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On the preparation and application of novel PVDF–POSS systems

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Abstract Novel systems based on poly(vinylidene fluoride) (PVDF) and polyhedral oligomeric silsesquioxane (POSS) have been prepared by grafting amino-containing POSS (POSS–NH_2) onto the surface of modified PVDF (PVDFm). Namely, the approach consists of a preliminary modification of PVDF by a chemical treatment with an alkaline solution, in order to obtain unsaturations, and a subsequent surface reaction of PVDFm with POSS molecules characterized by an amino group as reactive side. The level of polymer unsaturation, measured by Raman spectroscopy, turned out to be finely tuned by varying the dehydrofluorination reaction time. The surface grafting of POSS has been studied by SEM-EDS analysis, Raman and XPS spectroscopy. Indeed, while the level of modification of PVDFm has been found to decrease as a consequence of the reaction with POSS, thus indicating a likely saturation of double bonds by silsequioxane molecules, the Si concentration turned out to increase with increasing the concentration of the polymer surface unsaturation. The feasibility of the application of POSS grafting onto the surface of membranes, based on PVDFm, has also been verified.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) molecules, used as reagents, monomers, and polymers, are emerging as a new class of chemicals for the preparation of high-performance nanostructured plastics [1]. POSS is a cube-octameric molecule, which holds an inner inorganic Si–O–Si framework, externally covered by organic substituents [2–5]. POSS moiety incorporation, which can be performed via polymerization, grafting, blending, and so forth [6–12], results in relevant improvement of polymer properties, including glass transition and degradation temperatures, flammability, mechanical strength, and oxygen permeability [13–20].

It is important to underline that although most of the studies refer to POSS-based hybrids made from one-pot copolymerization, where POSS and organic monomers are mixed together prior to the copolymerization process, some works deal with the direct silsesquioxane molecule grafting to the polymer backbone. Indeed, while in the former approach any changes in POSS monomer structure and initial feed ratios can result in different degrees of polymerization, in the grafting method the molecular structure of the polymer backbone, including its molecular mass and polydispersity, is fixed and defined prior to the attaching of POSS. As an example, Fu et al. [21] developed a method to synthesize a novel organic/inorganic triblock copolymer polystyrene-butadiene-polystyrene (SBS) containing grafted POSS molecules, which allowed to make a series of polymers with different amounts of POSS without any change of the overall degree of polymerization or structure of the SBS backbone.

As far as the polymer matrix object of the present work, namely poly(vinylidene fluoride) (PVDF) is concerned, to the best of our knowledge, no report concerning the preparation of hybrids based on POSS has been published so far. On the other hand, the modification of the above polymer, which is widely applied in the polymer membrane field, was extensively studied mainly with the aim to

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change the fouling resistance [22–24] and separation properties [25–27]. Moreover, the modification of PVDF was also performed in order to vary its adhesion properties [28–30], particularly when used as biomaterial. Among the various methods applied to modify PVDF, such as chemical [22, 31] and plasma treatment [25, 28, 32], dip coating [31, 33], etc., the chemical grafting [26, 34–36] is one of the most effective approaches. Recently, very peculiar reactions, such as atom transfer radical polymerization (ATRP) [26] and reverse atom transfer radical polymerization (RATRP) [34], were applied for PVDF grafting. Indeed, RATRP was used by Chen et al. [34] to graft poly(methyl methacrylate) and poly(poly(ethylene glycol) methyl ether methacrylate) onto PVDF membrane surfaces, previously UV-treated. The pore size and pore size distribution of the resultant membranes turned out to be controlled by varying the polymerization time.

Clearly, as found for the above compounds, also the presence of POSS molecules directly grafted to PVDF, could from one side improve the mechanical and permeability properties of the resulting membranes and from the other modify their surface properties.

