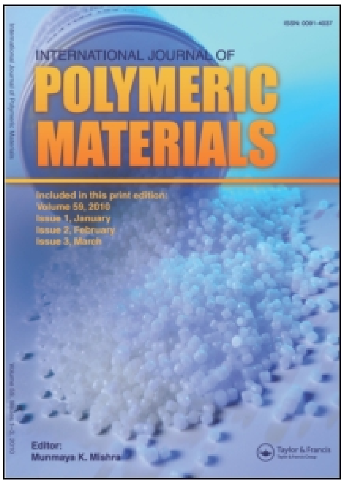

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Crystalline Structure and Phase Transformation in Powder Processing of Polyvinylidene Fluoride with Fillers*

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Structural investigations have been carried out in powder processed polyvinylidene fluoride containing various amounts of titanium dioxide and lead monoxide as fillers. The crystallinity was found to increase significantly at very low filler concentration (<3 percent) while it decreased monotonically with increasing filler concentrations above 5 percent. The phase transformation in the crystal structure was also noticed especially after sintering and the formation of beta phase was favourable in samples containing lead oxide. These various findings were also confirmed by infrared absorption studies and explained on the basis of deformation of the polymer during compaction together with preferential nucleation by the filler during the sintering step of the powder processing technique.

INTRODUCTION

Amongst the various fluoropolymers, polyvinylidene fluoride (PVDF) has drawn considerable attention in the recent years because of its remarkable piezoelectric and pyroelectric properties as well as its complicated polymorphism.[2] Amongst the four known crystalline phases, the β form exhibits the maximum piezoelectric

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activity and hence a number of studies have been carried out in last few years on the structure development, crystalline phase, orientation etc. as related to the processing conditions in this polymer. These have been reviewed earlier by Wada *et al.*[3] and more recently summarized by Lovinger.[4] In the attempts of producing/enhancing the β phase of the polymer, Richardson *et al.*[5] have studied the properties of PVDF drawn through conical die. The structure and piezoelectrocity of PVDF films obtained by solid state extrusion was investigated by Tasaka *et al.*[6] The structure development in melt spinning by PVDF fibres and tapes has been studied by Wang *et al.*[7] The phase transformation is an important aspect in PVDF processing but has been looked into only by a few authors. Sakaoku *et al.*[8] have reported the transmission electron micrographs of PVDF and phase transition during annealing. Tashiro *et al.* have studied the ferroelectric phase transition of PVDF by infra-red spectroscopy and x-ray diffraction.[9] It may be concluded from these various reports that the processing conditions play very important role in determining the crystalline phase present in the final product.

Although the piezoelectric activity of pure PVDF is sufficiently high, it is not as high as that of ceramic materials such as lead titanate, barium titanate etc.[10] On the other hand the latter materials do not have the advantages of flexibility, mechanical coupling factor etc. obtained in polymers. The piezoelectric composites consisting of the combination of these materials have been made in the past with mostly non crystallizing polymers such as crosslinked epoxies and rubbers.[11,12] The conventional processing of ceramic materials uses the powder metallurgical (P/M) technique consisting of high pressure compaction and sintering.[13] This technique can also be used for processing polymers[14] and in our recent investigation we have shown that fluoropolymers such as polytetrafluoroethylene (PTFE) can be moulded by this process and further, structural modifications take place during the same.[15] Hence it was thought that similar technique may be used for processing PVDF with incorporation of oxide based fillers such as titanium dioxide, lead monoxide, etc. which are related to piezoelectric ceramic materials. Lead monoxide has also some interesting charge storage properties which were reported earlier[16,17] and may yield interesting results in combination with PVDF. The crystalline structure and phase transformation were investigated in these composite materials and the results of these are reported in the following.

