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Multiporous Materials From Thermoreversible Poly(vinyledene fluoride) Gels

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Summary: Poly(vinylidene fluoride)(PVF_2) produces thermoreversible gels with alkyl diesters of general formula $(CH_2)_n$ $(COOEt)_2$ as well as with camphor, a naturally occurring ketone. These gels containing polymer-solvent intercalates yield multiporous materials when subjected to controlled solvent removal techniques. The micro and meso pores are attributed to polymer-solvent complexation while the macro pores are formed as a result of removal of the solvent trapped in the fibrillar network. PVF_2 –diethyl azelate (DEAZ, $n = 6$) and PVF_2 -camphor gels produce porous polymer network when dried by cyclohexane leaching. FESEM images exhibit porous network structures with fibrillar morphology. Mercury intrusion porosimetry (MIP) shows presence of pores having diameter in the range 4 nm–400μm for both the systems. The BJH pore size distribution curves for both systems confirm the presence of mesoporosity. The HK pore size distribution plots indicate that micropores are also created and it also puts evidence of single molecule solvent intercalation between the PVF_2 strands. The hysteresis between the extrusion and the intrusion curves indicates the presence of channel type/ink-bottle type structure in these systems.

Keywords: mercury intrusion porosimetry; multiporosity; N_2 adsorption porosimetry; polymer-solvent complex; thermoreversible gel

Introduction

Porous materials contain pores of different dimensions eg., nanometer (nm) to macrometer (μm) inside it. Such materials are very useful in catalysis, ion exchange resins, medical implants, low dielectric materials, super absorbents and in membranes.[1–5] According to IUPAC classification porous solids can be classified into three main categories depending on the pore diameter.[6,7] Microporous materials have pore diameter <2 nm, mesoporous materials have pores of diameter in the range 2–50 nm and for macroporous materials the pore diameter >50 nm. A combination of all these porosities in the same material may be termed as multiporous material.[8,9] Using supramolecular organization technique porosity in organic materials were introduced[10,11] but in these cases porosity is limited to a particular value of micro or mesoporosity. In polymeric systems porosity is developed using techniques like foaming,[12,13] temperature induced phase separation,[14,15] phase inversion[16,17] etc. In these methods the distribution of the pores is not large and macropores are generally produced. Multiporous materials may be needed in the separation process to separate impurities from industrial and municipal waste water where different sized impurities are present. They may be pesticides, insecticides and small molecular inorganics like arsenic, mercury, lead and iron salts. In this paper we report the preparation and characterization of multiporous materials from thermoreversible poly(vinylidene fluoride)(PVF_2) gels.

Thermoreversible polymer gels consist of fibrillar network structure obeying percolation model. So drying of these gels by keeping the gel structure intact would like to produce macropores. Also the fibrills

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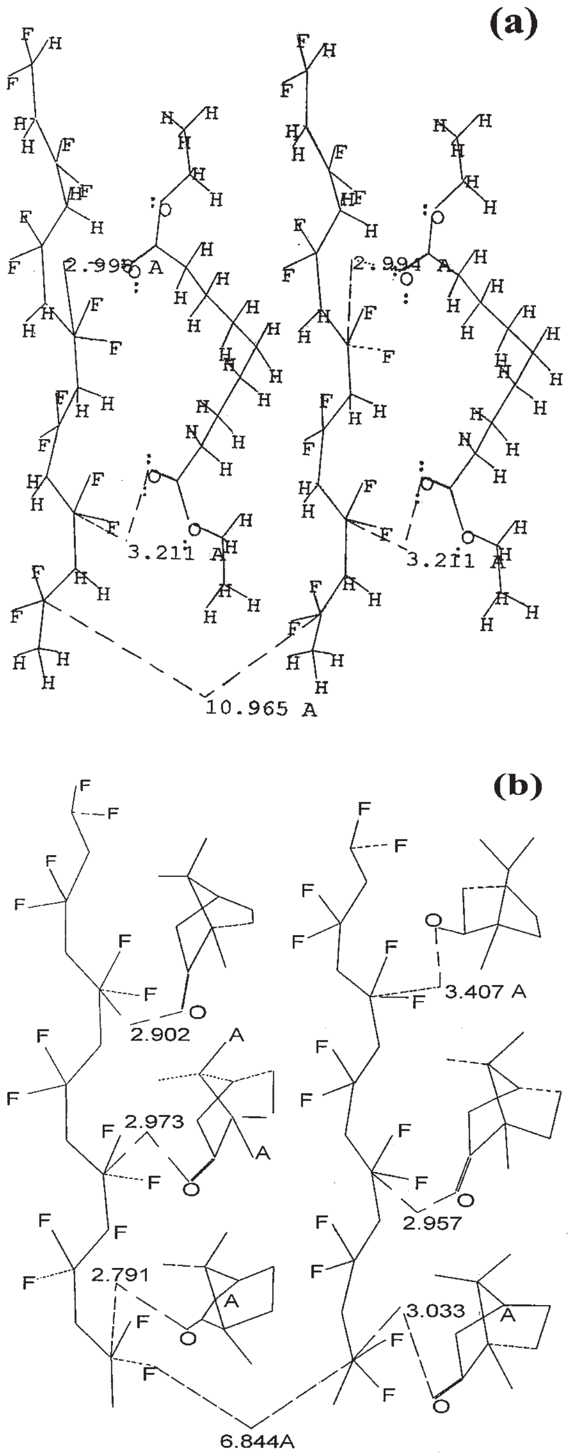