On these grounds, in the present work we report on the preparation of PVDF–POSS systems made of POSS molecules grafted onto the surface of modified PVDF (PVDFm). A correlation between the amounts of silsesquioxane retained by the PVDF powders and the level of polymer modification has been studied. The samples properties have been investigated by Raman, SEM-EDS analysis and XPS spectroscopy.

Experimental

Materials

Poly(vinylidene fluoride) was a commercial product (Foraflon 1000HD, Solvay). Aminopropylisobutyl-POSS was supplied by Hybrid Plastics.

N-methyl–2-pyrrolidone (NMP, 99%, Aldrich), tetrahydrofuran (THF, 99.9%, Aldrich), and methanol (MeOH, 99.8%, Aldrich) were used as received.

Methodology

The modification of PVDF was accomplished by a treatment with alkaline solutions. In a typical synthesis 5 g of PVDF and 25 mL of methanol solution containing 0.5 wt% of KOH were stirred under inert atmosphere at 70 °C. The reaction time was varied from 5 to 240 min. The dark brown product was collected by filtration, washed by methanol in soxhlet for 24 h and dried in vacuum oven at 60 °C.

The grafting of silsesquioxane molecules was carried out at solvent reflux, under inert atmosphere for 12 h, adding 1 g of PVDF to a solution of POSS–NH_2 in THF (0.05 mol/L). The reaction product was collected by filtration, washed with THF and dried in vacuum oven at 60 °C.

Porous PVDFm–POSS membranes were prepared either by using PVDFm powders, previously grafted with POSS–NH_2 or by applying directly the grafting reaction to PVDFm-based membranes.

Solutions, prepared by dissolving PVDF in NMP (20 wt%) at room temperature, were first cast on a glass plate by means of a proper knife to form thin films (thickness of ca. 350 μm) that were immersed in water at 20 °C to induce precipitation of the polymer and porous membrane formation. After 5-min immersion period, the membranes were detached from the plate and leached overnight under running water prior to characterization.

Characterization

A Leica Stereoscan 440 scanning electron microscope (SEM) was used to examine the POSS dispersion in PVDF powders and membranes. All specimens were coated with a thin layer of carbon before SEM observation. The amount of Si retained by the various PVDFm samples was measured by the above scanning electron microscopy, equipped with an EDS system (Oxford Link-Gem). The technique does not allow to evaluate the absolute atomic amount but the relative concentration only.

Modified PVDF samples before and after reaction with POSS–NH_2 have been characterized by RAMAN (Brooker RF100) spectroscopy.

XPS analyses have been performed using a PHI 5602 Multitechnique instrument, featuring a charge neutralizer and a monochromated Al X-ray source (1486.6 eV) set at 350 W anode power. The data were acquired in multiregion mode, with 23.50 eV pass energy, take-off angle of 45 degree and 0.05 eV energy resolution. Samples were prepared by pressing the powders onto a thick indium film; then, they were set into a pre-pumping chamber ($\cong 10^{-7}$ torr) for 10 min. and transferred in the main chamber ($\cong 10^{-9}$ torr) for analysis. PHI MultiPak software was used for data treatment and analysis.

Due to the intrinsic insulating nature of the samples and the need of a charge neutralization device, all XPS spectra have been software shifted to set the main carbon peak binding energy to 285.0 eV. Curve fits have been performed without smoothing, using gaussian templates and Shirley background subtraction.

Results and discussion

In order to modify PVDF by formation of groups capable of reacting with POSS molecules, a chemical dehydrofluorination with an alkaline solution has been accomplished. Namely, as already reported [37], the reaction of PVDF with organic or inorganic bases mainly leads to the elimination of HF and formation of unsaturations.

The level of polymer unsaturation has been changed by varying the reaction time from 5 to 240 min. Raman spectroscopy, as an effective technique for studying chemical structures containing double bonds, has been used to characterize the treated samples. Figure 1 shows the Raman spectra of neat PVDF (Fig. 1a) and of the treated samples, coded PVDFm (Fig. 1b, c, and d).

