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Actuators based on intrinsic conductive polymers/carbon nanoparticles nanocomposites

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ABSTRACT

New polyaniline (PANi) synthesis was performed starting from non-toxic N-phenil-p-phenylenediamine (aniline dimer) using reverse addition of monomer to oxidizing agent, the synthesis allows to produce highly soluble PANi. Several types of doped PANi were prepared to be used on electromechanical active actuators. Different techniques were used to include carbon nanoparticles such as carbon nanotubes and graphene. Bimorph solid state ionic actuators were prepared with these novel nanocomposites using a variety of supporting polymers.

Keywords: Polyaniline, Nanocomposites, Carbon Nanotubes, Graphene, Carbon Nanotubes, Sulphonated Polyether ether ketone, Polyvinylidene fluoride

1. INTRODUCTION

The interest in novel actuators is increasing, particularly for applications where conventional motors are inadequate in providing proper motions or when low voltage and low weight are the main requirements [1-3]. Typical examples are the biomedical devices, where lightweight actuators that can be operated safely by small portable batteries are required. Plastic and thus lightweight actuators, which can operate at low voltage, are a possible solution [4]. Ionic actuators are emerging as ideal candidates for these applications and, among the others, conducting polymers, ionic polymer metal composites and carbon nanoparticles are the most promising materials. Nevertheless, at present, no material stands out among the others; whilst each material may excel in some peculiar feature; many issues still have to be addressed before an overall winner can emerge. The idea of combining the properties of conducting polymers and carbon nanotubes (CNTs) in ionic actuators is attractive [5-7], as the firsts provide a large strain [5], while the seconds show a fast motion thanks to the excellent electrical properties of the CNTs [1]. An attempt to make actuators with an helix tube configuration using a composite of conducting polymers with carbon nanotubes prepared by mixing them in solvent has been previously reported [6] but, although these actuators present some advantages with respect to the ones made using pure conducting polymer, the need of a liquid electrolyte dramatically limits practical applications. A recent paper [7] reports a combination of carbon nanotube sheets, drawn from vertically aligned CNTs forests, and a conductive polymer, polypyrrole, by lamination; the authors demonstrate an increase of the actuator performance thanks to this combination of materials, but also this actuator is operated in liquid electrolyte and this is a major issue. Finally another group reported a combination of polyaniline (PANi), a conducting polymer, with carbon nanotubes operated with a solid electrolyte [8,9]; according to the authors the resulting actuators show a performance increase thanks to this composite material. In a previous paper [10] Biso et al. performed the oxidative polymerization of pyrrole directly on preformed bucky gel slurry in order to combine the remarkable properties of ionic actuators based on carbon nanotubes and polypyrrole.

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In this paper a new polymer, sulfonated polyetherketone (SPEEK), a conductive polymer, PANi, and two different carbon nanoparticles such as CNTs and graphene were used to produce actuators in combination with a solid electrolyte based on ionic liquids.

2. EXPERIMENTAL

2.1 Materials

N-phenyl-1,4-phenylendiamine 98%, that is the aniline dimer (DANI), ammonium persulfate (APS) 98%, 1-Chlorobutane 99% 1-Methylimidazole 98%, chloridric acid 37%wt, potassium exafluorophosphate 98%, sulfuric acid 98%wt, diethylether 99%, dimethylsulfoxide (DMSO) 99.9% and dimethylformamide (DMF) were purchased from Aldrich and used as received.

Polyether ketone (PEEK) VICTREX® PEEK 150G/151G was purchased from Victrex plc, Lancashire (United Kingdom) and used as received

Polyvinylidene fluoride (PVDF) KYNAR® was purchased from ARKEMA srl RHO (Italy).

Multiwall carbon nanotubes (MWNT) Nanocyl®-7000 supplied by Nanocyl Sambreville (Belgium) were used

2.2 PANi preparation

40 ml of a solution of DANI (4 mmol, 0.9212 g) in DMSO was added dropwise to 360 ml of a solution of APS (6 mmol, 1.369 g) in HCl 0.1 M. During the addition the solution first turned violet, then blue and finally dark green demonstrating the formation of PANi doped with HCl. After 3 hours, the precipitate was filtered and washed several times with distilled water and ethanol and finally dried at 60°C until constant weight was reached. The product was a green powder, the emeraldine salt of HCl. The obtained powder was de-doped by mixing the powder in a solution 0.1 M of NH_4OH for 24 h then the powder was filtered and washed with bidistilled water until neutral reaction was obtained. Finally the powder was dried at 60°C until constant weight was reached. The final product was a blue powder, the emeraldine salt of PANi.

