Pole Figure Analysis of Poly(vinyl Chloride) Samples: A First Approximation

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Synopsis

Pole figure analysis has been applied to different types of poly(vinyl chloride) (PVC) samples. Drawn samples of formulations containing increasing amounts of plasticizer show that the presence of plasticizer at concentrations exceeding 20 pph decreases the orientation of the crystalline phase for a given draw ratio. Cast and pressed films of PVC show incipient orientation in the plane of the films. This orientation can be removed to a great extent by immersing the films in diethyl ether. The method is experimentally feasible and the resolution achieved is determined by the automation of the equipment.

INTRODUCTION

Pole figure analysis and texture determination of certain semicrystalline polymers is well documented in the literature (see, for example, Ref. 1). However, in the case of poly(vinyl chloride) (PVC) no information other than an indirect mention in a paper on PVC gelation[2] has been published regarding this technique. Recent studies on antiplasticization of PVC[3] and on the interpretation of wide-angle x-ray diffraction (WAXD) profiles of PVC samples[4] have again made necessary the measurement of PVC pole figures. This paper reports these measurements; as a consequence of instrumental limitations and because of the low crystallinity of this polymer, the pole figures arrived at constitute a first approximation to the problem.

EXPERIMENTAL

Samples

The first requirement is that the value of the product of the linear absorption coefficient (μ) times the thickness of the sample (t) is in the vicinity of 1; otherwise the count rate will be too low and the baseline in the reflection mode excessively curved. The second requirement depends more on the particular equipment being used, but in general the sample must be sufficiently large in area so that it will always receive the whole incident radiation. The low 2θ values of the reflections of interest (200 and 100) can cause a large spread of the beam at certain sample orientations in reflection mode.

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Oriented samples were obtained from hot-pressed films of suspension polymerized PVC (Petroplas PP-140, by PEQUIVEN, El Tablazo, Maracaibo, Venezuela), with 0, 20, and 80 pph of dioctylphtalate. The films were stretched three times their original length at 100°C. Films were cast from THF solution on glass, and treated as indicated in Ref. 4. In one instance, a pressed-PVC film was left overnight in diethyl ether. Texture was measured on the same segment of film before and after immersion in diethyl ether.

Texture Goniometer

A Philips PW 1078 Texture Goniometer was adapted to a vertical diffractomer unit (PW 1050) mounted on a Philips PW 1730/10 generator fitted with a Cu tube. Since the PW 1078 texture accessory is designed primarily for