With respect to the virgin polymer, the spectra of the PVDFm samples show two new bands which are characteristics of the C=C stretching vibrational modes of polyenes. The first band has an intensity maximum at about 1,520 cm^{-1} but is very broad and asymmetric developing between 1,650 and 1,500 cm^{-1}, while the second is weaker and centered around 1,150 cm^{-1}.

Although a quantitative evaluation of the introduced modifications is very difficult, because the intensity of bands decreases as the length of the conjugated chains shortens [38], a qualitative evaluation of the unsaturation concentration has been attempted by calculating of the ratio between the area of the peak at 1,520 cm^{-1} which corresponds to the C=C stretching and that of the band, whose intensity maximum is at 1,430 cm^{-1}.

The results of the above evaluation, together with the solubility of the neat PVDF and of the PVDFm samples, are given in Table 1.

It is relevant to underline that the polymer level of unsaturation, namely the intensity of the band at 1,520 cm^{-1}, clearly follows the reaction time (t_r), as it increases by increasing the t_r. Moreover, apart from the sample PVDFm(240), prepared by applying a contact time of 240 min, all the other PVDFm powders are characterized by a good solubility in both DMF and NMP, which are the solvents generally used to prepare casting solutions. As far as the sample PVDFm(240) is concerned, the solubility turns out to be only partial at room temperature, although it tends to increase at higher temperatures. On this basis, it is possible to fine tune the level of PVDF unsaturation by applying the described technique.

Table 1 Characterization results of neat PVDF and PVDF samples modified by KOH treatment

Sample name	Reaction time (min)	Level of modification by Raman (1,520 cm^{-1}/1,430 cm^{-1})	Solubility at room temperature	
			DMF	NMP
PVDF(0)	0	0	+	+
PVDFm(5)	5	1.1	+	+
PVDFm(15)	15	2.3	+	+
PVDFm(240)	240	5.2	±[a]	±[a]

[a] Soluble at 50 °C

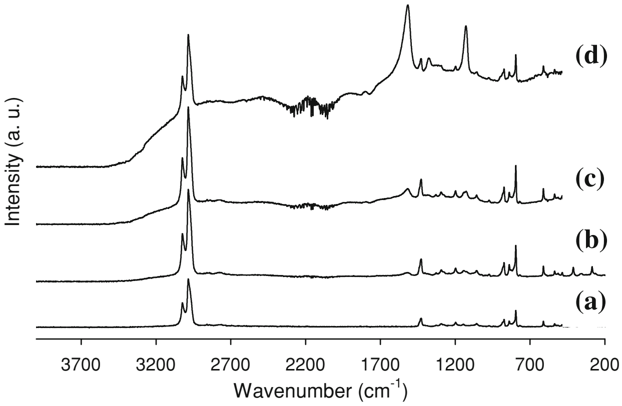

Fig. 1 Raman spectra of: (a) PVDF(0), (b) PVDFm(5), (c) PVDFm(15), and (d) PVDFm(240)

The PVDFm powders prepared have been used as polymer matrices in the reaction with POSS–NH$_2$. The reaction process has been monitored by Raman spectroscopy and by SEM-EDS, which allows to obtain the relative concentration of Si retained by PVDFm surface treated with amino POSS. In order to verify the capability of the untreated polymer to retain POSS, the reaction between a neat PVDF and the above silsesquioxane was also accomplished.

As an example Raman spectra of the sample PVDFm(15), before (Fig. 2a) and after (Fig. 2b) the reaction with POSS–NH$_2$ is shown in Fig. 2.

Considering the above spectra, it comes out that the peak at 1,520 cm^{-1} tends to disappear when PVDFm is treated with the above POSS molecules. Analogously to the previously mentioned evaluation method, the level of polymer unsaturation before and after the reaction with the silsesquioxane has been calculated by the ratio between the areas of the bands at 1,520 and 1,430 cm^{-1}. Table 2 summarizes the characteristics of neat PVDF and PVDFm samples before and after the reaction with amino POSS, in terms of percentage of retained Si, unsaturation concentration and solubility.

