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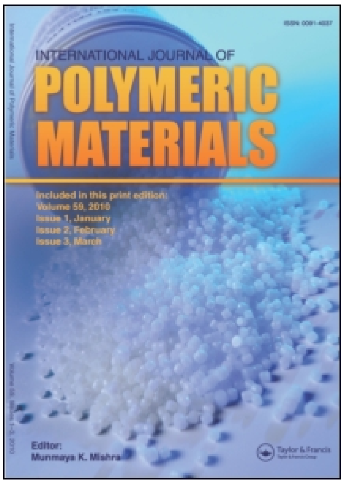

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Morphology of Plasticized Polyvinylchloride

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The morphology and the effect of plasticizer on the morphology of polyvinylchloride (PVC) were studied. Electron microscopy indicates that PVC contains aggregates on three size scales: 100 Å to 200 Å, 0.1 to 0.5μ and 1 to 10μ. The smallest of these structures are nodules which increase in size with the addition of plasticizer (DOP). This indicates that plasticizer diffuses into and disrupts the chain packing within these nodules. This has been confirmed by wide and small angle x-ray diffraction.

INTRODUCTION

Little is known about the structure of polymers with low crystallinity. Typically such polymers show one or more broad maxima in the wide angle x-ray diffraction region and are often referred to as "x-ray amorphous". Several possibilities exist for the structure of these polymers. They may consist of a few, small but perfect crystallites in an amorphous matrix, many, small imperfect crystallites or, as suggested by Bonart,[1] an irregular defective lamellar structure. This paper deals with the morphology of one such polymer, polyvinylchloride (PVC), and the effect of plasticizer on its morphology.

Many applications of PVC require that plasticizer be added to the resin. Furthermore, stabilizers are usually employed to improve heat and light stability. Determination of the effect of additives on the structure of PVC could provide an insight into the mechanism of plasticization.

PVC has been shown[2–5] to consist of nearly spherical particles which govern the flow characteristics of the melt. The exact size and nature of these particles depend on polymerization and processing conditions, i.e. pressure, temperature and shear. At low shear or at processing temperatures below 200°C a

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"macro-globular" structure is observed, which is 1–2μ in diameter (or larger depending on polymerization conditions.[3] At higher temperatures or shear this particle identity is lost and a smaller structure (0.1μ and smaller) becomes apparent.[2,3] Further increased shear provided by rolling leads to a formation of anistropic fibrillar structures.[2]

Bonart,[1] in a discussion of the paracrystalline state, presented the data of Geymayer which claimed the existence of "Lamellae" in plasticized, "x-ray amorphous" PVC. These lamellae had a step-height of 100–200 Å. Bonart also reported data of Hendus showing that the small angle spacings from plasticized PVC increased with percent plasticizer, suggesting that the plasticizer may preferentially collect between the lamellae. No small angle spacing was observed in unplasticized PVC.

The presence of lamellae in "x-ray amorphous" PVC is somewhat surprising. However, the presence of crystallinity in "x-ray amorphous" PVC has been reported by McKinney and Foltz[6] using results from differential thermal analysis. This they attributed to an alignment of short stereoregular chain segments of adjacent molecules. PVC with high crystallinity has been reported;[7–10] it is generally of low molecular weight.

EXPERIMENTAL

Sample Preparation

Samples of plasticized PVC-40TM† (number ave. MW = 50,000) was prepared by milling at 170°C for approximately 5 minutes. The plasticizers used were dioctylphthalate (DOP) and a chlorinated paraffin. Unplasticized samples of PVC were formed by heating to 190°C for approximately 5 minutes in a compression molding press.

X-ray Diffraction

Small angle x-ray diffraction (SAXD) scans were obtained using a Rigaku-Denki rotating anode (Cu Target) small angle unit equipped with a diffractometer. Intensities were measured every 0.01° using a step scan and punched directly onto a paper tape for computer processing. The background scan was obtained by placing the sample immediately following the first slit. This gave a profile of the main beam, i.e. that part which was neither scattered nor absorbed by the sample. The background scan was then subtracted from the raw data. The Lorentz correction factor for small angle diffraction was applied by multiplying the observed intensity (after subtraction of the background) by the square of the Bragg angle, θ.[11–13] Because of the high mass

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† TM—Trademark, Diamond Shamrock Company.

absorption coefficient of PVC, x-ray samples were necessarily cut very thin, usually 0.006 to 0.01 in. depending on plasticizer content.

