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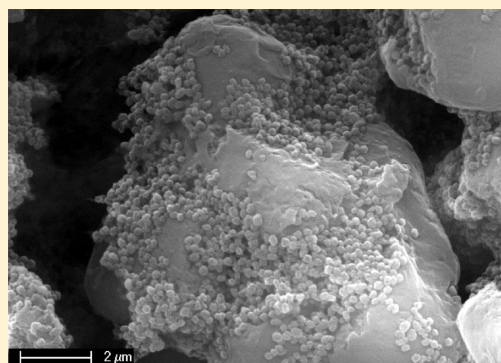
# Study of Polymer Particles Suspensions for Electrophoretic Deposition

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**ABSTRACT:** Recently a great interest has been expressed in electrophoretic deposition (EPD) of polymers, both as particles and as chains. It is generally accepted that also for polymer particles, the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is valid, therefore, in principle, polymer suspensions suitable for EPD could be easily obtained by dispersing polymer particles in an aqueous or nonaqueous medium. Nevertheless, this work demonstrated that in order to obtain good quality deposits based on poly(ether ether ketone) (PEEK) and poly(tetrafluoroethylene) (PTFE), some additives have to be used. In the case of PEEK, a dispersant providing citrate anions was successfully used, whereas for PTFE a steric suspension stabilization was reached by adding polyvinylpyrrolidone (PVP). In such a way, codeposition of PEEK and PTFE was achieved. The efficiency of the EPD process was demonstrated by means of differential scanning calorimetry (DSC) measurements. A thermal program consisting of heat/cool/heat cycles at a low rate was used in order to evaluate the crystalline amount of each polymer in the deposits. In order to explain the obtained results, it needed to also consider the dimension and structural characteristic of the polymer particles.



## ■ INTRODUCTION

In recent years, electrophoretic deposition (EPD) has been successfully applied to polymers, also together with ceramic particles.<sup>1–5</sup> Some efforts have been made in order to understand the interparticle interactions and the behavior of polymer particles when they were inserted in suspensions, more or less concentrated.<sup>6,7</sup> Particular interest was also focused on electrostatic interactions and on the validity of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory<sup>7,8</sup> when the suspension liquid was nonaqueous.<sup>9,10</sup>

On the other hand, several papers reported on the effect of an electric field on polymer chains, investigated by simulating the interface growth and the density profile of a polymer deposit on an impenetrable substrate.<sup>11–13</sup> Nevertheless, the actions of the additives are not clear, for example, a dispersant or a deflocculant, in a suspension where the polymer is in the form of a solid particle with a finite dimension rather than as a long chain. However, the considerable number of published papers on this subject demonstrates the large interest in the polymer deposition process, as the use of polymers is forever increasing, especially in the fields of bio-, nano-, and hybrid materials.<sup>14–16</sup>

Among polymers used for coating applications, a high performance polymer such as poly(ether ether ketone) (PEEK) is particularly attractive because it has excellent mechanical, chemical, and thermal properties in respect to other polymers. In spite of its outstanding properties, PEEK exhibits a high friction coefficient in dry sliding, which restricts its tribological applications. In order to reduce the friction coefficient of PEEK

and therefore to increase its range of applications, some solid lubricants, such as glass and carbon fibres, graphite or carbon nanotubes,<sup>17–20</sup> as well as polymers with low surface energy, such as poly(tetrafluoroethylene) (PTFE),<sup>21–23</sup> were added to the PEEK matrix.

Being interested in low friction coatings, we studied the possibility of obtaining PEEK-based coatings by the use of the EPD process, and also by mixing PEEK with other materials, both organic and inorganic. With respect to other deposition techniques such as thermal spraying or printing processes,<sup>24–31</sup> EPD does not induce polymer degradation, but produces coatings with low roughness, and is able to create patterned or miniaturized devices. Recently, EPD has demonstrated to be a suitable method to obtain polymer coatings based on PEEK.<sup>1–3,32,34,35</sup> Corni<sup>2,3</sup> has obtained good quality coatings by using EPD suspensions where PEEK particles were dispersed in ethylic alcohol without any additive. On the contrary, we observed a certain precipitation in PEEK powder suspensions when a dispersant was used.<sup>32</sup> This result is probably due to different PEEK powder characteristics. In order to get a good stabilization of an ethylic suspension containing PEEK particles, we used a mixture of citric acid and triethylamine (hereinafter referred to as CT), which has

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already been successfully used by the authors as dispersant in ceramic suspensions.<sup>33</sup>

Regarding PTFE, to the knowledge of the authors, the application of EPD to PTFE suspensions was reported in only two papers.<sup>4,5</sup> In one case, a commercial aqueous suspension of PTFE was used; in the other one, acetone was used as dispersion medium. In both the cases, PTFE was mixed with inorganic powders (ruthenium oxide and titanium oxide, respectively), which assisted the polymer particles in the deposition. As a relevant result, we prepared and used a suspension where only PTFE powder was present. In order to make possible EPD of PTFE, an organic dispersant, polyvinylpyrrolidone (PVP), was used.

In this paper we reported the study of electrophoretic polymer suspensions, by investigating the effect of CT and PVP on the stabilization on PEEK and PTFE suspensions, respectively. Moreover, the efficiency of the EPD process was evaluated by means of a thermal analysis of deposited coatings, performing a specific cycle of measurements. The proposed procedure is innovative and could be generally adopted to determine the amount of different polymers in a compound.