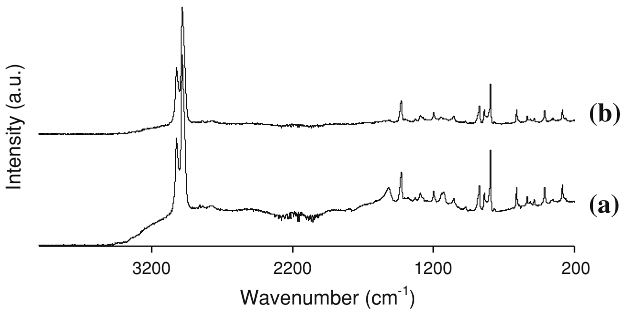

Fig. 2 Raman spectra of: (a) PVDFm(15), (b) PVDFm(15) + POSS–NH$_2$

Table 2 Characterization results of neat PVDF and PVDFm before and after the reaction with POSS–NH_2

Sample code	Level of modification by Raman (1,520 cm^{-1}/1,430 cm^{-1})		Content of Si[a] (%)	Solubility at 25 °C	
	Before reaction with POSS–NH_2	After reaction with POSS–NH_2		DMF	NMP
PVDF(0)	0	0	0	+	+
PVDFm(5)	1.1	0.2	0.5	+	+
PVDFm(15)	2.3	1.1	1	+	+
PVDFm(240)	5.2	2.4	3	+	+

[a] Calculated by SEM-EDS analysis

While the virgin PVDF seems not to be able to retain POSS, the Si concentration in the PVDFm samples turns out to depend on their modification level. Namely, the sample PVDFm(240), characterized by the highest concentration of unsaturations, shows the highest Si retention capability. It is also relevant to point out that