Wide angle x-ray diffraction (WAXD) scans were obtained on a General Electric diffractometer using CuK_α radiation.

Electron Microscopy

Because of the mobility of plasticizers and other additives in PVC, truly representative surface replicas were difficult to obtain; the plasticizer tended to exude to the surface and obstruct any structure which was present. In order to solve this problem, two methods were used for the preparation of samples for subsequent electron microscope observation. The first method consisted of fracturing the sample in a vacuum on a cold stage at liquid nitrogen temperature and immediately shadowing the sample with carbon-platinum at this temperature. The second method involved bombarding the surface with high energy gaseous ions, usually nitrogen or argon. The ions were generated by means of a high frequency induction coil, as described by Fischer and Goddar.[14] A 270 volt potential was placed across the plasma such that the positive ions were driven toward the sample. The specimen was again on a liquid nitrogen cold stage during ion etching and immediate Pt-C evaporation. The replicas were then stripped off with polyacrylic acid and prepared in the usual manner for electron microscopy. Both methods were successful in preventing plasticizer from exuding to the surface in most cases (exceptions will be discussed later).

EXPERIMENTAL RESULTS

Electron Microscopy

Electron micrographs of unplasticized PVC were obtained in order to compare the structure of PVC with no additives to that of the plasticized material. Figure 1(a) shows an electron micrograph of unplasticized PVC which was ion etched in the manner described previously. Large structures 1 to 2μ can be observed with a fine structure of about 200 Å. Figure 1(b) is a similar sample at higher magnification showing the structures on both the 1μ and 200 Å size scale. These micrographs are similar to those reported by Bonart,[1] except that the lamellar nature of the surface in the present work is not as obvious. Although in some areas of Figure 1(a) the surface does appear to be composed of lamellae, most areas of Figure 1(b) do not. This may be due, however, to a "smoothing" of the structure due to ion-etching.

No lamellar structures could be obtained, however, in milled PVC, which was plasticized with DOP. Figure 2(a) is a fracture surface of a sample

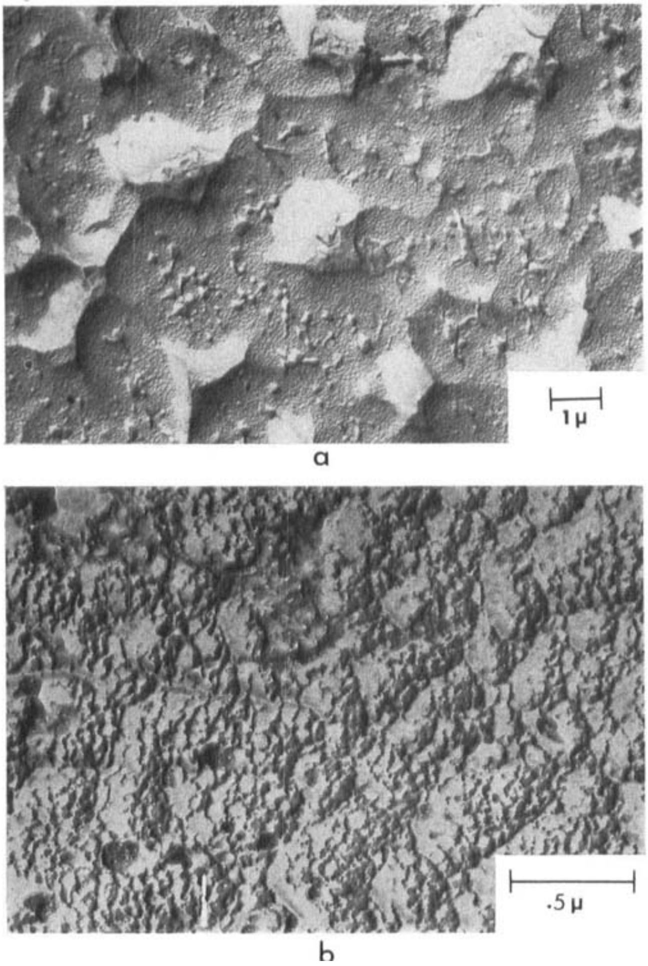

FIGURE 1 Electron micrographs of unplasticized PVC. (a) Surface replica of ion-etched material. (b) High magnification of an area similar to (a).

containing 10% DOP. Barely visible in the micrograph is a grainy or nodular structure of 120 Å ± 30 Å in diameter. (These values are the average diameter and standard deviation taken from a large number of measurements.) In addition to the nodules, structures which are roughly 0.1μ in size can be observed. The small nodules are more obvious in Figure 2(b), which is a fracture surface of PVC with 20% DOP (insert—high magnification). In this case the nodules are 130 Å ± 25 Å in diameter and an overall roughness is again present on the surface, with the size of the structure being about 0.1μ.

