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Characterization of Zr Phosphate/PVDF Nanocomposites by Vibrational Spectroscopy

Mario Casciola,[1] *Anna Donnadio,*[1] *Monica Pica,*[1] *Valeria Valentini,*[2]
*Paolo Piaggio**[2]

Summary: A study of the vibrational spectra obtained by various spectroscopic techniques (FTIR: T, ATR, PAS; FT-Raman) was performed on nanocomposites of α-zirconium phosphate [α-ZrP] in poly(vinylidenefluoride) [PVDF] matrices of different morphology and composition. As the morphology of both dense and porous nanocomposite materials was carefully observed by electron microscopy (SEM, TEM and EDS), the vibrational spectra could be discussed in order to highlight the effectiveness of each spectroscopic technique for the characterization of this type of samples. Some results are presented showing that, by using the proper technique for each type of material, vibrational spectroscopy is very useful not only to determine composition and homogeneity of the nanocomposite but also to understand more specific points like the chain conformation of the polymer matrix and its interaction with the inorganic particles.

Keywords: FTIR; nanocomposites; PVDF; Raman spectroscopy; zirconium phosphate

Introduction

Much attention has been recently devoted to the preparation of composites formed by nanoparticles uniformly dispersed within a polymeric matrix in order to obtain materials with better chemical-physical properties than the pure polymer.[1,2] A number of studies in the last years was devoted to obtain new materials by dispersing nanoclays into various polymeric matrices, showing that the greatest property enhancements are generally observed for exfoliated nanocomposites.[3–5] Less effort has been devoted to make nanocomposites with layered zirconium phosphates $Zr(O_3POH)_2$ both of α- and γ- type (hereafter α-ZrP and γ-ZrP, respectively), that can be easily exfoliated by intercalation reactions with short amines,[6] organic cations[7] and polar molecules[8] without altering appreciably the size of the layers. Moreover the acid proton of ZrP can be exchanged with other cations, while the replacement of the OH group leads to the formation of a large number of organic derivatives.[9] By combining these properties it would be possible to disperse ZrP nanoparticles with tailored properties in a polymer matrix in order to modify its characteristics or to enhance its usefulness for specific applications. To this end α-ZrP nanoparticles have been dispersed in proton conducting ionomers, namely Nafion[9–16] and sulfonated polyetherketones,[17–22] to improve the performance of proton exchange membrane fuel cells in terms of reduction of methanol cross-over and increase of working temperature above 100 °C. More recently, nanocomposites based on neutral polymers have been obtained by dispersing γ-ZrP in polyacrylamide,[23] and α-ZrP in epoxy resins[24,25] and polystyrene.[26] To our knowledge no studies are known concerning nanocomposites of ZrP in poly(vinylidenefluoride), hereafter (PVDF), which is a very important engineering material with unique

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[1] Dipartimento di Chimica, Laboratorio di Chimica Inorganica, Università di Perugia, Via Elce di Sotto, 8. 06123 Perugia, Italy

[2] Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31. 16146 Genova, Italy

chemical an physical properties.[27,28] In particular the modification of the hydrophobic nature of PVDF may be very important for applications in the membranes field,[29] while the stabilization of the trans planar conformation is of interest for various device applications based on the peculiar electric properties of this form.[30]

In any case the characterization of these nanocomposites requires reliable techniques to determine composition, structure, morphology and, if possible, interphase properties and nature of the interactions between the components. Fast and non-altering characterization, like IR/Raman spectroscopy, can be very useful and in particular the nanodispersed phase which, generally, cannot be easily analyzed by other important techniques like X-rays diffractometry. The usefulness of vibrational spectroscopy for the characterization of PVDF based materials and the study of the membrane formation process has been previously discussed.[31]

This paper offers the first results of a study of the vibrational spectra obtained by various spectroscopic techniques (FTIR: T, ATR, PAS; FT-Raman) on PVDF/α-ZrP nanocomposites of different morphology and composition. The effectiveness of each spectroscopic technique for the analysis of these nanocomposites is discussed by considering the results obtained by electron microscopy (SEM, TEM and EDX) as well. By choosing the best technique for each type of material, vibrational spectroscopy is an important and quick aid in following the preparation process as well as the determination of the composition of the nanocomposite. It is particularly important to verify that the final filler contents agrees with the stoichiometric expectations.