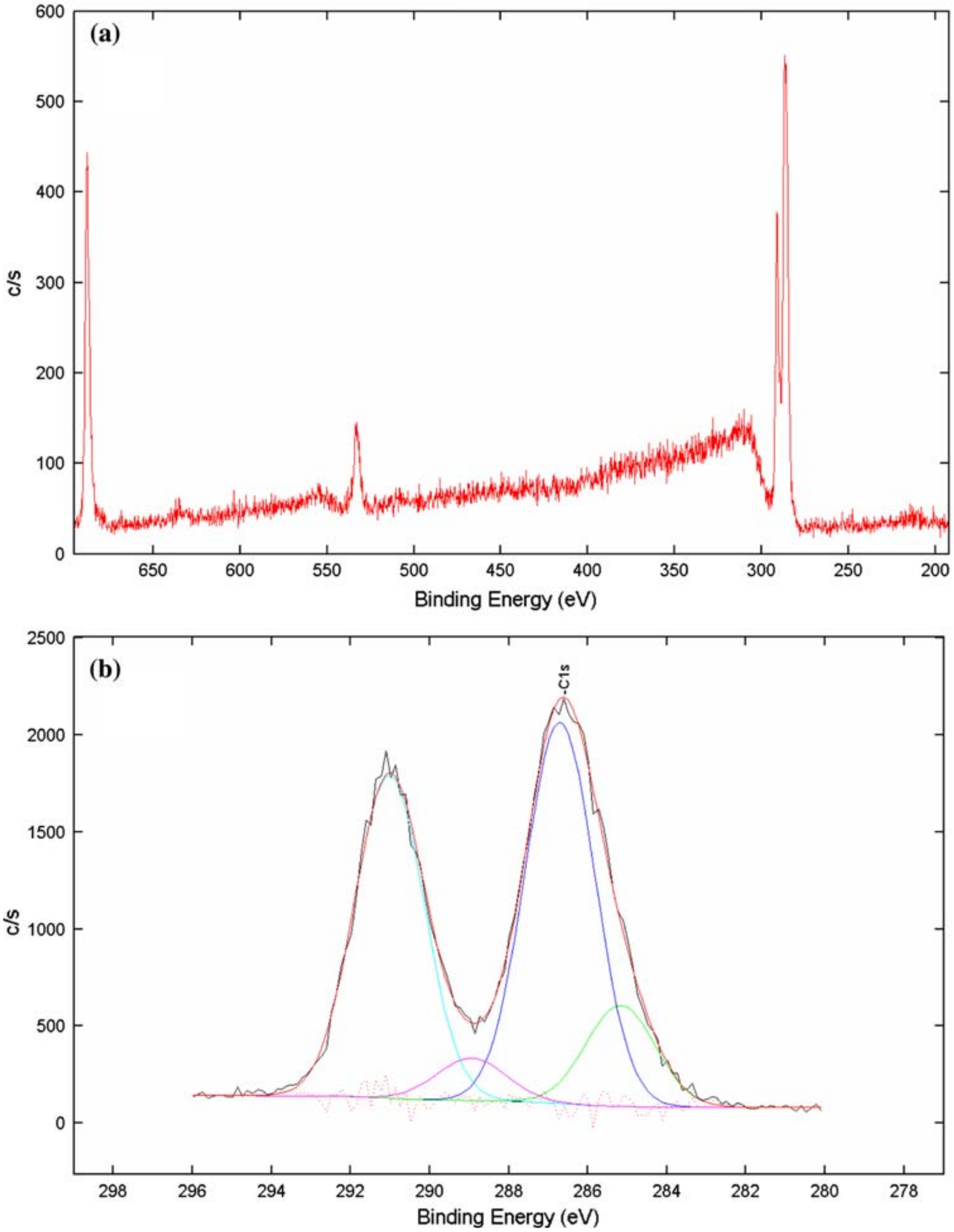

Fig. 3 **a** XPS survey and **b** C1s spectrum of PVDFm(240)

Table 3 Carbon peak assignment for neat PVDFm(240) and PVDFm(240) treated with amino POSS

Sample code	Peak	Binding energy	Relative concentration (%)	Assignment
PVDFm(240)	1	285.0	27.3	CH–CH
	2	286.6	38.5	CH–CF_2, C–OH
	3	288.8	8.4	C=O
	4	291.0	25.8	CF_2
PVDFm(240) + POSS	1	281.6	3.4	C–Si
	2	283.5	12.3	C–Si
	3	285.0	50.1	CH–CH
	4	286.2	19.2	C–N, C–OH
	5	287.9	4.8	C=O
	6	290.4	10.2	CF_2

