

Characterization of Polyetheretherketone Particle Suspensions for Electrophoretic Deposition

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ABSTRACT: Suspensions of polyetheretherketone (PEEK) using mixture of ethanol and isopropanol as solvent were prepared to carry out PEEK electrophoretic deposition (EPD). The rheological behavior and suspension structure of PEEK particles dispersed in co-solvents were investigated over a range of pH values (1–10) and shear rates ($\dot{\gamma} = 10^1 - 3 \times 10^2 \text{ s}^{-1}$). These PEEK suspensions generally exhibited a pseudoplastic flow behavior, indicating the occurrence of particle aggregation in the liquid medium. The maximum solids fraction (ϕ_m) showed an estimated value of $\phi_m = 2.9 \text{ wt } \%$. Using a suspension with 3 wt % PEEK concentration, PEEK coatings on stainless steel substrates were obtained by EPD at constant voltage condition. The influence of the electrolyte conductivity on PEEK EPD from ethanol–isopropanol suspensions was studied. Experimental results showed that high-conductivity ethanol-based suspensions yield non-uniform deposits, while low-conductivity suspensions resulted in uniform coatings. The difference in the deposition behavior is due to the different pH of the suspensions and the relationship of pH with suspension conductivity. pH = 8 was the optimal value for this system in terms of deposition results. The surfaces of EPD PEEK coatings were homogenous and a qualitatively good adhesion between the PEEK deposits and the substrate was confirmed. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40953.

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INTRODUCTION

Polyetheretherketone (PEEK) is a semicrystalline thermoplastic material with excellent mechanical properties and chemical resistance that are retained at high temperatures. Due to their chemical stability, this biomaterial is increasingly used in advanced biomedical applications.¹ For expanding application opportunities, there is an increasing demand in miniaturization, complexity and better control of the component dimensions and microstructures.^{1–3}

Electrophoretic deposition (EPD) is an effective method to fabricate polymeric and ceramic coatings and films from powder suspensions.⁴ EPD is being increasingly considered for preparation of biomaterial coatings.^{4,5} The motion of particles and fluids in DC fields has been the subject of study for over 100 years. But it is only during the last few years that the behavior of particles in AC fields, i.e., AC electrokinetics, has started to be studied in detail.^{6–9} EPD is based on the availability of charged particles suspended in aqueous or organic medium that migrate under the influence of an electric field (electrophoresis) and are deposited on the opposite charged electrode. EPD has several advantages for example the possibility to use substrates

with complex shape and the fact that easy control of the thickness of coatings is possible, in addition simple and low cost equipment is required.¹⁰

Several papers have been published on the preparation of thick PEEK films on stainless steel substrates by EPD.^{11–13} Organic solvents, e.g., mixtures of ethanol and isopropanol (IPA) have been used. Non aqueous processes have the advantage of avoiding the electrolysis of water and the gas evolution on the surface of the electrode during EPD. A good dispersion of PEEK particles using organic solvents is one key point in order to achieve good-quality coatings by EPD. This system presents several advantages including good chemical stability of the suspension and absence of electrochemical reactions and Joule heating on the electrodes.^{11,12,14}

Although there have been previous investigations of the microstructure of PEEK films obtained by EPD and the governing mechanisms of electrophoretic deposition,^{11,12} the rheological behavior of PEEK suspensions and the achievement of optimal compositions that produce uniform coatings have not been investigated in detail in previous researches. Indeed the rheological evaluation of PEEK suspensions is paramount in order to

obtain stable suspensions for EPD^{11,15,16} and consequently to achieve defect-free PEEK films by EPD. In the present study, we have investigated the rheological behavior of suspensions of PEEK particles in ethanol–isopropanol mixtures, and its influence on the quality of films obtained by EPD over a broad solids-concentration range was studied. Optimal suspension parameters which result in homogeneous PEEK deposits with high particle packing density were determined.

