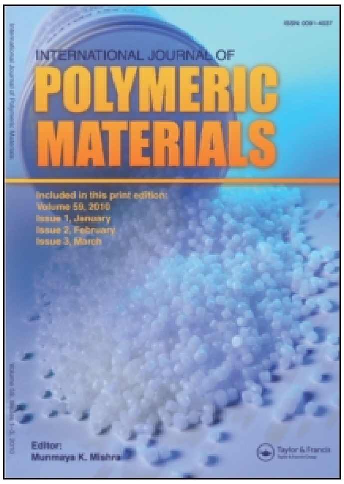

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Modification of Crystallinity and Structure in Powder Processing of Polytetra Fluoroethylene

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The modification of structure, crystallinity and orientation have been studied in powder processed polytetrafluoroethylene by various techniques. It was found that crystallinity (as determined from regression curve analysis) in unsintered samples decreased with increase of compaction pressure while in sintered specimen it increased with increase of pressure. The crystallinity was also found to vary inversely with logarithm of cooling rate. Microfocus X-ray diffraction revealed the orientation of *c*-axis lying preferentially in the plane perpendicular to applied pressure. There was slight variation in the lattice dimension especially the *c*-axis in completely sintered specimen. The infrared studies showed the presence of some of the bands depended upon the molding/sintering conditions. These various findings have been explained on the basis of compaction and recrystallization behaviour under constrained conditions.

1. INTRODUCTION

Although polytetrafluoroethylene (PTFE) is usually classified as a thermoplastic, it cannot be shaped into desired geometry by conventional melt processing techniques. This is mainly because the polymer remains in semi-solid gel state even at high temperatures

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(>370°C)[1] and thus goes beyond the scope of common molding machinery. Non-conventional techniques such as powder metallurgical (P/M) processing, flame spray, ram extrusion etc. have to be resorted to for fabricating objects from PTFE.[2,3]

In the P/M processing, the polymer is first compacted under high pressure at room temperature and preformed in green molds. These are then sintered at high temperature close to the melting point when large densification takes place and the final product obtained. The importance of this technique for processing polymers has only recently been realised and found application also for other polymers such as ultra high molecular weight polyethylene (UH MW-PE) polyphenylene sulfide (PPS) etc.[4,5] Inspite of this, very few studies have been reported on the fundamental understanding of the process, especially on the various structural modifications taking place at different stages of processing. It is only recently that the compaction behaviour of polymeric powders under high pressure conditions have been given serious considerations. Crawford *et al.*[6] have studied the density, microhardness and pressure distribution during solid phase compaction. Umeya and Hara[7] have investigated the rheological properties of compacted polystyrene powders. The powder processing of UHMW-PE was studied by Haldin and Kamal.[8]

In our recent investigations on powder processing of PPS[9] and its blends,[10] we found that the surface structure and crystallinity were greatly modified during the high pressure compaction and sintering steps. Even though the P/M technique is used routinely for processing PTFE, the structural modifications have not been investigated earlier.

The various parameters such as preforming pressure, sintering temperature, dwell time etc. are mostly optimised on the basis of the physical appearance and properties of the final product. However, based on our earlier studies, many changes in the structure, crystallinity, orientation or morphology are expected to take place at various stages of processing. The results of our investigations on the structure development in powder processing of PTFE are reported in the present paper.

II. EXPERIMENTAL

PTFE powder (Teflon) supplied by Coleman Asbestos Co. Ltd. India, was compressed in a single end compaction die having ultrasmooth surface (Perkin–Elmer Cat. No. 186–0025) using a 10 ton hydraulic press at various pressures ranging from 200 to 5000 kg/cm^2. Weighed amount of powder (0.2 gms) was charged into the die, the pressure raised to the final value within 3 sec, maintained constant for 30 seconds (dwell time) and released to ambient within a second, thus completing the compaction cycle. The cylindrical discs (2 mm thick $\times$ 1.1 cm^2 area) thus preformed were removed and passed through the thermal treatment (sintering) cycle which consisted of the following steps. The sample was placed in a ventilated furnace and the temperature was raised at the rate of 50°C/hr up to 310°C at which it was held for 20 mins. Temperature was then again increased at the same rate to ultimate value (between 350–370°C) and held constant for 1/2 hrs. It was then gradually decreased at the rate of 50°C/hr to room temperature ($\simeq$ 25°C). In some cases, the samples were directly removed from the furnace from ultimate temperature and allowed to self cool on a steel plate (rate $\simeq$ 50°/min) or plunged into water for fast quenching.

