

Porous Polymer Carbons. IV. Fused and Unfused Carbons from Poly(vinylidene Chloride)

It is well known that homopolymers and copolymers of vinylidene chloride yield, on heating to ca. 800–950°C, carbons of high adsorptive capacity. There are, however, still some uncertainties associated with the carbonization process and the properties of the resultant carbons. For instance, as recently emphasized by Dollimore and co-workers,¹ the term Saran carbon has been employed to describe products derived from vinylidene chloride-based polymers of various compositions, carbonized in different ways. The effect of the comonomer content of such linear polymers on the final carbon properties is not known. Recently, we have shown² that the micropore volume of 900°C carbons prepared from crosslinked vinylidene chloride/ethylene glycol dimethacrylate copolymers is a decreasing function of the methacrylate content, even though this component is eliminated during the pyrolysis at temperatures below those at which most of the micropores are developed. Further, if low molecular weight additives (plasticizers and stabilizers) are not removed before pyrolysis, the carbons may have reduced adsorptive capacities.³ Finally, there is the question as to whether poly(vinylidene chloride) carbons are typically fused (cokes) or unfused (chars). In this context, Everett and co-workers^{3,4} have shown that the temperature of the first-stage dehydrochlorination of Sarans is critically important in determining whether cokes or chars are produced on subsequent carbonization. Indeed, according to Bailey and Everett,³ the condition under which the first 10% of the hydrogen chloride is eliminated fixes the morphology of the final carbon. When the initial decomposition is carried out below ca. 180°C, the structure of the carbon subsequently produced is determined by the copolymer morphology, but above this temperature, the carbon no longer carries the traces of the polymer structure. This critical temperature is approximately that at which the polymer softens on rapid heating; the nature of the final carbon is thus considered to depend on whether the first stage of pyrolysis is made on a relatively crystalline solid or on a polymeric melt. Hestin and Bastick⁵ also show fused and unfused poly(vinylidene chloride) carbons, although they set the critical temperature range as 230–240°C. We wish to report here some further studies of the carbonization of vinylidene chloride homopolymer.

The homopolymers were prepared by suspension polymerization⁶; one (B/.000/.000) was free of diluent, while the other two samples (D/.000/.286A and -/B) were prepared in the presence of a 3:1 toluene/carbon tetrachloride diluent and differ only in the suspension stabilizers used. Preliminary experiments were made by heating the samples for four to five days under a flow of nitrogen; temperatures of 150°, 165°, 170°, 175°, 180°, 185°, and 190°C were used. After cooling, the samples (2–4 g) were removed from the oil bath and then placed in a vertical furnace (Stanton Redcroft VK2) and heated to 850°C at 10°/min and held at this temperature for 12 hr before cooling; again, a blanket of oxygen-free nitrogen was provided. The carbons were examined by scanning electron microscopy. Up to first stage temperatures of 175°C, the resultant carbons are perfect but shrunken pseudomorphs of the polymer (Fig. 1). At a first-stage isothermal of 180°C, the carbons exhibit a "peeling" effect (Fig. 2) identical to that reported by Everett⁴ for Saran powder at a rather lower temperature. By 190°C first-stage heating, there is some evidence of structural changes; for instance, Figure 3 shows a coarsening of the outer appearance and incipient fusion of beads in contact.

Further studies in this critical temperature region were made by holding samples for 24 hr at 190°C and 195°C in a scanning calorimeter prior to electron-microscopic investigation. Figure 4a shows scanning electron micrographs of the original polymer (D/.000/.286A). After heating at 190°C, the outer structure is somewhat coarser than in the polymer and the beads are starting to stick together (Fig. 4b). Heating to 195°C not only leads to progressive loss of the surface characteristics (Fig. 4c, i) and more interbead fusion (Fig. 4c, ii) but to extensive loss of the interior structure (Fig. 4c, iii). Taking 190°C and 195°C preheated samples up to 950°C in the furnace leads to little, if any, additional structural changes (Fig. 4d).