## EXPERIMENTAL DETAILS

PEEK powder (semicrystalline, particle size <10  $\mu\text{m}$ , 1.2 g/cm<sup>3</sup>, Victrex Manufacturing Ltd.) and PTFE powder (semicrystalline, particle size <1  $\mu\text{m}$ , 2.15 g/cm<sup>3</sup> at 25  $^{\circ}\text{C}$ , Aldrich) were used to prepare suspensions suitable for the EPD process. The solid content was fixed at 1 wt %. As liquid medium ethyl alcohol was used; as a dispersant, a solution of triethylamine and citric acid<sup>33</sup> was added to the PEEK suspension, whereas PVP (average molecular weight = 40.000) was added to the PTFE suspension. The suspensions were homogenized by using an ultrasonic processor with a power of 200 W for 30 min. Zeta potential and grain size measurements were conducted by using a Malvern Zetamaster Nano-ZS. The measurements were carried out on the suspensions diluted to a concentration of 0.2 g/L, suitable for light-scattering measurements. In order to evaluate the macroscopic effect of dispersant on polymer particles suspensions, viscosity was measured varying the dispersant content on a suspension with 40 wt % of solid content at a shear rate equal to 30 s<sup>-1</sup>, by Viscobasic Plus R. The referred variation of pH was carried out by adding some aliquot portions of HCl or NaOH.

Coatings based on PEEK and PTFE were obtained by using suspensions prepared by mixing the starting suspensions of PEEK and PTFE in three different ratios. EPD process parameters were optimized in order to obtain visually uniform coatings. Carbon paper substrates were used as coating supports and EPD depositions were performed at constant voltage conditions. The summary of the investigated samples is reported in Table 1. For all the coatings, the deposition time was 3 min. The powders and the EPD deposits were observed by a scanning electron microscope (SEM; Philips XL40 LaB6).

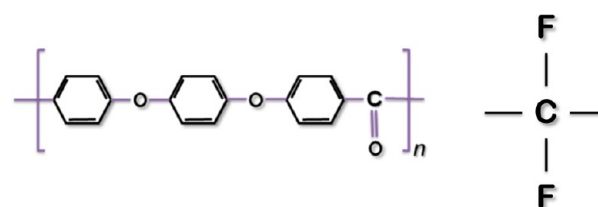
In order to evaluate the effectiveness of the two types of dispersant on the deposition process, the deposited particles were removed from the substrate after deposition and submitted to differential scanning calorimetry (DSC) measurements. The aim of these analyses was to determine the deposited amount of PEEK and PTFE and compare it with respect to the nominal concentration of the EPD suspensions. DSC measurements were performed by using TA-Instruments Q200. During thermal program, the analysis chamber was purged by a N<sub>2</sub> flux (50 mL/min).

**Table 1.** Composition of the Investigated Deposits and Voltage Applied for Deposition

name	% PEEK suspension	% PTFE suspension	voltage (V)
PEEK	100	0	100
MIX3	80	20	100
MIX1–100	50	50	100
MIX1–75	50	50	75
MIX1–50	50	50	50
MIX1–25	50	50	25
MIX2	20	80	100
PTFE	0	100	100

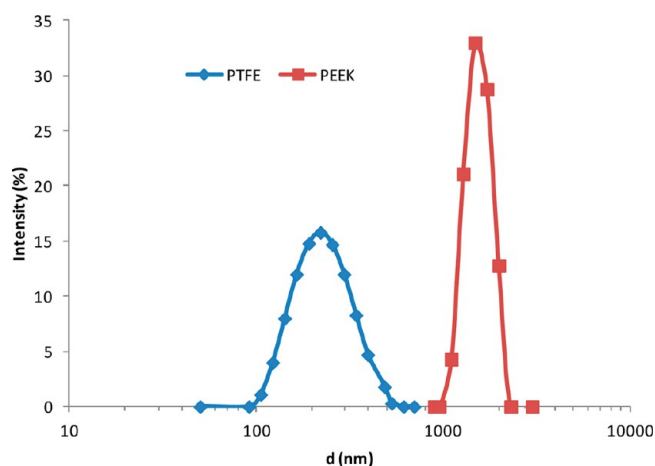
## RESULTS AND DISCUSSION

**Suspension Optimization.** PEEK is a polyaromatic semicrystalline thermoplastic polymer (typically with 30–40% crystallinity), formed by three aromatic rings and a carbonyl group. It is thermally stable up to 580  $^{\circ}\text{C}$ , with a glass transition temperature equal to 145  $^{\circ}\text{C}$ , a crystallization temperature equal to 250  $^{\circ}\text{C}$ , and a melting temperature equal to 340  $^{\circ}\text{C}$ . Polytetrafluoroethylene is a hydrophobic fluorocarbon compound, with a melting temperature equal to 325  $^{\circ}\text{C}$ . It is highly nonreactive, because of the strength of carbon–fluorine bonds, and so it is often used in containers for reactive and corrosive chemicals and as a lubricant. The chemical structure of PEEK and PTFE was shown in Figure 1.



