Thermal Stability of Poly(vinyl Chloride). VII. Influence of Particle Size

In a previous paper,[1] it was shown that the initial rate of the thermal dehydrochlorination of poly(vinyl chloride) under a stream of inert gas was very dependent not only on physical factors such as the rate of flow of the gas and the amount of polymer, which were not unknown facts, but also the surface area of the polymer (see ref. 1, Fig. 7). About this last point, it has been observed that the surface area was very much reduced during the heating process down to an immeasurable level, upon sintering of the powder. However, it has been suggested that the final morphology of the polymer which is smoothly degraded reflects the initial one.

In order to give better support to this hypothesis and to show more closely the influence of the morphology of the polymer upon its thermal degradation, a study has been made of three samples prepared using the same emulsion process, at the same temperature, but different only in the size of their spherical particles. It is well known[2] that it is easy to prepare such samples of uniform size distribution using seeding techniques and controlling the particle growth.[3] Most of the emulsifier has been eliminated by a series of six washings during which the powder was gently stirred in pure water during 1 hr and then decanted or separated by smooth centrifugation. After the last washing step, water was eliminated by freeze drying in order not to disturb the size distribution and avoid any agglomeration.

The samples were subjected to surface area measurements, using BET techniques, sodium titration (flame emission compared to a blank sample and after sulfonitric mineralization treatment), electron microscopic studies, and finally heat treated in various ways in argon atmosphere. The HCl evolved is titrated using differential conductivity measurements.[1] The results are reported in Table I and illustrated in Figures 1–6. It may be seen at first (Figs. 1–3) that the particles are spherical but not totally monodispersed. Two families may be seen, especially in the large particles, because the seeding process cannot avoid totally the formation of new growing particles. Secondly, the measured surface area tends to be smaller than the calculated one, on the basis of the average size of the particles. Probably, the difference comes from some agglomeration of the dried sample. But we can probably conclude that the particles are actually nonporous. The fact that the same values are obtained for large and medium particles is probably to be attributed to the second family of small particles. It appears also that the washing process is more efficient for large particles.

For heating treatment with programmed increasing temperature (heating rate 45°C/hr), it may be observed (Fig. 4) that the thermal stability of the particles increases with their size. The largest particles are more stable than a reference sample of polymer prepared according to the bulk process, which have been used throughout our previous studies.[1] These conclusions are

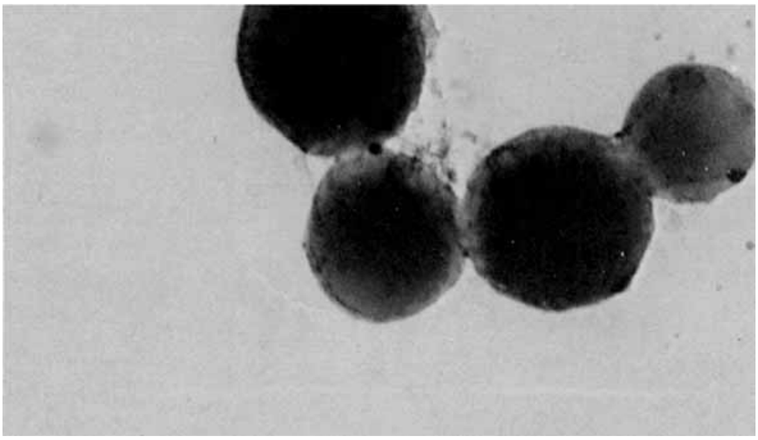

Fig. 1. Electron microscopy of fine particles.

TABLE I

			Sodium, ppm		Dehydrochlorination (after washing)			
					Induction period, hr		Rate, (ppm)/hr	
Sample	Average diameter, μ	Surface, area, m^2/g	Before washing	After washing	120°C	150°C	120°C	150°C
Fine	0.165	18	1170	337	0.6	0.4	133	605
Medium	0.28	6.3	487	150	3.5	0.6	47.5	550
Large	(0.66 0.165)	6.3	562	87	8	2.5	18.5	280