Finally, we show scanning electron micrographs of a sample which was not cooled to room temperature after the initial dehydrochlorination stage but was continued directly into full carbonization. A larger sample of D/.000/.286A was placed in the vertical furnace so as to extend beyond the central region of uniform temperature. The programmer was set to heat at

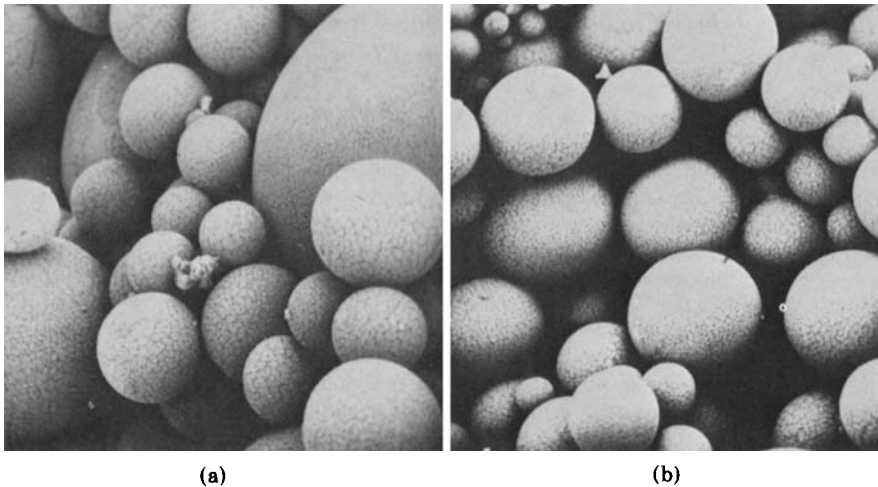


Fig. 1. Scanning electron microscopy of carbons: (a) D/.000/.286B/150°/850° ($\times 110$); (b) D/.000/.286B/170°/850° ($\times 77$).

1°/min to 200°C, to hold for 24 hr, and then to continue at 1.5°/min to 900°C. After 24 hr at full temperature, the sample was cooled and examined. The bottom part of the sample, which experienced a first-stage temperature of ca. 200°C, was a fused rod of carbon (Fig. 5a). It is just possible to distinguish (Fig. 5a, i) the outline of the original beads in the fused carbon. The top part of the specimen, which had been exposed to slightly lower temperatures, was readily reduced to the individual beads (Fig. 5b) on rubbing between finger and thumb; like the previous examples, these are almost identical in structure to the precursor polymer.

The CO₂ isotherms (195°K) were measured for both the fused and unfused parts of this carbon and are reproduced as Figure 6. Both carbons are highly microporous. The BET micropore volumes are the same at 248 cm³ S.T.P./g, but a Langmuir analysis (which we find superior for such microporous samples) gives the unfused carbon a noticeably higher micro-

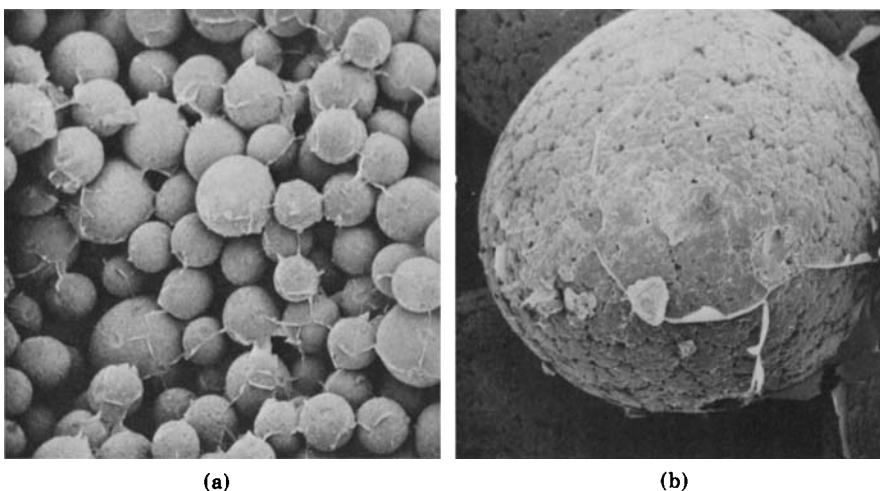


Fig. 2. Scanning electron microscopy of carbons D/.000/.286B/180°/850°: (a) ($\times 109$); (b) ($\times 545$).