Finally a careful analysis of the changes of the characteristic vibrational bands of each component in the nanocomposite spectra is of great help to understand more specific points like the chain conformation of the polymer matrix, the chemical structure of the inorganic particles and the presence of interactions between polymer and filler.

Experimental

The preparation of all samples started with casting a layer of the dispersion of both components in DMF on a glass plate. The components were obtained by mixing the proper amount of a PVDF solution and a α-ZrP gel in DMF.[26] Three different gels, indicated hereafter as A, B and C, have been derived by starting from crystalline, semicrystalline and amorphous α-ZrP powders, respectively.[26] The procedure used to obtain these gels is based on three main steps: a) intercalation of aqueous propylamine in α-ZrP so as to obtain a colloidal dispersion in water, b) deintercalation of propylamine by acid treatment with formation of a gel of α-ZrP in water and c) washing the gel with DMF, so as to replace water with DMF. Dense films were then obtained by evaporating the solvent in an oven while the asymmetric porous membranes were prepared by simple immersion in a water coagulation bath (phase inversion technique).[29] Similarly, by using 1-octanol as coagulant, membranes with a symmetric porous structure were obtained.[32] SEM images were collected by a SEM LEO, STEREOSCAN 440 scanning electron microscope, while TEM analysis was carried out by an HRTEM JEOL, JEM-2010 high resolution transmission electron microscope.

Bruker RFS10 and IFS66 instruments were used to obtain the FT-Raman and the FTIR spectra, respectively. Details of the ATR and PAS measurements are reported elsewhere.[32]

Results

A series of PVDF/α-ZrP nanocomposites in the three above described forms, containing from 2 to 15% of the inorganic component, have been investigated.

SEM observations of the particles obtained by drying the gels showed dramatically different sizes. Lamellas of several μm width and few tens nm thickness were typically observed in the case of gel A

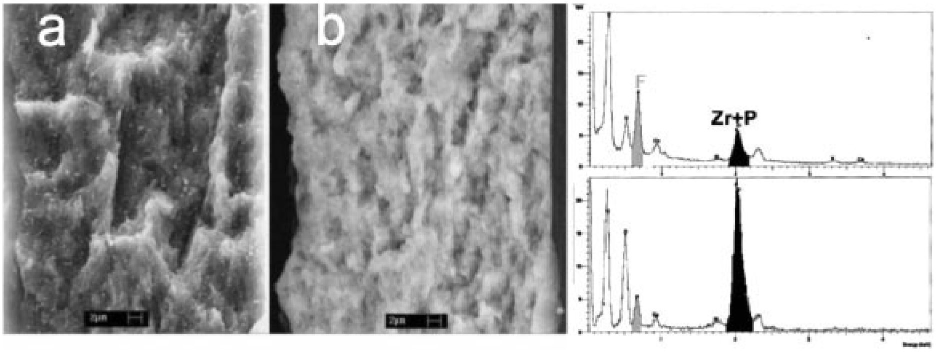

Figure 1.
Left: SEM micrographs of the cros-section of a dense PVDF nanocomposite film containing 7.5% α-ZrP (from gel A) observed by secondary electrons (a) and in backscattering (b). Right: SEM-EDX spectra corresponding to minimum (upper) and maximum (bottom) ZrP and F peaks ratios found.

while platelets of similar thickness but with about 300 nm diameter were found for the gel B. Finally gel C contained nanometric particles sizing 40–70 nm with a marked tendency to aggregate forming also large clots. In any case almost all the obtained nanocomposites showed a good or very good dispersion of α-ZrP in the PVDF matrix as no phase segregation was generally detected by SEM observations. A typical result is given by Figure 1 showing the case of a dense film containing 7.5% α-ZrP. It is apparent that neither image shows the presence of aggregates. Moreover the EDX spectra observed along the whole cross-section never indicated points with only the F peak or the $Zr + P$ unresolved peaks. The relative intensity of the two peaks changed point by point ranging between the values shown in the spectra of Figure 1.

The morphologies of the PVDF matrix were very similar to those observed in the case of the corresponding pure materials, i.e. polymer dense film and asymmetric[31] or symmetric[32] porous membranes. Appreciable changes were only observed for nanocomposites with filler content higher than 10%.

