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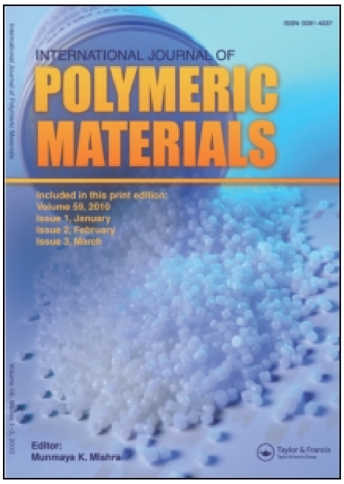

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The Processing Effect on the Morphology of Plasticized and Unplastized Polyvinyl Chloride

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The effect of processing conditions on the morphology of plasticized PVC was studied. A particulate nature was observed for all samples used but the distinctness, size, and regularity of the particulate structure depends on the processing conditions. The dynamic loss of the samples appears to depend on the particulate structure.

INTRODUCTION

Despite its commercial importance, little has been published on the effect of processing conditions on the physical properties of polyvinyl chloride (PVC); this is particularly the case for plasticized material. In this paper we present the initial results of an examination on the effect of processing conditions on the morphology of plasticized PVC.

For unplasticized samples Berens and Folt[1,2] have most closely approached the type of study suggested. They have shown that processing temperature (extrusion temperature and prior heat treatment) and shear rate affect the tensile properties of an extrudate as well as the extrusion characteristics. They interpreted their results in terms of particle-slippage flow at low processing temperatures with molecular deformation and particle merging occurring at higher temperatures. The particle size considered is that of the original emulsion polymerization particles, i.e., 0.1–1 micron.

Numerous papers have been published on the effect of plasticizers (various types and quantities) on the mechanical properties of PVC. The extraordinary creep properties of plasticized PVC are generally suggested to result from a three-dimensional gel network with small crystallites serving as the cross-links.[3] Variations in processing conditions would be expected to affect the nature of the crystalline regions and, correspondingly, the mechanical properties.

Previously in our laboratory, Gezovich and Geil,[4] using the techniques of freeze-fracture-replication, were for the first time able to observe the morphology of plasticized PVC. They reported a nodular structure for PVC samples plasticized, by milling at 170°C, with various amounts of the plasticizer di-octyl phthalate (DOP). The average size of the modules was about 120 Å for a sample plasticized with 10% DOP and increased with increasing DOP content to about 180 Å for a sample plasticized with 60% DOP. The observed diameters, assuming hexagonal packing, were in approximate agreement with corresponding, rather diffuse, small angle X-ray diffraction (SAXD) maxima. In addition, particles on the orders of 0.1 to 0.5 μ and 1 to 10 μ were observed in some of the samples; since the suspension polymer they used consists of porous particles on the order of 100 μ in size, the 0.1–0.5 μ and 1–10 μ particles are presumably sub-units of the polymerization particles. In this earlier work,[4] it was found that, occasionally, considerable variation in the morphological features were observed on similar samples prepared at different times with the same plasticizer as well as if different plasticizers were used, suggesting the structures observed were sensitive to processing conditions.

The present study is directed toward showing the effect of processing conditions on the morphology of plasticized PVC using several types of commercial PVC resins The results re-emphasize the importance of processing conditions on the morphology and suggest an interrelation between processing conditions, morphology and physical properties.

EXPERIMENTAL

Materials

Two commercial grade PVC resins, kindly supplied by their manufacturers were used, as listed below. Both samples contained 1% stabilizer mixed by dry blending.