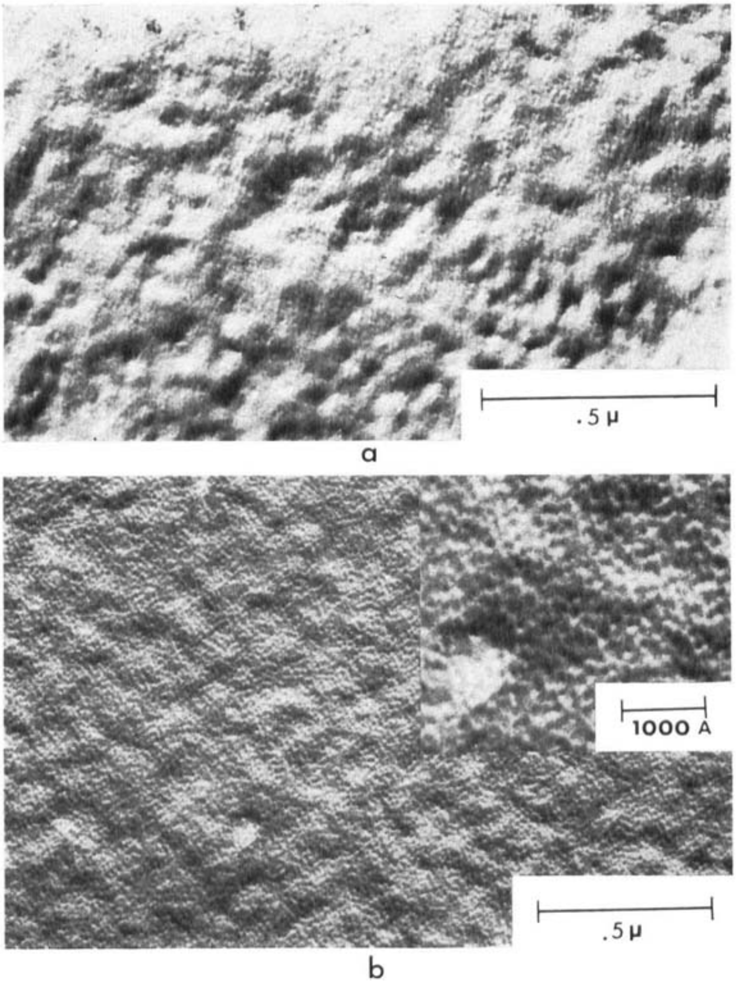

FIGURE 2 Fracture surfaces of PVC plasticized with DOP. (a) 10 wt. % DOP. (b) 20 wt. % DOP (insert—high magnification).

A fracture surface of a sample containing 40% DOP is shown in Figure 3(a) (insert left—high magnification). Nodules of 170 Å ± 20 Å in diameter and structures of 0.1μ in size can again be observed. The insert at the right of Figure 3(a) shows an area of a similar sample where the large structure is dominant and the 170 Å nodules can barely be seen. Figure 3(b) represents a fracture surface of a PVC sample with 60% DOP (insert—high magnification). The nodules are now 180 Å ± 20 Å in diameter. The 0.1μ structures