**Figure 1.** Chemical structures of PEEK (on the left) and PTFE (on the right).

The dimension and the morphology of the two powders were rather different, as evaluated by SEM observation (SEM images were not reported here) and grain size distribution measurements (Figure 2). PTFE powder was dimensionally monodisperse, rounded, and regular, with a mean dimension of



**Figure 2.** Grain size distribution of PTFE and PEEK particles measured by the dynamic light scattering technique.

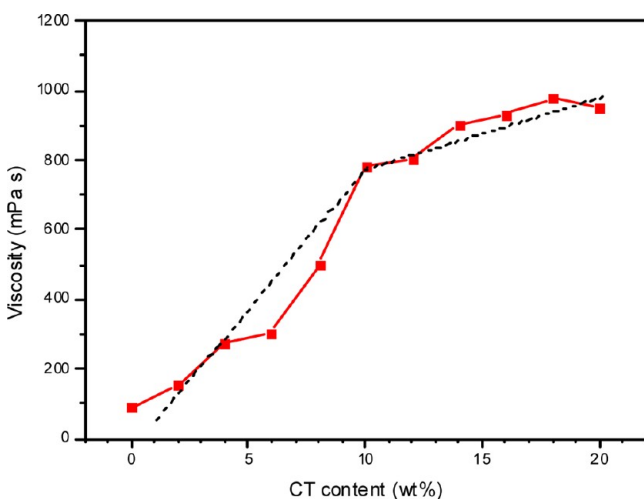
about 300 nm, whereas PEEK powder had an irregular shape, with a dimension distribution ranging approximately from 0.3 to 6  $\mu\text{m}$ .

To prepare CT, a quantity of 0.5 M citric acid was dissolved in deionized water; to this solution, 2 M triethylamine was added. This solution was used as the dispersant for PEEK suspensions. In the CT solution, water was preferred to ethyl alcohol because of the better solubility of the chemicals in an aqueous medium. In the past, CT was successfully used in ceramic suspensions containing alumina or zirconia powder,<sup>33</sup> as it produced an efficient electrostatic repulsion between ceramic particles. In fact, the conjunction of an amine with high basicity and a carboxylic acid promoted the deprotonation of the acid groups and therefore the production of the citrate anion  $\text{COO}^-$ . The citrate anion was adsorbed on the ceramic particle surface, which therefore was charged negatively.<sup>33</sup>

CT demonstrated to be efficient also in the dispersion of PEEK particles,<sup>32,34,35</sup> improving the stabilization and increasing the zeta potential of PEEK suspensions. Ma et al.<sup>7</sup> affirmed that the classical colloidal theories describing the particle behavior in suspension can be applied to polymer particulates. When a polymer particle is immersed in a nonaqueous solvent, it could acquire surface charges principally by dissociation and ionization of surface groups. Besides this electrostatic effect, Ma proposed that in polymer particle suspensions, a certain degree of steric stabilization can occur due to loosed polymer chains extending externally to the particulate.

According to this point of view, we believe that the citrate anions acted as an electrostatic capping agent toward the PEEK particles, providing an absorption of negative charges from the surface chains. Evidence of this phenomenon was provided by some considerations on viscosity, zeta potential, and conductivity measurements.

First, the viscosity of a 40 wt % PEEK suspension was evaluated at shear rate constant (Figure 3). The amount of

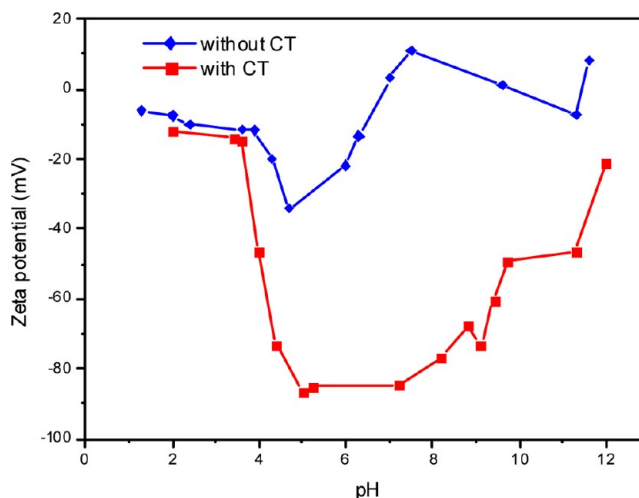


**Figure 3.** PEEK suspension viscosity as a function of the CT content.

PEEK content was intentionally chosen so high in order to have appreciable values of viscosity. From this measurement, it was possible to note that up to a certain content of CT, namely, 10 wt %, the viscosity increased linearly with a moderate rate. This increase could be attributed to repulsive interactions between the PEEK particles having negative charges on surface, which therefore could hamper the particle sliding. At higher values of

the CT content, the viscosity rate slowed down, indicating a reduction of the CT action, maybe due to a threshold in the CT addition that further limited the interaction with PEEK chains.