The crystalline content in the P/M processed samples was determined from wide angle x-ray diffraction (WAXS) data obtained by using Philips PW 1730 diffractometer with Cu K-target and β-Ni filter. The infra-red absorption spectra in the range of 200–4000 cm^{-1} were recorded by means of Perkin–Elmer 283B Spectrophotometer using very thin free standing specimen (thickness $\sim -10\ \mu$) processed in the same manner as above. For orientation studies, use was made of microfocus single crystal X-ray diffraction unit CAD-4 Diffractis 586, with samples sectioned in appropriate configuration.

III. RESULTS AND DISCUSSION

PTFE is known to exist in hexagonal form in the temperature range of 19°–30°C while in other phases namely trilinic below 19°C and pseudohexagonal above 30°C.[11] Since all the measurements were carried out in samples held at room temperature ($\simeq$25°C) one may restrict to a single phase for the present studies.

In order to investigate the changes in crystalline structure and content in the P/M processed samples, WAXS scans were recorded in the 2θ range of 10–70°. The pattern consisted of very strong peak at $2\theta \simeq 18°$ which had an intensity five times or more than the other

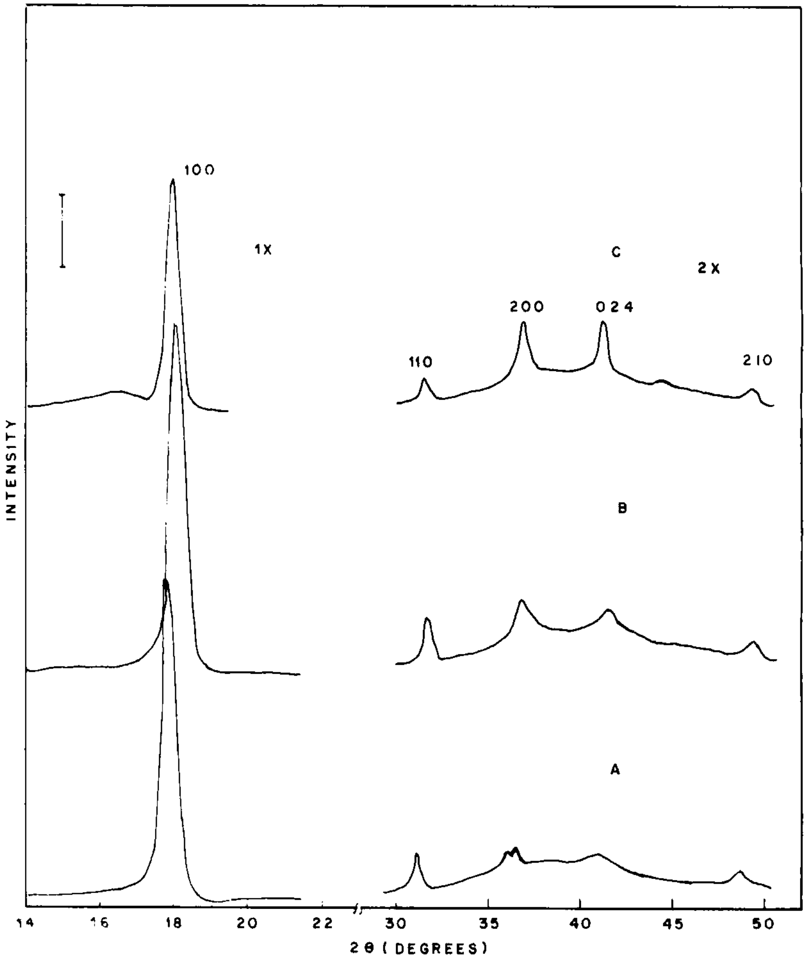

FIGURE 1 X-ray diffractometer scans for PTFE samples molded at 3000 kg/cm^2. Curve A is for unsintered samples, B for heat treated at 310°C and C for samples passed through complete sintering cycle (360°C).

peaks and hence in order to note small differences, higher sensitivity was chosen for the range of 25–70 degrees. Figure 1 shows the WAXS scan obtained for samples moulded at 3000 kg/cm^2. The curves, "A" is for unsintered sample, "B" for samples heat treated up to 310°C and "C" for samples passed through complete sintering cycle (360°C).