Code	Trade Name	Manufacturer	Polymerization Method	$\bar{M}n$	$\bar{M}w$
A	Geon 103	B. F. Goodrich	Suspension	69,730	154,000
C	PVC-40	Diamond Shamrock	Suspension	50,000	—

Sample Preparation

The plasticized samples were prepared with the cooperation of the two suppliers by milling on a two roll mill under conditions we requested. Although the temperature of the mill rolls and milling time were specified for all samples, it is certain that the processing conditions for the different mills were not identical. In addition, the mill roll temperature is usually lower than the actual milling temperature of the sample, which is difficult to measure or control accurately. Consequently, a certain degree of variation in processing is expected not only for samples prepared on different mills but also for the, presumably, same conditions on the same mill. Therefore, direct comparison of the two suppliers' samples is not possible; rather, similar trends are to be sought. Technical literature of the manufacturers suggests a mill roll temperature of 127–143°C for sample A and ca. 160°C for sample C.

Plasticized PVC recovers almost completely from extensive deformation even at elevated temperature. Consequently, premanently orientated samples are difficult to obtain. In the present work, dumbell-shaped samples were stretched at room temperature to the highest extent possible before break, then annealed at 55°C while taut for a period of time, usually overnight. The samples were then similarly restretched and annealed several times. Even after repeated application of stress-relaxation, the samples recovered to a certain extent when finally released at room temperature. The maximum residual extension was usually not much higher than ca. 100% with respect to the original length.

Electron Microscopy

Electron micrographs were obtained with replicas of fracture surfaces. The replication technique is the same as that described by Gezovich and Geil[4] and is thus described only briefly.

Plasticized samples were fractured *in vacuo* on a cold stage at liquid nitrogen temperature (using a Denton Freeze Etching Apparatus) and immediately shadowed with platinum-carbon at this temperature. In so doing, the plasticizer was prevented from migrating to the surface and obscuring the surface structure. Following warming to room temperature the replicas were stripped with polyacrylic acid. After dissolution of the polyacrylic acid by floating on water, the replicas were picked up on copper grids.

Dynamic Mechanical Measurement

The temperature dependence of the dynamic mechanical loss (Tan δ) was measured using a Vibron Model DDV-II at a frequency of 110 cycles per second and rate of heating of approximately 1°C/sec. Test pieces were microtomed from the as-milled samples to a thickness of ca. 0.5 mm with a length from 3 to 5 cm.

X-ray Diffraction

Wide angle X-ray diffraction (WAXD) data were obtained in a conventional flat plate camera and on a General Electric diffractometer. Small angle X-ray diffraction (SAXD) scans were run on Rigaku Denki equipment, using plasticized samples prepared both by milling (and subsequent microtoming) and solvent casting. In the solvent cast films, using a mixture of solvent, plasticizer and polymer, the plasticizer is presumed to be uniformly dispersed.

EXPERIMENTAL RESULTS

Electron Microscopy

Distinct structual changes were observed on fracture surfaces of samples A and C plasticized with DOP by means of milling, as described above, at various mill roll temperatures. The changes appeared to follow a general pattern for the two suspension polymerized resins. The appearance of fracture surfaces of samples milled at relatively low mill temperatures, 150°C or lower, seem to depend on the resin used; type C samples consisted of irregular particles, in the size range from 0.5 to 0.1 μ, while type A samples generally showed considerable evidence of micro-deformation. In a few cases, small nodules 100–200 Å in diameter were seen. Fracture surfaces of all samples milled at intermediate mill roll temperatures, near 160°C, were completely covered with relatively well defined, small nodules on the order of 100 Å in diameter. The small nodules in many samples appeared to be arranged in larger structures varying from 0.05 to 0.1 μ. These samples, in general, fracture in an apparently brittle fashion. Fracture surfaces of samples milled at higher mill temperatures, 180°C or higher, had a surface roughness on the 500 Å size scale; in some cases well-defined particles of this size were seen.

The structural changes described above can be seen most clearly in Figure 1(a, b and c) which are from sample C plasticized with 20 wt. % DOP at mill temperatures of 140, 160 and 180°C, respectively. The basic morphological structure and average nodule diameter (ca. 130 Å) observed on Figure 1b are the same as those for the similar samples in the earlier work from our laboratory (Figure 2b, Ref. 4). Samples were also milled at 130 and 190°C; they closely resemble the micrographs shown for mill temperatures of 140 and 180°C.