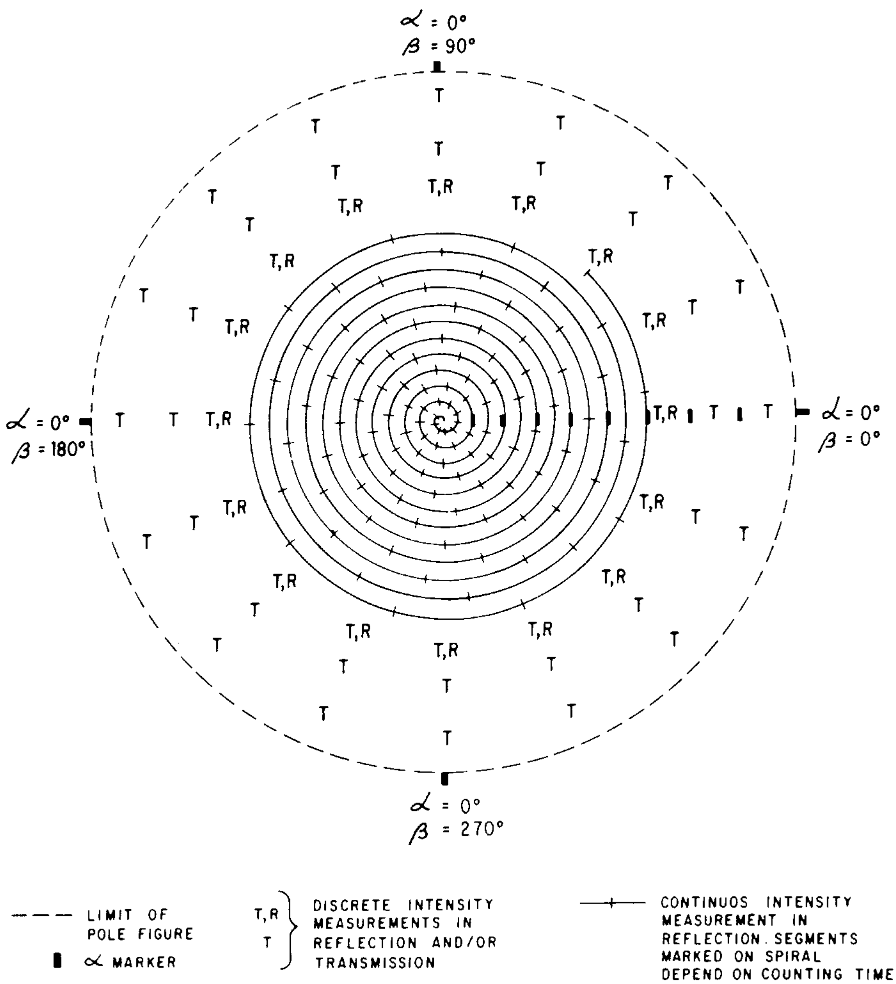
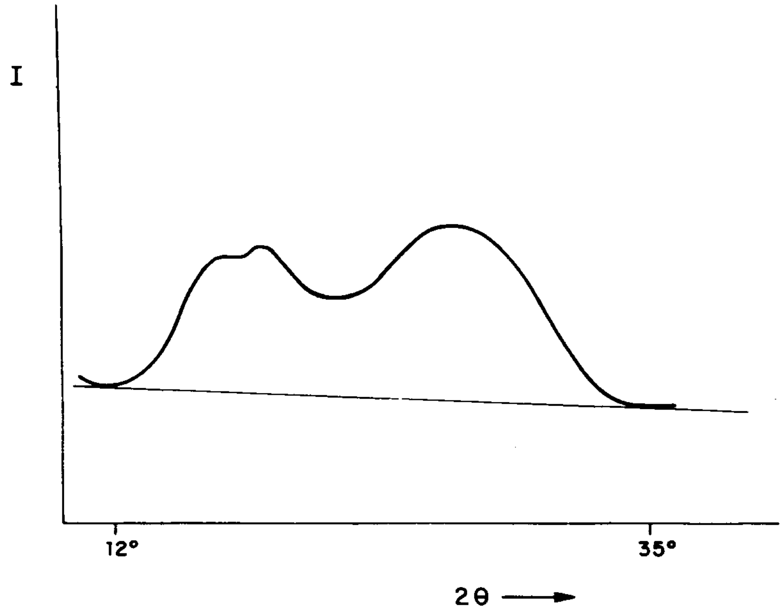
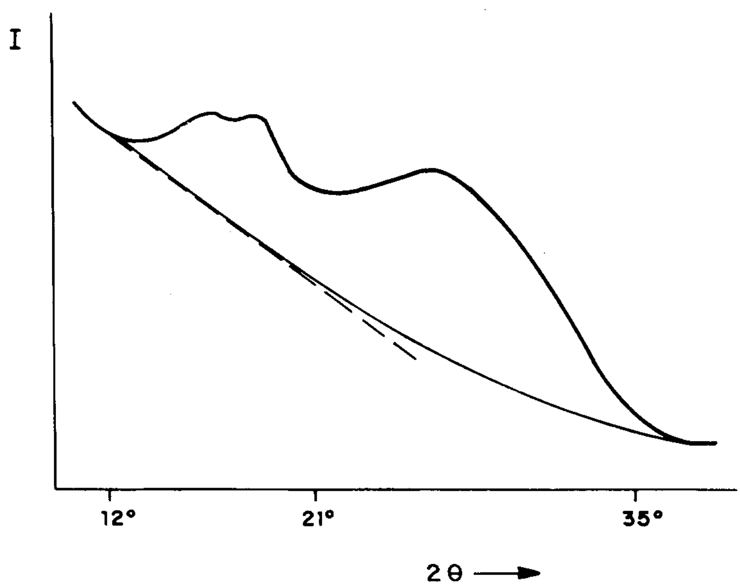


Fig. 1. Areas and discrete points on pole figure where measurements of intensity are taken: (_____) limit of pole figure; (■) α marker, (______) continuous intensity measurement in reflection segments marked on spiral, depending on counting time. T, R and T = discrete intensity measurements in reflection and/or transmission.



(a)



(b)

Fig. 2. Background for (a) transmission, (b) reflection in unoriented films, and (c) reflection in drawn films.

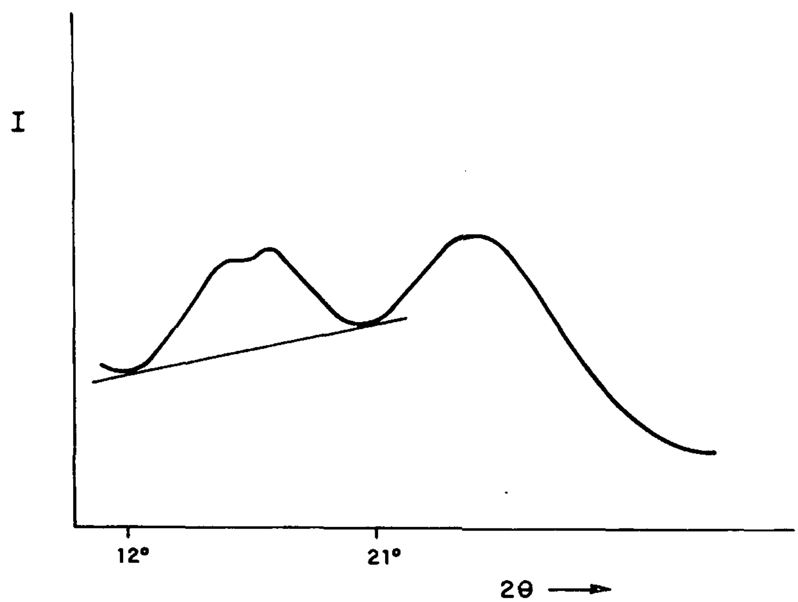
metal specimens where measurements are carried out mainly in the reflectance mode, some adjustments are necessary. The most important of these are:

1. Shift in the calibrated scale so that transmission measurements can be carried out from $\alpha = 0°$ to $+40°$ (using the sign convention of Ref. 1).
2. Reducing the exit collimator slit size during measurements in reflection so that the beam area will not spread out excessively at certain critical angles. This was done on a trial and error basis, setting the 2θ value at 6° and checking the incident area on the fluorescent screen provided by the manufacturer.

All other precautions pertinent to the correct alignment of the goniometer were applied (see, e.g., Ref. 5).

Data Acquisition

Data was stored either on the teletype connected to the equipment, or direct on an IBM personal computer. Calculations were performed using a spreadsheet format (Lotus 1-2-3, Lotus Development Corp.). The final pole figures are plotted on the PC screen thanks to a program originally developed by Carlos Ribeiro and Miguel Luna of the Centro Científico Tecnológico of IBM Venezuela. The program has been further adapted by Héctor Veloso of the Universidad Simón Bolívar, Caracas, Venezeuela.



(c)

Fig. 2. (*Continued from the previous page.*)

Intensity Measurements

All samples are first scanned at $2\theta = 0.1°$ intervals in the range 12–35° (2θ), at 100 s counting times. This is necessary to determine the exact position of the 200 and 110 reflections, and to establish the baseline slope for each sample. Once the 2θ values of the reflections are determined, two ways were used to arrive at the pole figures of the sample.

1. Fixed time measurements of 100 or 400 s are taken at discrete alpha and beta orientation values of the sample, both in reflection and transmission modes. Because of the number of measurements involved, only a quarter of the pole figure is scanned and a fourfold symmetry is assumed for the sample under study.
2. The whole pole figure amenable to measurement in reflection mode is scanned, using the spiral tracking movement of the PW 1078 Texture Goniometer at a 5° pitch. During this time intensity measurements are accumulated every 100 s. Thus, instead of discrete intensity values, an

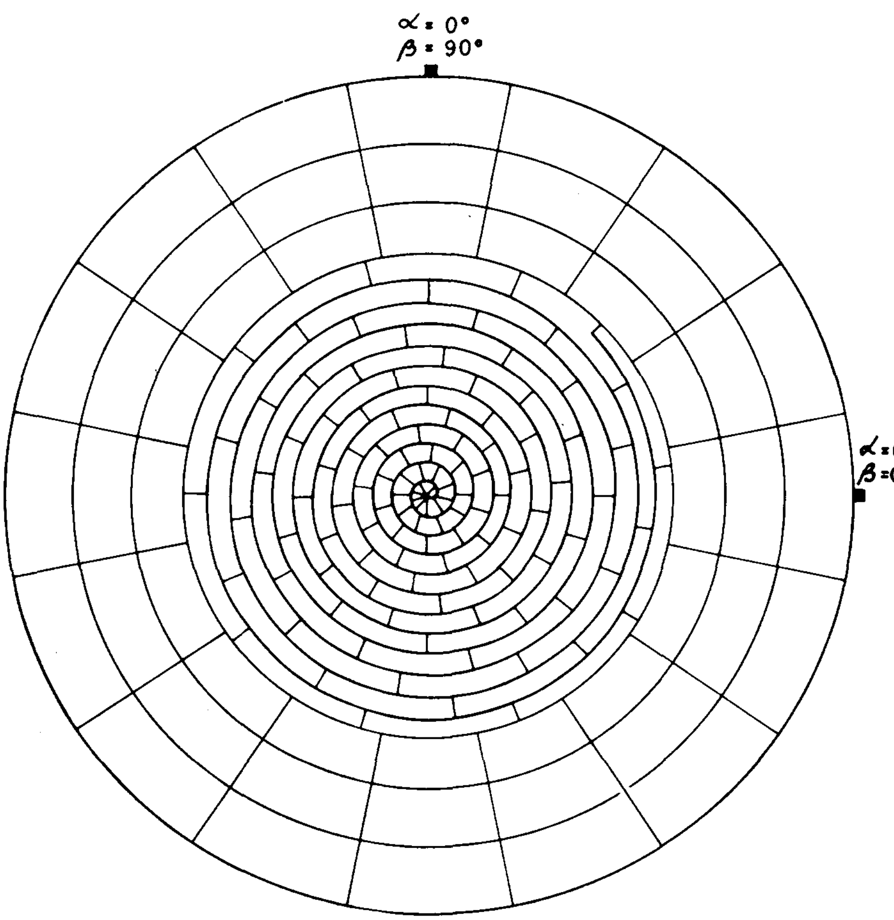
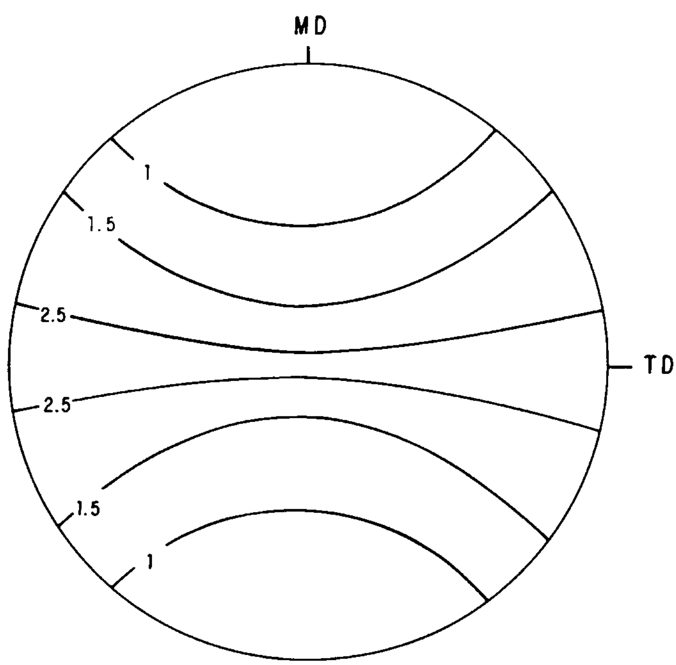