EXPERIMENTAL

Starting Materials

The powder used in the present work was PEEK of particle size < 25 μm , (Victrex® Manufacturing, South Yorkshire, UK). A co-solvent suspension containing 5% isopropanol and 95% ethanol (>99.7%) was used. In contrast to researches of Wang et al.¹¹ and Corni et al.,¹² who employed pure solvents, we used a co-solvent system because the addition of a aliquot of isopropyl alcohol induces the solvation of PEEK particles and consequently, deposits obtained by EPD should exhibit improved homogeneity and better adherence to the substrate

PEEK powders were added in variable concentrations. This powder has been used in previous EPD studies.^{10,11} The pH values of suspensions were adjusted by using HNO_3 and NH_3 (Tetrahydroxide) for the acidic and alkaline ranges, respectively. Each suspension employed was ultrasonically dispersed for 20 min in order to ensure a good dispersion of the particles. The suspensions used to evaluate rheological properties were prepared incorporating a broad range of solid loading, i.e., 1–7 wt %. The EPD process was carried out using stainless AISI 316L foils (0.2 mm of thickness) as substrates, employing a PASCO power supply SE-9721A (PASCO Instrument, Roseville, USA).

The dependence of deposited weight as function of time was estimated by comparing the electrode weight before and after deposition.

Rheological Characterization

Rheological properties of the PEEK powder suspensions were determined at room temperature (303 K) using a Brookfield LV-DV-III rheometer, equipped with ultra-low sampler adapter (UL Adapter), and conical spindle. Assays were performed on triplicate. All suspensions used in this study were stabilised by magnetic stirring during 40 min. The experimental process was controlled using Rheocalc® software and measurements were performed with steady increment of the shear rate ($\dot{\gamma}$). Rheological properties were always measured 20 s after the viscometer reached the desired shear rate. The suspensions typically reached an equilibrium stress in less than 10 s, this duration is hence sufficient to ensure that the sample rheological properties were taken under steady-state conditions. The rate was increased in 4.5 rpm steps each 15 s over a shear rate range 10–298 s^{-1} . The shear rate was subsequently decreased to the initial value at the same rate. The effect of pH on suspension stability was investigated using suspensions that led to good-quality PEEK films, in terms of macroscopic homogeneity and compactness of the deposits and exhibiting sufficient adherence to the substrate. The pH effect on suspension viscosity was investigated in the pH range 1–14. The dependence of PEEK

suspension conductivity on pH values was determined using a Delta CO044 conductivity meter.

Electrophoretic Deposition of PEEK

For EPD, suspensions with solid concentration of 1, 3, 5, 7 wt % were chosen. Co-solvent suspensions based on 5% isopropanol (IPA) and 95% ethanol containing PEEK powders were used. In the previous section the advantage of using a small amount of IPA was mentioned. The stability of the suspensions was enhanced by sonically stirring for 45 min before the tests. A glass beaker was used as the container for the EPD cell. Stainless steel planar substrate (15 \times 10 mm^2 cross section, 2 mm thickness) was used as the cathode, knowing that PEEK particles in suspension would acquire a positive charge for $\text{pH} > 5$, and negative charge for $\text{pH} < 5$ (isoelectric point $\text{pH} = 4.5$).^{2,11} The separation between electrodes (d) was 2 cm. The counter electrode was planar stainless steel foil with the same dimensions as the cathode. Before electrophoretic deposition, all substrates were cleansed with acetone and mechanically polished using abrasive paper with different granulometry.

After EPD, the samples were carefully removed from the suspension and slowly dried in air for 24 h in order to minimise cracking during drying. Uniform PEEK coatings on stainless steel substrates were obtained after sintering the electrophoretic deposited samples in air at 350°C for 30 min.

Characterization of PEEK Coatings

The “green” (unsintered) PEEK deposits were characterised by visual inspection and scanning electron microscopy (SEM Philips 515). The samples were coated with gold before SEM examination. SEM was used to characterize the uniformity of the coating microstructure and to determine the presence of microcracks, residual porosity as well as to evaluate the structural homogeneity and thickness of the deposits.