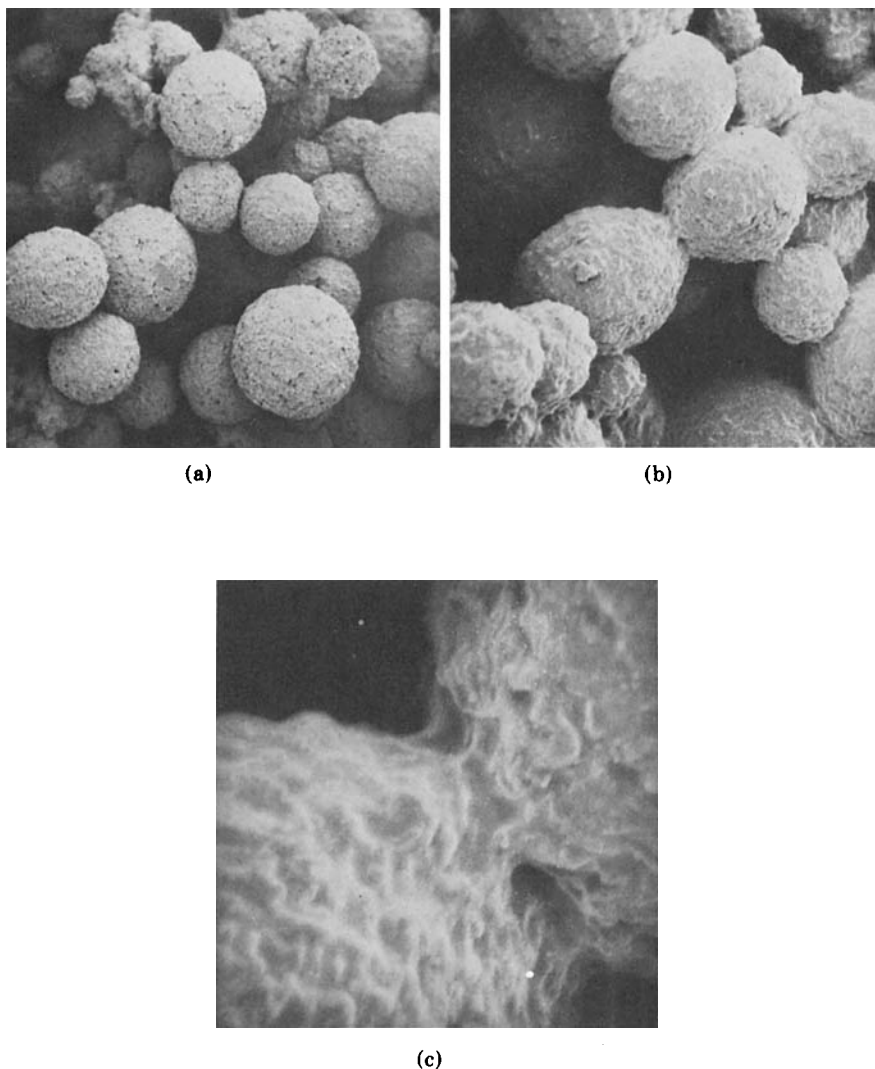
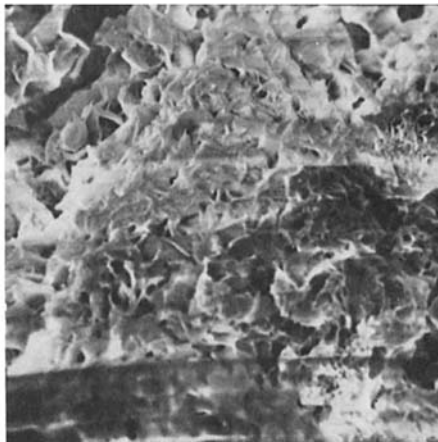
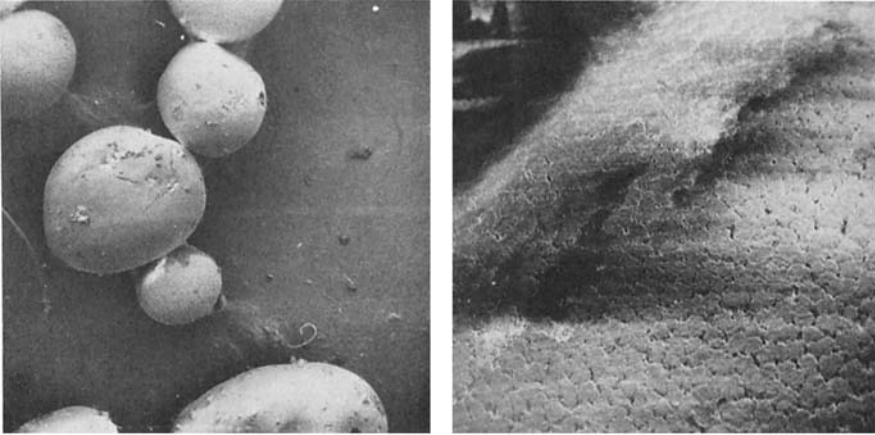