It is seen by comparison of A with B and C that although the general features of the patterns are similar, there is a slight shift in the peak position for heated samples. A careful analysis of the WAXS data was carried out for the assignments of various reflections. It was found, that the pattern for unsintered samples conformed to the reflections from a hexagonal lattice with unit cell dimensions of $a = 5.66$ Å and $c = 19.5$ Å. On the other hand, the sintered ones (or heat treated > 310°C) had also a hexagonal type structure but with lattice parameters of $a = 5.61$ A° and $c = 16.8$ A°. The various interplanar spacings observed and calculated are shown in Table I for both cases. The experiment was repeated several times and same results were obtained thus reconfirming the structures indicated at each stage. The two types of hexagonal lattices have been reported for PTFE (drawn samples) in literature by different authors.[12,13] However, the exact origin for these differences is not described. Further, the history of the samples for which these have been recorded is also not reported. The difference in lattice parameters in the same structure of the polymer when studied under different sample configuration has been noted earlier. In polyethylene terephthalate for example,[14] differences are found in the XRD patterns when studied in film or fibre form. Both have triclinic type of structure but the lattice parameters are apparently different. One cannot ascribe this to new phase formation or mere refinement in measurements. PTFE has a high pressure phase with

TABLE I

WAXS data on powder processed PTFE

Unsintered (3000 *kg/cm*²)					*Sintered* (*above* 320°*C*)				
2θ	I	d(A°)	h kl	d_{calc}(A°)	2θ	I	d(A°)	h kl	d_{calc}(A°)
17.7	VVS	5.018	100	4.9	18.2	VVS	4.868	100	4.858
31.3	m	2.854	110	2.83	31.8	m	2.81	110	2.805
36.4	ms	2.465	200	2.45	37	ms	2.426	200	2.429
37	m	2.426	021	2.43	41.5	m	2.173	024	2.103
41	w	2.198	024	2.18	44.5	w	2.033	018	1.927
48.8	w	1.864	210	1.85	49.5	w	1.839	210	1.836
56	w	1.644	300	1.633	57.5	w	1.600	300	1.619
65.8	w	1.417	220	1.415	66.2	w	1.409	220	1.402

* Calculated with hexagonal lattice $a = 5.66$, $C = 19.5$

† Calculated with hexagonal lattice: $a = 5.61$, $C = 16.8$

orthorhombic configuration (polyethylene like)[15] but since there were no new reflections which could be ascribed to this type of structure in the present case, one has to rule out the possibility of this phase occurring in the sample.

Another note worthy difference is seen in the variation of intensities of different peaks with thermal treatment. By comparing A and C of Figure 1, it can be seen that whereas the intensity of 100 reflection decreases, the peaks corresponding to 021/200 and 024 planes (at 2θ of 37° and 41° respectively) increase in height when the sintering process is completed.

The 100 reflection is as such unusually strong in unsintered samples, overshadowing the amorphous halo, which on the other hand can be distinctly seen in the sintered specimens. It thus appears that some form of orientation (axial or planar) is induced during the compaction or sintering steps, in addition to the formation of amorphous phase. The effect of cooling rate on the WAXS scan is shown in Figure 2, where A, B and C correspond to a cooling rate of 300°/sec. (fast quench), 50°C/min (self cool) and 50°/hr (oven control cooling) respectively. It is seen that the various peak positions are same in all cases. However, the intensities of the reflections especially 100, 021/200 and 024 are increasing with decrease of cooling rate suggesting that the crystallinity is enhanced as the samples are cooled slowly. This was true irrespective of the value of final temperature (320°C) or dwell time used in the sintering process.