Fig. 3. Areas in pole figure over which the intensities measured in Figure 1 are assumed to be representative.

intensity average is measured over continuous areas of the pole figure. In transmission mode, and for certain reflection measurements in the transition zone, discrete intensity values are taken at chosen alpha and beta values. This is schematically illustrated in Figure 1.

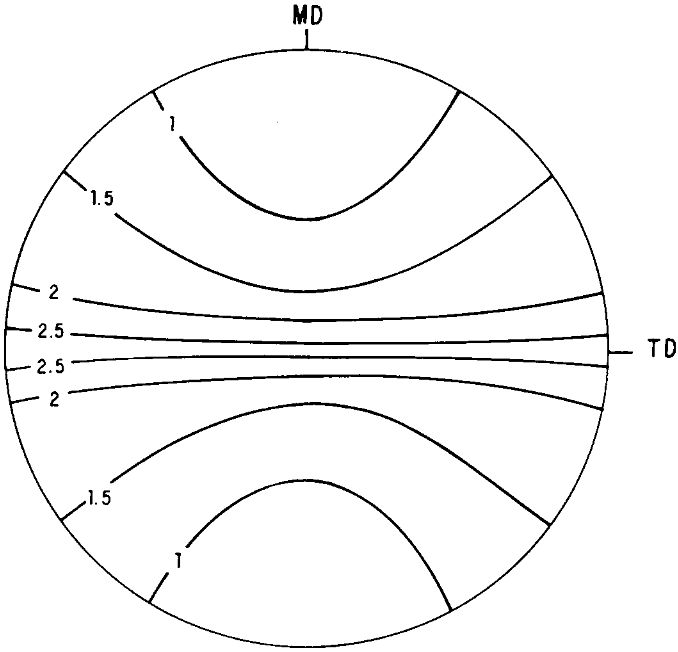
Data Treatment

The first step is to determine how the background count is to be estimated at each 2θ value corresponding to the 200 and 110 reflections. In transmission the background is a straight line, so an interpolation is carried out using background values measured at 12° and 35° (2θ) [see Fig. 2(a)]. In the reflection mode, the background is not linear but curved [see Fig. 2(b)]. In samples with little or no orientation, the background of interest could be approximated by a straight line of virtually constant slope for the series of samples under study. This particular coincidence cannot be taken as evidence of a general application of this procedure. In the case of highly oriented samples the fact that there is a broad amorphous peak centered around 17° (2θ) and also contributions, albeit small, from the DOP complicates the problem. In this case a completely arbitrary background was chosen by drawing a straight line between the points shown in Figure 2(c).



(a)

Fig. 4. Pole figure measured on top right-hand quadrant then extrapolated assuming fourfold symmetry of 300% drawn samples of: (a) PVC, commercial suspension grade; (b) PVC with 20 pph DOP; (c) PVC with 80 pph DOP.