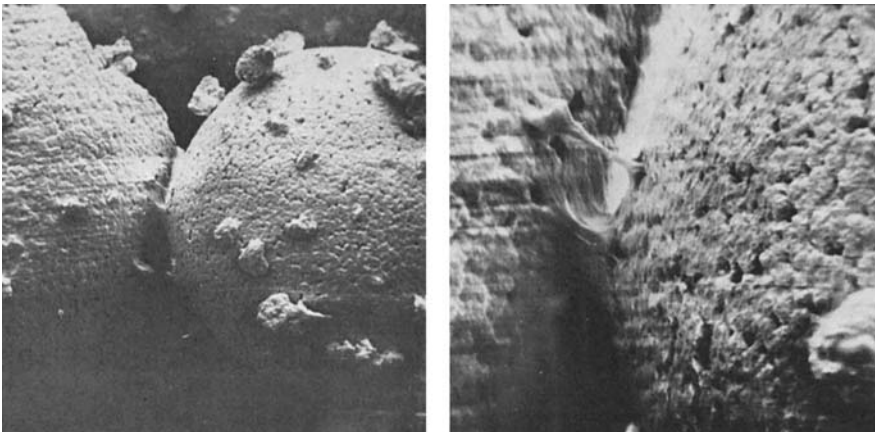
Fig. 3. Scanning electron microscopy of carbons: (a) B/.000/.000/185°/850° ($\times 605$); (b) B/.000/.000/190°/850° ($\times 1,160$); (c) B/.000/.000/190°/850° ($\times 5,810$).

porosity; expressed as pore volumes, the figures are $0.56 \text{ cm}^3/\text{g}$ and $0.49 \text{ cm}^3/\text{g}$, respectively. Thus, the development of high microporosity in a poly(vinylidene chloride) carbon does not depend on fusion occurring during carbonization. Further, although crosslinked vinylidene chloride copolymers yield carbons of lower microporosities, this cannot be a simple consequence of the chemical crosslinks preventing polymer melting during first-stage dehydrochlorination. Since these crosslinking moieties are eliminated at $350^\circ\text{--}450^\circ\text{C}$, a latent control of micropore development, like that of the gross structural features, seems to lie at temperatures well below the temperatures of actual micropore formation.