Scheme 1.
MMX model of single solvent intercalation in (a) PVF_2-DEAZ and (b) PVF_2-camphor gels.

are produced due to polymer-solvent comlexation and molecular model of the complexes are presented in Scheme 1(a) and (b). From the molecular models it is apparent that single molecule solvent intercalation between the polymer strands may produce a pore size of diameter 1.1 nm and 6.8 Å for PVF_2 –diethyl azelate (DEAZ) and PVF_2-camphor gels respectively. However, double, tripple or multiple solvent molecule intercalation would be possible between two polymer strands and these would produce pores of different meso dimensions. Thus by a proper drying of thermoreversible polymer gels multiporous materials can be produced.

Poly(vinylidene fluoride) is highly used as membrane material for its excellent chemical resistance, good thermal properties and easier processability.[18] When grafted with poly(acrylic acid) and poly(ethylene glycol) pH sensitive and antifouling membranes are produced, respectively.[19,20] The average pore size of these membranes are 1600 nm, thus they are essentially macroporous. By proper drying of PVF_2 gels micro and mesoporosity may be introduced in these materials as discussed earlier. For this purpose we have used two types of gels e.g, PVF_2 –liquid solvent (diethyl azelate) gel and PVF_2 –solid solvent (camphor) gel. After proper drying of the gels the resulting porous materials are characterized by field emission scanning electron microscopy (FESEM), Mercury Intrusion Porosimetry (MIP) and N_2 Adsorption Porosimetry.

Experimental Part

Samples

Poly (vinylidene fluoride) (PVF_2) is a product of Aldrich Chemical Co. Inc. The weight average molecular weight ($\overline{M}_w$) of the sample is 1,80,000 g/mole and polydispersity index is 2.54 as obtained from GPC. The PVF_2 sample was recrystallized from its 0.2% solution in acetophenone, washed with methanol and finally dried in vacuum at 60 °C for three days. The diester diethyl azelate (DEAZ) was purchased from Lancaster synthesis, Morecambe, England and were used as received. D-L camphor was purchased from S. D. Fine Chemicals Ltd., Mumbai and was purified by sublimation procedure in vacuum at 50 °C.

Porous Materials Preparation

PVF_2 and camphor were taken in a thick walled-glassed tube (8 mm in diameter and I mm thick) and were sealed. The sealed tubes were melted at 210 °C in an oven for 30 min with constant shaking to make homogeneous. The transparent melt was then quenched to room temperature (30 °C). The solid mass thus obtained was taken out from the tube and poured into a round bottomed flask containing cyclohexane. The cyclohexane was replaced by every twelve hours. This solvent replacement was carried out untill all the camphor was extracted from the gel (~10 days). It was then dried in air and finally in vacuum at 30 °C for three days. Complete removal of camphor was confirmed from the absence of >C=O stretching frequency (1740 cm^{-1}) in the FT IR spectrum of the samples. The PVF_2 -diethyl azelate gels were prepared in a sealed tube by melting the samples at 210 °C for 30 minutes and then quenched to 30 °C. A transparent gel was obtained. They were then cut into pieces and dipped into cyclohexane for 10 days with occasional change of cyclohexane. It was finally replaced with methanol by dipping the gel in methanol for 1 day and dried in vacuum at 40 °C for 4 days.