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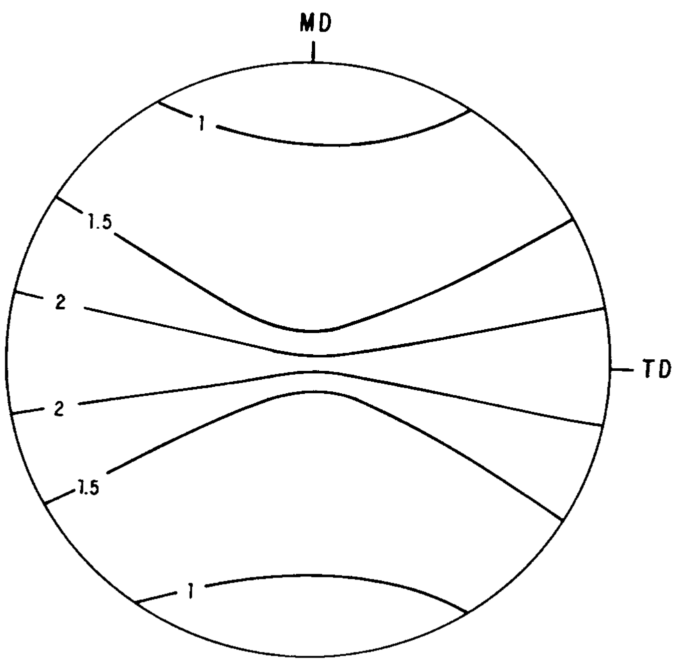


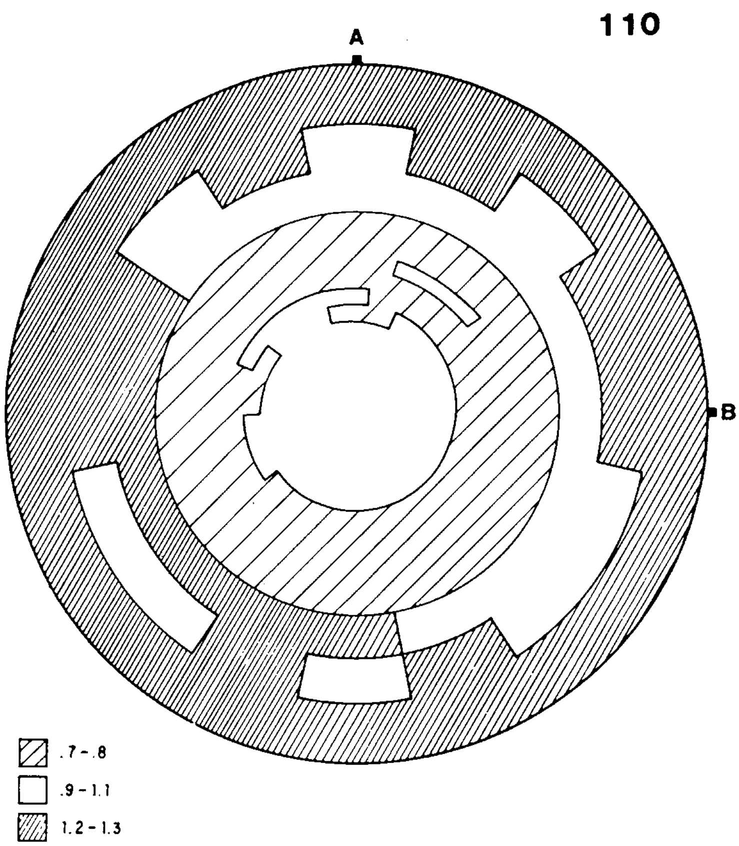
(c)

Fig. 4. (*Continued from the previous page.*)

Once the absolute intensities are obtained this way, the values are corrected according to accepted procedures.[1] An average intensity value (I) is calculated from the total intensity values measured for each sample. This necessarily involves the assumption that each $I(\alpha, \beta)$ value is representative of an area in the pole figure where $\Delta\alpha$ can vary from 5° to 10°, and $\Delta\beta$ from 22.5° to 37.5° (see Fig. 3). In other procedures[1] much lower intervals are achieved through interpolation, for example. For the present case, Figure 3 indicates the scope of the resolution of the pole figures as will be presented in the results.

Correlation between Pole Figures and Crystal Orientation

The accepted unit cell for PVC is orthorhombic with the following dimensions: a = 10.24 Å, b = 5.24 Å and 5.08 Å.[6] The WAXD profile of commercial PVC samples presents only two clearly identifiable reflections of sufficient intensity: the 200 and the 110 reflections. All the others are either too broad and overlap extensively or they are too weak for practical purposes (i.e., the 020 reflection; see Refs. 4 and 6 for more details).



(a)