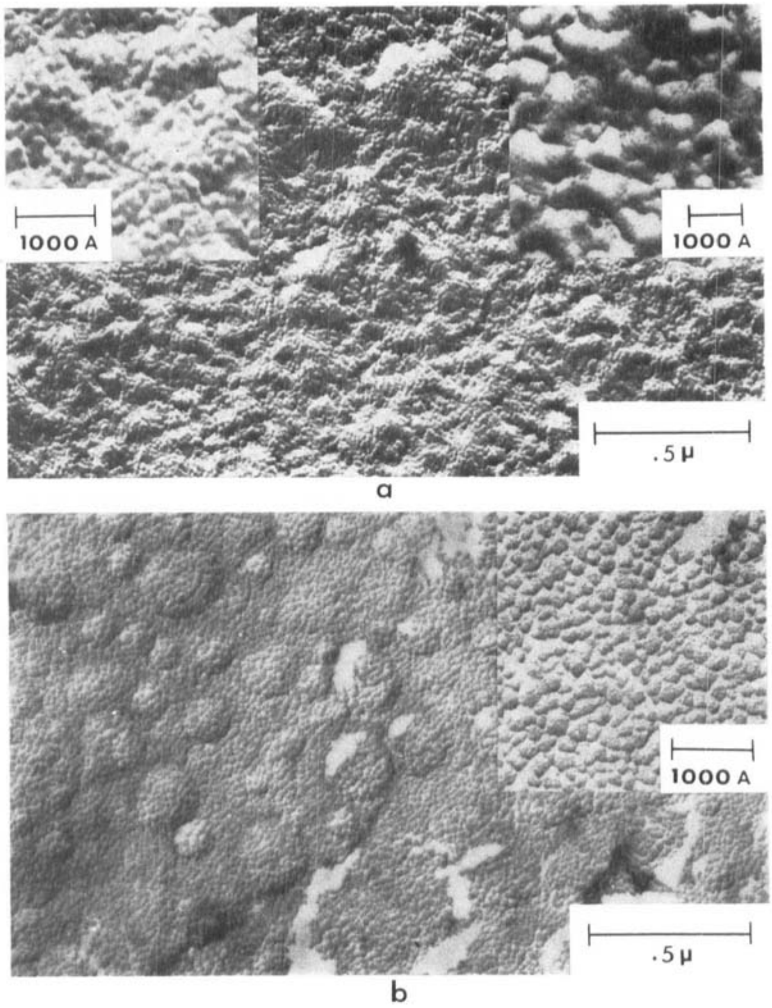

FIGURE 3 Fracture surfaces of PVC plasticized with DOP. (a) 40 wt. % DOP (insert left—high magnification of similar area, insert right—area showing almost complete absence of 170 Å structure). (b) 60 wt. % DOP (insert—high magnification).

seem to exist in this case as separate, almost spherical units. However, on other areas of the same sample they are similar to those of the samples with 20% DOP and 40% DOP. Thus, it is not felt that this uniformity is singularly characteristic of the 60% DOP sample.

As in the case of fracture surfaces of other so-called glassy polymers[15–17] parabolic surface features can be observed in many (but not all) areas. A

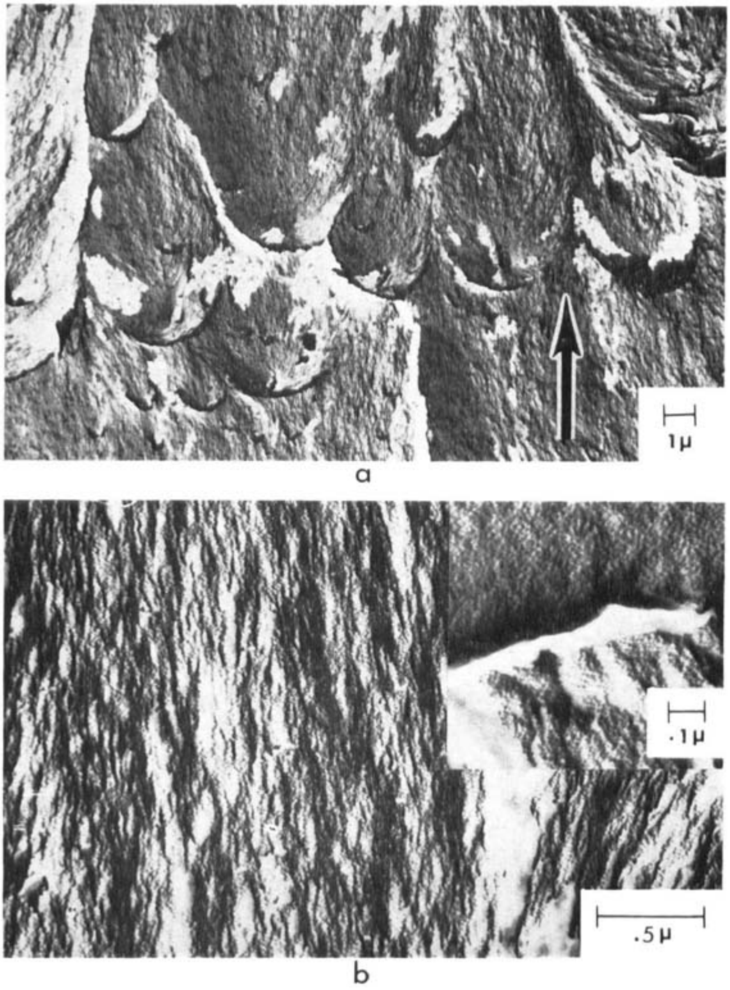

FIGURE 4 Fracture surfaces of PVC plasticized with 20 wt. % DOP. (a) Area showing parabolic surface features. (b) High magnification of similar area showing tear lines. (Insert—boundary between "smooth" and striated regions).