In order to determine the crystallinity from the WAXS data, there are several methods available for analysis.[16] Amongst others, C_i can be determined from the ratio of the areas under main crystalline peaks (θ_c) to the area of the amorphous halo (ϕ_a) as

$$C_i = \phi_c/(\phi_c + \phi_a) \tag{1}$$

On the other hand, in regression curve analysis a series of samples with different values of crystallinity are studied and the plot of ϕ_a vs ϕ_c (equivalent to I_a *vs* I_c) is made to give a regression curve. The crystallinity index is determined as

$$C_i = \left[1 + \frac{Q}{P}\left(\frac{\phi_a}{\phi_c}\right)\right]^{-1} \tag{2}$$

where P and Q are constants determined from the regression curve

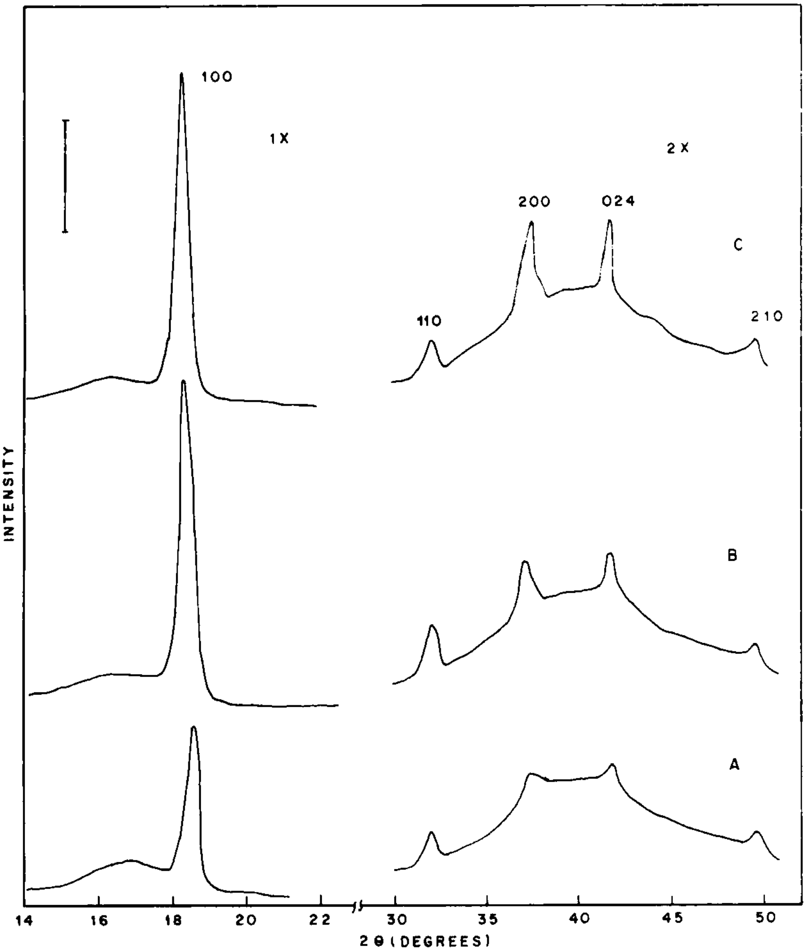

FIGURE 2 Effect of cooling rate on the WAXS scans of PTFE. Curves A, B and C correspond to cooling rate of 300°C/sec, 50°C/min and 50°C/hr respectively.

as $Q = 1/I_a$ (100) and $P = 1/I_c$ (100), that is, the points of 100 percent amorphous or crystalline contents. Such analysis was carried out in the present case by obtaining samples prepared with different processing conditions of compaction pressure, sintering temperature or cooling rate. The X-ray data was corrected for background, Compton scattering geometrical factors etc. and ϕ_a and ϕ_c were

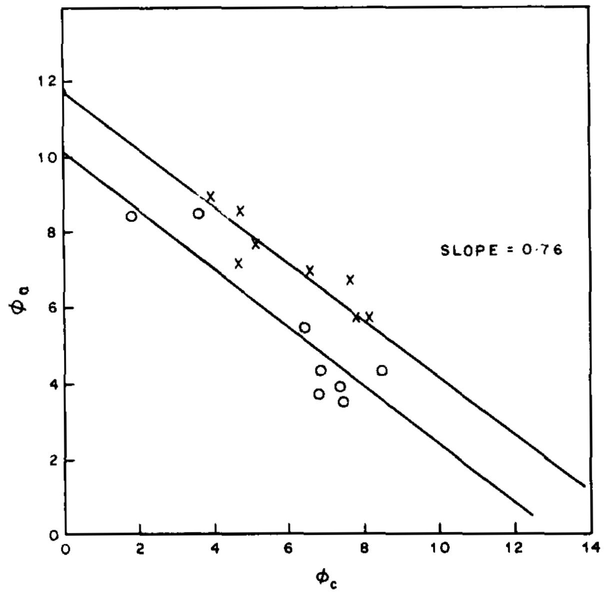

FIGURE 3 Regression curve for the determination of crystallinity in PTFE.