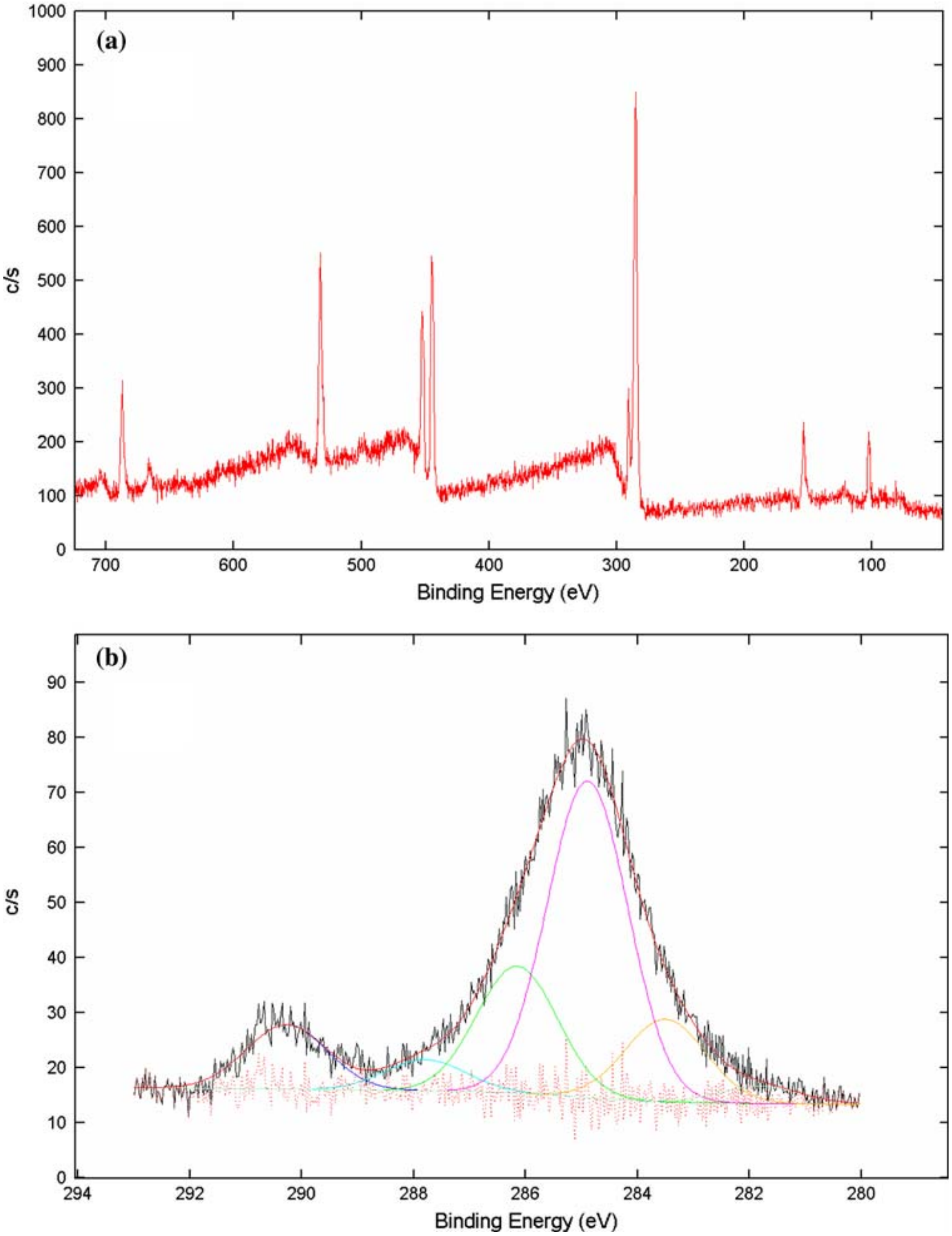

Fig. 4 **a** XPS survey and **b** C1s spectrum of PVDFm(240) + POSS–NH_2

the content of PVDFm unsaturations tends to decrease as a consequence of the reaction with POSS, thus indicating a likely saturation of double bonds by silsesquioxane molecules.

Another polymer feature, which seems to be influenced by the presence of POSS grafted to the polymer chain is the solubility. Indeed, the sample PVDFm(240) after the reaction with amino POSS enhances its solubility both in NMP and DMF. This phenomenon might be due to the organic substituents of POSS molecules, which can affect the final solubility of the system PVDF–POSS.

In order to further validate the above findings, XPS characterization has also been performed. XPS measurements might be helpful to clarify the mechanism of POSS incorporation to the polymer as it allows an evaluation of chemical changes.

The sample PVDFm(240), characterized by the highest level of unsaturation, has been studied by the above method. Figure 3 shows XPS survey (Fig. 3a) and the C1s spectrum (Fig. 3b).

While the C1s spectrum of neat PVDF includes two peaks at a binding energy of 285 (C–C and C–H) and 291 eV (CF_2) that of PVDFm indicates that carbon is present in the form of C–OH, C–H/C–C, CF_2, and C=O. The assignments used are presented in Table 3.