typical area for a sample with 20% DOP is shown in Figure 4(a). Figure 4(b) is a higher magnification of a similar region. These parabolic features are due to secondary crack growth initiating ahead of the primary crack growth front.[15,18] Striations can be observed more or less parallel to the direction of crack propagation (arrow Figure 4(a)). These striations appear to represent slight level differences in the fracture surface. However, the nodular structures observed in the "smooth" area are also present in the striated regions. The insert to Figure 4(b) shows a boundary between the regions. The striations are directed radially from the focus of each of the hyperbolas. These foci are the points of initiation of the secondary fractures. The change from a smooth to rough crack surface occurs at the secondary crack boundaries which grew in the opposite direction to the primary crack growth. When this boundary is reached the crack changes level and the secondary crack becomes the primary crack. The insert to Figure 4(b) shows such a boundary.

Results from ion-etching the DOP plasticized material were inconclusive. The reason for this is not known exactly, except that perhaps enough heat was produced at the surface due to the etching to allow the plasticizer to flow and obscure the structure.

Ion-etching was successful to an extent, however, for material which was plasticized with a chlorinated paraffin. Figure 5 shows such an etched surface. Uniform, nearly spherical particles which are 0.2–0.4μ in diameter can be seen over the entire surface. No fine structure, such as that found on unplasticized or DOP plasticized PVC is observed on the surface of these particles. These particles tend to cluster in groups of two or more to form large structures up to several microns in size. The insert on Figure 5 shows the ion-etched surface when the sample is allowed to return to room temperature before Pt–C shadowing. This indicates that plasticizer exuded to the surface upon warming to room temperature. Fracture surfaces of these materials yielded similar results; no fine structure could be observed on the surface of the particles.

X-ray Diffraction

The relatively uniform 100–200 Å nodular structures obtained from electron microscopy of DOP plasticized PVC suggest that these structures may be giving rise to the observed small angle x-ray diffraction peaks. Figure 6 shows SAXD diffractometer scans for 0, 20, 40, and 60 wt. per cent DOP. The Lorentz correction and background subtraction were performed on these data and the results plotted in Figure 7. The unplasticized sample resulted in a curve with extremely low intensity, indicating that the scattering curve is about the same as the background, i.e. very little scattering is present in the small angle region. As the amount of plasticizer is increased, a broad peak appears at approximately $2\theta = 1°$. The peak becomes sharper and moves toward the main beam as the percentage of plasticizer is increased further. This indicates that the small angle spacing increases as the amount of plasticizer is increased, in general agreement with the results of electron microscopy and those reported by Bonart.[1] This will be discussed later in somewhat more detail.