RESULTS AND DISCUSSION

Rheological Characterization

The behavior of a fluid defined by rheological studies can be described implementing different mathematical models that relate the shear stress and shear rate. Among the commonly used models to characterize plastic and pseudoplastic fluids the Power Law and the Herschel-Buckley model¹⁵ are usually applied.

In the present study, the rheological behavior of suspensions was visualized employing shear stress vs. shear rate plots. The resulting curves were modelled in terms of Power Law with exponent (flow index) n (shear-thinning: $0 < n < 1$ or shear thickening: $1 < n < \infty$) and constant K , using the following equation:

$$\sigma = K \cdot \dot{\gamma}^n \quad (1)$$

where σ = shear stress (Pa), K = consistence index, taken as $K = 1$ in this study, $\dot{\gamma}$ = shear rate (s^{-1}), n = flow index.

This behavior is considered a special case of the Herschel–Bulkey model where K and n are structure-dependent parameters that can be determined experimentally.^{16–19} Figure 1 shows the shear stress vs. shear rate dependence of the PEEK colloidal suspensions with different solids content. Figure 2 shows the viscosity variation of the suspensions in ethanol/isopropanol for different concentrations (ascendant branch).

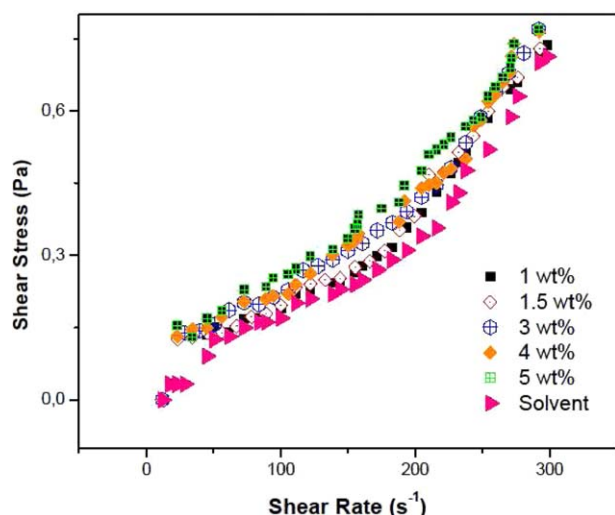


Figure 1. Shear stress vs. shear rate plot of pure solvent and PEEK suspensions at different concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEEK suspensions with 1, 3, and 5 wt % of solid exhibited a similar behavior. In those cases, suspensions with low PEEK concentration, a pseudoplastic behaviour at low shear rate range was observed. Values of $K < 0.79$ justify this behaviour.

All concentrations studied exhibited a decrease in the apparent viscosity up to $\sim 50 \text{ s}^{-1}$ shear rate, then, the viscosity increased, except for the suspension with 7 wt % PEEK for which the viscosity decreased in the complete range of shear rates evaluated (not plotted). This result indicated the existence of particle aggregations in the suspensions, and an increased degree or particle interactions as ϕ increased. The flow behavior changed for the case of suspensions with high concentration of solid, indicating a higher resistance to flow.

This effect is not noticed at concentrations $< 7 \text{ wt} \%$ which might be due to the fact that PEEK particles remain in stable