EXPERIMENTAL

PVDF powder (Dyflor 2000) supplied by Dynamit Nobel Chemicals, West Germany, was dry blended with the filler powders, namely titanium dioxide (TiO_2, Rutile pigment grade) and lead monoxide (PbO, yellow, reagent grade) in an agate pestle mortar. Compositions ranging from zero to 25 percent by weight for fillers were used in these studies. The original particle size of the polymer and filler powder was determined from scanning electron microscopic observation and it was (average size) 40 μm, 2 μm and 4 μm for PVDF, TiO_2 and PbO respectively. The blended powder was compacted in a single end compaction die using a 10 ton hydraulic press at a pressure of 3000 kg/cm^2 and a dwell time of 30 seconds. Smooth, tough and well compacted discs (2 mm thick × 1.1 cm^2) could be produced by this method. These were then sintered in an electric oven at 180°C (just below the melting point of the polymer) for 15 minutes with the heating and cooling rate of about 100°C/hr without any additional pressure. The details of other experimental conditions were same as those reported earlier.[15]

The crystalline content of the P/M processed samples was determined from wide angle x-ray diffraction (WAXS) data obtained using Philips PW 1730 diffractometer with CuK_α target and β-Ni filter. In order to study the infra-red absorption, films were grown on smooth glass substrates (corning glass) by evaporation of the solution (5 percent by weight) of the polymer in pure dimethyl formamide at 80°C followed by thorough drying. The fillers were added to the solution when necessary in required quantities. The infra-red spectra were recorded on the free standing films with the help of Pye–Unichem spectrophotometer. For orientation studies, microfocus single crystal x-ray diffractometer CAD-4 Diffractis 586 was used with samples sectioned in appropriate configuration.

RESULTS AND DISCUSSION

The wide angle x-ray diffraction scan (WAXS) recorded in the 2 θ region of 14 to 40 degrees for samples containing PbO as the filler is shown in figure 1. The curve I represents the WAXS for pure PVDF powder, curve II that for moulded PVDF containing 0.5 wt.% PbO before sintering and curve III for the same moulded

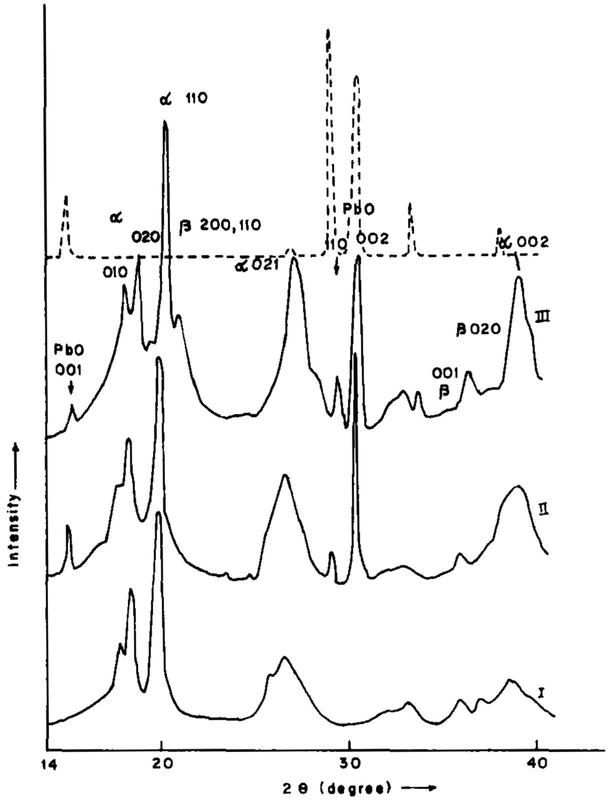

FIGURE 1 Wide angle X-ray diffraction pattern of PVDF powder (curve I), PVDF with PbO (0.5 wt %) before sintering (curve II) and after sintering (curve III). The dotted curve is for PbO powder alone.

sample after sintering. Since the crystalline structures of both the polymer and the filler are well established, the assignments of the various diffraction peaks can easily be carried out. The α form of PVDF, which is most readily obtained, has a monoclinic configuration with unit cell dimensions of $a = 4.96$ A°, $b = 9.64$ A° and $c = 4.62$ A° and angle $\beta = 90°$. The various diffraction peaks of curve I conform to this crystal structure and thus it may be concluded that the starting material consists mainly of α form of PVDF. The WAXS of the moulded unsintered specimen containing PbO revealed some additional sharp peaks at $2\,\theta$ values of 15, 29 and