Microscopy

For scanning electron microscopy (SEM) a thin film of PVF_2 gel was melt casted and dried as above, gold coated with a gold layer of thickness 40 nm by the sputtering technique in an argon atmosphere and was observed in a SEM apparatus (Hitachi S-2300). The morphology of dried PVF_2 –camphor and PVF_2-DEAZ gels were also viewed in a FESEM apparatus (JEOL, JSM-6700F) without any metal coating at an accelerating voltage 1 kV.

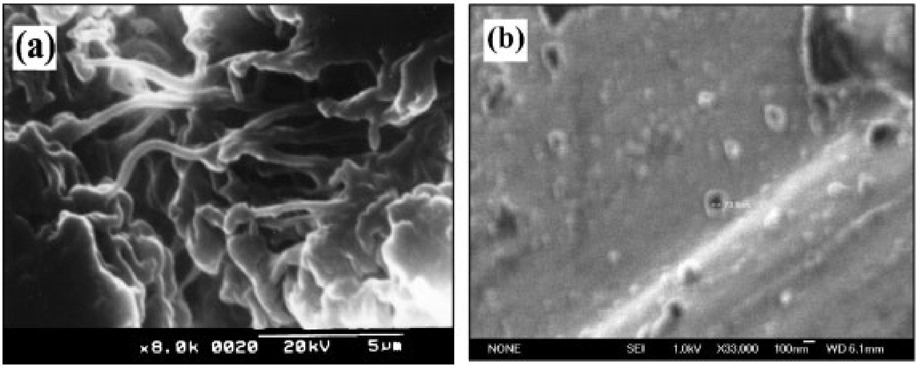

Figure 1.
(a) SEM and (b) FESEM pictures of dried PVF$_2$-DEAZ gel ($W_{PVF2} = 0.10$).

Porosity Characterization

For porosity measurement both mercury intrusion porosimetry (MIP) and N_2 adsorption porosimetry were used. MIP was used to measure pores having diameter lying in the range 4 nm–400 µm. To measure the pores of diameter below 4 nm N_2 adsorption porosimetry was used. The MIP was done using the instrument Poremaster-60 (Quantachrome Instrument). The sample was first taken in a penetrometer (stem volume 0.5 cm^3) and inserted into the low-pressure station where mercury pressure was gradually increased from an initial 0.5 psi to 50 psi. Both intrusion and extrusion runs were recorded. The penetrometer was then taken out and some of the mercury was replaced by silicon oil and the entire system was then placed in the high-pressure station. In this station the pressure was increased to 60,000 psi then also both intrusion and extrusion runs were recorded. The data were analyzed by Porewin-32 software. The nitrogen adsorption porosimetry was done with Quantachrome Autosorb 1-2C instrument (Quantachrome Instruments. USA). BJH (Barett-Joyner-Halenda)[21] and HK (Horvath-Kawazoe)[22] methods were used to measure the diameter as well as the pore size distribution of meso and micro pores, respectively using Autosorb 1 software.

Thermal Characterization

The melting point and enthalpy of fusion of the dried gels were measured using a differential scanning calorimeter [Diamond DSC (Perkin Elmer)] under N_2 atmosphere. The samples were heated from 50 °C to 230 °C at the rate 40 °C/min. The

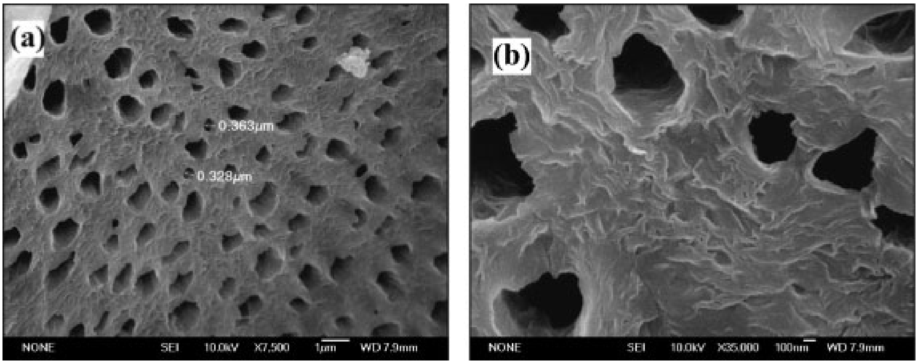

Figure 2.
FESEM pictures of (a) dried PVF$_2$-camphor gel ($W_{PVF2} = 0.25$) and (b) the same picture in higher magnification.