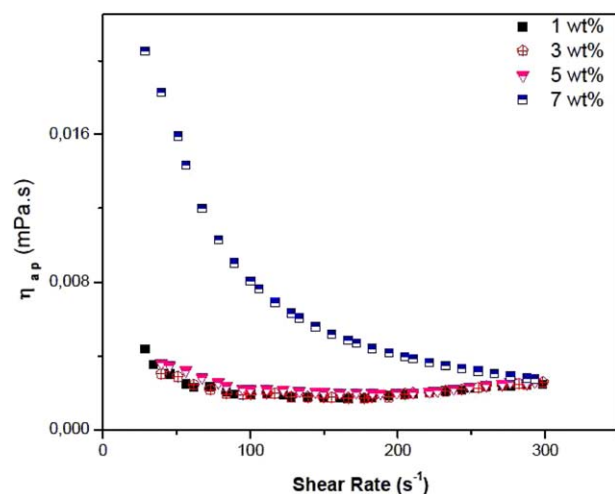


Figure 2. Apparent viscosity vs. shear rate of PEEK suspensions in ethanol/isopropanol co-solvent with different solid (PEEK) concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

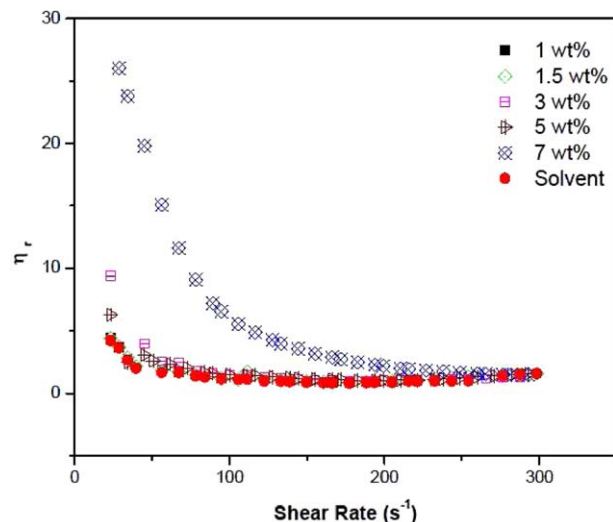


Figure 3. Relative viscosity vs. shear rate of PEEK suspensions in ethanol/isopropanol co-solvent with different solid (PEEK) concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

suspension. The relative viscosity (η_r), defined as the relation between suspension viscosity (η_s) and pure solvent viscosity (η_o), is shown in Figure 3 for all concentrations of suspensions investigated. The maximum solids concentration (ϕ_m) at which the suspension behaves as solid is estimated by extrapolating the fitted linear line to $(1 - \eta_r^{-1/2}) - \phi$ dependence. ϕ_m can be estimated by extrapolating the fitted linear line to $(1 - \eta_r^{-1/2}) \rightarrow 1$. As shown in Figure 4, the experimentally determined $1 - \eta_r^{-1/2}$ values appear linearly proportional to ϕ over the range of solids loading studied, which is similar to previous results obtained for titania suspension.¹⁹ The correlation is high, with $R = 0.9991$ for $\gamma = 100 \text{ s}^{-1}$. Extrapolating the $1 - \eta_r^{-1/2}$ values to 1, the value found for our system is 2.9 wt %, which corresponds to the minimum solid concentration at which the suspension is stable.

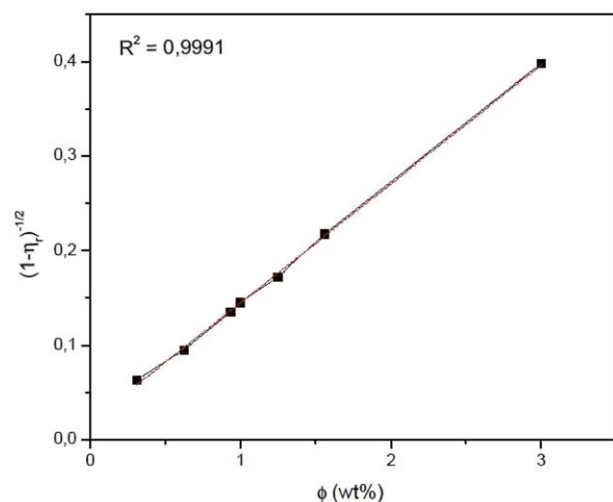


Figure 4. Deposited solid fraction as function of relative viscosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