30.5 degrees in the scanned region. These again could be assigned to the diffraction from the lead oxide particles containing orthorhombic crystals with unit cell dimensions[18] of $a = 5.89$ A°, $b =$ 4.775 A° and $c = 5.48$ A°, the indexing being indicated in the figure. It is however, interesting to note that the relative intensities of the various peaks, especially at 17.6 degrees corresponding to 100 reflection from PVDF and 29 and 30.5 degrees corresponding to 110, 002 reflections respectively from PbO are very much different in the moulded samples than that observed in powder/loose form (curve I and dotted curve). This suggests that there may be some form of orientation of the crystallites taking place during the high pressure moulding. This was confirmed by taking the microfocus transmitted x-ray diffraction photographs with beam normal and parallel to the mould surfaces in diametrically sectioned samples. The photographs being on instant polaroid paper, have not been reproduced here. However, semicircular arcs were clearly noticed in the reflections corresponding to PbO, clearly indicative of orientation of these crystallites.

Significant changes take place in the WAXS after sintering the specimen. As seen from curve III of Figure 1, not only the intensities of the various reflections similar as indicated in curve I and II change but also there are additional peaks at 2θ of 20.5, 35.4 and 36.5 degrees. There is also a slight shift in th position of the major peak occuring at 2θ of 19.9 degrees which may be due to the overlap of the reflection observed at 20.5 degrees. A careful analysis of the WAXS data revealed that these various new peaks could be assigned to the reflections (as shown in the figure) occuring in the β phase of PVDF with orthorhombic configuration having unit cell dimensions[2] of $a = 8.58$ A°, $b = 4.91$ A°, and $c = 2.56$ A°. The assignment of other peaks in the curve III was same as that for curves I and II namely the various reflections from α phase PVDF and orthorhombic PbO. However, it may be noticed that the intensities of some peaks such as $\alpha(100)$, $\alpha(021)$ of PVDF increase while the 001 and 002 peaks of PbO decrease after sintering suggesting that the crystallites may have moved from the oriented position to more random configuration after heat treatment. It may be mentioned here that with the increase of filler concentration up to 25 percent by weight, the general findings in the WAXS data were the same as mentioned above only with the difference that

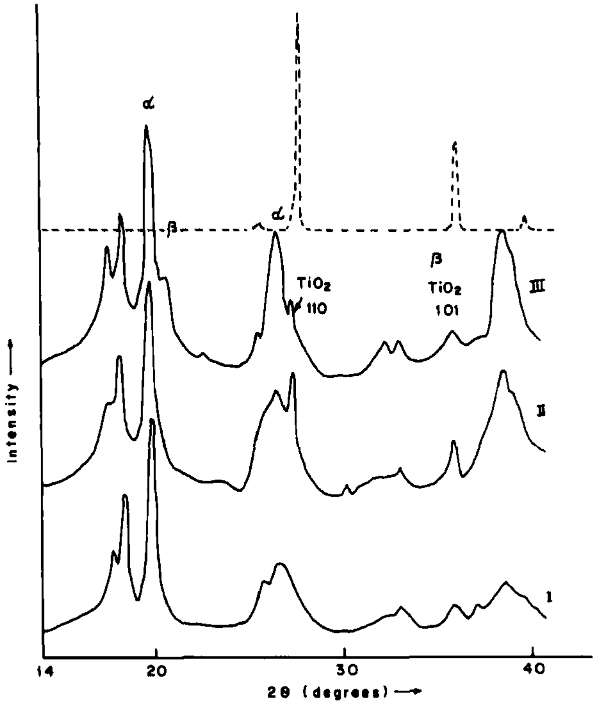

FIGURE 2 Wide angle X-ray diffraction of PVDF with TiO_2 (1.0 wt %) before sintering (curve II) and after sintering (curve III). The dotted curve is for TiO_2 alone and curve I for PVDF powder alone shown for comparison.

higher intensities were noted for reflections corresponding to PbO and an overall lowering of intensities was noted for reflections from PVDF , which is expected since the mass fractions of the components in the composite change accordingly.