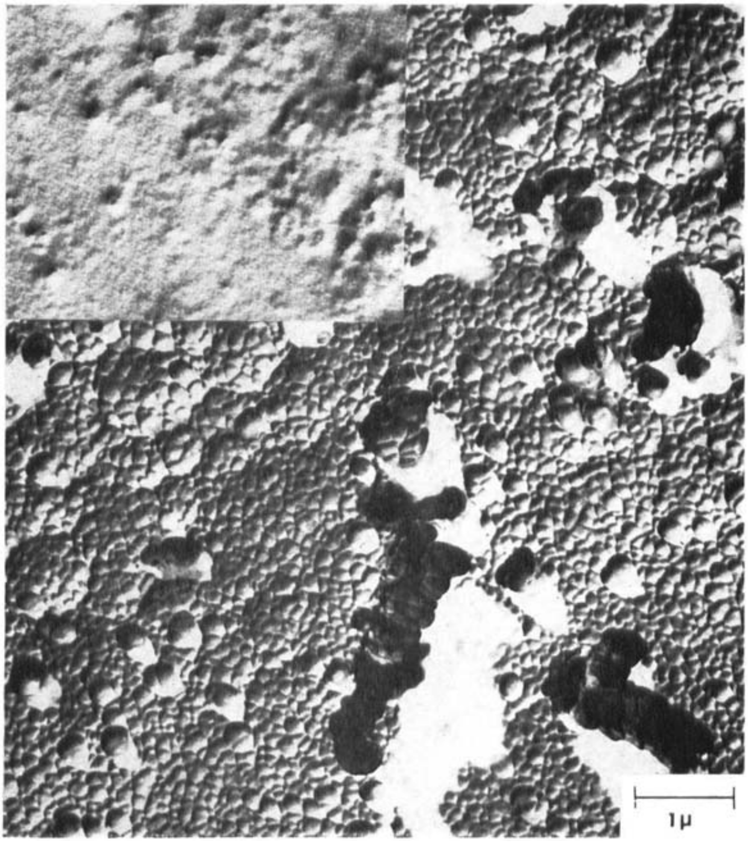

FIGURE 5 Surface replica of PVC plasticized with 30 wt. % chlorinated paraffin. The surface was ion-etched and shadowed at −195°C. (Insert—similar surface which was shadowed after warming to room temperature).

Similar results for PVC plasticized with a chlorinated paraffin (20 wt. %) are shown in Figure 8.

WAXD scans of PVC as a function of weight per cent DOP are shown in Figure 9. At low weight per cent DOP the patterns consist of two broad maxima centered at approximately $2\theta = 17°$ and $2\theta = 24°$. These correspond closely to the (200) and (010) reflections ($2\theta = 17°$) and the (210) reflection ($2\theta = 24°$) as reported by Natta and Corradini.[19] The breadth of the peaks in the present case indicates that the crystallites are small and/or imperfect. As DOP is added, the maximum at $2\theta = 24°$ begins to weaken and disappears completely at 60 wt. % DOP, leaving only one very broad maximum centered at approximately $2\theta = 19°$. This broad maximum at high plasticizer

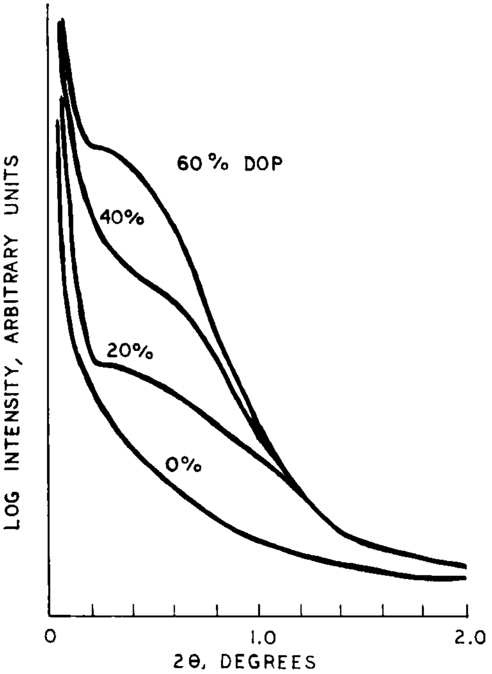

FIGURE 6 SAXD scans of PVC as a function of weight per cent DOP.

content presumably corresponds to an average interchain distance (ca. 4.7 Å) in a nearly amorphous system. A broad peak of unknown origin was observed at $2\theta = 6°$. This peak also decreased in intensity with increasing plasticizer content.

DISCUSSION

Interpretation of the SAXD results and comparison with the electron microscope are complicated by the fact that the system is not an ordered lattice or a dilute solution but a random collection of densely packed spherical particles. Thus, not only must the structure factor of the individual particles be considered but also the particle interactions. However, approximate information can be obtained by applying Bragg's law to the diffuse peak. In this way an order to magnitude approximation can be made of a characteristic average distance between the particles.[20] A precise physical interpretation of this dimension cannot be made.[20,21] On the other hand, the relative change in this dimension can be determined as plasticizer is added and compared with changes in nodular size observed by means of electron microscopy.

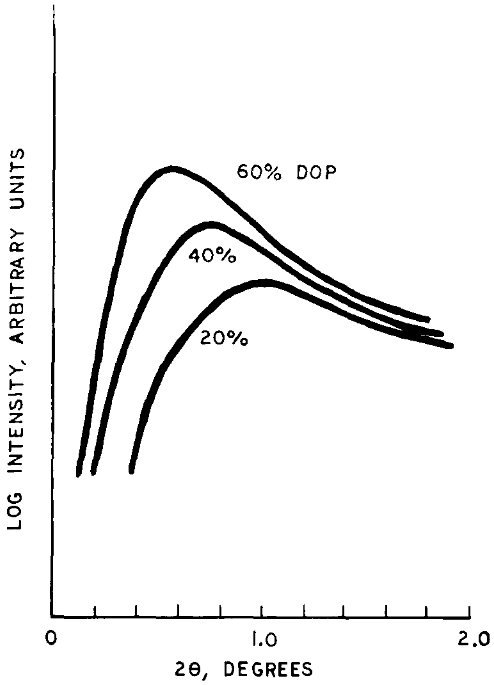

FIGURE 7 Corrected SAXD scans for DOP plasticized PVC.

