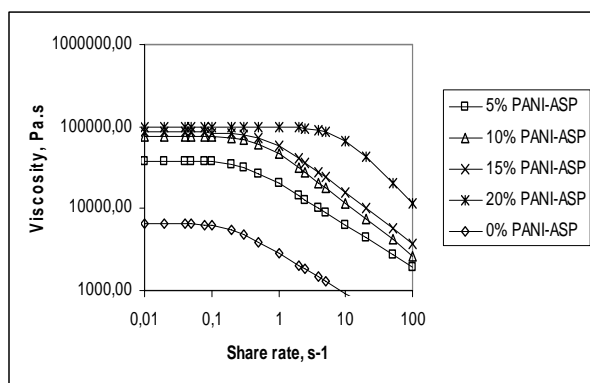


Figure 2. The dependence of the η on γ

The parameter zero share rates, n decreased with PANI content. These curves clearly demonstrate a Newtonian region at low shear rates and a well-defined power-law region at higher shear rates. With increasing shear rate, the conformations of the intercalated chains are also expected to change as PANI layers align parallel to the flow field.

4. Conclusions

The viscosity of dispersion decreases with the increase of rotation speed and increases with PANI content. The rheological behaviour of dispersions depends on the anion nature of PANI. The calculated values of η_0 , t_1 , and $(1 - n)$ increased with PANI content.

Furthermore, we observed $(1 - n)$ and η increase drastically for 15 wt % content and exhibit a sharp transition from the Newtonian plateau region to the power-law region.

The electrical conductivity of the composites was improved with increasing amount of PANI and the resistance of melamine formaldehyde dispersions decreases. The dispersions of PANI powder in melamine formaldehyde resins allowed obtaining of semiconductive dispersions because the resistance is situated in domain of about 10-5 Ohm. Therefore, a low value of resistance indicate a semiconductive dispersion which allowed to use the dispersion like a semiconductive coatings with a large application domain, in modern industry and it can be used to remove the electrostatic charges, and for the shielding effects (i.e. Faraday screen, protective coat for the high voltage cables, etc.).

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