In order to distinguish the inorganic nanoparticles from the polymer, TEM measurement of ultra thin sections were performed as shown by Figure 2. Here, the darker traces indicate the α-ZrP dispersed into the lighter PVDF matrix. It is apparent that the material obtained from gel A contains large lamellas of nanometric thickness while that derived from gel C presents nanoparticles that are more or less aggregated.

The results of the TEM-EDX mappings of the F or $Zr + P$ peaks, shown in Figure 3, confirm the nanosize of the α-ZrP particles or lamellas as well as their close contact with the polymer matrix. Moreover, as can be seen from Figure 3 no appreciable separation of the organic and inorganic materials occurred after membrane treatment with 1 M HCl.

The appreciable thickness and/or porosity of a large part of the prepared nanocomposites generally hinders the acquisition of good transmission FTIR spectra over a wide wave-number range. This type of measurement however can be performed for many samples in the 4000-1500 cm^{-1} transmission window of PVDF and could be of practical interest as it allows one to determine the presence of CH, OH and NH stretching bands, i.e. remnants of the various steps in the preparation process.

Several problems affected the acquisition of FTIR-ATR spectra of good quality as the optical contact on the ZnSe crystal strongly depends on the actual roughness of the sample surface. Therefore, due to the low reproducibility of the surface morphology between the different samples, reliable

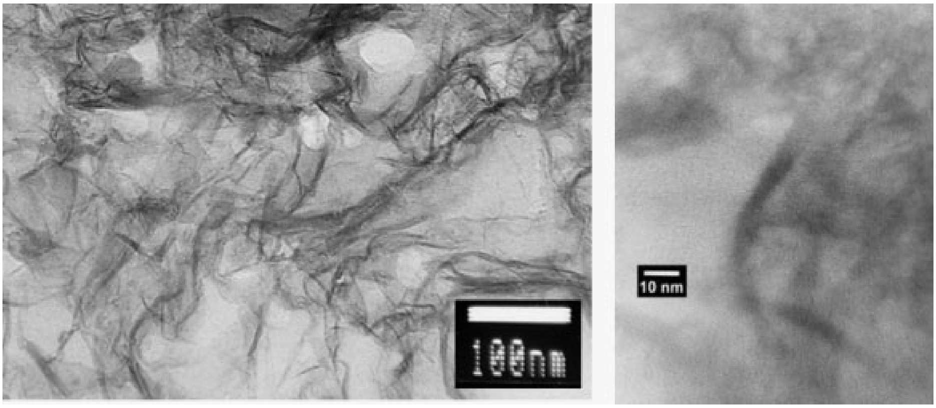

Figure 2.
TEM micrographs of ultra thin sections of PVDF /α-ZrP nanocomposites. Left: symmetric porous film containing 7% α-ZrP (from gel A). Right: asymmetric membrane containing 7% α-ZrP (from gel C).

quantitative measurements cannot be made by this technique. This fact is particularly relevant in the case of the macroporous surfaces and the coarse side of dense films.

On the other hand the ATR spectra can offer very important qualitative information. In the case of asymmetric membranes, due to the very low penetration depth, it is possible to distinguish the different conformations of the polymer chains at the two sides of the membrane. The ATR spectra show that the very thin selective layer is formed by PVDF in the form II (trans-gauche) as is the case of the corresponding materials of pure polymer.[31]

FTIR-ATR spectra of fairly good quality were obtained by analyzing the smooth side of dense films and gave very important