Therefore, in order to evaluate the zeta potential and to investigate the effect of CT on PEEK particles, it was decided to add a CT content equal to 10 wt %. In Figure 4 is reported the



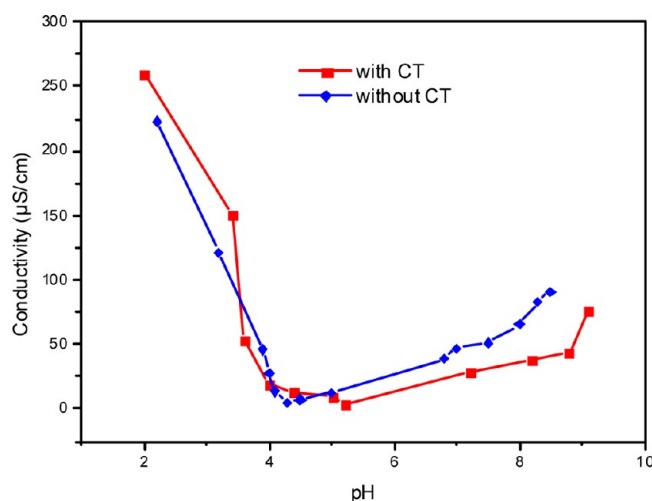
**Figure 4.** Zeta potential of PEEK suspension as a function of pH, with and without 10 wt % CT.

zeta potential of a 1 wt % PEEK suspension with and without the addition of 10 wt % CT, when the pH was varied. First, we observed that in the presence of CT, the zeta potential values of the PEEK suspension were always negative, meaning that actually the citrate anion interacted with surface chains of PEEK, making them negatively charged. Moreover, CT increased the absolute value of the zeta potential, especially in the pH range between 4 and 8. This fact is attractive for EPD, since during the deposition process a variation of local pH near the electrodes occurs, both in aqueous and nonaqueous suspensions.<sup>36,37</sup> As De speculated,<sup>37</sup>  $[\text{H}^+]$  decreases toward the cathode because of the continuous depletion (discharge) of  $\text{H}^+$  in the cathodic reaction of an EPD cell, inducing a local increase of pH. In our case, negatively charged PEEK particles moved toward the anode, where  $[\text{H}^+]$  increases and consequently pH decreases. For deposition, the PEEK suspension as prepared (pH = 4.4), was used. Therefore, when PEEK particles approached the anode, they were affected by a pH decrease and so suffered an appreciable reduction of zeta potential, which facilitated the particle coagulation on the anode.<sup>37</sup>

As high values of zeta potential generally correspond to a good stabilization, we concluded that the CT dispersant was able to perform a suitable electrostatic stabilization of PEEK particles in ethyl alcohol.

Finally, in order to confirm the proposed dispersion mechanism of PEEK particles in the presence of the CT, conductivity measurements were performed on PEEK suspensions with and without CT, respectively, when the pH was varied (Figure 5). When the CT was absent in the PEEK suspension, principally the electrolytic charges added for varying pH contributed to conductivity, as without CT the PEEK particles demonstrated having a low zeta potential. When the CT was present in suspension together with the added electrolytic charges, we observed a decrease of the conductivity

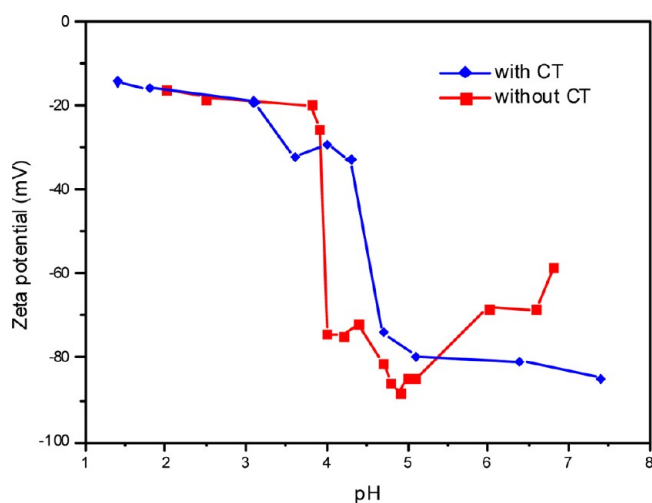




**Figure 5.** PEEK suspension conductivity as function of pH with and without 10 wt % CT.

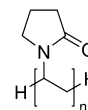
for pH >7 with respect to the suspension without CT. This result was attributed to the electrostatic interaction between the PEEK particles surface negatively charged by citrate anions and  $\text{OH}^-$  added to suspension to increase pH. Therefore, we deduced that the interaction between PEEK particle surfaces and citrate anions of CT conferred a negative charge to PEEK particles giving stabilization to the PEEK suspension and making the PEEK particles able to move under an applied electric field. All things considered, the CT content to add to PEEK suspension was fixed equal to 10 wt %.

PTFE molecules are structurally different from those of PEEK. The PTFE chain is linear with electronegative F atoms surrounding C atoms. Therefore the electrostatic interaction with the citrate anion is, in principle, hardly possible. Actually, the zeta potential of the 1 wt % PTFE suspension with and without addition of CT dispersant was almost similar (Figure 6) up to pH = 5. For higher pH values, the zeta potential assumed less negative values when CT was absent. Moreover, we noticed that at pH values higher than 8, the PTFE particles precipitated drastically as soon as NaOH was added, making it impossible to measure the zeta potential.



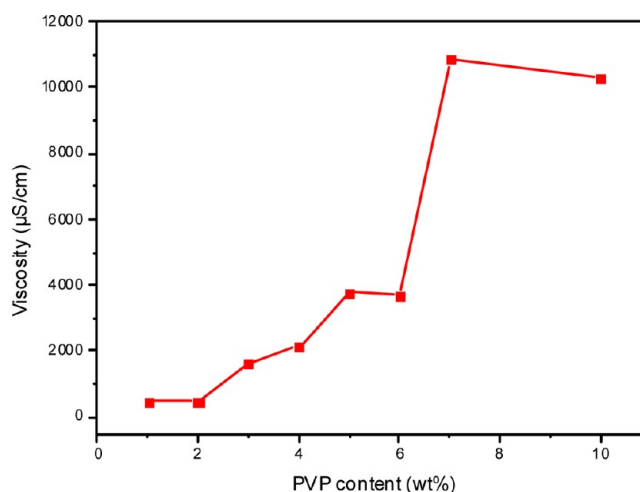
**Figure 6.** Zeta potential of the PTFE suspension as a function of pH, with and without 10 wt % CT.