Figure 2 shows the typical WAXS scan for PVDF–TiO_2 system. The curve I is for PVDF alone, curve II for PVDF with 1.0 wt.% TiO_2 before sintering and curve III is the same sample after sintering. In this case also it may be seen that the incorporation of TiO_2 and subsequent moulding gives rise to additional peaks (cf curve III) similar to those noted for PVDF–PbO system that is at 2θ of 20.5, 35.4 and 36.5 degrees. These again can be assigned to the reflections from the β phase of PVDF. Other new reflections at 27.6, 36 and 39.8 degrees correspond to 110, 101 and 200 reflection from TiO_2 (Rutile) having tetragonal configuration with unit cell dimensions[19] of $a = 4.594$ A° and $c = 2.958$ A°. Although the β phase formation takes place, it may be mentioned that for the same filler concentration (by weight), the intensities of the peaks corresponding to this phase are much smaller for PVDF–PbO system. Further there does not seem to be any significant difference in the relative peak heights of the reflections from TiO_2 in moulded form as compared with the loose form (dotted curve) suggesting that there is very little development of any orientation. This is in contrast to the pronounced changes in intensity and development of orientation in PbO containing PVDF observed earlier.

Since the major reflections from the polymeric phase in the WAXS scan do not overlap on those from the filler phase (another reason for choosing these fillers) in both the systems, one can easily estimate the crystallinity (C_i) of the polymeric phase in the moulded composites using conventional methods of analysing the WAXS for pure polymers.[20] The crystallinity was estimated from the areas under the major crystalline peaks (ϕ_c) and the amorphous halo (ϕ_a) which were obtained from the WAXS data in the 2θ range of 16 to 28 degrees after correction for background, Crompton scattering etc. Figure 3 shows the crystallinity of PVDF phase as a function of filler concentration for samples containing PbO (curve A) and TiO_2 (curve B) before sintering and those after sintering (curves A′ and B′ respectively). The dashed line at C_i value of 45 percent is for original polymer powder. The value of C_i in moulded polymer with zero filler content is lower, that is 35 percent when the same applied pressure as for other samples is used. It is interesting to see that the crystallinity increases slightly (but not above the original value) in unsintered samples with the increase of filler content up to three percent but with further filler loading, the crystallinity infact decreases considerably. This is true for both the fillers used. After the sintering process however, the crystallinity in samples with low filler content (below 2 percent) increases considerably exceeding even that of original powder. There is also an overall increase of crystallinity for all levels of filler loading in sintered samples. Further, this enhancement of crystallinity is more pronounced in the case of PbO filled PVDF than for TiO–PVDF system.

The various phenomena taking place in powder processing of semicrystalline polymers which lead to the decrease of crystallinity

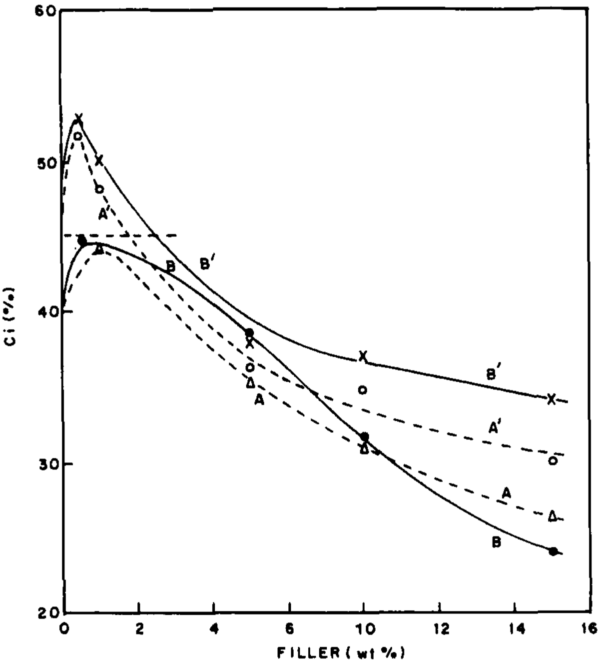

FIGURE 3 Variation of crystallinity in PVDF with filler concentration. Curves A and A' are for samples with PbO before and after sintering respectively. Curves B and B correspond to PVDF–TiO_2 system before and after sintering respectively.