obtained using 2θ range of 10–70°. Figure 3 shows the regression curve obtained for two series of samples (heat treated or untreated) and it is seen that the plot of ϕ_a and ϕ_c is a linear graph with slope of 0.74 (or $Q/P = 1.4$). The crystallinity is hence given by

$$C_i = [1 + 1.4(\phi_a/\phi_c)]^{-1} \tag{3}$$

rather than equation (1) where essentially P/Q is assumed to be unity. This can be easily understood in terms of the differences in the scattering co-efficients for the amorphous and crystalline components of the polymer i.e. $P \neq Q$ for the same mass.

The crystallinities (C_i) in various samples prepared at different preforming pressures or at different cooling rates was determined using the above relation (3). Figure 4 shows the C_i values for green moulds, (C_g), and the ultimate crystallinity (C_u) in samples sintered under same conditions (360°C, 50°/min) but prepared at different preforming pressures. The 2θ range of 10–70 degrees was used for these calculations. If one takes the intensity of 100 reflection alone (curve I Figure 4) or only this peak for calculation of crystallinity

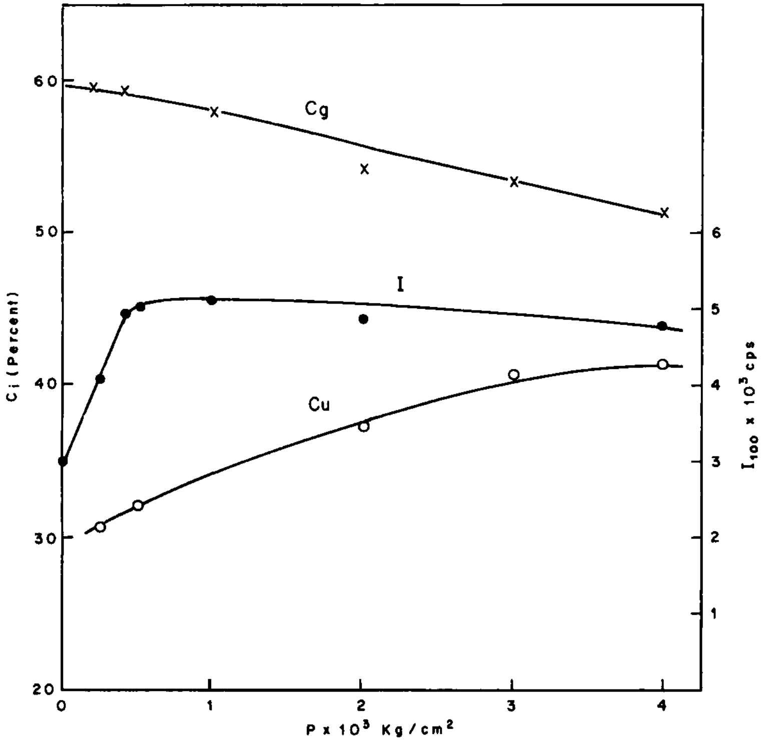

FIGURE 4 The variation of crystallinity with molding pressure. C_g corresponds to unsintered molds, and C_u represents sintered molds with same cooling rate. The curve I corresponds to the intensity of the main (100 reflection) peak.

then it would appear that C_i increases initially up to a pressure of 1000 kg/cm^2 above which it remains more or less constant. However, as indicated in Figures 1 and 2 there are changes taking place in the higher 2θ range (25–70°) which need to be considered while estimating the crystallinity. C_g and C_u were estimated keeping these points in view.

It is seen that C_g decreases slightly from 61% to 53% with increase of preforming pressure but C_u on the other hand increases from 32% to 44% when the preforming pressure is increased from 200 kg/cm^2 to 4000 kg/cm^2. The decrease in crystallinity with increase of pressure in the green molds is similar to that observed by us in the polyphenylene sulfide[9] which also has a high glass transition temperature. The compaction was carried out at 25°C, much below the glass transition temperature (127°C) of the polymer. Hence, similar types of mechanisms may be involved for attributing the changes in crystallinity. These consist of particle deformation, plastic flow and increase of amorphous phase during recrystallization. During the process of single end compaction, as the punch presses down, restacking of lightly held particles takes place. After the initial rearrangement a stage is reached when the punch cannot move further without causing particle deformation. Mostly the deformation occurs at the contact points due to increasing compressive force and build up of internal pressure. Finally, the elastic limit is reached and plastic flow begins. There could also be local heating and softening taking place at the contact points. PTFE as such is known to flow even at low deformation pressures.