2.3 SPEEK preparation

10 g of PEEK were dissolved in 100 g of concentrated sulfuric acid at room temperature for 68h thus the temperature was increased to 60°C for 4 hours in order to complete the reaction. The obtained red viscous solution was cooled and it was added dropwise in deionized water to precipitate the SPEEK. The obtained polymer was washed several times with bidistilled water in order to remove the remaining sulfuric acid. The resulting precipitate was dried at 60 °C until constant weight was reached.

2.4 Synthesis of Ionic liquid (IL) [BMIM][PF_6]

Synthesis of 1-Methyl-3-Buthyl-Imidazolium Cloride [BMIM][Cl]. 1-Chlorobutane (64 mL, 0.95 mol) and 1-Methylimidazole (50 mL, 0.63 mol) were added to a flask fitted with a reflux condenser for 24h at 80 °C with stirring until two phases formed.

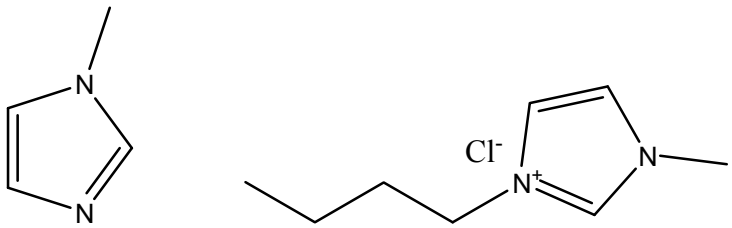

Figure 1.1-Methylimidazole (left) and 1-Methyl-3-Buthyl-Imidazolium Chloride (right)

The top phase, containing unreacted starting material, was decanted and diethyl ether (50 mL) was added with thorough mixing (solvent extraction repeated twice). The bottom phase was washed with diethylether (4 x 25mL), heated at 40 °C under vacuum using rotovapor for about 8h. The resulting product was a slightly yellow viscous liquid (85 g, yield 86%).

Synthesis of 1-Methyl-3-Buthyl-Imidazolium Hexafluorophosphate [BMIM][PF_6]. The product of the first step (25 g, 0.15 mol) is transferred in a flask (250 mL). Then acetone (150 mL) and KPF_6 (31 g, 0.17 mol) are added. The mixture was stirred at room temperature for 24h. The resulting white waxy solid precipitate was removed by filtration, washing with acetone.

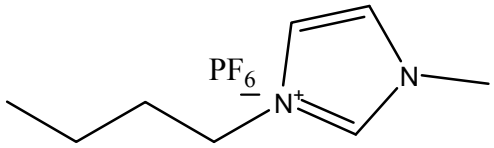

Figure 2. 1-Methyl-3-Buthyl-Imidazolium Hexafluorophosphate

The organic part was collected, removing the solvent under vacuum using the rotovapor for about 2h. The product was a colorless and viscous liquid.

2.5 Graphene dispersion in DMF

Graphene dispersion was obtained from the graphite exfoliation as previously reported in literature[11]. In a vial, 40 mg of graphite were added to 10 mL of DMF; this solution was sonicated for 4 hours in a refrigerant bath (15 °C). After that, the solutions were centrifuged twice for 1 hour at 4500 rpm: between the first and the second centrifugation, the liquid phase was separated from the solid phase and more solvent was added.

Figure 3. Graphene dispersion in DMF

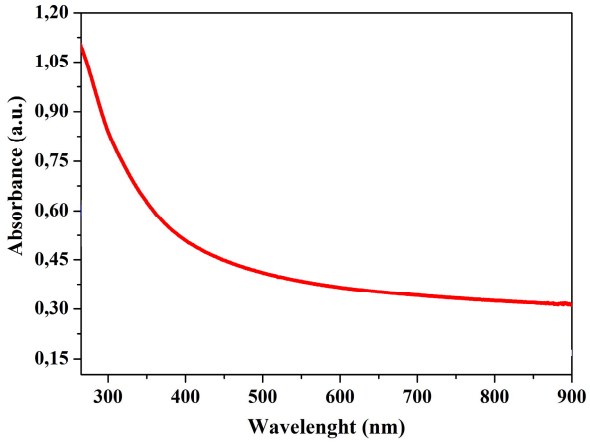

Figure 4. UV-Vis spectrum of graphene dispersion in DMF

It is possible to evaluate the concentration of ghaphene in solution by means of UV-Vis spectroscopy, knowing the molar extinction coefficient. Its value, according to literature, is 2.46 $Lg^{-1}m^{-1}$ at 660 nm [11]. Since the absorbance measured in DMF at 660 nm is 0.350 a.u., the graphene dispersion concentration is 0.14 g/L. The graphene dispersion was employed as filler in order to increase the electrode conductivity.