Samples of type C resins were also milled at 140, 160 and 180°C with 40% DOP plasticizer. The micrographs for the 140 and 160°C samples are essentially identical to those in Figures 1a and 1b. The variation in particle size in the 140° sample was too large to permit meaningful comparison of particle size. In the 160°C sample, as found by Gezovich and Geil, the nodules were somewhat larger in the 40% DOP sample than in the 20% sample. At 180°C roughness on the 500 Å size scale was present but the particles were less well defined than in Figure 1c.

At 160°C the appearance of sample A with 20% DOP (Figure 2b) is nearly identical to that for sample C (Figure 1b). Despite being a different resin, the small nodules are again ca. 130 Å in diameter and are arranged in 0.05 to 0.1 μ diameter particles. At 140°C (Figure 2a), however, although 0.05 to 0.1 μ particles are visible, they are much less well defined than in Figure 1a. There is some evidence of microdeformation. At 180°C (Figure 1c) there is also some evidence of 0.05 to 0.1 μ particles, although considerably less well defined than in the corresponding sample C (Figure 1c); granularity is also noted on the 30–50 Å scale. This is the only sample for which this size granularity was seen and it may be an artifact due to granulation of the shadowing material. One of these samples was also milled at 160°C for 10 minutes, twice as long as the sample in Figure 2b. No evidence of the ca. 130 Å particles was seen; the 0.05 to 0.1 μ particles, however, remained.

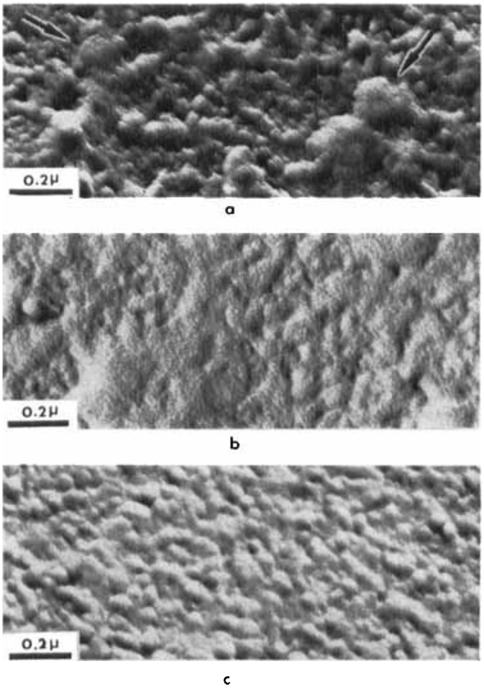

FIGURE 1 Sample C plasticized by milling with 20% DOP. a, mill temperature 140°C. b, mill temperature 160°C. c, mill temperature 180°C.

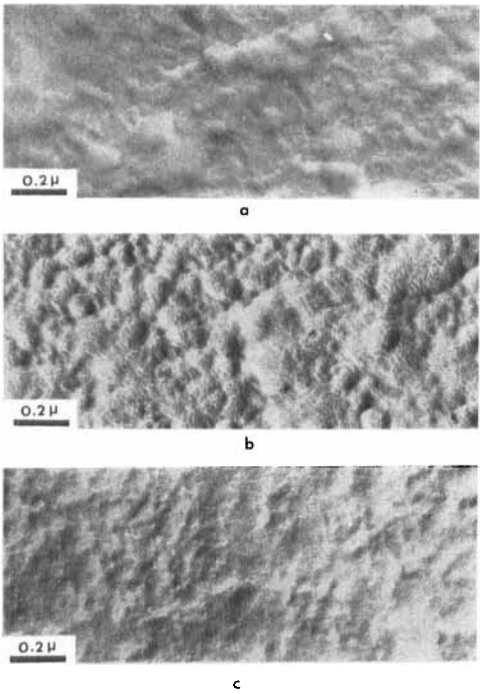

FIGURE 2 Sample A-1 plasticized by milling with 20% DOP. a, mill temperature 140°C. b, mill temperature 160°C. c, mill temperature 180°C.