The crystallinity of the final product (C_u) after complete sintering however depends also upon the thermal treatment given. The sintering was carried out at the same final temperature (360°C), dwell time ($\frac{1}{2}$ hr) and cooling rate (50°/hr) in all cases. One may hence understand the increase of crystallinity with increase of compaction pressure as follows. The polymer after compaction or preforming process, is in a highly strained state and the amount of internal stress depends upon the pressure used during the compaction step.

These stresses may be relieved during the thermal treatment, however, depending upon the degree of densification, the rearrangement of molecules and/or crystallites is restricted especially for high pressure molded samples, which have higher degree of orientation than low pressure molded samples. Strain induced crystallization can also take place in the pre-oriented specimen.[17] If one considers the net drop in crystallinity after curing, it is seen from Figure 4, that this drop is less for high pressure molded samples than the low pressure ones. This is mainly due to the restrictive mobility of the chains/crystallites mentioned above. It is interesting to note that these changes occur mainly for samples processed through the complete curing cycle. In the samples heat treated only up to 310°C, there was practically no change in crystallinity though the lattice dimensions altered slightly as indicated in the early discussions.

The effect of cooling rate on the final crystallinity of the sintered

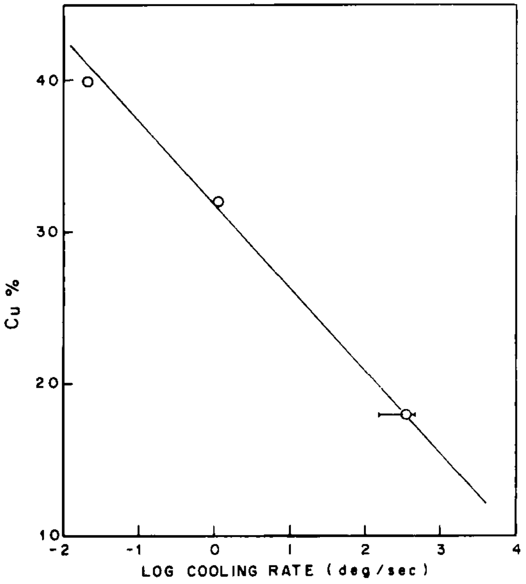

FIGURE 5 Effect of cooling rate on ultimate crystallinity in sintered specimen. Same molding pressure (3000 kg/cm^2) used for all.

samples is shown in Figure 5 as a plot of C_u vs logarithm of cooling rate. Same compaction pressure (3000 kg/cm^2), ultimate temperature (360°C) and heating rate (50°C/hr) were used for all cases. Error bars are shown for high cooling rates especially when samples are quenched in cold water since it was difficult to monitor the exact sample temperature due to changes taking place within a few seconds. For slower cooling rates however, the rate could be monitored accurately. It is seen from the figure that the graph is a linear one with a negative slope suggesting that very slow cooling rate, can yield highly crystalline products. Further it can be noted that C_u depends much more critically on the cooling rate than on other processing parameters. It is to be noted here that the cooling rates recommended for PTFE processing are indeed in the range of 10°C to 20°C/hour in order to facilitate high crystallinity in the end product.

In order to investigate the presence of any orientation microfocus X-ray diffraction stationary patterns (photographed on flat plate)

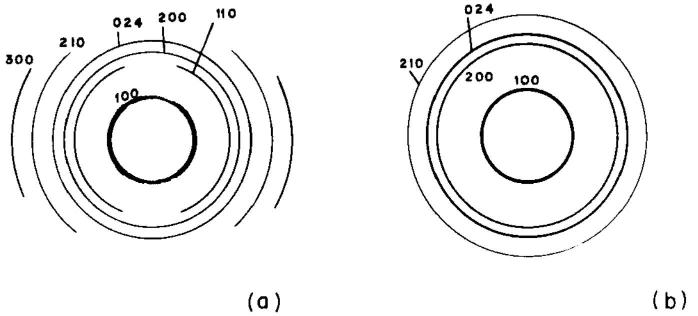

FIGURE 6 Microfocus X-ray diffraction stationary photographs for P/M processed PTFE. a. beam direction parallel to mold surface. b. beam direction normal to mold surface.