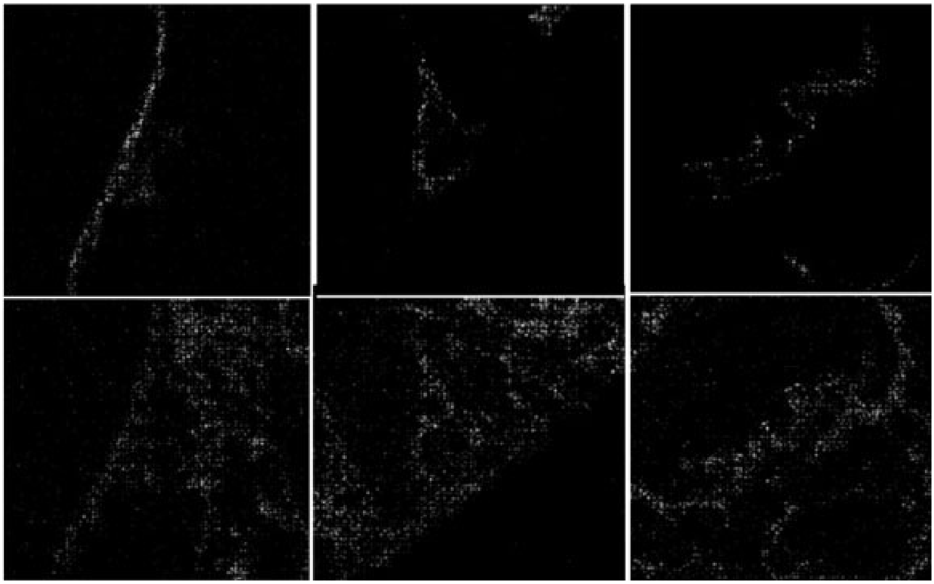

Figure 3.
TEM-EDX mapping of three different zones (about 2×2 μm) of ultra thin sections of PVDF asymmetric membrane containing 14% α-ZrP (from gel A) after treatment with HCl, obtained by counts of the Zr + P unresolved peak (above) and of the F peak (below).

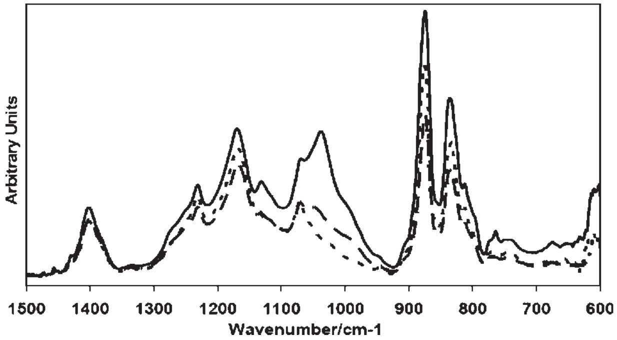

Figure 4.
FTIR-ATR spectra of nanocomposite PVDF films with different α-ZrP (from gel A) content; full line = 7%, dashed line = 4% and dotted line = 0%.

information with regard to the vibrational structure of the inorganic component.

Figure 4 shows the spectra of nanocomposite dense films of different α-ZrP content and clearly indicates that the P-O absorption in the stretching region can be resolved in three main contributions: a very strong band at 1038 cm^{-1}, a shoulder around 1000 cm^{-1} and a band at 1131 cm^{-1}.

These spectral features are notably different from what is observed in the spectra of the crystalline α-ZrP powders. In fact the maximum of the very strong P-O band is observed at 1070–1060 and 1054 cm^{-1} in the case of the starting material and the powder obtained by drying the gel, respectively. In addition to this appreciable redshift, the P-O stretching main band in the spectra of α-ZrP nanocomposite dense materials seems to be very intense when taking the low filler content into account.

New and more dramatic differences were observed for porous nanocomposites membranes which can be well investigated by FTIR-PAS. The spectra of asymmetric and symmetric membranes are shown in Figure 5 and Figure 6, respectively.

In the P-O stretching region, all the spectra of the porous nanocomposite materials show a broad and very intense band at 990 cm^{-1}, which is very different from the band observed in the spectra of the dense nanocomposite films as well as of the α-ZrP powders. The redshift with respect to the strongest band of crystalline α-ZrP is 60–70 cm^{-1} indicating that a marked rearrangement of the P-O bonding in the phosphate units occurred.

The high intensity despite the low phosphate concentration seems to indicate that a large dipole moment is associated with the vibrational transition. These changes are clearly assignable to a different vibrational structure of the phosphate groups in the nanosized particles or lamella and, probably, due to field interactions with the polymer chains. In the latter case the fairly large bandwidth could be associated with a distribution of the distance of the interacting groups of PVDF and α-ZrP. All these findings suggest the establishment of some dipole interaction between the P-O(H) bonds on the surface of external ZrP layers and the CH_2-CF_2 units, magnified by the high specific area of the α-ZrP nanolamella.

It is noteworthy also to observe that no qualitatively difference can be observed for the P-O band in the spectra of the two different types of porous nanocomposites which have been prepared by the phase inversion method using non-solvents of very different polarity and different washing procedures. This can be considered proof that the presence of alterations of the phosphate units is not due to solvents or possible contaminants.