Unfortunately, these observations do not lead to an understanding of how the micropores arise. If the micropore content is proportional to the amount of crystalline lamellae in the parent polymer, introduction of comonomer will reduce the crystallinity and, hence, the microporosity. However, on this picture, the unfused and fused samples described above would be expected to differ markedly in microporosity since the initial degradation would be of a partially



(a)



(b)

Fig. 4 (continued)

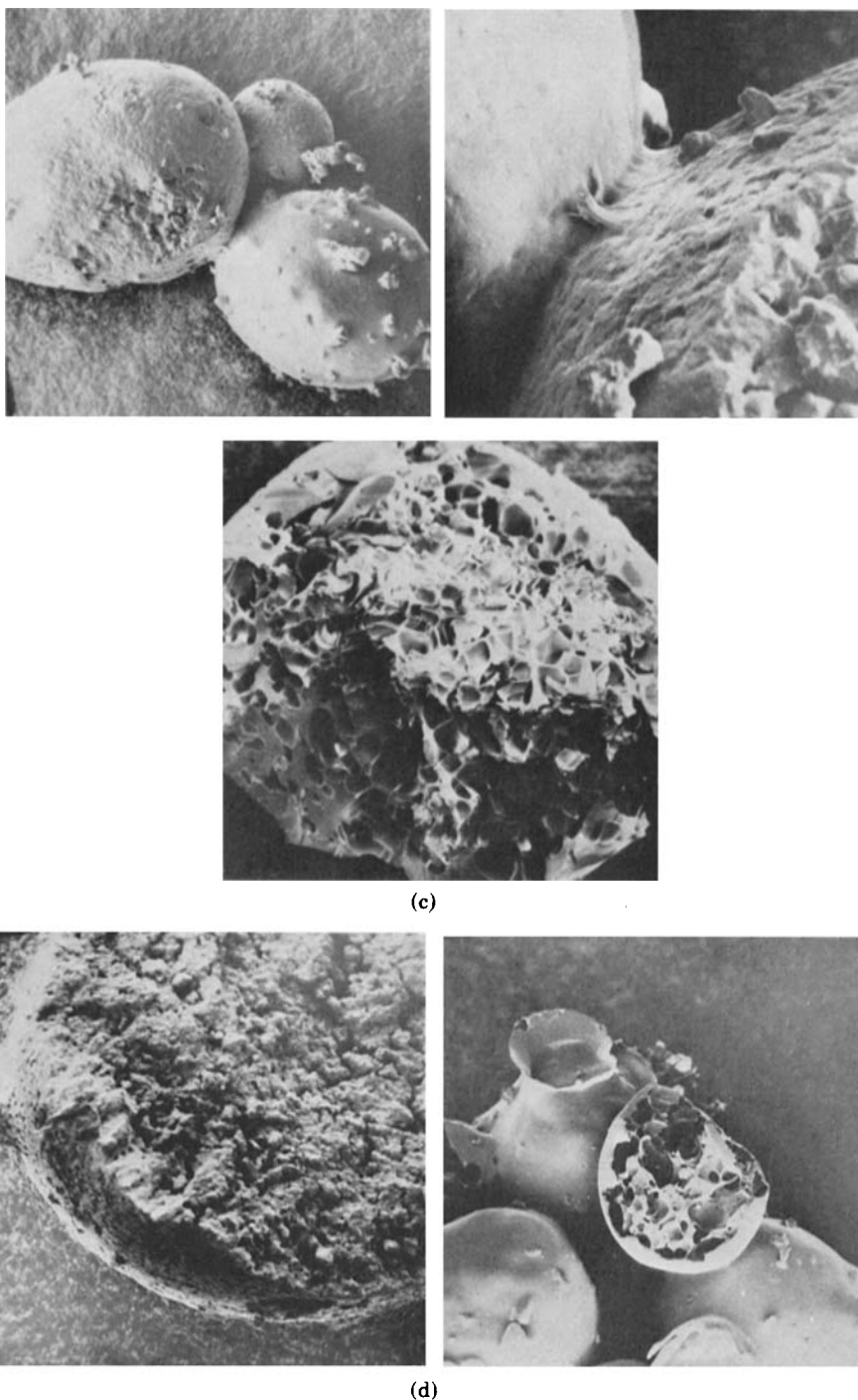


Fig. 4. Scanning electron microscopy of polymers and carbons: (a) polymer D/.000/.286A, (i) whole bead ($\times 31$), (ii) outer surface ($\times 915$), (iii) fracture surface ($\times 3100$); (b) 190° semicarbon D/.000/.286A/190, (i) ($\times 322$), (ii) ($\times 1310$); (c) 195° semicarbon D/.000/.286A/195°, (i) ($\times 131$), (ii) ($\times 640$), (iii) interior ($\times 330$); (d) 950° carbons, (i) D/.000/.286A/190°/950° ($\times 265$), (ii) D/.000/.286A/195°/900° fused ($\times 105$).