were taken on appropriate sections of the samples *P/M* processed in the above manner. Figure 6(a) shows the typical pattern (transmission) obtained with beam direction parallel to mold surface and Figure 6(b) is the type of photograph obtained for beam direction normal to the mold surface. The sample was sectioned diametrically 2 mm wide at the center. It is clearly seen that in addition to the normal polycrystalline ring type pattern, a few arcs are present in some reflections (100, 200) and also the number of reflections recorded depends on the beam direction/sample geometry, indicating the presence of preferred orientation of crystallites in the specimen. From the direction of the beam and sample configuration it could be deduced that the *c*-axis or the long axis lies preferrably in the plane parallel to the mold surface. i.e. perpendicular to the direction of the applied pressure. Thus it seems that the polymer chains (which are parallel to *c*-axis) are positioned along the diameter of the sample. These findings together with the unusually strong intensities noted for some of the reflections in the WAXS data, clearly support the suggestion of orientation induced in the powder processing of PTFE.

The infrared studies were carried out on free standing films ($<10\ \mu$) molded and sintered in the same manner as bulk samples. Major changes in the spectra were observed in the spectral region of 1000–200 cm^{-1}. Figure 7 shows the transmission spectra of unsintered films molded at low pressure (L), high pressure (H) and sintered specimen (cooling rate 60°/hr). It is seen that prominent

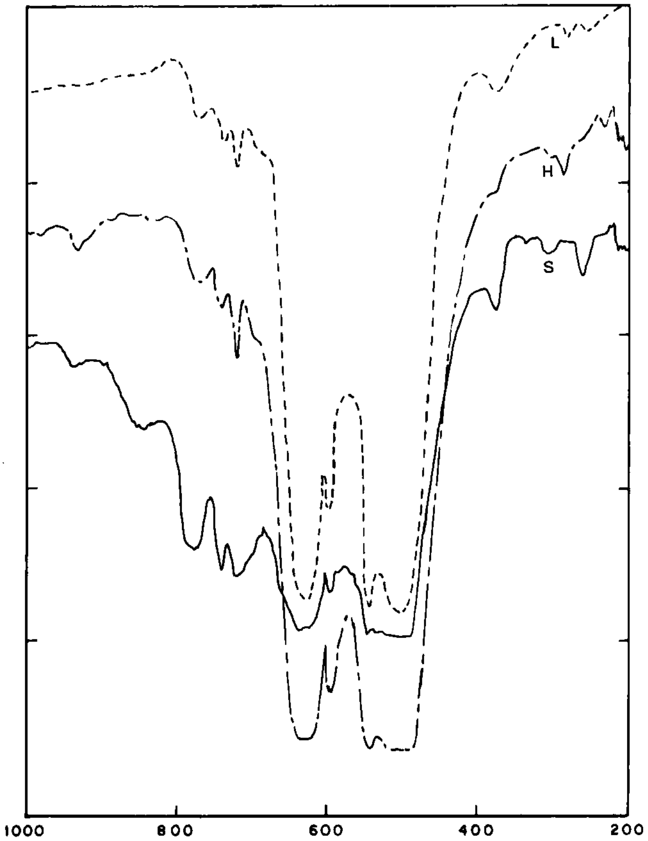

FIGURE 7 Transmission infrared absorption spectra of PTFE films. L corresponds to low pressure (500 kg/cm^2) H corresponds to high pressure (3000 kg/cm^2) unsintered and S corresponds to sintered (360°C) samples.

peaks appear at 850 cm^{-1}, 700 cm^{-1}, 375 cm^{-1}, and 260 cm^{-1} for the sintered samples while these are not present in the unsintered specimen. Also the relative intensities of the other peaks such as 740 cm^{-1}, 630 cm^{-1} and 595 cm^{-1} bands are considerably changed by high pressure compaction and sintering.