have been described earlier by us elsewhere.[14,15] The essential features of the process are that during the single end compaction of the polymer under high pressure, the polymer particle initially get restacked, then deformed and ultimately at sufficiently high pressure made to cold flow mostly along the radial direction perpendicular to the applied pressure. Some local heating due to friction at contact points may also take place. All these processes contribute to increase in structural changes of the polymer in general and a decrease of crystallinity in particular. These observations have been found to be true in a number of polymers such a polyphenylene sulfide,[14] polytetrafluoroethylene,[15] Nylon 6 etc.[21] This is the reason for the decrease of crystallinity in the moulded PVDF at zero filler loading. In the filled case however, the situation is slightly different

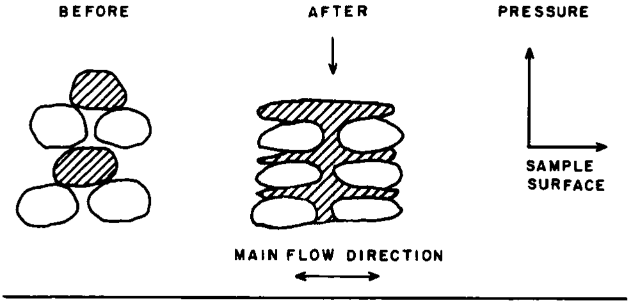

FIGURE 4 Schematic representation of high pressure powder compaction process of polymer containing filler. The shaded portion corresponds to polymer while the unshaded ones are filler particles.

because the presence of filler particles can cause shearing, nucleation, variation in pressure transfer characteristics etc. The compaction process of polymer powder containing filler is a complex phenomenon but for simplicity one can depict it is shown in Figure 4. The shaded portions are the polymer and unshaded portions the filler particles respectively. On application of pressure, the polymer being easily deformable material, is squeezed between the interparticulate gaps of the filler particles to form a continuous matrix. The movement and restacking of filler particles will also cause shear deformation of the polymer. These various processes being similar to those occuring in solid state extrusion through narrow die/nozzel or cold drawing, will cause similar structural changes in the polymeric solid. In particular case of PVDF such processes are known to give rise to the formation of β phase crystals.[5,22,23] In the present case the percentage of β phase content in the samples was estimated from the ratio of intensities of the major peaks of α phase ($2\theta = 19.9$ degrees) and β phase ($2\theta = 20.5$ degrees). Figure 5 shows the amount of β phase present in these specimen as a function of filler concentration. Curves A and B are for the unsintered samples containing PbO and TiO_2 repectively, whereas the curves A' and B' are for unsintered samples containing same respective fillers. It is seen that in unsintered case, the amount of β phase gradually increases with decrease of filler content and tends to a limiting value of about 20 percent for TiO_2 and 30 percent for

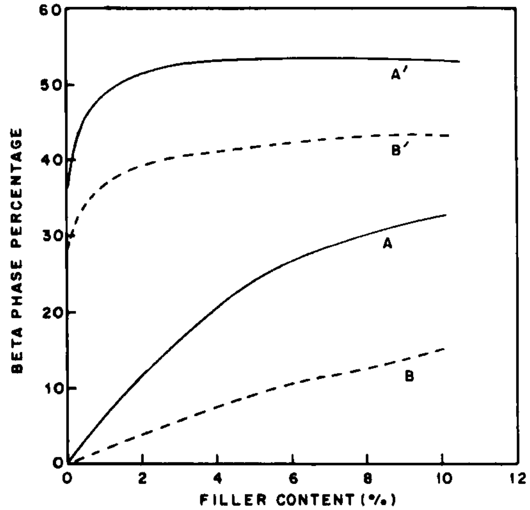

FIGURE 5 The variation of beta phase content in powder processed PVDF with filler content. Curves A and A' are for samples with PbO before and after sintering respectively while curves *B* and *B* are the respective curves for PVDF–TiO_2 system.