All things considered, we deduced that the electrostatic interaction that occurred between the dispersant and PTFE particles was poor. On the other hand, a suspension containing only PTFE particles and ethyl alcohol without any dispersant was unstable and produced electrophoretic deposits of low quality. For this reason, a steric dispersant, such as PVP, was used. PVP is an amphiphilic polymer (Figure 7) with an effective action in dispersing both aqueous and nonaqueous ceramic and polymer suspensions.<sup>38–41</sup>



**Figure 7.** Chemical structure of PVP.

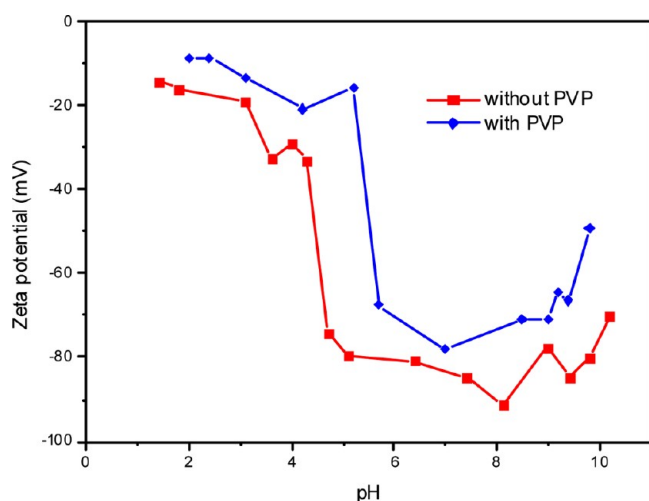
Some papers have highlighted the intermolecular hydrogen bonds between the carbonyl group of PVP and electronegative groups, for example, hydroxyl radicals.<sup>41</sup> We hypothesized that a steric stabilization of PTFE suspension could be induced by a similar behavior between  $\text{F}^-$  of PTFE and hydrogen atoms of PVP chains. An appreciable effect of the presence of PVP in PTFE suspension was observed on viscosity (Figure 8). For the



**Figure 8.** PTFE suspension viscosity as a function of the PVP content.

addition of up to 6 wt % PVP, the PTFE viscosity increased quite linearly, but the increasing rate grew exceptionally, reaching very high values. We believe that at the beginning of PVP addition, there were a large number of accessible sites for the interaction between PVP and PTFE. When the PVP amount increased, a lower number of  $\text{F}^-$  was available, and therefore PVP chains remained nonbonded in the suspension, hampering the motion of PTFE particles.

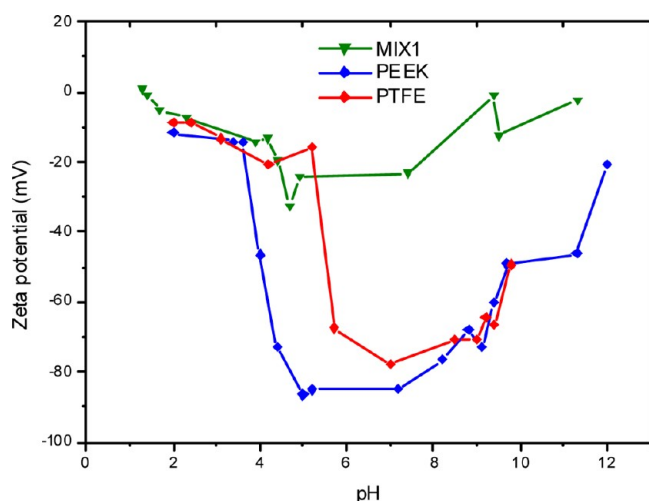
With regard to zeta potential, no relevant differences were observed on its values measured on 1 wt % PTFE suspension with and without PVP (Figure 9), except for a curve shift toward slightly lower values. This fact could be due to a lower number of sites on surface chains of PTFE particles, available for interaction with electrolytic charges, when PVP was added in the suspension. All the experimental results confirmed that PVP had a positive effect on PTFE suspension, producing a steric stabilization. Therefore, in order to obtain a suitable EPD PTFE suspension, the PVP amount to add was chosen equal to 5 wt % with respect to powder.



**Figure 9.** PTFE suspension zeta potential as a function of pH with and without 5 wt % PVP.

Since the aim of our work was to produce coatings containing PEEK and PTFE, new suspensions were obtained mixing the previously optimized suspensions of PEEK and PTFE. The aliquot portions of PEEK and PTFE suspensions were such as that the nominal content of polymer powders were those reported in Table 1, corresponding to weight ratios 4:1, 1:1, and 1:4 between PEEK and PTFE.

The zeta potential of the suspension containing PEEK and PTFE in a ratio of 1:1 at varying pH was reported in Figure 10.