Figures 3a and 3b are from sample A plasticized with 28.6% DOP (40 parts DOP per 100 parts resin) at mill roll temperatures of 154 and 165°C, respectively. Considerable microdeformation occurred during fracture of the sample milled at 154°C (Figure 3a), resulting in numerous fibrils protuding from its surface. At 165°C (Figure 3b) one again finds the surface covered with small nodules, similar to those in Figures 1b and 2b. However, the average diameter of the nodules appeared to have increased to ca. 150 Å. Figures 3c and 3d are from different areas of an A sample milled at 143°C; this is the only sample that did not follow the general pattern described previously. Structures on the scale of 0.1 μ in Figure 3c appear as distinct units with the ca. 150 Å nodules being somewhat visible, whereas in Figure 3d, the 150 Å nodules are relatively well defined while the larger structures (ca. 0.1 μ) are not as clearly identifiable. This sample is unique in that, while the 0.1 μ particles are seen in the other samples milled at comparable temperatures, as shown in Figures 1a and 2a, the smaller nodules are not as clearly observed.

Samples were also milled at 143°C with 10, 16.67 and 37.5% DOP (10, 20 and 60 parts DOP per 100 parts resin). All of these samples resembled

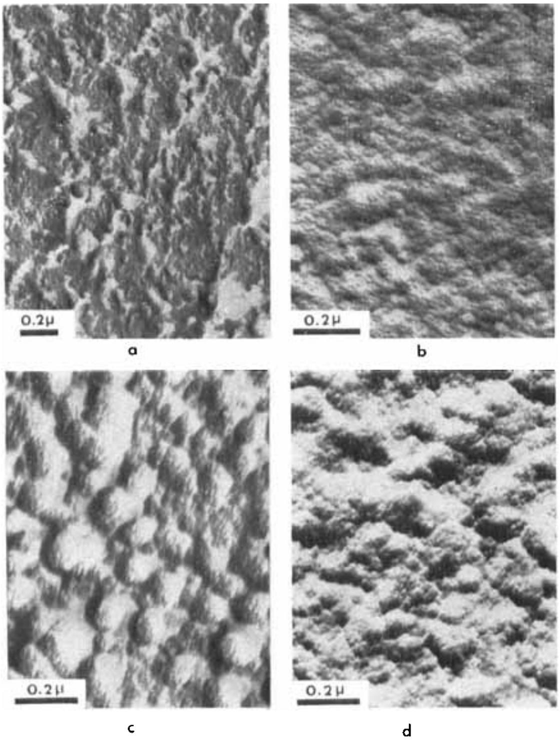

FIGURE 3 Sample A-1 plasticized by milling with 28.6% DOP. a, mill temperature 154°C. b, mill temperature 165°C. c, mill temperature 143°C. d, mill temperature 143°C.

that in Figure 3a rather than 3c or 3d. We are unable, at this time, to explain this apparent discrepancy.

Figure 4a is from a sample milled at 165°C with 28.6% DOP (similar to that shown in Figure 3b) and subsequently compression-molded at 143°C for 5 minutes before fracture; the ca. 150 Å nodules are no longer observable. Instead, particles on the scale from 0.05 to 0.1 μ, varying considerably in size, and rather smooth in appearance, can be seen. This sample was drawn to a total extension of about 100% by repeated stress-relaxation cycles, as described above. On the fracture surface of the resulting sample (Figure 4b) the 150 Å diameter nodules are again clearly seen, aligned in rows or fibrils on the order of 1000 Å long. The size distribution of the nodules, however, is considerably wider than in the original sample (Figure 3b).