PbO. For the sintered samples the limiting value of β phase percentage is attained even at small amount of filler and this limiting value is much higher for PbO (50%) than for TiO_2 as the filler. Thus, in the sintered case the increase of β phase is more favourable especially with PbO as the filler. These findings suggest that apart from the cold drawing/extension which may be taking place during compaction, the recrystallization process during sintering in presence of fillers also plays an important role in governing the crystal phase predominant in the final mould.

Now, PVDF has very interesting polymorphism. It is known to crystallize in four forms α, β, γ and δ, also designated as form II, I, III and IV respectively. The α phase is most commonly occurring one, obtained when crystallization takes place from melt and solution.[2] The β is formed when the polymer film, rod or sheet is drawn/extended uniaxially or biaxially or when crystallization is carried out under high pressure.[23,24] The γ phase obtained by crystallization of some typical solutions.[25,26] The fourth phase (δ) has been found when the α phase is subjected to high electric field.[27] In the recent investigations reported by Gelfandbein and Perlman,[28] it was found that the substrate material plays an important role in deciding the crystalline phase of the solution grown films. These authors have suggested that lattice mismatch may also be an important factor for this behaviour. The expitaxial crystallization of PVDF on (001) surface of potassium bromide can also produce β phase.[29] These observations together with the present findings seem to suggest that nucleation phenomena assisted by the additives may also be important for the enhancement of β phase of PVDF. It is well known that fine dispersion of small particles in low concentration (<1 percent) act as one of the best nucleating agents in crystallization of polymers.[30] The high crystallinity in sintered samples at low concentration of filler (particle size 2–4 μm) also suggests the same. Further, if one compares the lattice parameters of orthorhonbic PbO ($a = 5.89$, $b = 4.775$, $c = 5.48$ A°) with those of β phase ($a = 8.58$ A°, $b = 4.91$ and $c = 2.56$ A°) it can be seen that there is a close fit of the b-axes and 2c (β) with c (PbO) axes, that is, the lattice mismatch is less than six percent. Additionally, there seems to be a strong interaction between the polymer and filler particle for PbO as evidenced by the development of orientation. In the case of TiO_2 on the other hand, the lattice mismatch between β phase orthorhombic PVDF crystal and TiO_2 (Rutile) tetragonal one with $a = 4.594$ and $c = 2.958$ is seven percent for b-axis and more than sixteen percent for c-axes. Thus the nucleation of the β phase is likely to be more favourable than the α phase by the PbO particles. The fact that not only the crystallinity was found to be high but also the β phase content was also large in PVDF–PbO system clearly are in support of these remarks.

In order to further confirm the importance of nucleation behaviour in determining the phase in PVDF, infra-red absorption was studied in this films grown on glass plate from dimethylformamide solution containing small amount of PbO particles (1% of polymer). Figure 6 shows the infra-red transmission spectra in the region 1200–200 cm^{-1} for as grown films containing PbO curve A, pure powder polymer in nujol mull (curve B) and the films containing PbO after heat treatment at 180°C (curve C) to simulate earlier conditions. The various phases of PVDF have characteristic absorption bands in this region of infra-red.[31,32] It can be clearly seen from Figure 6 that the absorption bands characteristic of α