Moreover, as the above discussed 990 cm^{-1} band can be assimilated to the band shoulder observed in the spectra of the dense nanocomposites (Figure 4), some local formation of these PVDF/α-ZrP

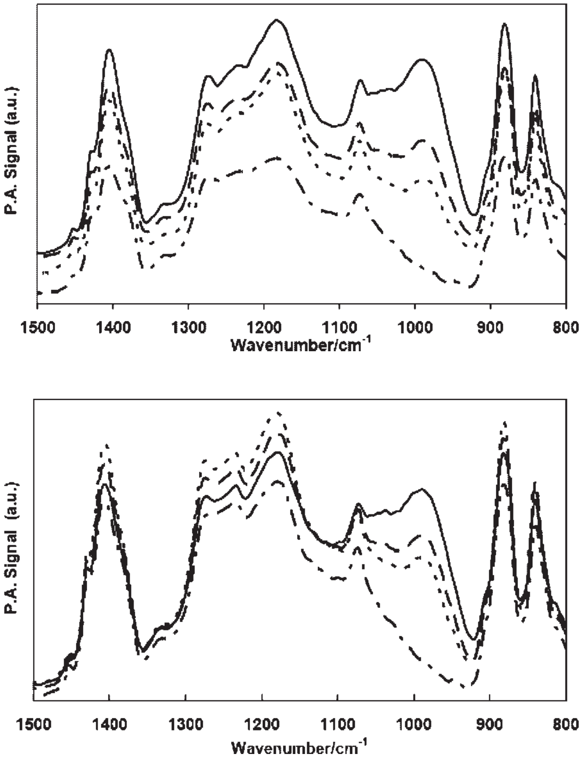

Figure 5.

FTIR-PAS spectra of a nanocomposite PVDF asymmetric membrane with different α-ZrP (from gel A) content; above = macroporous side, below = selective side. Full line = 15%, dashed line = 7%, dotted line = 4% and dashed-dotted line = 0%.

structures, typical for materials obtained by phase inversion, can occur also during the slower solvent evaporation process.

In order to obtain deeper insight into this matter several chemical or physical treatments of the different nanocomposites have been performed and some results are given for asymmetric membranes in Figure 7 and Figure 8. The membranes are treated with HCl or heated up to the PVDF melting temperature, respectively.

Figure 7 clearly shows that the P-O stretching bands of porous nanocomposites completely changed after the acid treatment indicating that the water permeates the membrane pores and that the filler nanoparticles are accessible to ions or solutes.

The α-ZrP nanoparticles (or nanolamella) are not destroyed by the acid treatment and remain well inserted into the PVDF matrix, as already said by discussing Figure 3. It seems reasonable to assume that the spectral changes originated from notable changes in the phosphate groups and/or strong modifications of the polymer/filler interactions.

Figure 7 unambiguously shows that after the HCl treatment the 990 cm^{-1} band, very strong in the IR and very weak in the Raman spectrum, vanishes while a band at about 1050 cm^{-1}, active in both IR and Raman spectra, appears with appreciable intensity. These findings clearly indicate that the P-O stretching modes are strongly changed after the acid treatment. A mode with a very strong dipole moment vanishes and a spectral structure more similar to that present in the α-ZrP original materials appears.

These changes can be explained by considering the possible presence of residual propylammonium ions (not completely removed when the gel is washed with

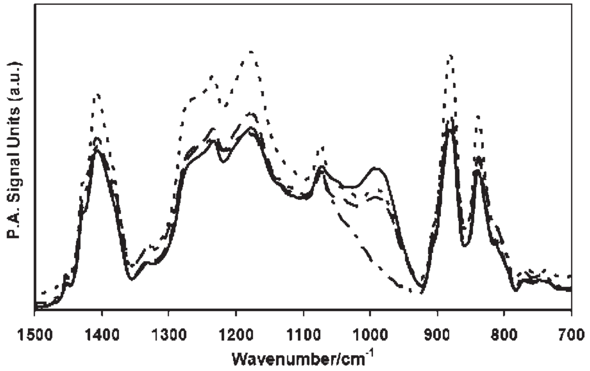

Figure 6.
FTIR-PAS spectra of nanocomposite PVDF symmetric membrane with different α-ZrP (from gel A) content; full line = 12.5%, dashed line = 7.5%, dotted line = 4% and dashed-dotted line = 0%.