As reported by Ross et al. [39, 40], it is important to underline that the component at 286.6 eV could represent a contribution from the secondary shift experienced by the CH_2 groups that are adjacent to CF_2 and primary C–OH.

Figure 4 shows XPS survey and C1s spectrum of the sample PVDFm(240) treated with amino POSS.

By curve-fitting analysis, the C1s spectrum of the above sample, shown in Fig. 4b, can be deconvoluted into six components at BE 281.6, 283.5, 285.0, 286.2, 287.9, 290.4 eV which can be assigned to C–Si, C–C/C–H, C–N/C–OH, C=O, and CF_2, respectively. Analysing the above results, it comes out that the percentage of CH–CH increases with respect to neat PVDF and new peaks due to C–Si emerge. Taking into account that the unreacted POSS has been completely eliminated by the purification process, the modification of C1s spectrum of the composite sample must be due to silesquioxane molecules linked to the polymer. Indeed, the CH–CH increase can be explained by considering the contribution of the pendant groups of POSS and the disappearance of unsaturation by the grafting reaction. Moreover, apart from CH–CH, the relative ratio of the other groups is similar to that found in neat PVDFm. Indeed, it is relevant to underline that the peak at 286.2 might be due not only to C–OH but also to C–N. Namely, the peak of the legand POSS–PVDF (C–N) might overlay that of C–OH.

In the light of the above results, among the possible reactions which involve double bonds of the polymer matrix and POSS amino group, the addition seems to be the more likely event to occur (Fig. 5) [41].

PVDF–POSS systems have been used to prepare both porous and dense membranes. Unfortunately, as the grafting reaction occurs only on the powder surface, the concentration of Si in the resulting membranes, prepared after the complete solubilization of PVDFm–POSS systems in NMP, has been found to be very low (<2wt%).

In order to overcome this problem, a direct grafting reaction of POSS onto porous membranes has been attempted. It is important to underline that due to the scarce solubility of PVDFm characterized by a high level of unsaturation, partially dehydrofluorinated samples have been used for the above purpose. Indeed, the reaction between POSS–NH_2 and porous membranes has been carried out in the same conditions used for the powders.

Both porous membrane cross-sections and surfaces have been examined in detail by SEM. Figure 6 compares the micrographs of membrane cross-sections obtained by secondary electrons (SE) emission and those by back scattering (BS) emission.

Back scattering electron emission allowed to identify the presence and distribution of Si in the polymer matrix and hence to study POSS dispersion in the membranes. It is relevant to underline that the Si distribution is homogeneous along the membrane cross-section, being the relative concentration ca. 2 wt%, and no visible POSS aggregates are present. Although the above results