**Figure 10.** Zeta potential of PEEK, PTFE, and 1:1 PEEK/PTFE (MIX1) suspensions as a function of pH.

It is possible to notice that the zeta potential of the mixed suspension was lower than the other ones. This detrimental effect was attributed to the negative effect of PVP on PEEK, which probably hampered the motion of PEEK particles. This was confirmed by the reduced value of zeta potential measured on a PEEK suspension prepared by adding 5 wt % PVP (Table 2). Nevertheless, the EPD process performed by using the mixed suspensions produced interesting results, as discussed in the following section.

**Electrophoretic Deposition.** Once the PEEK and PTFE suspensions were optimized, their suitability for EPD had to be verified, especially whether they were efficient for codeposition

**Table 2.** Zeta Potential of Different Suspensions Containing PEEK Particles

suspension	zeta potential (mV)
PEEK in ethyl alcohol	$-24.5 \pm 2.8$
PEEK in ethyl alcohol +10 wt % CT	$-80.6 \pm 4.1$
PEEK in ethyl alcohol +5 wt % PVP	$-10.8 \pm 5.1$
PEEK in ethyl alcohol +5 wt % PVP + 10 wt % CT	$-58.0 \pm 4.6$

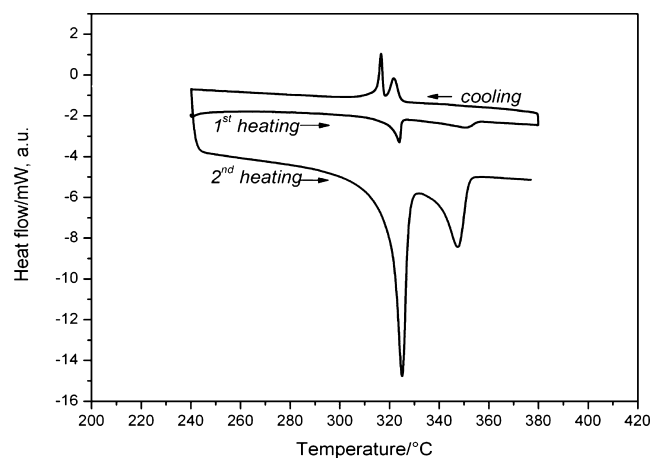
of the two polymers. To this aim, coatings based on only PEEK and only PTFE were deposited on carbon paper. The direct current (DC) voltage applied was varied between 25 and 100 V, but the best uniformity of coatings was visually reached at the maximum voltage for both the materials. Then, several deposits were produced with a fixed deposition time of 3 min, in order to have enough mass for the subsequent DSC analysis. Before a new deposition, the suspension was briefly magnetically stirred. The used suspensions were a mixture of determinate aliquot portions of the two suspensions, in order to have 4:1, 1:1, and 1:4 as nominal weight ratios between PEEK and PTFE.

To determine the quantity of both polymers present in each coating through the determination of their crystalline phase, DSC measurements were performed on the deposited mass after removing from the substrate. It is known that, assuming that the heat capacity of a polymer is substantially independent from the temperature, it is possible to calculate the mass fraction crystallinity ( $\chi$ ) by evaluating the melting enthalpy from the DSC thermogram, according to the following formula:

$$\chi = \frac{H_m}{H_f}$$

where  $H_m$  is the melting enthalpy, calculated as the area under the crystal melting transition per unit weight, and  $H_f$  is the theoretical heat of fusion for a pure crystalline phase, equal to 130 J/g and 82 J/g for PEEK and PTFE, respectively.

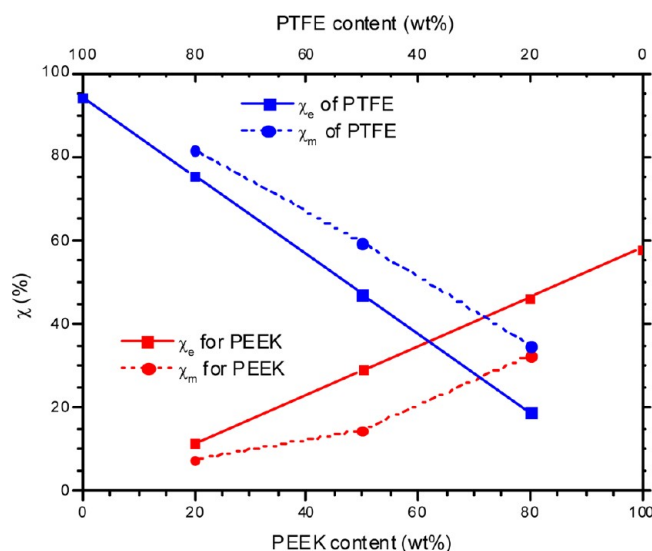
First, a sort of calibration curve was determined by evaluating the crystallinity of known amounts of the polymer powders. A thermal program consisting of a heat/cool/heat cycle performed in sequence, was executed using a rate of 5 °C/min during the first heating and cooling, and a rate of 10 °C/min during the second heating, corresponding to DSC measurement (Figure 11).



**Figure 11.** DSC thermograms of 50 wt % PEEK/50 wt % PTFE powder cycled at 5 °C/min (second heating at 10 °C/min).

There were two reasons for this composed thermal program. The first heating, and especially the low rate cooling, were performed to increase polymer crystallinity. In such a way, the DSC signal was sharpened, and mistakes due to evaluation of peak areas in thermograms were lowered. Moreover, the increase of the crystalline phase reduced the amorphous one, which was, however, present in both the polymers, and which was hardly evaluable and consequently not attributable. Therefore, this procedure was used in order to lower the mistakes in the determination of the PEEK and PTFE content.