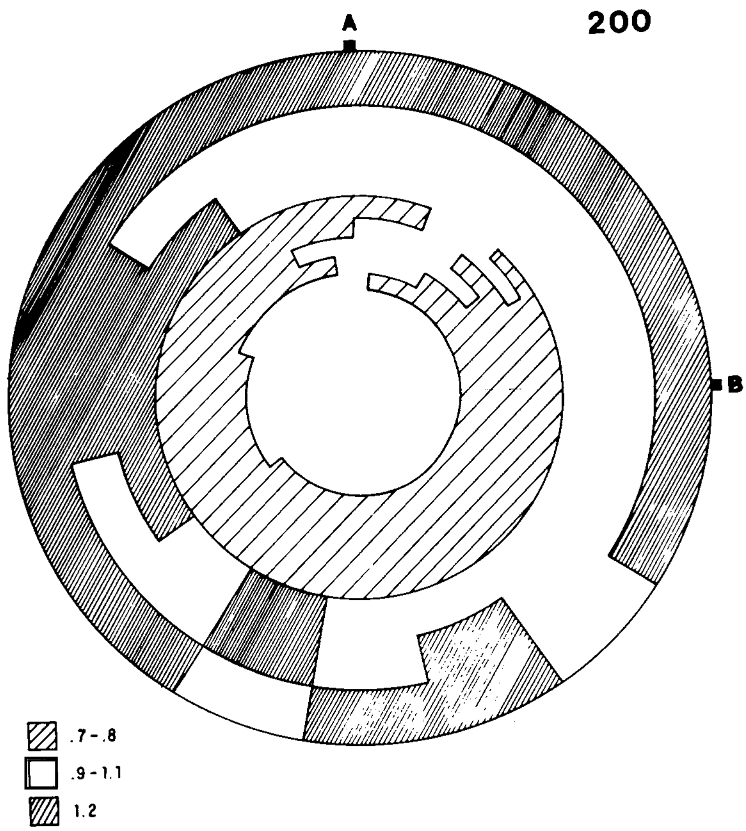
Fig. 5. Pole figure measured over all quadrants of PVC film cast from THF solution: (a) 200 plane; (b) 110 plane.

The use of the 200 and 110 pole figures to detect crystal texture had already been tried out with success in the case of PVC gels.[2] While with the present data it is possible to arrive at approximate $\langle \cos^2 \phi_{hkl,z} \rangle$ values, in the discussion that follows only a qualitative approach is used, since the experimental data have been extrapolated over wide areas of the pole figures.

RESULTS

Pole Figures of PVC Samples Drawn 300% at 100°C

Even though the main interest of the paper is the detection of orientation in cast films of PVC, initial measurements were carried out on oriented systems so as to gauge the degree of increase in pole densities that could be detected from the method being employed. The choice of formulations under study (0, 20, and 80 pph) could also reflect the influence of plasticizer on the orientation of the crystalline regions in drawn PVC. The experimental measurements shown in Figure 4 were carried out on the top right-hand quadrant, and fourfold symmetry was assumed in order to draw the whole figure.



(b)

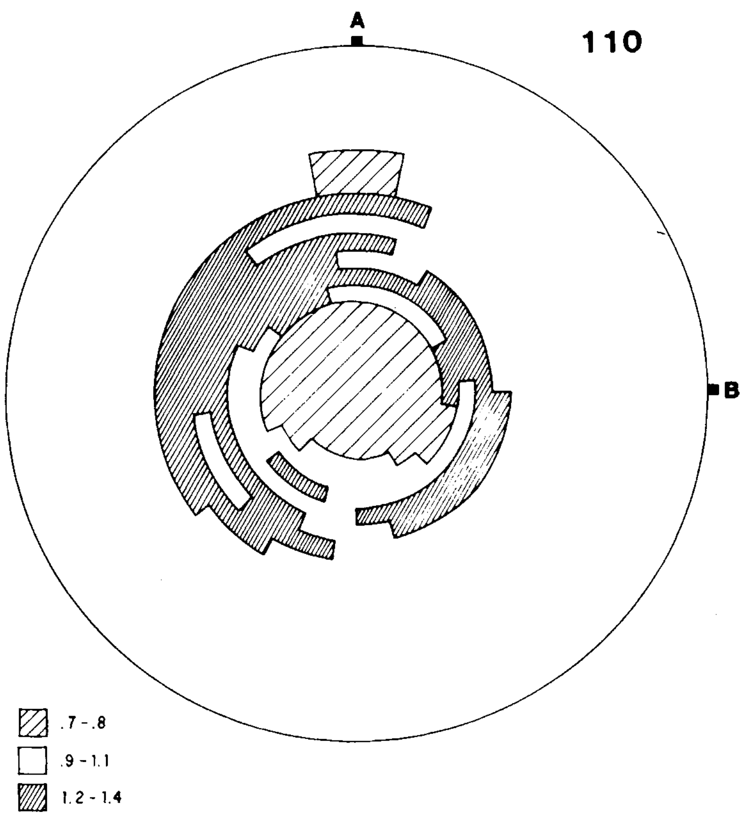
Fig. 5. (*Continued from the previous page.*)

The 110 pole figures shown in Figure 4 evidence an axial or fiber texture around the *c*-axis. Figure 4(c) shows less orientation along the TD direction than the other two. Pole figures of these same samples for the 200 plane show practically the same orientation.

The tendency as shown by the few samples studied is that while the overall fiber texture is maintained, the presence of plasticizer at a concentration of 80 pph lowers the degree of orientation achieved by the crystalline phase, for a given value of draw ratio.