DMF) and of associated deprotonated phosphate groups that after the HCl treatment undergo protonation of the external oxygen atoms (restoring of the P-OH groups). In fact, also if no bands characteristic of the propylammonium were observed, they would be masked by the PVDF absorptions.

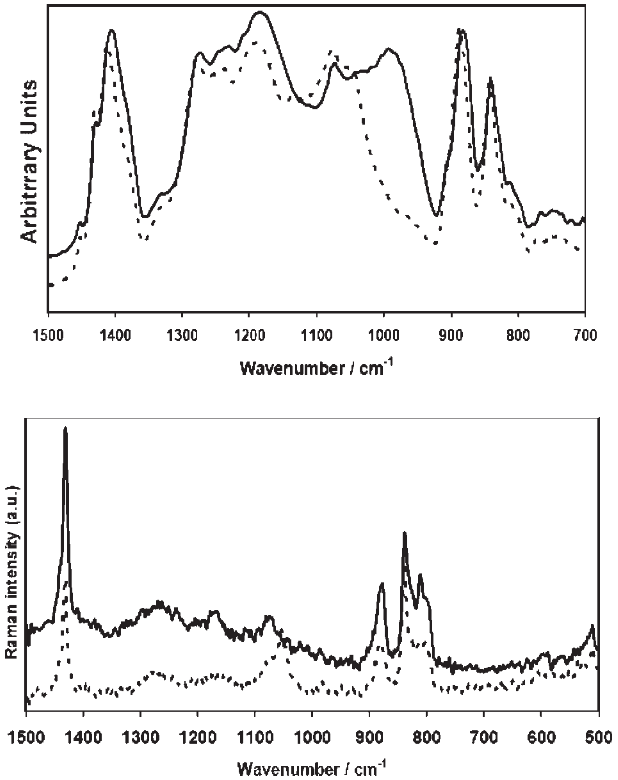

Figure 7.
FTIR-PAS spectra (above) and FT-Raman spectra (below) of an asymmetric membrane containing 14% α-ZrP (from gel A); full line = as prepared , dotted line = after acid treatment (HCl).

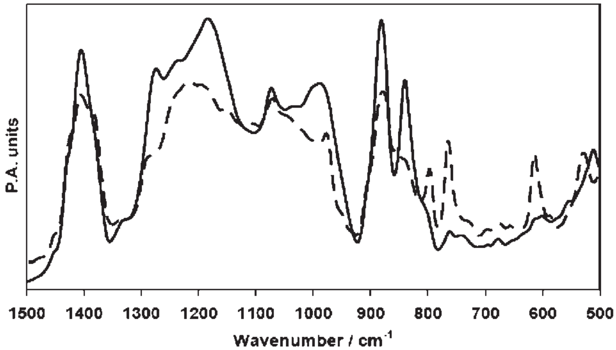

Figure 8.
FTIR-PAS spectra of a PVDF asymmetric nanocomposite membrane containing 12% α-ZrP (from gel A), before (full line) and after (dotted line) heating to 180 °C.

However, other interface effects have to be present as Figure 8 demonstrates that similar spectral changes were also observed after the thermally induced conformational transitions of PVDF. In fact the spectra of Figure 8 unambiguously show that after the heating process the PVDF form II bands at 974, 795, 795 and 615 cm^{-1} appear,[31] i.e. the PVDF chain conformation, containing the all trans sequence, typical of the as cast form, changed into the trans-gauche structure proper of form II. It is also apparent that together with these changes of the PVDF bands, a collapse of the very strong P-O band occurs leaving a broad less intense absorption band between 1070 and 950 cm^{-1}.

Similar observations were made in the case of dense nanocomposite films that, after transition, give IR spectra qualitatively very similar to those of the porous nanocomposites. In fact as shown in Figure 9a broad featureless absorption around 1000 cm^{-1} appears superimposed to the characteristic bands of the PVDF form II, replacing the more structured band, with maximum at 1038 cm^{-1}, present in the spectrum of the as cast nanocomposite film.

For a sound interpretation of these important points some work is still needed. First, attempts will be made to obtain new α-ZrP gels in DMF by improving the deintercalation of the propylamine during the preparation. A second effort regards the assignment of the vibrational spectra of the phosphate group in differently intercalated α-ZrP. Significant help could derive from new investigation of these PVDF/α-ZrP nanocomposites by other techniques, such as solid state NMR.