On 100% PEEK powder, the determined crystallinity weight ( $\chi$ ) was 58.0%, whereas on 100% PTFE powder it was 94.3%. Assuming these values as a reference, the estimated values of crystallinity ( $\chi_e$ ) on the mixtures of PEEK and PTFE powders were calculated proportionally with the nominal amount of polymer powder present in the mixture. In Figure 12, besides

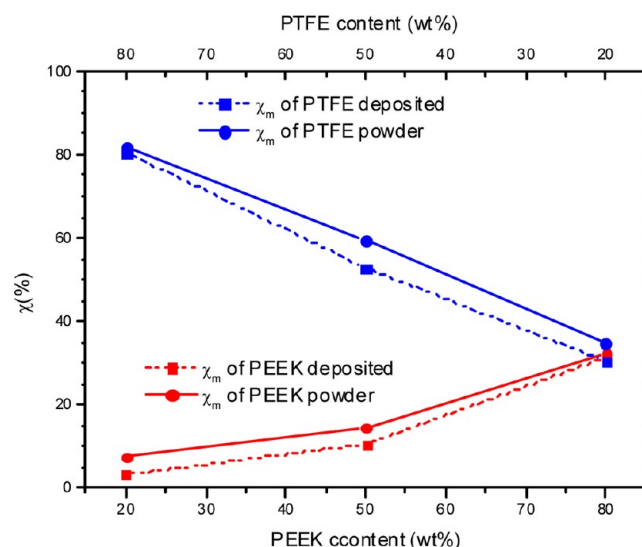


**Figure 12.** Estimated and measured values of crystallinity for PEEK/PTFE powder mixtures.

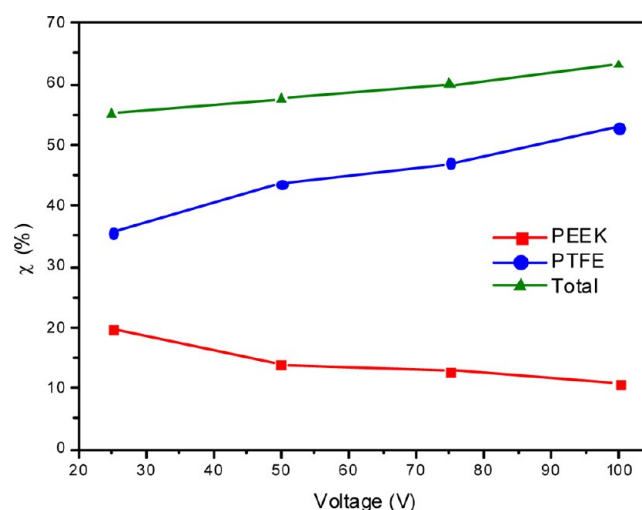
$\chi_e$ , the measured amount of crystalline phase ( $\chi_m$ ) for PEEK and PTFE mixtures with 4:4, 1:1, and 1:4 as weight ratios were reported. It is possible to note that for PEEK,  $\chi_m$  was always lower than  $\chi_e$ . On the contrary, for PTFE,  $\chi_m$  was always higher than  $\chi_e$ . It seems that the presence of PTFE influenced the crystallinity of PEEK and vice versa, as confirmed by the literature.<sup>42</sup>

Analogous measurements were performed on the PEEK and PTFE mass, removed after deposition at 100 V (Figure 13). As a result, when the nominal weight percent in suspension was the highest,  $\chi_m$  was equal to that measured on powder, both for PEEK and PTFE. In the same way, when the nominal weight percent in suspension was the lowest,  $\chi_m$  diverged from that of powder. This could indicate that the widest presence of one of the two polymers hampered that of the other one during the motion toward the deposit electrode, independently from the nominal zeta potential value of PEEK or PTFE.

Finally, the suspension containing PEEK and PTFE in a ratio of 1:1 was used to deposit at different applied voltages, precisely 25, 50, and 75 V. Also in this case, the deposited mass was analyzed in order to deduce the voltage influence on the produced deposit. In Figure 14, both the total  $\chi_m$ , and that of PEEK and PTFE, separately, were reported. The trend of  $\chi_m$  increased with the applied voltage, according to the theory, but