2.6 Single layers preparation

PVDF [BMIM][PF_6]. In a mixture of 0.5 g of PVDF and 0.5 g of [BMIM][PF_6], 20 mL of DMF were added in order to prepare the polymeric substrate of the actuator. The solution was cast on a Petri dish (5.5 cm of diameter) at 85 °C. The solvent evaporation produced a homogeneous film. The obtained material was preheated at 150 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

PVDF PANi-CSA [BMIM][PF_6]. In a mixture of 140 mg of PVDF, 140 mg of [BMIM][PF_6] and 70 mg of PANi-CSA, 10 mL of DMF were added in order to prepare the polymeric substrate of the actuator. The solution was cast on a Petri dish (5.5 cm of diameter) at 85 °C. The obtained material was preheated at 150 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

PVDF PANi-CSA MWNT [BMIM][PF_6]. In a mixture of 70 mg of PVDF, 35 mg of MWCNTs, 35 mg of PANi-CSA and 70 mg of [BMIM][PF_6], 10 mL of DMF were added, in order to prepare the polymeric electrode of the actuator. The mixture was subjected to probe sonication for 30 min to obtain the gel, then the solution was ready to be cast on a Petri dish (5.5 cm of diameter) at 85 °C. The obtained material was preheated at 150 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

SPEEK [BMIM][PF_6]. In a mixture of 0.5 g of SPEEK and 0.5 g of [BMIM][PF_6], 20 mL of DMF were added in order to prepare the polymeric substrate of the actuator. The solution was cast on a Petri dish (5.5 cm of diameter) at 85 °C. The solvent evaporation produced homogeneous film. The obtained material was preheated at 135 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

SPEEK PANi-CSA [BMIM][PF_6]. In a mixture of 140 mg of SPEEK, 140 mg of [BMIM][PF_6] and 70 mg of PANi-CSA, 10 mL of DMF were added in order to prepare the polymeric substrate of the actuator. The solution was cast on a Petri dish (5.5 cm of diameter) at 85 °C. The obtained material was preheated at 135 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

SPEEK PANi-CSA MWNT [BMIM][PF6]. In a mixture of 70 mg of SPEEK, 35 mg of MWCNTs, 35 mg of PANi-CSA and 70 mg of [BMIM][PF_6], 10 mL of DMF were added in order to prepare the polymeric electrode of the actuator. The mixture was subjected to probe sonication for 30 min to obtain the gel, then the solution was ready to be cast on a Petri dish (5.5 cm of diameter) at 85 °C. The obtained material was preheated at 135 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

SPEEK PANi-CSA Graphene [BMIM][PF_6]. In a mixture of 70 mg of SPEEK, 35 mg of Graphene previously obtained, 35 mg of PANi-CSA and 70 mg of [BMIM][PF_6] were added to 10 mL of DMF. The solution was casted on a Petri dish (5.5 cm of diameter) at 85 °C. The obtained material was preheated at 135 °C for 5 minutes and then pressed using a pressure of about 140 $Kgcm^{-2}$ for 5 minutes. The obtained films have a thickness of about 0.025 mm.

2.7 Tri-layer actuator assembling

The SPEEK-based sandwiches were composed by two electrode sheets 0.025 mm thick and the electrolyte film 0.025 mm thick was pressed at T = 135 °C using a pressure of about 140 $Kgcm^{-2}$ for 20 minutes.

The PVDF-based sandwiches were composed by two electrode sheets 0.025 mm thick and the electrolyte film 0.025 mm thick was pressed at T = 150 °C using a pressure of about 140 $Kgcm^{-2}$ for 20 minutes.

2.8 Characterizations

Fourier Transformed Infrared Spectroscopy (FT-IR) transmittance spectra were collected on a Nicolet 5700 FTIR Spectrometer (ThermoFisher). The samples were prepared via casting on Si wafer. 64 scans were signal-averaged at a resolution of 2 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1}.

X-ray photo- electron spectroscopy (XPS) was performed on SPEEK film casted from DMF solution with a VG EscaLab 220i spectrometer using a standard AlKα X-ray source (300 W).

UV-vis Electronic absorption spectra of the samples were recorded in dimethylformamide (DMF) solution in the wavelength range of 190–800 nm at room temperature using a Cary 5000 UV–vis-NIR spectrometer.

Differential Scanning Calorimetry (DSC) analyses were performed with DSC Q20 TA Instruments (New Castle, DE, USA) with a double heating cycle from -40 to 180°C at 10°C/min separated by a single cooling cycle at 10°C/min with isothermal step for 3 minutes at 180 and -40°C. The thermal history of samples was erased by the preliminary heating cycle at 10°C/min. The amount of material in the DSC samples was 6–8 mg. An empty pan was used as a reference.

Field Emission Scanning Electron Microscope (FE-SEM) examinations were performed with a Zeiss SupraTM 40 (FE-SEM).