A few studies on the infrared absorption of PTFE have been reported in the past. Long and Krimm[18] have recorded the spectrum using commercial films of various thicknesses and oriented by drawing. They have noted that the bands in 900 cm^{-1} to 700 cm^{-1} region are sensitive to the polarization of radiation, that is, whether parallel or perpendicular to the draw direction. Moynihan[19] has reported the spectrum of microtomed specimen from commercial molded bars and attributed the bands in the region of 850 cm^{-1} 703 cm^{-1} to amorphous part of the polymer. Haslam et al[20] also report similar type of spectrum for microtomed films. Jackobson[21] has investigated the infrared absorption in PTFE at high pressure using diamond anvil cell and noted the loss of series of bands between 800 cm^{-1} – 700 cm^{-1} and also bands at 620 cm^{-1}, 550 cm^{-1} and 1260 cm^{-1} (shoulder) at high pressure. This was attributed by the author to phase change. In our case however the compaction was carried out at high pressure but the infrared studies were made at normal conditions. Nonetheless, it is seen that there are practically no prominent bands noted in this region for unsintered specimen (especially the low pressure molded ones). Unless the high pressure phase gets locked in and continues to remain even at normal working conditions, the changes observed cannot be attributed to new phase formation. Further, the high pressure phase being orthorhombic, it will give rise to new reflections in WAX pattern which were not detected in the present case. Thus one may attribute these bands to contribution from amorphous phase and/or orientation induced during high pressure compaction. Krimm[22] has given a detailed discussion on the assignment of infrared bands of PTFE and shown that the absorption at 638 cm^{-1} and 625 cm^{-1} is sensitive to the twist in the backbone of polymer chain. Also their occurrence depends upon whether 15 monomer units or 13 monomer units are included in the repeat distance.

Considering the fact that there is slight splitting in the band at 630 cm^{-1} and also there is change in the *c*-axis dimension (from WAXS studies), together with the evidence of presence of orientation, it seems quite likely that the bands are sensitive to the macroscopic stretching of polymer chain. Clark and Muus[22] have indicated that at the crystalline transition points of 19°C and 30°C, untwisting of polymer chain takes place. In the hexagonal lattice, the motion of the molecular chain is restricted to small angle oscillations but at the second crystalline transition (30°C) the restraint on the molecular conformation imposed by the lattice is lost.

This may lead to increase in the number of modes and hence the presence of new bands in sintered specimen.

IV. SUMMARY AND CONCLUSIONS

The modification of structure, crystallinity and orientation have been studied in powder processed polytetrafluoro ethylene (PTFE) by various techniques. It was found that although the crystal structure is similar in high pressure compacted unsintered samples to those in heat treated sintered ones, the lattice constants, especially the c-axis of the hexagonal unit cell are different in the two cases. The crystallinity as determined from the areas of amorphous halo and crystalline peaks using the relation $C_i = [1 + 1.4(\phi_a/\phi_c)]^{-1}$ was found to be dependent on processing conditions. The C_i in unsintered samples decreased with increase of compaction pressure while in samples sintered under same conditions C_i increased with increase of pressure. The crystallinity was found to vary inversely with logarithm of cooling rate i.e. very slow cooling rates yielded samples with highest crystallinity. The microfocus X-ray diffraction studies revealed the presence of orientation of the lattice with c-axis lying preferentially in the plane perpendicular to the direction of applied pressure.

The infrared studies on thin specimen revealed the occurrence of new peaks in sintered samples in the region of 1000 cm^{-1} to 600 cm^{-1} which were attributed to the formation of amorphous phase as well as some orientation/deformation of the lattice.

It may be of interest to note here that high pressure compaction modifies the crystallinity of the polymer in such a way that same value of C_i may be achieved in sintered samples by increase of pressure. This can be deduced by extrapolating the curve C_g and C_u of Figure 4 towards high pressure region. Thus one may possibly make a final product by applying very high pressure compaction alone.

Some of the earlier findings on the dependence of the properties such as tensile strength, density, mold shrinkage etc. on preforming pressure may now be understood in the light of present findings. Since for the same sintering conditions (temperature, rate of cooling etc.) higher preforming pressure gives rise to higher crystallinity and orientation in the sample, tensile strength and environmental stress crack resistance (ESCR) would be expected to increase and the mold shrinkage would decrease with increase of preforming pressure. This indeed has been found to be true for PTFE. Ref. 23, 24.

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