higher heating rate was chosen to avoid any melt recrystallization of the PVF_2 sample.

Results and Discussion

Microscopy

In Figure 1(a, b) the SEM and FESEM pictures of PVF_2 DEAZ gel ($W_{PVF2} = 0.1$) are presented.

Figure 1(a) corroborates the presence of macropores of large diameter (400 nm – 2 μm) with fibrillar network structure and Figure 1(b) indicates the presence of mesopores of 50 –100 nm.

In Figure 2(a, b) the FESEM picture of PVF_2 camphor gel ($W_{PVF2} = 0.25$) dried by cyclohexane leaching method are presented. It is apparent from the Figure 2(a) that macropores of different dimensions

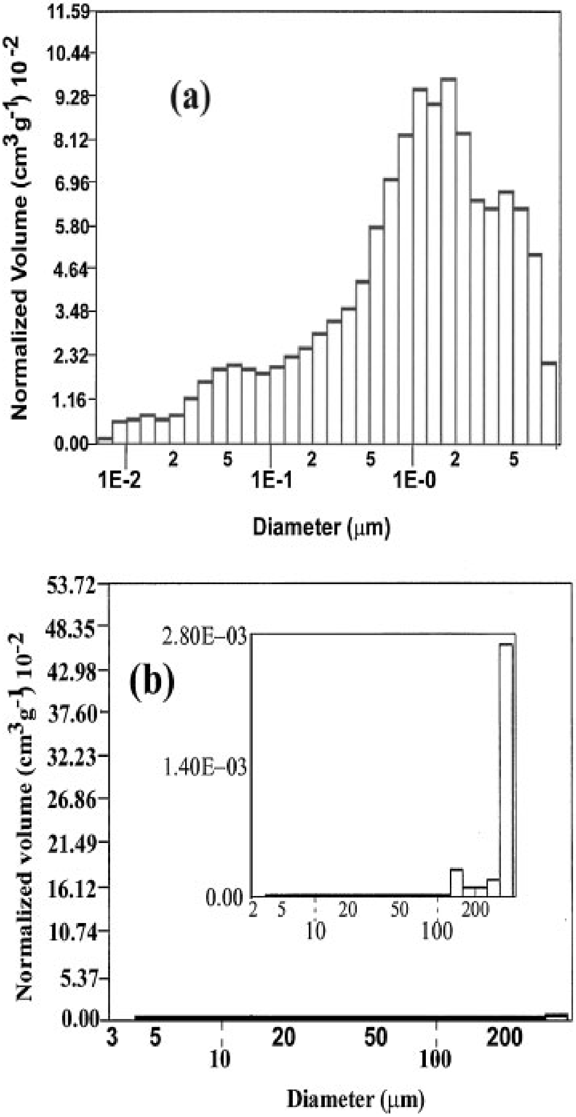

Figure 3.

(a) High pressure and (b) low-pressure MIP histograms of dried PVF_2 –DEAZ gel ($W_{PVF2} = 0.25$) [Inset of (b) Y scale enlarged].

(200 nm to 1 μm) are present in this system. The five times enlarged micrograph of the same sample is shown in Figure 2(b) where the mesopores of dimensions 50 nm–100 nm are clearly seen. This type of porous morphology is also observed for other compositions of the gel. Thus it can be inferred from above micrographs that meso and macropores are present in PVF_2 films dried from PVF_2-camphor and PVF_2-DEAZ gels.

Mercury Intrusion Porosimetry

To get a quantitative idea of the porosity of the samples the MIP intrusion histograms with both high-pressure and low-pressure techniques are shown in Figure 3 and Figure 4.