3. RESULTS AND DISCUSSION

3.1 Infrared analyses

The FT-IR spectrum for SPEEK is reported in Figure 5. PSS shows the characteristic peak of aromatic ring, of ketone/ether groups and of the sulfonation. At 3483 cm^{-1} the νSO_3-H is present and this band, the stretching of S=O (1190 cm^{-1} $\nu_{as}SO_3^-$, 1080 cm^{-1} $\nu_sSO_3^-$) and the ν C-SO_3^- at 628 cm^{-1} confirm the succesful PEEK sulfonation. The other peaks confirm the presence of SPEEK aromatic rings (3100-3000 cm^{-1} band νC-H_{arom} 1596 and 1492 cm^{-1} the two $\nu C=C_{arom}$) and the two functional groups, the keton (1646 cm^{-1} νC=O) and the ether group (1225 cm^{-1} νC-O-C_{as} and -1025 cm^{-1} νC-O-C_s).

In Figure 6 the FT-IR spectrum of PANi emeraldine base is reported. At 3230 cm^{-1} the ν_{NH} of secondary aromatic amine is present. In the 3100-3000 region the ν_{CH} of PANi aromatic rings are present. The PANi spectrum exhibits a band at 1592 cm^{-1} attributed to $\nu_{C=N}$ stretching of quinoid diimine unit (the oxidised form of PANi). C–C aromatic ring stretching of the benzenoid diamine unit (the reduced form of PANi) appears at 1503 cm^{-1}. At 1306 cm^{-1} the ν_{C-N} is present confirming the presence of benzenoid rings. The 1150 peak is the N=quinoid=N absorption while the 835 cm^{-1} peak is the out of plane bending for para-disubstituted benzene. Finally the 748 cm^{-1} band is due to the out-of-plane band of CH of the quinoid rings.

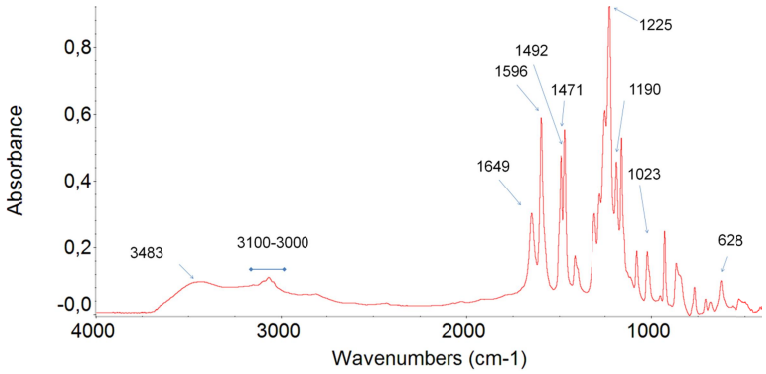

Figure 5. FT-IR analyses of SPEEK

The FT-IR spectrum for PANi doped with CSA is reported in Figure 7. PANi-CSA shows the characteristic peak of PANi and the ketone and sulfonic groups of CSA. At 3452 cm^{-1} the νSO_3-H with the stretching of S=O (1231 cm^{-1} $\nu_{as}SO_3^-$, 1039 cm^{-1} $\nu_sSO_3^-$) confirms the presence of sulfonic salt. The other CSA peaks confirm the presence of aliphatic ring (3000-2850 cm^{-1} band νC-$H_{aliphatic}$ and the tensioned aliphatic keton (1741 cm^{-1} νC=O). The PANi in the emeraldine salt form has the following absorbance. At 3255 cm^{-1} the ν_{NH} of secondary aromatic amine is present. In the 3100-3000 region the ν_{CH} of PANi aromatic rings. At 1573 cm^{-1} the $\nu_{C=N}$ stretching of quinoid diimine unit (the oxidised form of PANi) is present. C–C aromatic ring stretching of the benzenoid diamine unit (the reduced form of PANi) appears at 1500 cm^{-1}. At 1314 cm^{-1} the ν_{C-N} confirms the presence of benzenoid rings. The 1163 peak is the N=quinoid=N absorption while the 829 cm^{-1} peak is the out of plane bending for para-disubstituted benzene. Finally the 750 cm^{-1} band is due to the out-of-plane band of CH of the quinoid rings.