The FT-Raman spectra of the α-ZrP/PVDF nanocomposites, not here reported, presented fairly weak P-O bands which, with a very small blueshift, reproduce the frequency observed in the IR spectra, confirming a vibrational structure of the phosphate groups very different from that in the α-ZrP powders. However the S/N ratio observed in the FT-Raman spectra of the nanocomposites is appreciably lower than for the pure PVDF. This is even worse in the case of porous materials and in general is associated to a broad background luminescence. Nevertheless, the PVDF bands in the 840–780 cm^{-1} region, being conformation-dependent,[31] can be complementary to the IR bands. This can help to determine the distribution of the PVDF forms in the nanocomposites.

Finally some remarks about the effectiveness of vibrational spectroscopy for quantitative purposes can also be made. The problems affecting transmission and ATR measurements have already been mentioned while those regarding PAS spectra are related to their dependence on both the optical and thermal properties of the observed materials.[31] Therefore it is difficult both to determine the effective

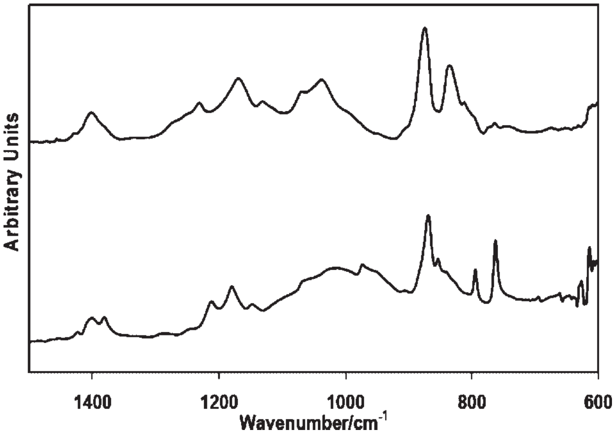

Figure 9.
FTIR-ATR spectra of a dense PVDF nanocomposite film containing 7.5% α-ZrP (from gel B); upper = as cast film, lower = after heating to 180 °C.

sample volume analyzed and obtain reliable analytical relations of the photoacoustic signal intensity as a function of concentration. Nevertheless, by plotting the intensity[33] of the 990 cm^{-1} phosphate band vs the α-ZrP concentration,[34] a fairly regular trend was observed among the same type of samples, like those reported in Figure 5 and Figure 6. These findings indicate that, for porous materials with similar morphology, the PAS spectrum can be used for the quantitative evaluation of the α-ZrP contents. The broadness of the 990 cm^{-1} band and the presence of the 1073 cm^{-1} PVDF band affect the accuracy of the measurement, especially when the lowest phosphate concentrations are considered.

Conclusions

Vibrational spectra are very useful in the study of polymer based nanocomposites if the proper sampling techniques are used. In the case of α-ZrP/PVDF materials, both FTIR and FT-Raman spectra highlight the structural differences of the polymeric matrix and the phosphate units in the nanocomposite with respect to the structures observed for the starting materials. Careful analysis of the observed spectral differences helps understand the modifications induced by chemical or physical treatments.

In particular by analyzing the shape of several PVDF bands it is possible to determine the type of chain conformation induced by the preparation process as well as by the filler contents. Moreover, the strong P-O stretching bands are valuable in the investigation of the rearrangement of the phosphate groups due to nanosize effects and/or boundary interactions. In order to get a better understanding of this very important point new studies of the vibrational spectra of α-ZrP and, possibly, of α-ZrP intercalated by model molecules, must be done. A detailed vibrational analysis of anhydrous, monohydrated and D_2O exchanged α-ZrP will be reported elsewhere.

Despite the plethora of qualitative information, vibrational spectra are less effective for quantitative analysis of the considered nanocomposites. In fact, the nature of the samples in many cases makes it difficult to obtain transmission measurements (except for the study of the OH stretching bands of the phosphate groups or of the intercalated molecules in a fairly transparent region of PVDF).

However some useful quantitative information can be obtained by the PAS spectra in the case of porous nanocomposites with the same polymer morphology.

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[33] normalized to the 1400 cm^{-1} PVDF band, common to all the conformations
[34] the indicated filler concentration of the nanocomposites reflects the stoichiometric expectations. The fairly good correspondence to the actual composition was verified by TG analysis of several nanocomposites of each type.