For easier comparison between the PVF_2 –DEAZ and PVF_2 –camphor systems both the figures are presented in the same scale. The high-pressure mercury intrusion histogram of dried PVF_2-DEAZ gel

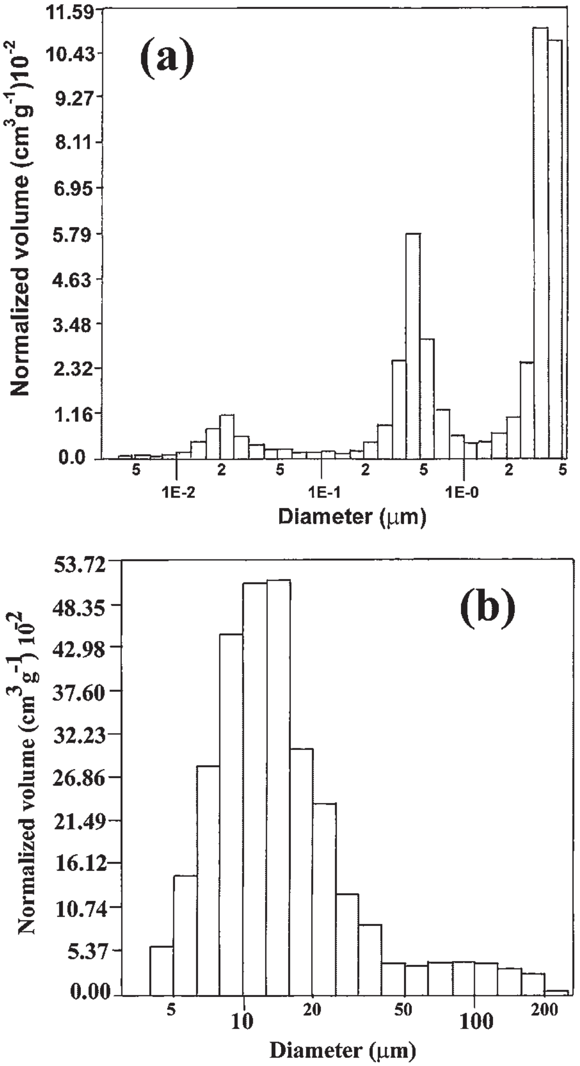

Figure 4.
(a) High pressure and (b) low-pressure MIP histograms of dried PVF_2 -camphor gel ($W_{PVF2} = 0.25$).

($W_{PVF2} = 0.25$) indicates the presence of both mesoporosity and macroporosity (6 nm to 10 μm) in the sample whereas the low-pressure intrusion histogram indicates the presence of pores of diameter 100–400 μm. The later value may be partly contributed from the interparticle porosity apart from the contribution of fibrillar network structure. It is noteworthy to mention that the macropore concentration is much smaller than that of mesopores. Nonetheless it may be inferred that both meso and macroporosity are present in the sample.

The high-pressure and low-pressure mercury intrusion histograms of dried PVF_2–camphor system ($W_{PVF2} = 0.25$) are presented in Figure 4. The high-pressure histogram indicates the presence of pores of diameter 4 nm to 5 μm but the low-pressure histogram indicates pores lying in the range 4 μm to 200 μm. Comparison of normalized pore volume indicates macropores are present in large amount than mesopores in both the systems.

Figure 5(a, b) show the hysteresis loop of extrusion and intrusion of mercury of dried PVF_2-DEAZ ($W_{PVF2} = 0.25$) and PVF_2 –camphor ($W_{PVF2} = 0.25$) gels. In both the systems a significant amount of hysteresis is observed indicating the presence of interconnected channel type or ‘‘ink-bottle’’ type pores.[23] The interconnectivity between the pores may be supported from the three dimensional percolation model obeyed by these gels.[24–26] Such materials would be very much useful for diffusion/sorption process.[27]