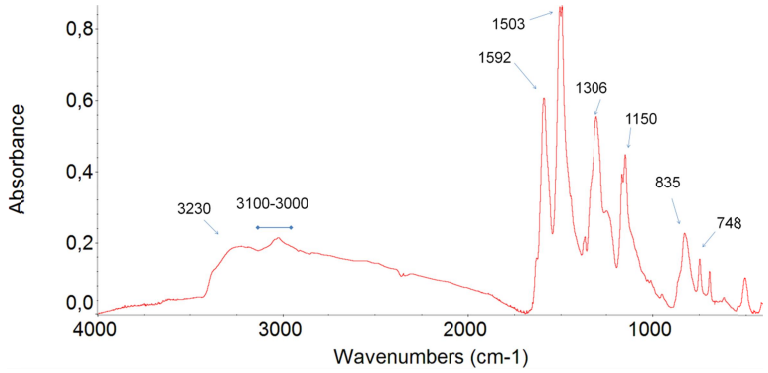

Figure 6. FT-IR analyses of PANi emeraldine base

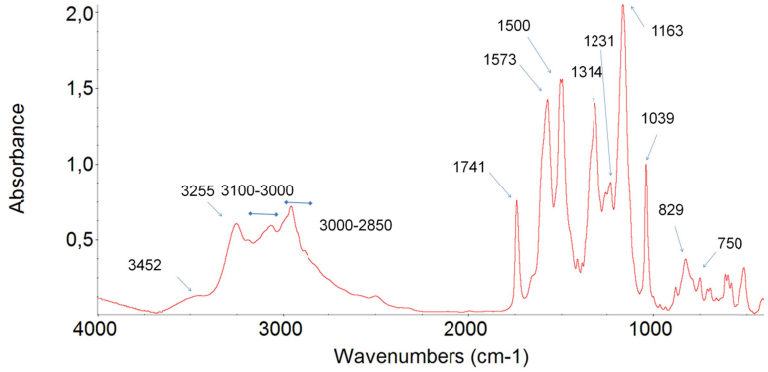

Figure 7. FT-IR analyses of PANi CSA emeraldine salt

3.2 UV-vis

In Figure 8 the UV–vis spectra of PANi emeraldine base in DMF solution is reported. In DMF, as for the majority of available solvents, PANi adopts compact-coil conformation. In such case, the main bands are the π- π* transition at c.a. 330 nm and the absorption band at c.a. 600–650 nm arising from n-p transition [12,13] is observed confirming the formation of PANi from the synthesis starting from DANI in aqueous solution [4].

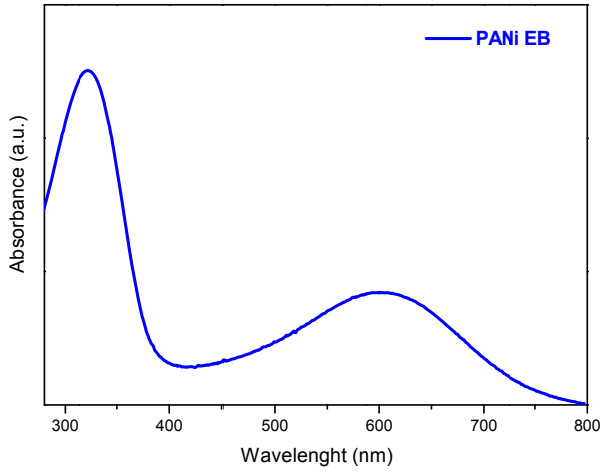

Figure 8. UV-vis spectra of PANi emeraldine base

3.3 XPS

The XPS analysis was used in order to evaluate the percentage of sulfonation of PEEK. The data are reported in The results for the PVDF samples are resumed in Table 2. PVDF has a melting temperature (T_m) of about 171°C, once the ionic liquid is added the T_m decreases to about 146-148 °C while the heat of fusion (ΔH), normalized for the weight fraction, is practically unchanged. Thus it can be supposed that the ionic liquid behaves as a solvent decreasing the melting temperature of PVDF. Similar results were obtained for the crystallization temperature (T_c): the addition of the ionic liquid decreases the temperature from 136 °C to 102 °C.

Table 2. The general formula of PEEK is $C_{13}O_2H_8$ (two benzenoid rings, an ether group and a keton group) due to the alternated ether/ketone functional groups. In the presence of 100 % sulfonic functionalization, the ratio between sulfur and carbon should be 1 sulfur atom every 6.5 atoms of carbon. The percentage of functionalization thus can be found by the formula:

$$\%f = 6.5 * 100 * \frac{atomic\%_S}{atomic\%_C} \quad (1)$$

Where %f is the percentage of functionalization, atomic%$_S$ and atomic%$_c$ are the atomic percentage of respectively sulfur and carbon.

Table 1 . XPS analyses of SPEEK sample

Sample	atomic %
C	69.40
O	26.85
S	3.74

The %f evaluated using equation (1) is about 35%, confirming a good percentage of functionalization. A higher percentage would decrease the mechanical properties typical of the pristine PEEK.

3.4 Differential scanning calorimeter

The calorimetric analyses were used in order to understand the thermal properties, both for the preparation of the trilayer actuator and to understand the thermal properties of the final actuator.

The results for the PVDF samples are resumed in Table 2. PVDF has a melting temperature (T_m) of about 171°C, once the ionic liquid is added the T_m decreases to about 146-148 °C while the heat of fusion (ΔH), normalized for the weight fraction, is practically unchanged. Thus it can be supposed that the ionic liquid behaves as a solvent decreasing the melting temperature of PVDF. Similar results were obtained for the crystallization temperature (T_c): the addition of the ionic liquid decreases the temperature from 136 °C to 102 °C.