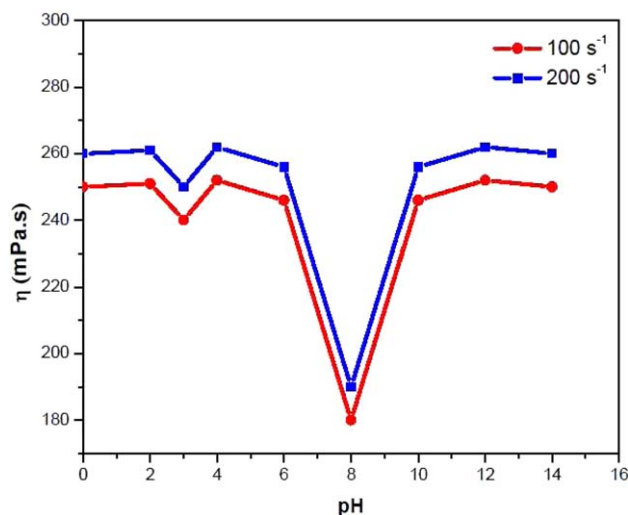


Figure 5. Viscosity vs. pH of 3 wt % PEEK suspensions in ethanol/isopropanol co-solvent at two different shear rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of pH

In order to determine the effect of pH on suspension stability the optimal suspension concentration in terms of rheological behaviour (3 wt % PEEK) was evaluated. It was determined that the suspension with 3 wt % of PEEK exhibited pH = 7.90. Figure 5 shows viscosity measurements obtained at shear rates of 100 and 200 s⁻¹. In the plot of viscosity vs. pH, an optimum pH value at which a minimum viscosity occurs was observed. The minimum viscosity point corresponds to the point of transition from attractive to repulsive particle interaction that is consistent with pH ~ 8. The fact that the suspension shows the lowest viscosity at pH = 8.0 is attributed to the extension of the polymer chains that contribute to the steric stabilization. For other pH values, the suspension displays a higher viscosity in the range evaluated. For the investigated PEEK suspension, pH

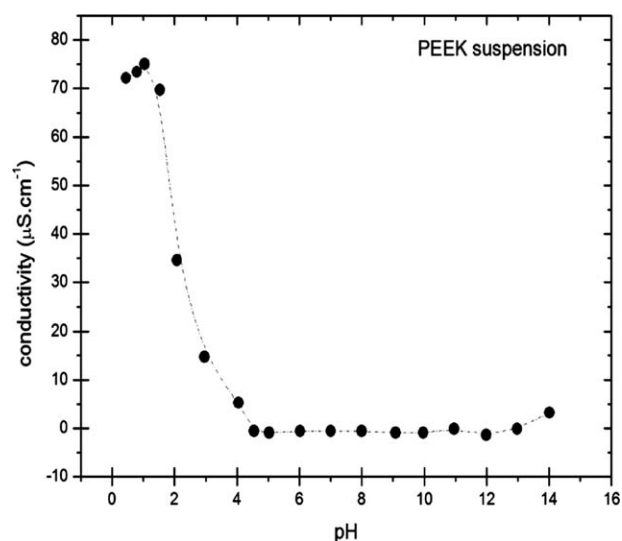


Figure 6. The dependence of the conductivity of PEEK suspensions on pH value.

≈ 3 is another point at which the viscosity decreases more, however to a lesser extent than observed at pH 8. The possible causes for this behaviour are likely related to reflocculation, particle size effects, or pH-dependant surface charge. All these factors are known to increase the viscosity of suspensions.² Clearly, the suspension pH has marked effects on the rheology behaviour and consequently on suspension stability. Interestingly, the present data confirm the results of the pH ranges used for EPD of PEEK in ethanol systems in previous investigations, which were determined by trial and error.^{11,12}