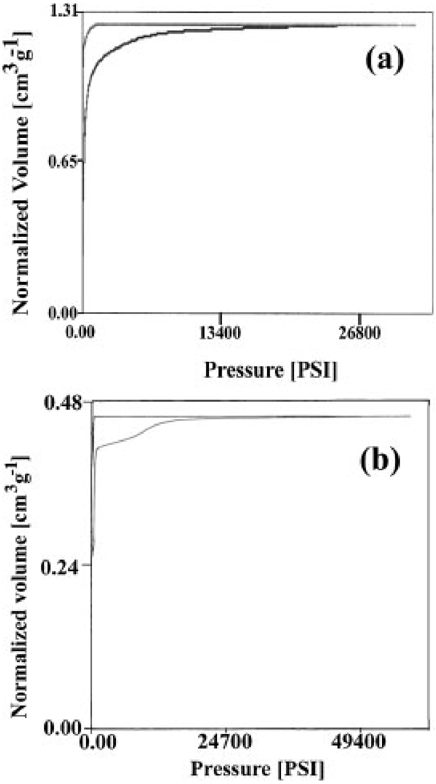

Figure 5.
MIP hysteresis profile of (a) dried PVF_2-DEAZ ($W_{PVF2} = 0.25$) and (b) dried PVF_2-camphor gel ($W_{PVF2} = 0.25$).

N_2 Adsorption Porosimetry

In the MIP method the lowest diameter of pore that can be determined accurately is 3.5 nm.[8] So we have studied nitrogen adsorption porosimetry to measure pores of lower diameter. In Figure 6(a) and 6(b) the BJH pore size distribution of dried PVF_2-DEAZ gel and dried PVF_2-camphor gel ($W_{PVF2} = 0.25$) are presented, respectively. From the Figure 6(b) it is apparent that there is a trimodal distribution of pore size with maximum population of 2.7 nm, 3.4 nm and 9.5 nm. This is really interesting that three different types of pores are present in this dried PVF_2-camphor gel. These differently sized mesopores are thereby produced from four, five and thirteen camphor molecules intercalation between the PVF_2 strands. On the other hand for PVF_2-DEAZ system the maximum occurs at 4.3 nm with a hump at 7.9 nm. These results, therefore, indicate approximately four and seven diethyl azelate (DEAZ) molecules intercalation between the PVF_2 strands as the single DEAZ intercalation separates two PVF_2 strands by a distance equal to 10.96 Å. Thus from these pore volume distribution plots mainly pores of two different sizes are observed showing multiple solvent molecule intercalation between two PVF_2 strands.

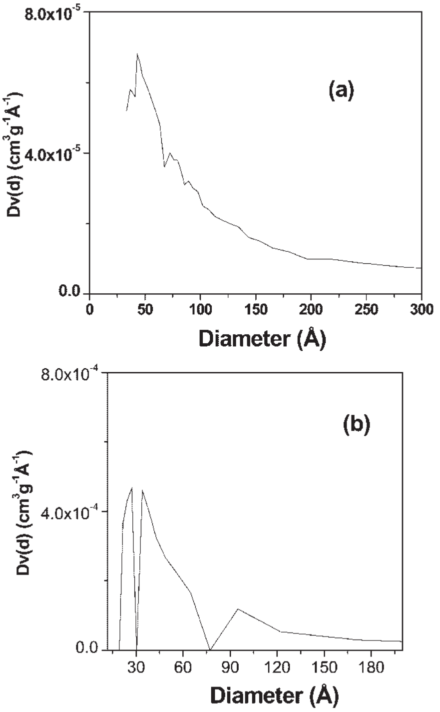

Figure 6.
BJH pore size distribution of (a) dried PVF_2-DEAZ ($W_{PVF2} = 0.25$) and (b) dried PVF_2-camphor gel ($W_{PVF2} = 0.25$).

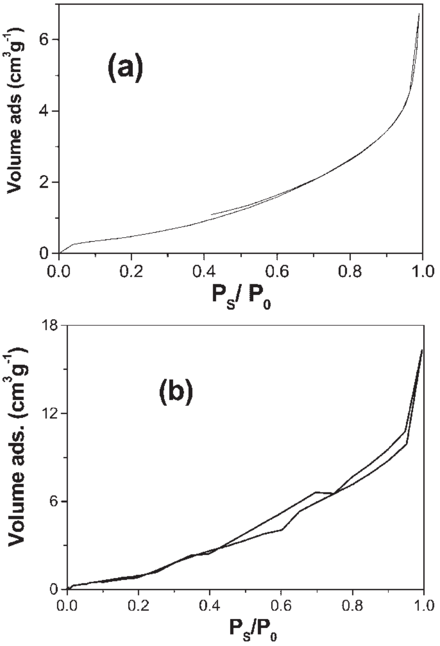

Figure 7.
BET adsorption isotherm of (a) dried PVF_2-DEAZ ($W_{PVF2} = 0.25$) and (b) dried PVF_2-camphor gel ($W_{PVF2} = 0.25$).