Table 2. DSC analysis of PVDF-based samples

Sample	T_m(°C)	ΔH (J/g)*	T_c (°C)
PVDF	171	51.29	136
PVDF_IL	146	22.83	102
PVDF_PANi_IL	146	22.87	102
PVDF_PANi_MWNT_IL	148	16.81	102

* The weight used for the evaluation is not normalized for the PVDF fraction

SPEEK is an amorphous polymer, and to our knowledge no data on glass transition temperature were reported in literature. The DSC curves change the slope in a wide range of temperatures and no definite glass transition temperature is evident (Figure 10). A slight change is recognizable at about 100 °C. No variations were reported from the addition of the carbon particles, PANi or ionic liquid. However, a temperature of about 135 °C during hot pressing, allows to produce homogeneous films.

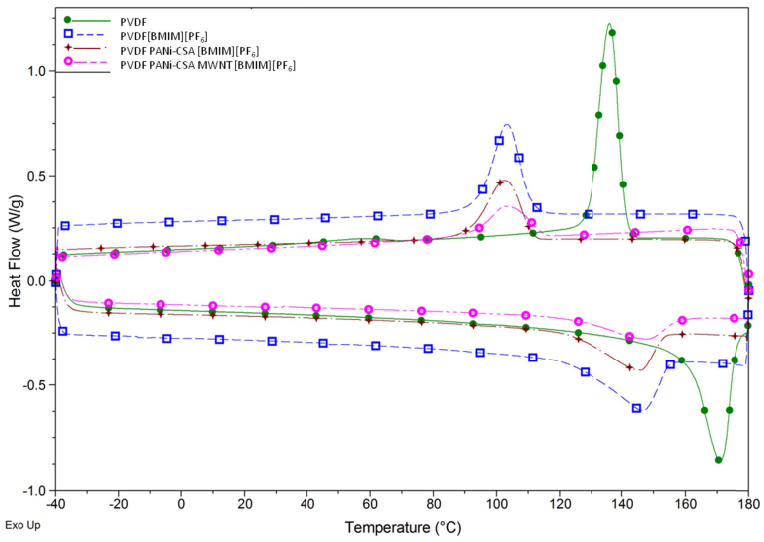

Figure 9. DSC of PVDF samples: cooling and 2nd heating curves

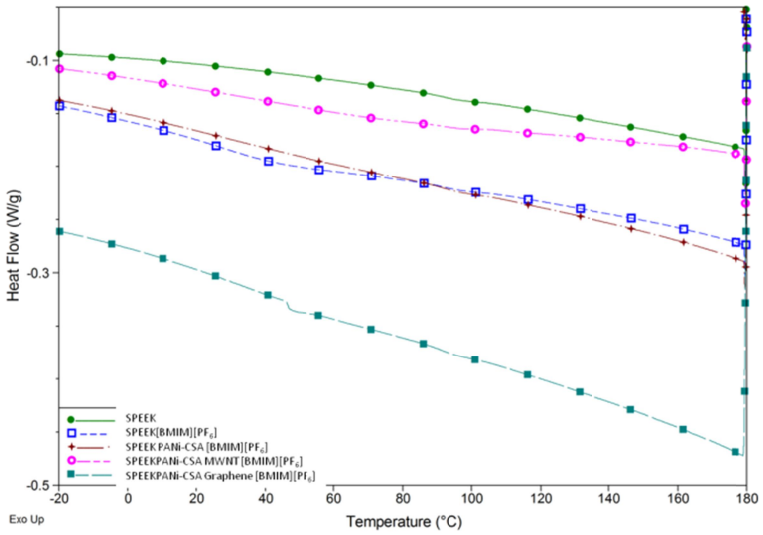

Figure 10. DSC of SPEEK samples: 2nd heating curves

3.5 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM analyses were performed in order to assess the homogeneity of the different films and the dispersion of the cabon particles inside the polymers.

The PVDF based composites (Figure 11) show a good final morphology. The PVDF [BMIM][PF_6] (Figure 11a,b) did not show leaching, thus the ionic liquid is finely linked to the polymer substrate. The addition of PANi causes the formation of a separated phase in which the PANi assumes a globular structure within the PVDF polymer matrix and, taking into account the different relative volume, the ionic liquid should be mainly in the PVDF matrix. The addition of MWNT modifies the morphology of the final product, and in this case it is impossible to distinguish the presence of different phases in the samples; no MWNT aggregates were present (Figure 11e,f). The isolated nanotubes were quite recognizable, thus it can be affirmed that a homogeneous, well dispersed composite was obtained.