**Figure 13.** Measured values of crystallinity for PEEK/PTFE deposits compared with powder mixtures.

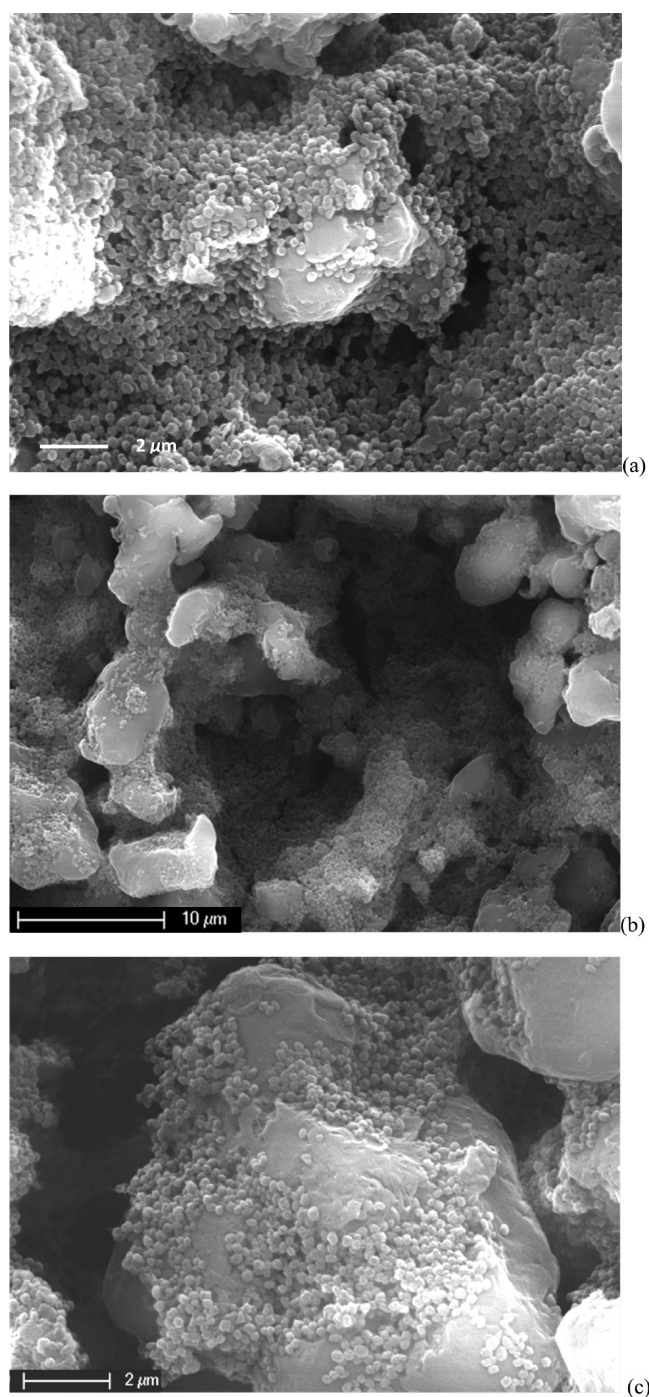


**Figure 14.** Measured values of crystallinity of PEEK, PTFE, and their sum measured in deposits obtained at different applied voltages.

the behavior of PEEK and PTFE was singularly different. In fact, the  $\chi_m$  of PTFE increased with the voltage with a rate higher than the total  $\chi_m$ , whereas  $\chi_m$  of PEEK decreased with respect to the voltage. That means when the voltage was low, the deposit of PEEK particles was promoted to the detriment of PTFE. On the contrary, the deposit of PTFE particles rose at high voltage.

We attributed this behavior not to electrophoretic properties of suspensions, but rather to the dimension of the two powders. As PTFE particles are very small in comparison with PEEK, a packing result was facilitated, since PTFE particles could be easily inserted between those of PEEK. This fact was obviously favored by applying a high voltage, which contributed to make a more disordered distribution of PEEK particles inside the deposit, and produced a greater porosity. As a confirmation, SEM images acquired on sample MIX1–100 was reported in Figure 15. PEEK particles are disorderly distributed, whereas PTFE particles were able to insert in the cavities and fill up them, as far as to cover PEEK particles.





**Figure 15.** SEM images at different magnifications of the surface of sample MIX1-100, prepared by applying 100 V at the 1:1 PEEK:PTFE suspension. In panel c, the different dimensions of PEEK and PTFE particles is well highlighted, as PTFE particles are lain on PEEK.

From these results, it is possible to conclude that the suspensions containing PEEK and PTFE particles were suitable to be used for EPD. Moreover, their composition was appropriate for a good dispersion of both polymer particles and for their codeposition. By using the DSC results, it could be possible to establish the opportune aliquot portion of each suspension to mix in order to obtain a planned amount of each polymer in the deposit.

## CONCLUSION

PEEK and PTFE particles were used to prepare suitable EPD suspensions. Due to different molecular structures, the stabilization of the suspension containing PEEK was based on electrostatic interactions with the citrate anion of the used dispersant, whereas the PTFE particles were sterically stabilized thanks to the addition of PVP. The composition of both the polymer suspensions was determined taking into account zeta potential and viscosity measurements.

The EPD process was applied on these polymer suspensions, used both singularly and as mixtures, and uniform coatings were obtained by using a DC applied voltage equal to 100 V. By means of DSC measurements, the amount of the polymer crystalline portion was determined. When in the suspension the polymer content was high, nominally 80%, its crystalline amount in the coating was approximately equal to that expected. On the contrary, when the polymer content in the suspension was low, nominally 20%, the polymer crystalline quantity was lower than that expected. This result was found for both the polymers, meaning that the widest presence of one of the two polymers hampered that of the other one, during the motion toward the deposit electrode. Therefore, in this case, although the zeta potential of both the polymer suspensions had almost the same maximized value, this was not definitely sufficient to ensure that the polymer particles were deposited in the same amount during the codeposition. In fact, the motion of particles and their arrangement on substrate were affected also by the particle dimension, the polymer molecular structure, and their content in the suspensions. Nevertheless, thanks to the proposed DSC procedure, it could be possible to establish the proportion of suspensions in order to have planned composition of the coating. The same procedure could be generally adopted to determine the amount of different polymers in a compound.

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### Author Contributions

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### Notes

The authors declare no competing financial interest.

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