SAXD scans from plasticized samples were similar to those reported previously.[4] In particular, no difference was seen in the scans from the samples

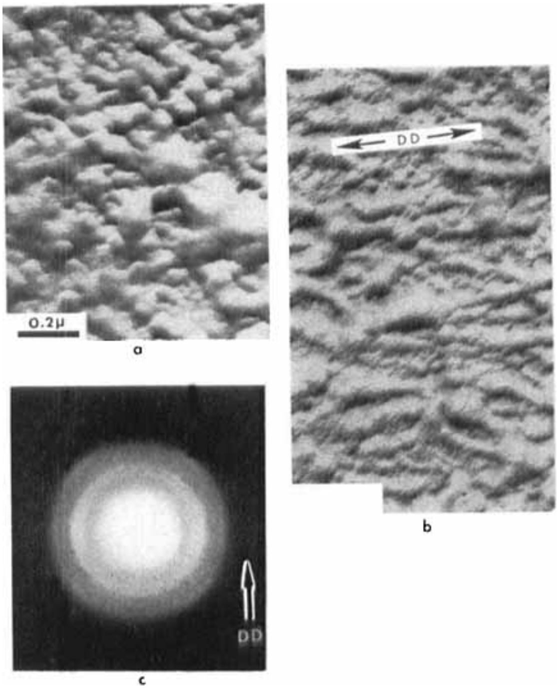

FIGURE 4 Sample A-1 plasticized with 28.6% DOP milled at 165°C. a, molded at 143°C for 5 min. b, molded and deformed, ca. 100% Elongation. c, WAXD pattern of deformed sample.

shown in Figures 3a and 3b although they have apparently different morphologies. Solvent cast samples (with 10, 20, 40 and 60% DOP plasticizer, the plasticizer presumably being uniformly dispersed) also yielded scans similar to those previously described; i.e., a diffuse maxima was observed whose spacing increased with plasticizer content. In addition, no anisotropy was observed by SAXD for the oriented plasticized PVC shown in Figure 4b.

Of concern in the plasticized samples is whether or not the plasticizer has been completely dispersed in the amorphous regions of the polymers. DTA scans of many of the samples utilized in this work were furnished to us by Dr. E. Collins and L. Chandler of B. F. Goodrich. Table 1 lists the values for *Tg* that they report. The presence of two *Tg* values is believed to indicate a lack of uniform dispersion of the plasticizer. The visibility of the 0.05 to 0.1 μ size particles appears to be related to the uniformity of dispersion, the A samples milled at 140 and 160°C with 20% DOP have poorly defined particles and show only one *Tg*, whereas the other samples have reasonably well defined

TABLE 1

DTA characterization of plasticized samples*

Sample Code	Percent DOP	Mill Temp. 0°C	Milling Time (min.)	Glass Transition °C	
				Initial Heat	Reheat
A	20	140	5	31	25
		160	5	29	29
		160	5 (Repeat)	15 & 27	24
		160	10	31	26
		180	5	29	22
C	20	140	5	24 & 39	24
		160	5	24 & 40	24
		160	5 (Repeat)	22 & 37	23
		180	5	26 & 37	24

*Supplied by E. Collins and L. Chandler, B. F. Goodrich Co., Avon Lake, Ohio.

particles and two T_gs. However, there seems to be no relationship between the presence of the small nodules and the number of T_gs.

Dynamic Mechanical Measurements

All samples for which a dynamic mechanical spectrum was obtained showed a well defined primary relaxation; i.e., Tg; the magnitude and temperature of the Tan δ maxima is listed in Table 2. The Tan δ–temperature curves for three plasticized C samples are shown in Figure 5. They typify the changes in the dynamic mechanical spectrum with processing condition.