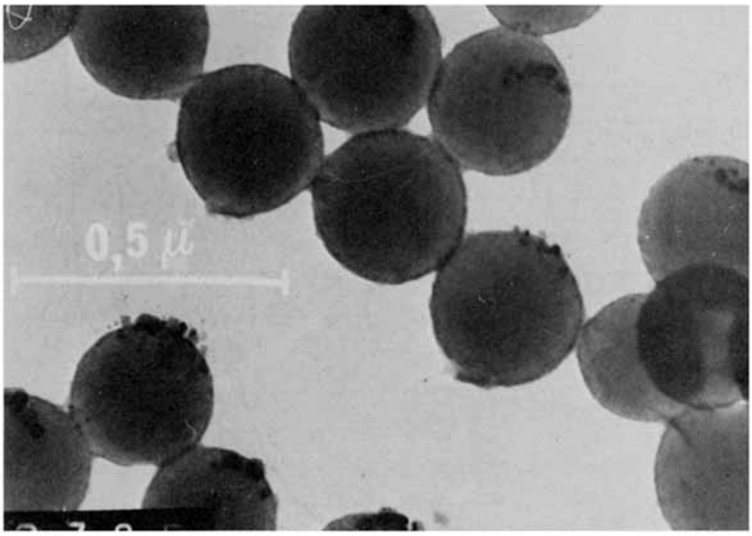

Fig. 2. Electron microscopy of medium particles.

verified in isothermal heat treatment at 120°C (Fig. 5). The induction period is dependent, as shown for fine particles, upon the amount of residual sodium but depends mostly on the size of the particles (see Table I). The rate is not dependent upon the sodium content but depends very much on the size.

Surprisingly, it seems that the second family of small grains in the large particles has no effect upon the degradation; possibly they are totally free of sodium, and then the initiation of the thermal degradation would have been produced by the sodium only in the large particles. A steady state would be established in each particle with a steady concentration of dissolved HCl in equilibrium with the vapor pressure of the HCl surrounding the particle; the rate is then a function of the surface area and also on the diffusion rate in the particle. Such features assume that an ionic dehydrochlorination process is probably dominant at this temperature. It would have been interesting to measure the probable steady concentration of HCl; but it is certainly very low, and we have not succeeded in carrying out reproducible measurements. So, quantitative checking of the above hypothesis would not be meaningful.

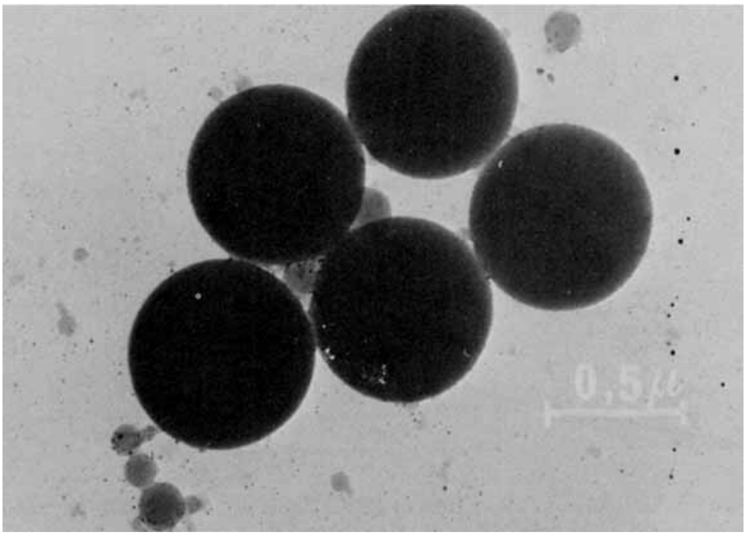

Fig. 3. Electron microscopy of large particles.

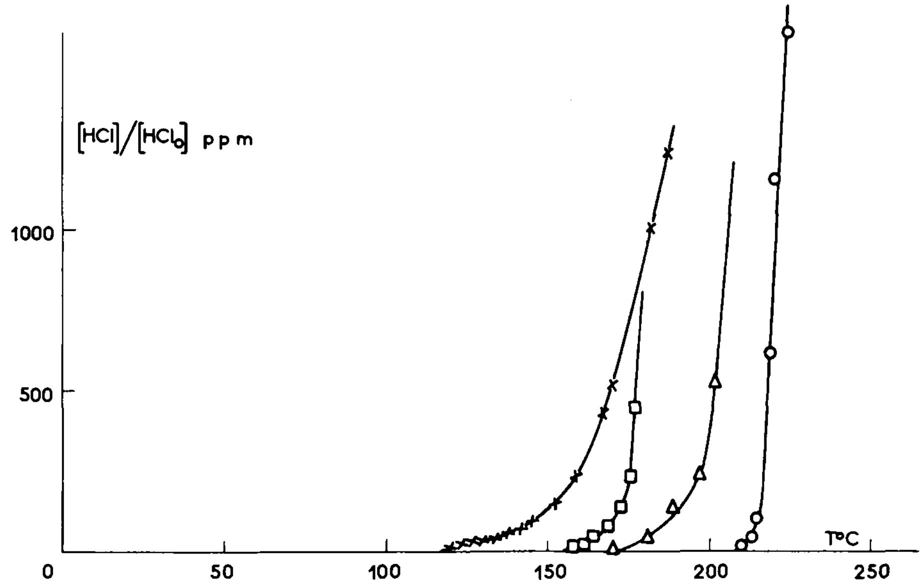

Fig. 4. Dehydrochlorination ratio vs. temperature. Linear heating rate 45°C/hr; argon atmosphere, 6 l./hr; 100 mg PVC: (X) fine particle; (□) medium particle; (○) large particle; (△) bulk process polymer.