TABLE I

Comparison of spacings observed in SAXD and electron microscopy for PVC plasticized with DOP

Percent by weight DOP	Angular position of SAXD maxima, $2\theta_M$	Diameter of spheres assuming a dilute solution	Characteristic average distance assuming Bragg diffraction	Diameter of particles assuming a hexagonal close-packed lattice	Diameter of particles measured from electron microscopy
10%	—	—	—	—	120 Å
20%	1.02°	149 Å	88 Å	118 Å	130 Å
50%	0.77°	194 Å	115 Å	141 Å	170 Å
60%	0.58°	257 Å	152 Å	187 Å	180 Å

Table I shows the results of assuming independent spherical particles and Bragg law scattering for PVC plasticized with DOP. For a dilute solution of uniform spheres,[20]

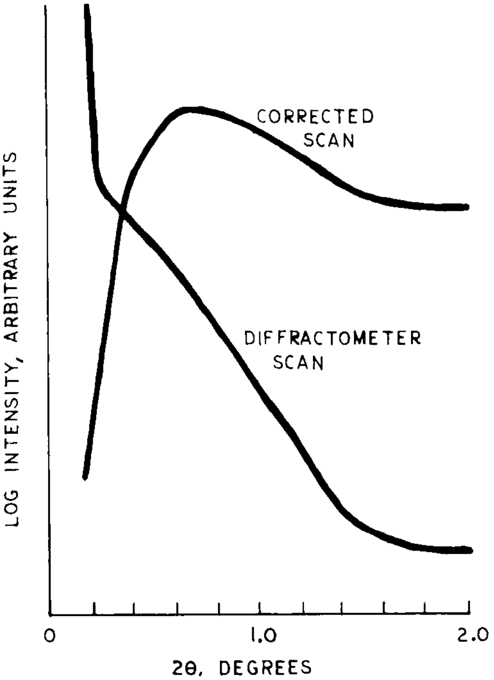

FIGURE 8 SAXD and corrected SAXD scans for PVC containing 30 wt. % of a chlorinated paraffin.

$$\alpha = \frac{4\,a \sin \theta_M}{\lambda}$$

where: α = 5.31 (position of the first maxima in the theoretical scattering function of uniform spheres)

θ_M = half-angle of maximum intensity

λ = wavelength of radiation (1.54 Å)

a = radius of spherical particle

The value of d calculated from Bragg's law can be assumed to represent either a characteristic average distance between particles, or the distance between closest spaced planes in a hexagonal lattice of spheres. In the latter case the diameter of the spheres is 1.23 times d.[22]

The best agreement with electron microscopy is obtained when the material is assumed to consist of spheres placed in a perfect hexagonal close-packed lattice. The dilute solution approximation yields values which are larger than those observed from microscopic examination while the characteristic

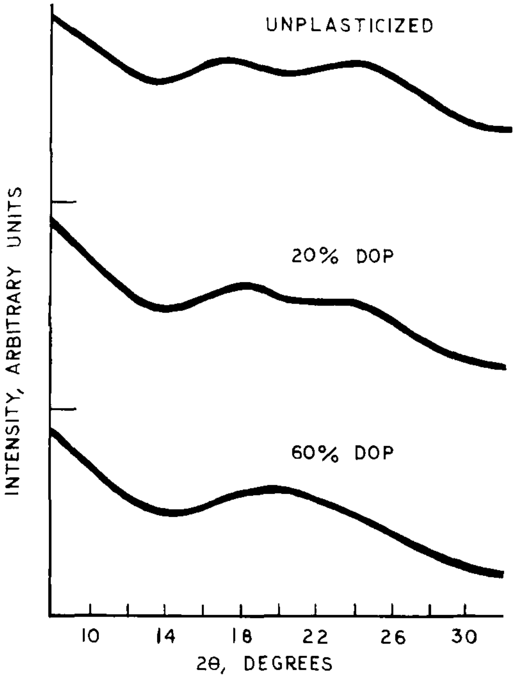

FIGURE 9 WAXD scans of PVC as a function of weight per cent DOP.

distance approximation yields smaller values. However, the trend is the same in all cases; the characteristic distance increases as DOP is added to the system. This qualitative agreement leads to the conclusion that the nodules observed on the fracture surfaces are responsible for the maxima observed in Figure 7. Lamellae are not needed to describe the scattering in our samples. The increase in the size of the nodules and the change in the WAXD patterns suggests that the plasticizer diffuses into and disrupts the chain packing within these nodules.