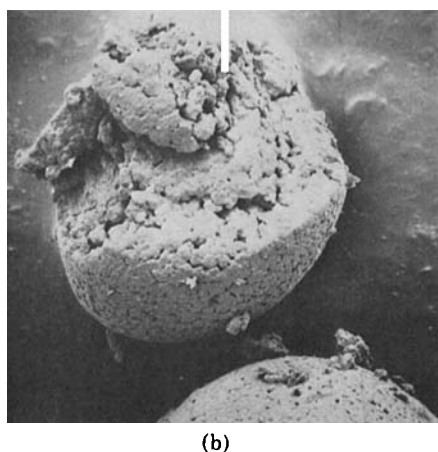
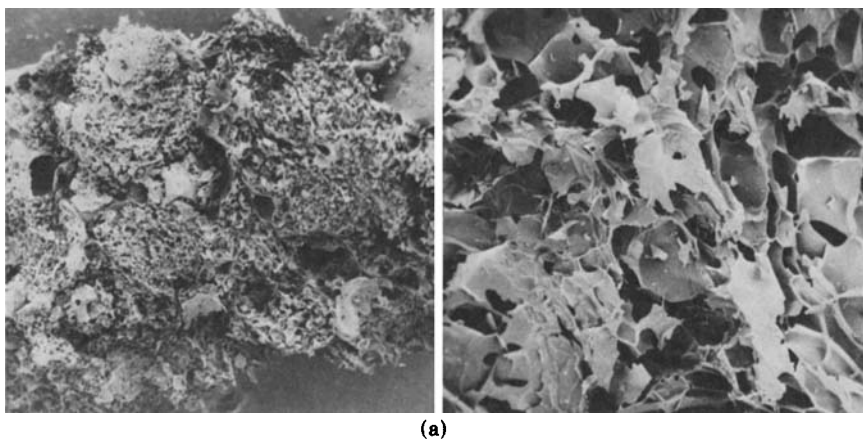


Fig. 5. Scanning electron microscopy of carbon D/.000/.286A/900°: (a) fused, (i) ($\times 32$), (ii) ($\times 317$), (b) unfused ($\times 296$).

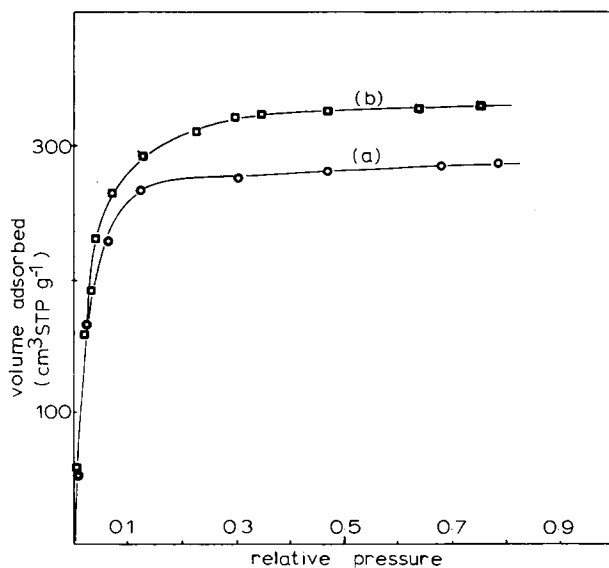


Fig. 6. Adsorption isotherm (CO_2 , 195°K) of carbon: (a) D/.000/.286A/900° fused; (b) D/.000/.286A/900° unfused.

crystalline solid and an amorphous melt, respectively. Again, if micropores are cracks resulting from reorganization during stage II, it would be reasonable to consider that the fused and unfused semicarbonbons would differ in their ability to adapt to the internal stresses resulting from further dehydrochlorination.

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