The influence of electrolyte conductivity on the electrophoretic deposition of PEEK particles from ethanol suspensions was studied. The obtained results demonstrate that the pH value (adjusted by the addition of small amount of acid and alkaline in suspension) has an obvious influence on conductivity of PEEK suspensions. Deposition experiments showed that high-conductivity ethanol-based suspensions yield non-uniform deposits, while low conductivity suspensions result in uniform coatings. Considering that stable suspensions for EPD process were only obtained at pH 8, a low conductivity for this pH value was confirmed, this is agreement with results of other investigations. Ferrari and Moreno,¹³ for example, proposed that the conductivity of the suspension is a key factor and needs to be taken into account in EPD experiments. If the suspension is too conductive, particle motion is very low, and if the suspension is too resistive, the particles charge electronically and the stability is lost. The suitable region of conductivity is however expected to be different for different systems. In our case, the result is likely due to the protons (H⁺) present in the acid medium which can join the free unshared electrons of the PEEK surface thus preventing the formation of hydrogen bonds with the solvent. Then, PEEK particles settle and the deposition rate on the substrate decreases. Figure 6 shows the dependence of the conductivity of PEEK suspension on pH values, which indicates that the conductivity is very low when the pH is higher than pH ≈ 4, a value close to the isoelectric point (pH ≈ 5).¹¹ The failure of deposition of PEEK powders on the

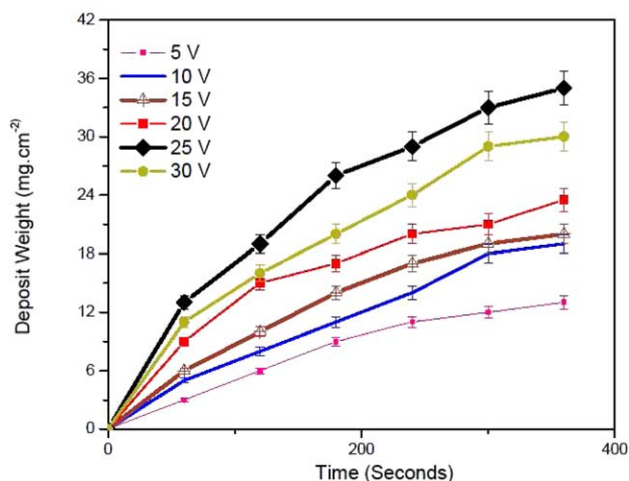


Figure 7. Deposited weight vs. deposition time for EPD of PEEK at different voltages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

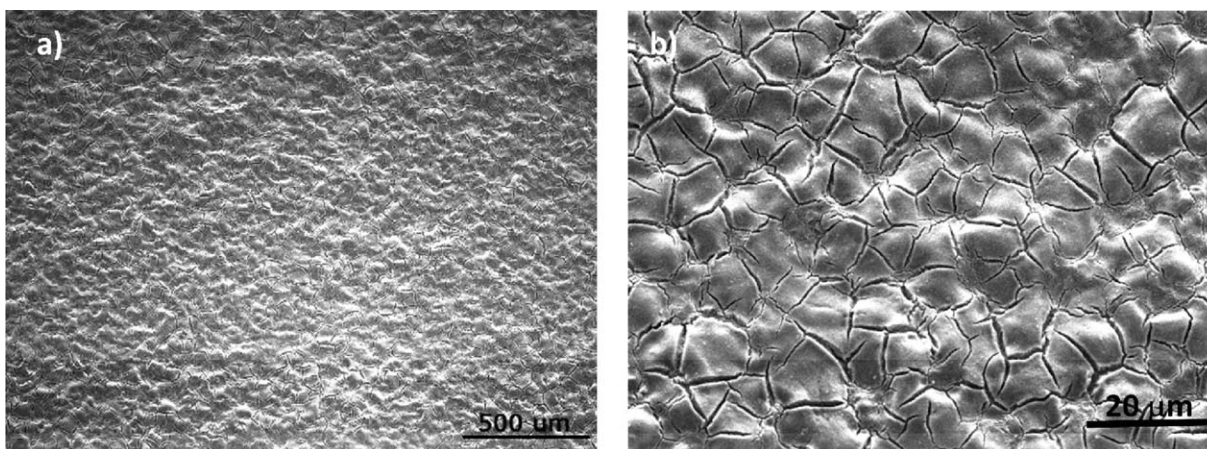


Figure 8. SEM micrographs of PEEK coating on stainless steel (Top view) at different magnifications: a) low and b) high magnification, the presence of some cracks is observed on the coating surface.