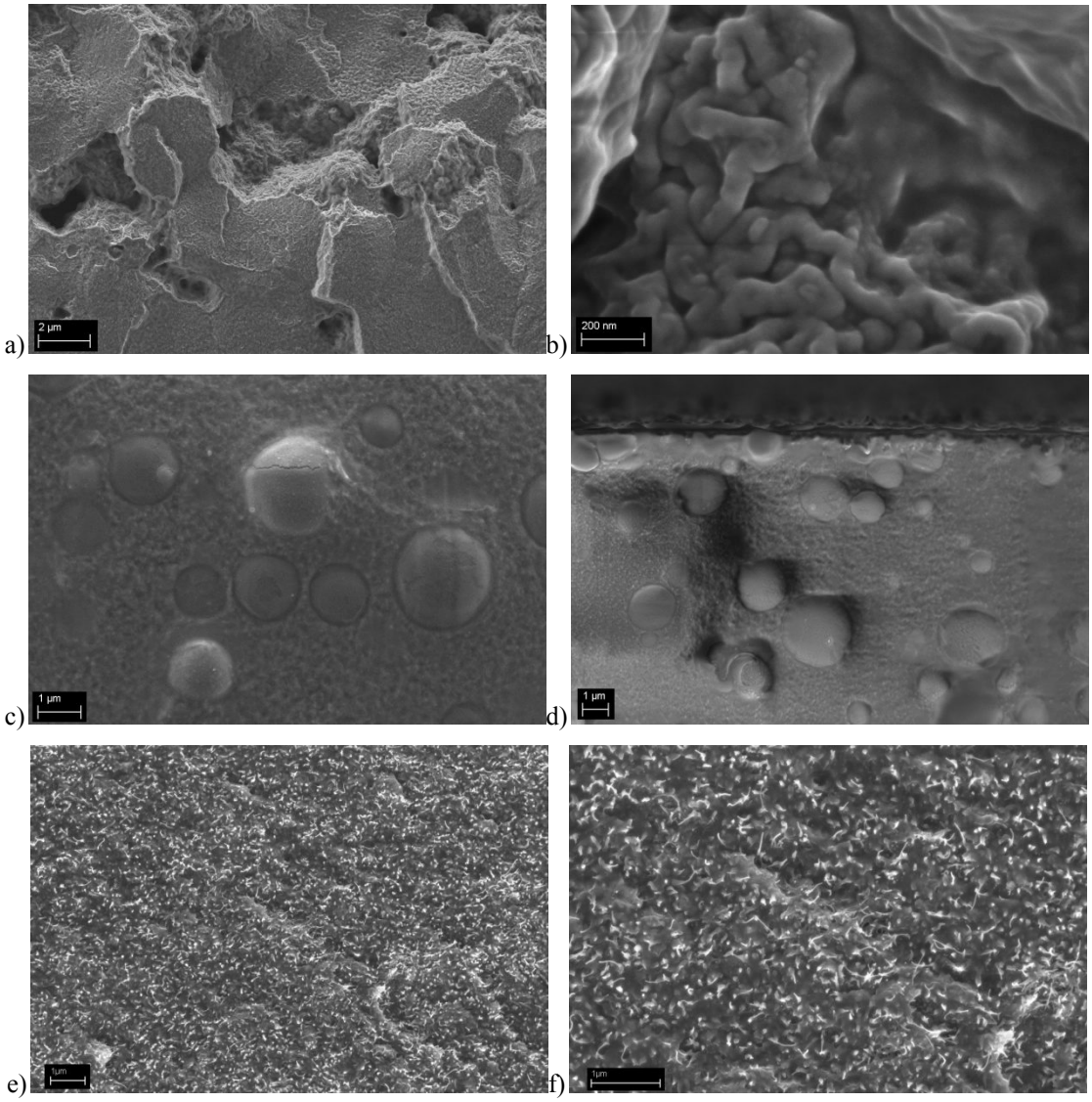

Figure 11. FE-SEM analyses of a)b)PVDF [BMIM][PF_6]c)d) PVDF PANi [BMIM][PF_6]e)f) PVDF PANi MWNT [BMIM][PF_6]

The SPEEK based composites (Figure 12) have a better final morphology. As expected from a completely amorphous sulfonated polymer such as SPEEK, its blend with ionic liquid is completely homogeneous (Figure 12a,b). On the contrary of PVDF, the addition of PANi did not change the morphology, because the SPEEK sulfonic groups can react with PANi and work as secondary doping agent forming a single phase. The addition of MWNT did not modify the morphology of the final product. The main difference is the presence of isolated nanotubes: they were well dispersed and recognizable. Finally the addition of well exfoliated graphene did not change the morphology of the matrix. It is quite difficult to recognize the single graphene sheets, however it could be possible that the lamellar-like particle measured in Figure 12h is a few layer graphene nanoparticle. In order to confirm this finding further characterizations involving the use of transmission electron microscopy will be performed.