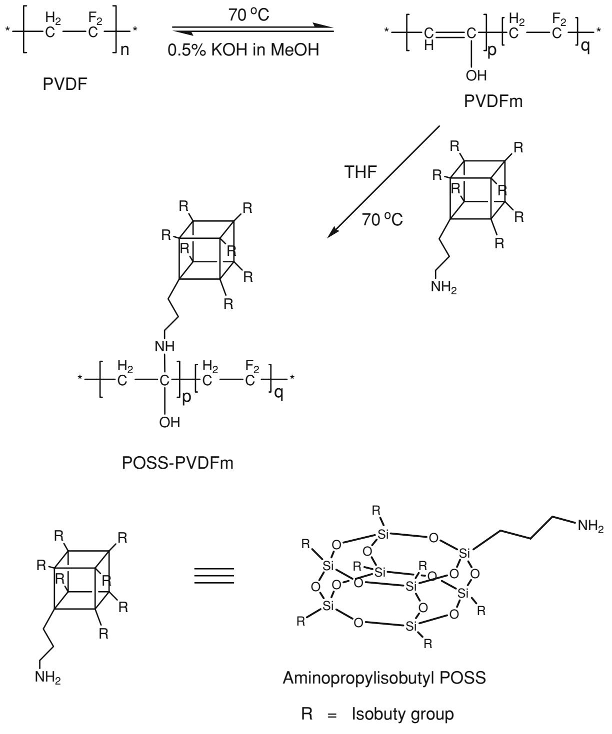

Fig. 5 Reaction between PVDFm and POSS–NH_2

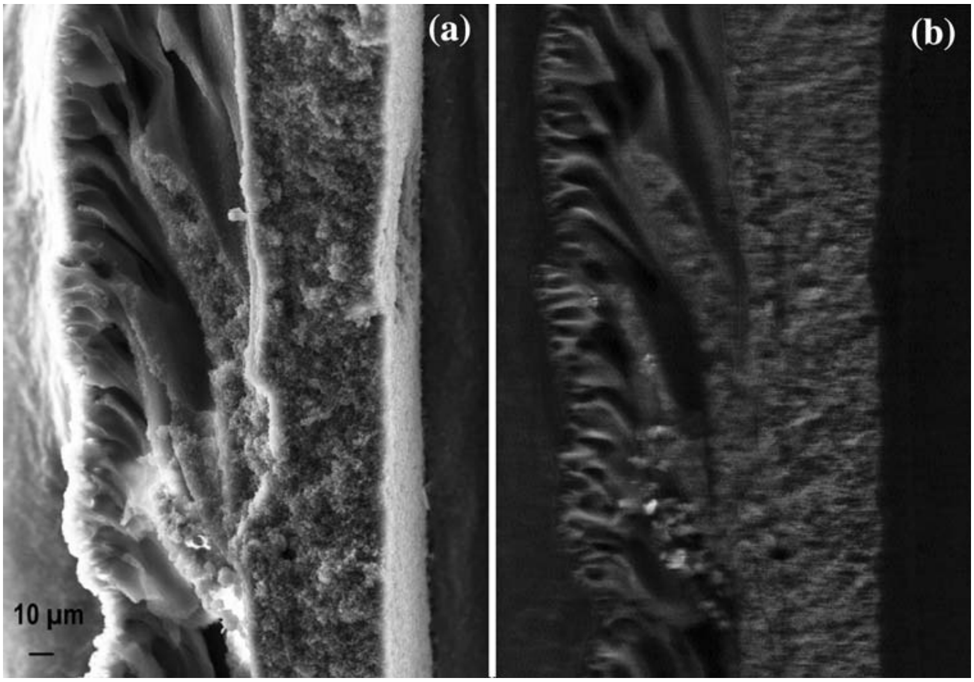

Fig. 6 SEM micrographs of PVDF membrane based on PVDFm(15) after reaction with POSS–NH_2: **a** SE emission, **b** BS emission

are only preliminary, they demonstrate the possibility to prepare directly hybrid membranes based on PVDFm and POSS.

Conclusions

A method to prepare PVDF–POSS systems, characterized by silsesquioxane molecules grafted onto the polymer surface has been developed. This approach consists of a preliminary modification of PVDF by a chemical treatment with an alkaline solution, in order to obtain unsaturations, and a subsequent surface reaction of the PVDFm with POSS molecules characterized by an amino group as reactive side.

Both Raman and SEM-EDS analysis have evidenced the possibility to fine tune the amount of Si retained by the PVDF surface by varying the level of modification, namely by changing the contact time of alkaline treatment. Indeed, XPS measurements have demonstrated the chemical modification of the polymer surface due to the reaction with POSS molecules.

Uniform Si concentration both on the membrane surface and on its cross-section has been obtained by carrying out chemical grafting of POSS–NH_2 using directly porous membranes based on PVDFm.

The performances and properties of the above membranes will be the topic of a forthcoming paper [42], focused on the specific role of POSS on the membrane features.

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