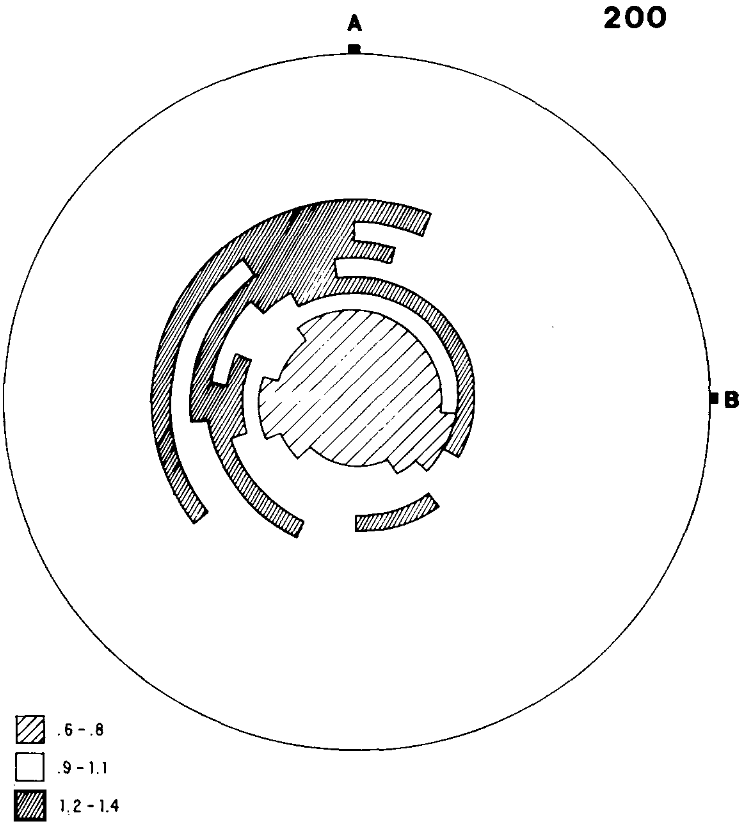
Pole Figures of PVC Pressed and Cast Films

The interpretation of WAXD patterns of PVC samples is influenced by the fact that planar orientation in some samples may be the cause of unexpected variations in the relative intensities of the 110 and 200 reflections.[4] In prior work on PVC gels it was shown that in those systems there was indeed a marked tendency for PVC films derived from gels to acquire a measurable planar orientation of the crystallites in the film plane.[2]



(a)

Fig. 6. Pole figure measured over all quadrants of PVC hot-pressed film: (a) 200 plane; (b) 110 plane.



(b)

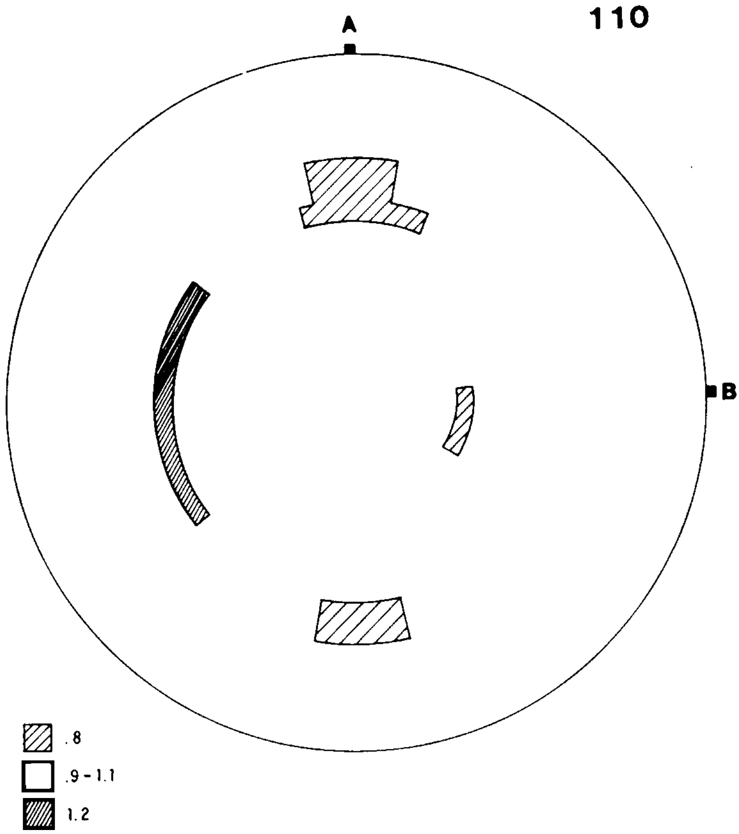
Fig. 6. (*Continued from the previous page.*)

For this reason special emphasis was placed on measuring pole intensities over the whole pole figure for samples of PVC which were known to show variations in the relative intensities of the 200 and 110 reflections. In the pole figures that follow, A and B simply denote arbitrary but orthogonal directions in the film plane of the samples.

Figure 5(a) and (b) correspond to a film cast from THF solution. The tendency for both pole figures to show slightly higher than average pole densities at lower alpha values would indicate a slight preference for the *c*-axis to orient perpendicular to the film plane in this sample. The other fact to be singled out is that there is no remarked difference between the orientation of the two planes.