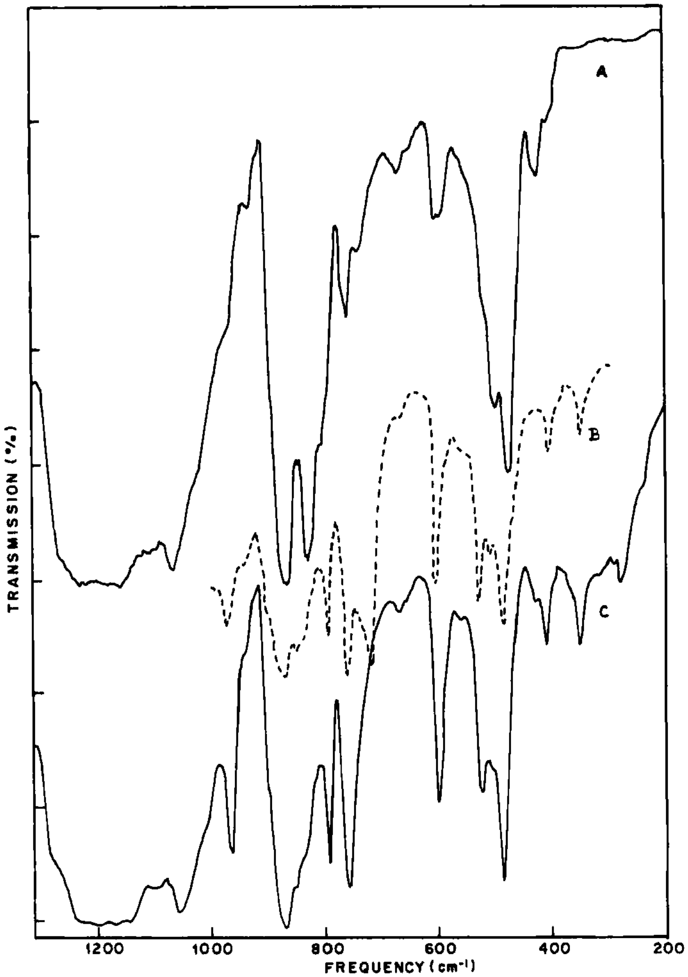

FIGURE 6 The infrared transmission spectra for PVDF film containing 1.0 wt % PbO grown from solution; curve *A* is for sample before heat treatment, curve *C* is for that after heat treatment while the dotted curve (*B*) is for original PVDF powder in nujol mull.

phase namely 976 cm^{-1}, 766 cm^{-1}, 612 cm^{-1} and 488 cm^{-1} have decreased in intensity whilst those of β phase namly 842 cm^{-1}, 512 cm^{-1} and 446 cm^{-1} have increased in intensity in the case of PVDF films containing PbO. The pure polymer shows a spectrum characteristic high α phase content. It may be mentioned that the heat treatment of the pure polymer without application of pressure or electric field close to melting point generally causes all phases to transform to α phase.[33,34] However, it is interesting to note in the present case that even when the films have been heated to high temperature and then cooled, retain the β-phase. This again is in support of the above hypothesis based on nucleation phenomena.

Thus, from the above discussions it appears that there are two main sources for the increase of β phase in powder processing of PVDF containing fine particulate fillers. These are (a) the cold flow and shearing of the polymer between the filler particles during compaction and (b) nucleation of the b phase during sintering and recrystallization of the polymer by the appropriate crystals the filler material. The first process can take place in majority of fillers, so long as they are hard and do not deform during high pressure moulding. The second process however, is restricted to some special fillers having appropriate dimensions and crystal lattice parameters close to that of the polymer under consideration. The latter process is also responsible for the high crystallinity especially at low filler content. The process (a) on the other hand is also a cause for decrease in overall crystallinity at high filler loading under the same moulding conditions because of the increase of pressure transfer and energy dessipation to the polymer with increasing amount of filler, especially during high pressure compaction. These various factors have to be taken into consideration for obtaining a composite of PVDF containing high amount of β phase as well as crystallinity.