TABLE 2

Magnitude and location of dynamic mechanical loss (Tan δ) as measured by Vibron (Plasticized Sample)

Sample Code	Percent DOP	Mill Temp.	Milling Time	$(\text{Tan }\delta)_{max}$	$(T°C)_{max}$
A	20	140	5	0.72	65
		160	5	0.75	65
		160	10	0.74	65
		180	5	0.71	65
C	20	130	5	0.68	64
		140	5	0.67	66
		160	5	0.83	65
		160	10	0.73	64
		180	5	0.75	64
		190	5	0.75	63

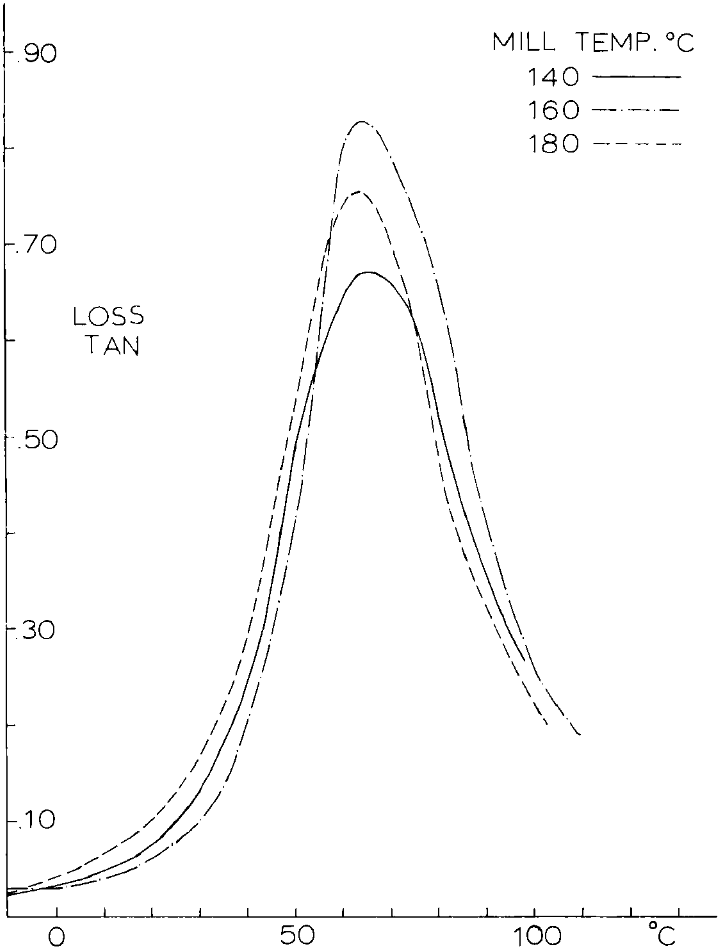

FIGURE 5 Tan δ-temperature plot for sample C plasticized with 20% DOP by milling at various temperatures.

As expected, the peak shifts with plasticizer content. In addition, however, the height of the peak depends on the milling temperature, being the highest for the 160°C sample. It should be noted that the temperature listed for T_{max} is that determined by a thermocouple in the vicinity of the sample; although the actual temperatures of the sample may be somewhat lower, the relative change should be correct.

WAXD

The resolution of WAXD scans is very poor due to the diffuse nature of the diffraction and the high mass absorption coefficient of PVC. No significant differences were observed in WAXD diffractometer scans for plasticized samples having different morphologies as determined by electron microscopy and dynamic mechanical properties. In addition, WAXD scans were run of solution plasticized samples; i.e., solvent was evaporated from varying mixtures of plasticizer (10, 20, 40 and 60 parts per hundred) and type A resin. The scans were similar to those above; in particular the spacings were the same as for unplasticized polymer, suggesting that the plasticizer does not interact with the ordered regions giving rise to the pattern.

A flat plate pattern (Figure 4c) obtained for the oriented plasticized PVC is similar to that reported in the literature for oriented, plasticized PVC[3] and indicates that there is only a moderate alignment of the molecules in the draw direction. One also notes that there is a nearly uniform background, for angles less than that of the 210 reflection. The diffuse Bragg reflections are not superimposed on an additional, obvious amorphous halo suggesting that a much larger variation in inter- and intra-molecular spacings are present in the disordered regions of PVC than in most semicrystalline or amorphous polymers.