In the Figure 7(a) and (b) the N_2 adsorption isotherms of dried PVF_2-DEAZ gel ($W_{PVF2} = 0.25$) and dried PVF_2-camphor gel ($W_{PVF2} = 0.25$) systems are presented. it is apparent that there are hysteresis in both the systems indicating the presence of interconnected and "ink-bottle" type pore structures even in the mesopores.[23]

In Figure 8 the HK pore size distribution plot[22] is presented for PVF_2-camphor system. It is apparent from the figure that pores of dimension 6.3 Å, 9.5 Å, 14.2 Å and 18.4 Å are present in the dried gel of polymer wieght fraction (W_{PVF2}) = 0.10. This certainly corroborates single molecule intercalation of camphor between the two PVF_2 strands (from MMX program such intercalation results in pores of diameter 6.8 Å). However, larger size micropores are present in greater proportion than the pore of diameter 6.3 Å and they may be created from two or multiple camphor molecules intercalated structures. These results, therefore, support polymer-solvent complexation during thermoreversible gel formation.

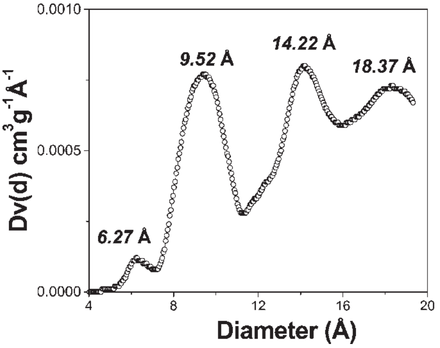

Figure 8.
HK pore size distribution of dried PVF_2-camphor gel ($W_{PVF2} = 0.1$).

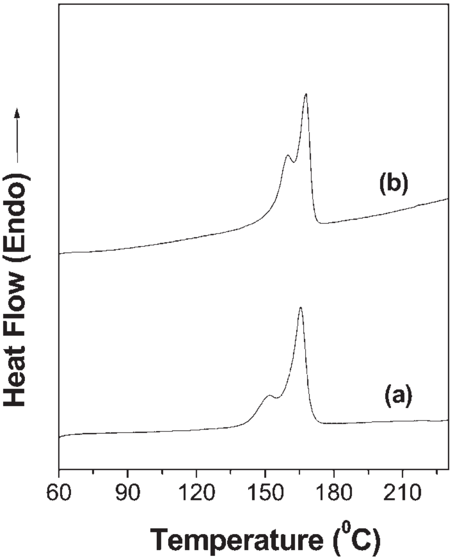

Figure 9.
DSC thermograms of as prepared (a) dried PVF_2 –DEAZ gel ($W_{PVF2} = 0.1$) and (b) dried PVF_2 camphor gel ($W_{PVF2} = 0.1$) at the heating rate 40°/min.

Thermal Study

In Figure 9 the thermal properties of the dried PVF_2-DEAZ ($W_{PVF2} = 0.1$) and PVF_2-camphor ($W_{PVF2} = 0.1$) gels are compared. In each thermogram there are two peaks. The lower temperature peak is due to the melting of crystals at porous surface whereas the higher temperature peak corresponds to melting of bulk polymer. This is because the porous part has higher surface energy (due to large surface area) and consequently it melts at lower temperature than the bulk sample.[28]

Conclusion

Thus from the above results it may be concluded that porosity of micro, meso and macro sizes can be developed in poly(vinylidene fluoride) by proper drying of their thermoreversible gels. The materials show hysteresis in both MIP and N_2 adsorption porosimetry indicating the presence of interconnected or ink-bottle type of pore structures in both meso and macro pores. The HK plot of PVF_2-camphor system concludes single camphor molecule intercalation between the PVF_2 strands .Thus the present work puts direct evidence of single and multiple solvent molecule intercalation between the PVF_2 strands during thermoreversible gelation.

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