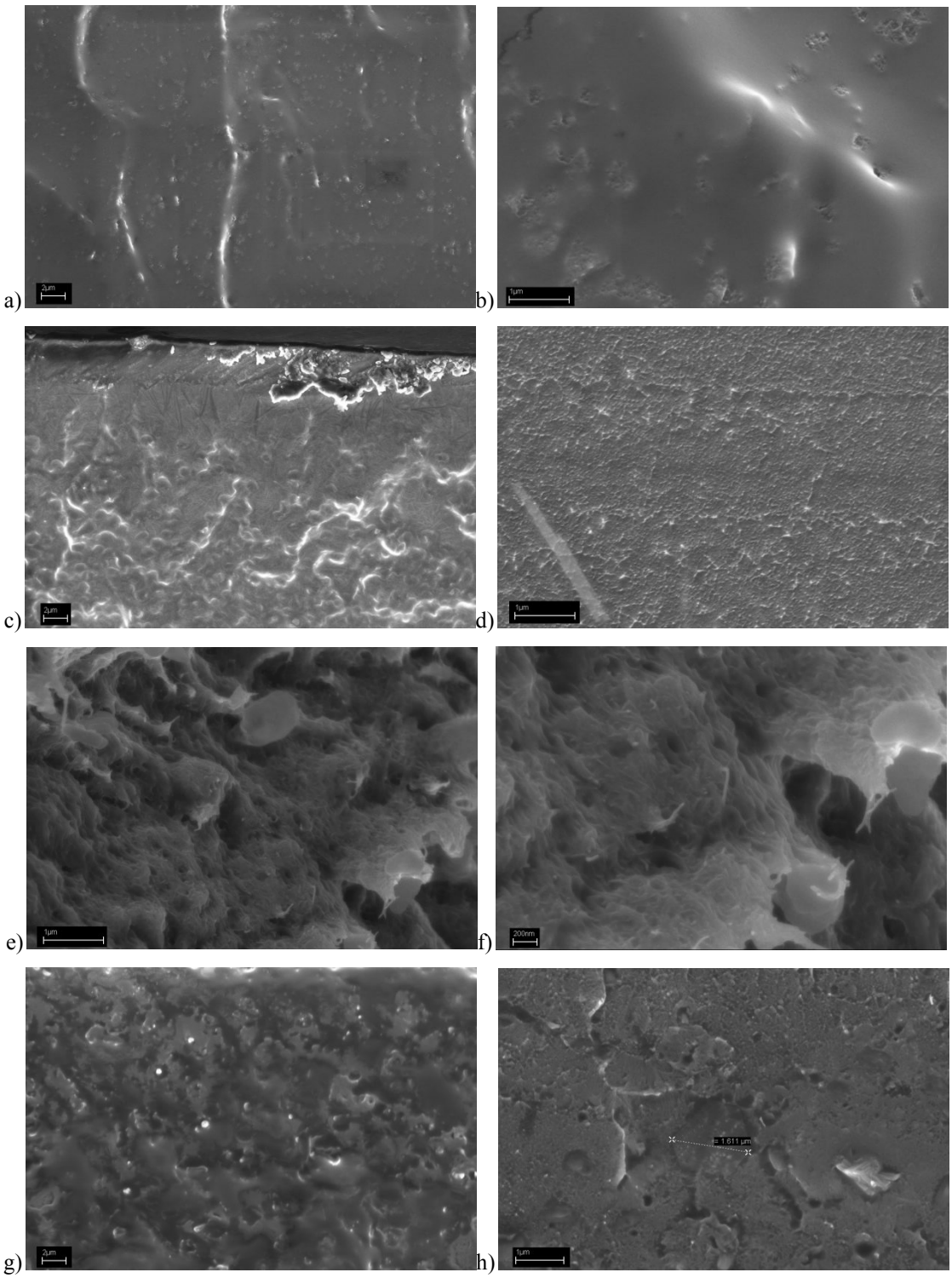

Figure 12. FE-SEM analyses of a)b) SPEEK [BMIM][PF_6] c)d) SPEEK PANi [BMIM][PF_6] e)f) SPEEK PANi MWNT [BMIM][PF_6] g)h)SPEEK PANi Graphene [BMIM][PF_6]

4. CONCLUSIONS

Novel hybrid materials with ionic liquid electrolyte, containing carbon nanoparticles, PANi and matrix polymer such as SPEEK or PVDF were prepared. By further processing, we were able to prepare bimorph actuators. The preliminary characterizations on these materials show the formation of homogenous blends containing the well-dispersed nanoparticles. The resulting devices will thus benefit from the combination of the actuating characteristics of both CNTs and conducting polymer. Moreover SPEEK, the new polymer used demonstrate better mechanical properties than PVDF allowing the production of stiffer actuators. Preliminary characterizations are in progress in order to study the actuation properties of these compounds.

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