References

1. N. Murayama and H. Obara, *Japan. J. Appl. Phys.* **22,** Suppl. 22, 3 (1983).
2. A. J. Lovinger, *Developments in Crystalline Polymers*–1 Ed. D. C. Bassett, Applied Science Publishers, London, 1982, p. 195.
3. J. Wada, *Electronic Properties of Polymers,* Ed. J. Mort and G. Pfister, John Wiley, New York, 1982, pp. 109.
4. A. J. Lovinger, *Science,* **200,** 115 (1983).
5. A. Richardson, P. S. Hope and I. M. Ward, *J. Poly. Sci. Polym. Phys. Ed.* **21,** 2525 (1983).

6. S. Tasaka, J. Niki, T. Ojio and S. Miyata, *Polym. J.* **16,** 41 (1984).
7. Y. Wang, M. Cakmak and J. L. White, *J. Appl. Polym. Sci.* **30,** 2615 (1985).
8. K. Sakaoku, T. Itoh and S. Kimimura, *Japan. J. Appl. Phys.* Pt. 2, **24,** 175 (1985).
9. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro, *Polym. Bull.* **10,** 464 (1983).
10. B. Jaffe W. R. Cooke and H. Jaffe, *Piezoelectric Ceramics,* Academic Press, New York (1971).
11. H. Banno, *Ferroelectrics* **50,** 3 (1983).
12. N. M. Shorrocks, M. E. Brown, R. W. Whatmore and F. W. Ainger, *Ferroelectrics,* **54,** 555 (1984).
13. W. D. Kingery, H. D. Brown and D. R. Ulhman, *Introduction to Ceramics,* John Wiley, New York, 1976.
14. S. Radhakrishnan and V. M. Nadkarni, *Polym. Eng. Sci.* **24,** 1383 (1984).
15. S. Radhakrishnan and V. M. Nadkarni, *Int. J. Polym. Mater.* **11,** (1985).
16. S. Radhakrishnan, M. N. Kamalaseman and P. C. Mehendru *J. Mater. Sci.* **18,** 1912 (1983).
17. S. Radhakrishnan, M. N. Kamalasanan and P. C. Mehendru *Materials Lett.* **1,** 11 (1982).
18. R. W. G. Wykoff, *Crystal structures,* vol. 1, Interscience Publishers, New York 1963, pp. 137.
19. R. W. G. Wyckoff,
20. L. E. Alexander, '*X-ray Diffraction Methods in Polymer Science*', John Wiley, New York (1969).
21. S. Radhakrishnan, *Agnew Makromol. Chem.* **141,** 49 (1986).
22. J. Humpherys, I. M. Ward, E. L. Nix, J. C. McGarth and T. Emi, *J. Appl. Polym. Sci.* **30,** 4069 (1985).
23. K. Matsushige, K. Nagata, S. Imada and T. Takemura, *Polymer,* **21,** 1391 (1980).
24. K. Matsushige and T. Takemura, *J. Cryst. Growth* **48,** 343 (1980).
25. A. J. Lovinger and H. D. Keith, *Macromolecules,* **12,** 919 (1979).
26. D. T. Grubb, P. Cebe, K. W. Choi, *Ferroelectrics* **57,** 121 (1984).
27. D. Naegele, D. Yoon and M. G. Broadhurst, *Macromolecules,* **11,** 1297 (1978).
28. V. Gelfandbein and M. M. Perlman, *J. Mater. Sci.* **18,** 3138 (1983).
29. A. J. Lovinger, Polymer **22,** 412 (1981).
30. B. Wunderlich, *Macromolecular Physics,* vol. 2, academic Press, New York, 1976, pp. 49.
31. K. Tashiro, M. Kobayashi and H. Tadokoro, *Macromolecular* **14,** 1757 (1981).
32. M. A. Bachman, W. L. Gordon, J. L. Koenig and J. B. Lando, *J. Appl. Phys.* **50,** 6106 (1979).
33. K. Tashiro, K. Takauo, M. Kobayashi, Y. Chatani and H. Tadokoro, *Polymer* **24,** 199 (1983).
34. G. T. Davis, T. Furukawa, A. J. Lovinger and M. G. Broadhurst, *Macromolecules,* **15,** 329 (1982).