At higher temperature (150°C, Fig. 6), the same trends are true also, but the differences between the samples are smaller, especially for the rate. But then, the morphology of the sample is probably more affected by the heat treatment because the crystalline parts of the sample begin to melt. Further, the radical dehydrochlorination mechanism is probably much more important and the steady conditions are then very different.

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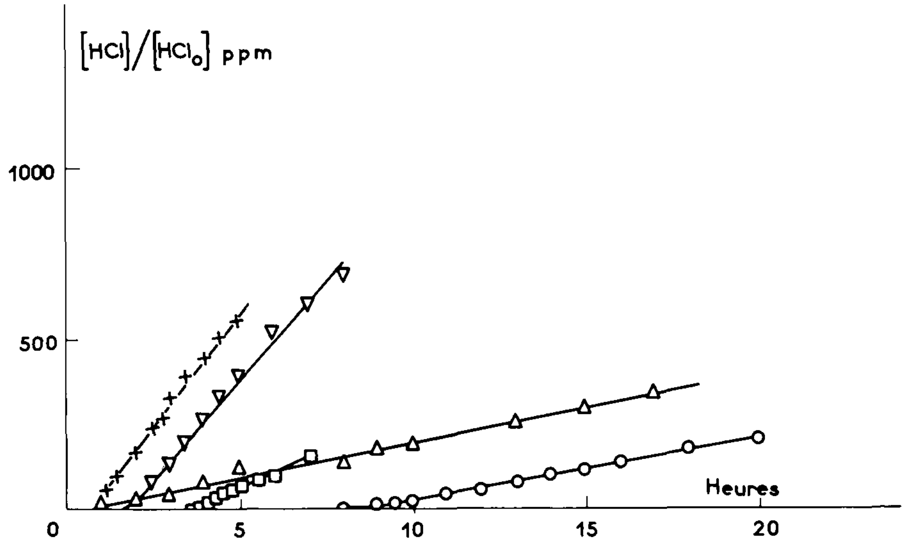

Fig. 5. Dehydrochlorination ratio vs. time at 120°C; argon atmosphere; 6 l./hr; 100 mg PVC: fine particle after washing (X) and before washing (▽); medium particle after washing (□); large particle after washing (○); bulk process polymer (△).

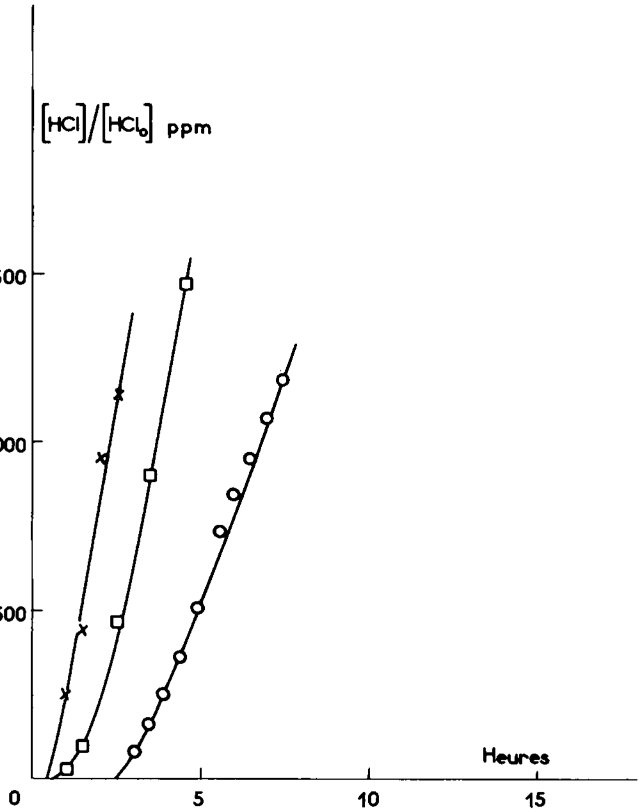

Fig. 6. Dehydrochlorination ratio vs. time at 150°C; argon atmosphere; 6 l./hr; 100 mg PVC: fine (X), medium (□), large (O) particles, bulk process polymer (△).

References

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