Figure 6(a) and (b) corresponds to a film pressed on a hot plate. The concentration of pole densities towards $\alpha = 40°$ would indicate that in this case the *c*-axis tends to orient towards the plane of the film. The similarity is not so evident between the orientation of both planes. However, overall both pole figures show the same tendency.

The effect of soaking films in cold ether is to effectively remove nearly all orientation, as shown in Figure 7(a) and (b).



(a)

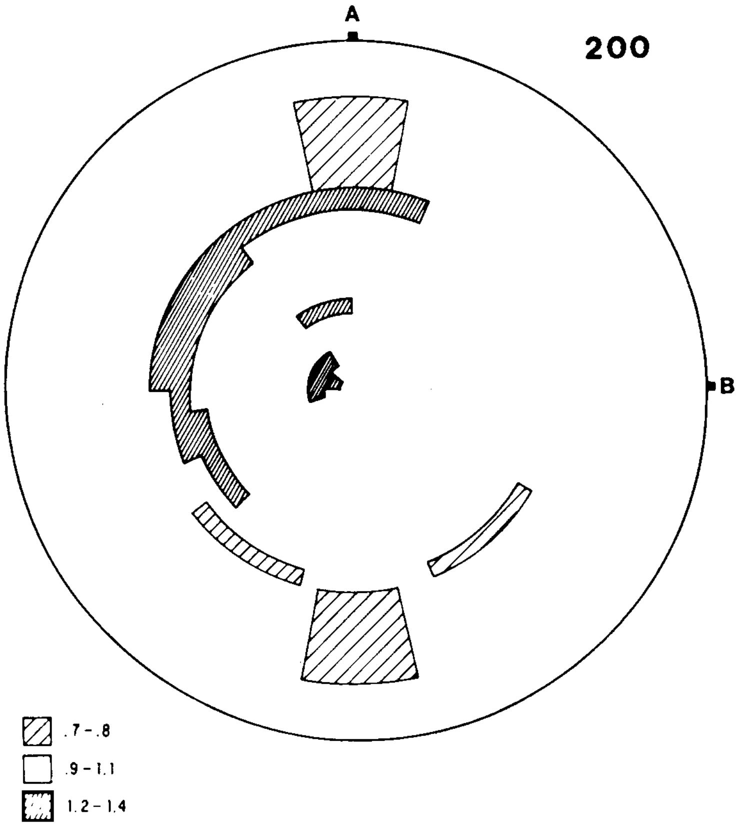
Fig. 7. Pole figure measured over all quadrants of same PVC hot-pressed film as in Figure 6, after immersion overnight in dietyl ether: (a) 200 plane; (b) 110 plane.

DISCUSSION

One obvious drawback to the pole figures presented in this paper is the low resolution in $\Delta\beta$ (intervals are in the range of 30°C), while the resolution in $\Delta\alpha$ is within the norm in reflection mode (5°), and somewhat higher in the transmission measured zone of the pole figure (10°). As to intensity counts, they are usually in the range of 40,000 (background) to 10,000 (signal), which gives an error below 5%. The long experimental times makes it even more necessary to ensure a very good generator voltage stability over long periods of time. Any spurious signals will influence unduly the pole figure, as a consequence of the low resolution employed. However, none of these considerations make the method impractical, and with increasing equipment sophistication it is certainly a feasible measurement to undertake.

The main purpose of the present set of measurements was not so much to determine texture in drawn PVC samples, but in detecting a preferential orientation of the 200 plane or 110 plane in nominally unoriented samples.

The pole figures show that both cast film and hot-pressed film possess incipient orientation, and that diethyl ether can relax the films and eliminate



(b)

Fig. 7. *(Continued from the previous page.)*

most of the residual orientation. The measurements did not detect any marked difference in the orientation of one plane as against the other. These two observations are of great importance for the interpretation of WAXD profiles of PVC.

First of all, many crystallinity measurements are reported from solvent cast or hot-pressed samples. As shown by the present results, steps must be taken to eliminate the inherent orientation of samples prepared this way. Immersion in cold diethyl ether is a proven manner for removing this orientation. Secondly in gel films there was clear evidence for *a*-axis orientation in the plane of the film. The direct consequence of this particular texture is that in flat plate WAXD photographs taken with the incident beam perpendicular to the film sample plane, the intensity of the 200 reflection is stronger than that of the 110 reflection.[2]

In the samples studied in this paper, not much evidence has been found, even if their corresponding WAXD diffractometer traces also show a stronger intensity of the 200 reflection than expected (see Ref. 4). This apparent contradiction can be explained in one of two ways: either the method as applied is not capable of detecting the *a*-axis orientation, or the intensity ratio of the 200 vs. the 110 reflection in WAXD profiles of certain samples is not determined by the crystal texture but rather by the amount present of a mesomorphous phase. The reasoning behind the latter statement is the subject of a separate paper (Ref. 4).

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