DISCUSSION

Although the mechanism of plasticization is not completely understood, it is generally believed that plasticized PVC consists of a three-dimensional network with crystallites being the cross-links. The plasticizer is presumed to solvate the amorphous segments but not affect the crystallites which remain to hold the polymer together and restrict long-term creep.[5] In addition to examining the effect of processing on the morphology of plasticized PVC, we also need to consider whether the above suggestion is compatible with our observation.

In all of the plasticized samples, A and C, regardless of the milling temperature, there is evidence of a 0.05 to 0.1 μ particle. These may be related to the 500 Å particles observed to some extent in unplasticized PVC.[6] There is some suggestion that the distinctness of these particles may depend on the uniformity of dispersion of the plasticizer; i.e., the 20% plasticized type C samples, in which the 500–1000 Å particles are clearly visible, show two *Tg* peaks suggesting poor dispersion, whereas the 140° and 180°C 20% plasticized type A samples in which the 500–1000 Å particles are poorly defined, show only one peak. The situation for the A sample milled at 160°C is not clear; one sample gave two peaks and another only one. The 500–1000 Å particles are relatively clearly defined in the sample used for the electron microscopy.

These particles are also seen in the samples with higher plasticizer content; in fact, they were noted in all of the DOP plasticized samples examined by

Gezovich and Geil (from 10% to 60% DOP).[4] In neither case, however, can the size of the particles be correlated with the plasticizer content; they vary considerably in size within a given sample, as well as varying somewhat from sample to sample in no regular manner.

Of perhaps the most interest in attempting to relate physical properties to morphology is our observation that the small nodules, first observed by Gezovich and Geil,[4] are present only for a limited range of processing condition. Unfortunately, we were able to examine only suspension polymerized resins that had been processed in this range and thus do not know if similar nodules would be present in plasticized bulk and emulsion polymerized polymers. Coincident with the presence of the nodules, one also finds the height of the *Tg* mechancial loss maxima is greatest for samples processed in the same range.

Consider now the relationships of these nodules to the proposed crystallites. If the crystals are assumed perfect, the crystallite size in PVC is sufficiently small that each nodule might contain one or more ordered regions; each nodule might also, however, represent a single, highly defective crystal. The increase in size of the nodules with increasing plasticizer content indicates the plasticizer is solvating at least some molecules within each nodule, rather than solvating only internodular material. X-ray diffraction, on the other hand, shows that the ordered regions contributing to the diffraction pattern are not solvated by the plasticizer; the intermolecular spacing remains constant. In addition, nearly identical WAXD scans were obtained from all of the plasticized samples we examined (i.e., whether or not the nodules were seen). We also note that the nodules appear essentially identical for the two resins from different sources (A and C) which were processed in, presumably, a similar manner; that they are not seen in a sample milled at the same temperature for a longer period of time, nor in one that was compression molded at a relatively low temperature after milling, but that they reappear when the latter sample is drawn. In addition, DTA suggests the presence of material plasticized to two different degrees in some of the samples.

The observed results could be explained in terms of a crystalline core at the center of each nodule, which is not affected by the plasticization, and with the surface of the nodule being more difficult to plasticize than the internodular material. With sufficient time or at a high enough temperature, the nodules apparently merge to a degree leaving the core unaffected. However, at low milling temperatures, in most of the samples, the nodular structure was also not seen, possibly because of a greater similarity in mechanical properties of internodular and nodular surface material. We point out, however, that this explanation is not completely satisfactory; the SAXD results suggest similar electron density fluctuation in samples for which no nodules are seen in electron microscopy. The nodules themselves may result from the original polymerization process; their size is such that they would correspond to ca. 3–4 molecules for the samples we used.

Although considerably more work is needed, and suggested, by the above results, which should be considered as illustrating the possibilities of morphological research on PVC, it is evident that processing has produced significant differences in morphology, differences which are correlatable with the magnitude of the *Tg* loss maxima. In addition to further research on the morphological features of the various types of resins, the electron microscopy observations need to be correlated with other mechanical properties and X-ray measurements of crystal size and perfection.

Acknowledgements

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