cathode at low pH value (pH 5) in our experiment may also result from the disturbance of the free H^+ ions released at the cathode in the form of H_2 . On the other hand, at $pH > 5$ we successfully deposited PEEK powders on the anode within the experimental range.

EPD Process

For electrophoretic deposition of PEEK the same suspension concentrations employed for rheological characterization were used in order to assess the synergic effects of suspension concentration, voltage and deposition time on the quality of PEEK coatings. According to preliminary experiences, using a co-solvent suspension of 5% isopropanol and 95% ethanol with added 3 wt % of PEEK powder and applying a continuous voltage in the range 20–25 V, it was possible to obtain homogeneous PEEK coatings by EPD. The anodic deposition of PEEK particles confirmed that the carried charge on the PEEK particle surface is negative for pH values below 5. In Figure 7 the results of PEEK deposited weight as function of different applied voltages and deposition times are presented. The results show that initially the deposited weight increases with deposition time (150 s); and then the deposited weight deviates from linearity indicating a decrease of deposition rate as the coating thickness increases (Figure 7). This behavior is typical for EPD processes under the conditions employed here.^{11,12}

For PEEK concentrations lower than 1 wt %, it was not possible to observe deposits on the stainless steel substrates for all voltages tested. For polymer concentrations above 5 wt %, and for applied voltages of 25 V, the particles were deposited mainly on the edges of the substrate. It was thus confirmed that the best quality films in terms of coating homogeneity and efficient coverage of the substrate were obtained using 3 wt % PEEK suspensions under constant voltage (25 V) and deposition times of 90 to 120 s. SEM micrographs of PEEK films in “green” state, electrophoretically deposited for 120 s, are shown in Figure 8(a,b), respectively. The cracks on the coating surface can be produced during the drying step. In future researches these aspects of the coating processes will be further investigated. It is

relevant to compare the present results with those of Corni et al.¹² whose best deposition conditions to obtain PEEK coatings on stainless steel using ethanol-based suspensions (with different solids concentrations and applied voltages) involved deposition time of 7 min, higher to the one required in the present study. Moreover, it is interesting that in the present investigation no additives, such as dispersants, were required. The advantage it is that the additive-free suspension allows to work at relatively low voltages, in contrast to previous investigation¹⁵ in which a high voltage was necessary (100 V) to produce uniform PEEK coatings.

CONCLUSIONS

Experimental work and theoretical analyses were performed to investigate the rheological behavior of ethanol-based suspensions containing PEEK particles. Mixtures of ethanol-isopropanol were used as co-solvent in order to formulate suitable suspensions for EPD. The effects of PEEK particle concentration and pH on suspension rheology were studied and the following conclusions were obtained:

- For suspensions with low solids concentration a pseudoplastic behaviour at low shear rate range was observed.
- The maximum solids concentration (ϕ_m) was determined from empirical viscosity-concentration relationship, the value $\phi_m = 2.9$ wt % was found for this system.
- The optimum pH in terms of suspension stability, a which the minimum of viscosity occurs, was determined to be $pH = 8$.
- The best quality of PEEK films manufactured by EPD in terms of coating uniformity was obtained employing suspensions with 3 wt % solids under constant voltage (25 V), electrode distance of 2 cm and deposition times of 90–120 s.

The present results are relevant to design EPD experiments to produce PEEK-based composite coatings, e.g., including inorganic bioactive particles, which are relevant for applications in the orthopedic field and are the focus of current studies.

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