The presence of two seemingly different morphologies on fracture surfaces of other glassy polymers has been previously documented[18] and represents regions of slow ("smooth") and fast ("striated") crack propagation. The lines observable in the striated areas are tear lines marking boundaries between fractures on different levels within the parabolas.[18]

DOP plasticized PVC has been shown to contain "agglomerates" on at least three size scales. The 100–200 Å nodules, which give rise to the SAXD maxima, presumably are the basic building blocks of the material. These nodules aggregate to form larger structures 0.1μ to about 1μ in diameter. Many times these structures are spherical, often they are not. These "particles" are presumably related to the original latex particles in unplasticized PVC. In some cases (PVC plasticized with a chlorinated paraffin and in many areas of DOP plasticized PVC, see Figure 3(a)—right insert), the small nodules are not observable and the larger structure is the dominant feature. A number of these structures often cluster to form large "macroglobules" of approximately 0.5 to 2μ in size.

The question remains, however, as to why lamellar-type morphology is observed in some cases (unplasticized PVC in the present work and plasticized PVC described by Bonart[1]) and not in others. The only conclusion that can be drawn is that these structures are extremely sensitive to processing conditions, as has been reported previously,[2,3] and that a systematic structural analysis with regard to milling, pressing, etc. is needed.

Acknowledgement

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References

1. R. Bonart, *Kolloid Z.* **213**, 1 (1956).
2. L. I. Vidyaikina, N. A. Okladnov, and B. P. Shtarkman, *Polymer Sci., U.S.S.R.* **8** 425 (1966).
3. A. R. Berens and V. L. Folt, *Trans. Soc. Rheol.* **11**, 95 (1967).
4. A. R. Berens and V. L. Folt, *Poly Eng. Sci.* **8**, 5 (1968).
5. M. Chmelarova, J. Zdarsky, and S. Modry, *Kolloid Z. Z. Polymere* **221**, 65 (1967).
6. P. V. McKinney and C. R. Foltz, *J. Appl. Poly. Sci.* **11**, 1189 (1967).
7. A. Utsuo and R. S. Stein, *Polymer Letters* **3**, 49 (1965).
8. R. J. Clark, *J. Poly. Sci.* **51**, S71 (1961).
9. V. I. Zegelman, M. N. Shlykova, S. V. Svetozarskii, and Y. N. Zel'berman, *Polymer Sci. U.S.S.R.* **10**, 133 (1968).
10. R. W. Smith and C. E. Wilkes, *Polymer Letters* **5**, 433 (1967).
11. O. Kratky, *International Series of Monographs on Electromagnetic Waves*, Vol. 5 edited by Milton Kerku (Pergamon Press, 1963), pp. 459–476.
12. C. G. Vonk and G. Kortleve, *Kolloid Z. Z. Polymere* **220**, 19 (1967).
13. B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley, 1959), pp. 124–130.
14. F. W. Fischer and H. Goddar, *J. Poly. Sci., C* **16**, 4405 (1969).
15. J. P. Berry, *J. of App. Phys.* **33**, 1741 (1962).
16. R. P. Kambour, *J. Poly. Sci., A*1 **3**, 1713 (1965).
17. R. P. Kambour, *J. Poly. Sci., A*2 **4**, 17 (1966).
18. I. Wolock and S. B. Newman, in *Fracture Processes in Polymer Solids*, edited by Bernard Rosen (Interscience, New York, 1964), pp. 235–244.
19. G. Natta and P. Gorradini, *J. Poly. Sci.* **20**, 251 (1956).
20. M. B. Webb, *Handbuck der Physik*, Vol. 32 (Springer-Verlag, 1956).
21. A. Guinier and G. Fournet, *Small-angle Scattering of X-rays* (Wiley, New York and London, 1955), pp. 135–148.
22. P. A. Hiltner and I. M. Krieger, *J. Phys. Chem.* **73**, 2386 (1969).