LETTERS TO THE EDITOR

Carbonization of Irradiated Polyvinyl Chloride

STUDIES have been made on the physical and crystallographic properties of carbons formed by the heating of polyvinyl chloride, $(C_2H_3Cl)_n$, called for convenience PVC.[1, 2]. Upon pyrolysis, PVC loses essentially all of its HCl at or below 225°C, leaving a residue still relatively rich in hydrogen.[3] As a result, further heating yields large quantities of tar, with the residue remaining viscous up to about 450°C.[4] Loss of hydrogen and hydrocarbons continues up to at least 800°C, producing a carbon yield equal to about 15% of the starting polymer weight.[3]

Franklin concluded from X-ray diffraction studies [2, 4] that in the PVC carbon heated to 1000°C, 85% of the carbon is in the form of graphite-like layers 18A in average diameter and the remaining 15% is in an amorphous form. The graphite-like layers which show parallelism are grouped, on the average, in packets of four or five. On the basis of the good graphitizability of this carbon and its relatively high density of 1.99 g/cm³, it was concluded that neighboring packets are well aligned. Consistent with the relatively small amount of amorphous material, the crystallites in PVC carbon are crosslinked only to a minor extent. As expected from the relatively close parallelism of the graphite-like layers and the small amount of crosslinking of these layers, the surface area of PVC carbons, as measured by gas adsorption, is low.[1] For example, the area measured by Kr adsorption at 77°K for the 700°C carbon is 0.6 m²/g. Carbons produced from PVC also do not exhibit significant molecular sieve properties.

It has previously been shown that substantial crosslinking can be produced in carbons resulting from PVC either when its dehydrochlorination between 200–250°C takes place in the presence of oxygen[5] or when it is mixed with polyvinylidene chloride (PVDC),[6] which itself undergoes extensive crosslinking upon carbonization. It has been shown that PVC can be crosslinked when subjected to nuclear radiation at ambient temperatures in the absence of oxygen.[7] Concurrent with the observed crosslinking, the irradiated PVC evolves gas (primarily HCl) and steadily darkens in color.

In the present study, irradiated PVC samples have been subsequently carbonized to investigate the possibility of producing carbons of increased surface area, which also might exhibit molecular sieve properties. The PVC samples used were $\frac{1}{2}$ in. in diameter by 2 in. long. Their formulation was 100 parts PVC, 2 parts dibutyltin bis(isooctyl thioglycolate), 2 parts calcium stearate, and 1 part N,N-ethylene-bis-stearamide.

Using a Co^{60} source at the Penn. State Nuclear Reactor Facility, samples were irradiated at a dose rate of about 0.7×10^6 rads/hr. Samples were encapsulated and placed in a test tube which was lowered into the source through a 3 in. tube. Irradiations were carried out near room temperature (RT). Previous swelling measurements[8, 9] indicated that the G value for crosslinking by Co^{60} radiation (RT) was about 0.5. Crosslinking appeared to increase linearly with dose up to about 4×10^8 rad. (Usefulness of swelling measurements is limited at higher doses.) About 30% of the available chlorine was lost by irradiation to 4×10^8 rad.[9] the rate of loss being much lower at higher doses. The gel point was determined to be about 20 mrads.

The irradiated samples were carbonized in a flowing stream of high purity N_2 using the following heating cycle: 20 to 170°C, 2 hr; 170 to 190°C, 1 hr; 190 to 210°C, 0.5 hr; and 210 to 900°C, 2 hr. Samples were soaked at 900°C for 1 hr. Carbonized samples were ground and measurements made on the 65×325 mesh material. Surface areas were calculated from CO_2 and N_2 isotherms (using the BET equation), measured at 195 and 77°K respectively. One hour was allowed for equilibration of each adsorption point.

Carbonization yields increased from 14.5% for the unirradiated PVC to 20.6% for the PVC receiving the maximum radiation, that is 6.4×10^8 rads. The increased yields partly reflect the prior loss of HCl during irradiation. Figure 1 presents results for the change in surface area of the carbons with extent of PVC irradiation, as measured by CO_2 adsorption. The specific surface area of the unirradiated PVC carbon is 0.79 m²/g. Irradiation of the PVC between 0.27×10^8 and 6.4×10^8 rad. substantially increases the surface area of the carbons subsequently produced. Maximum radiation resulted in producing a carbon with the maximum area
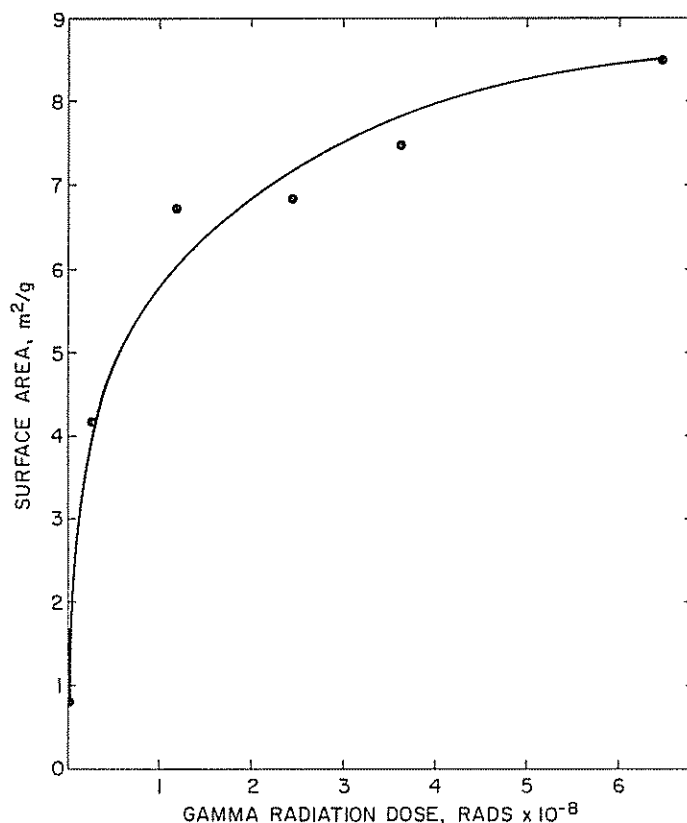
FIG. 1. Effect of irradiation of PVC on the surface areas of carbons subsequently produced. Area measured by CO_2 adsorption at 195°K.

attained, 8.5 m^2/g; it appears that additional radiation would result in little further increase in area.

The carbon from the PVC sample irradiated to 1.2×10^8 rad. has an N_2 area of only 0.1 m^2/g. Thus, it is clear that most of the surface area in this carbon, and presumably the other samples derived from irradiated PVC, is contributed by molecular sized pores in the 4–5A range.[10] Despite this generation of some molecular sieve character, the surface area of the carbons is still very low compared to those produced from thermosetting resin systems. For example, molecular sieve carbons having areas of 1200 m^2/g can be produced by carbonizing un-irradiated PVDC.[6] It is conjectured that irradiation of PVC in the presence of oxygen might significantly increase the surface area of the carbons subsequently produced. Whether these carbons would retain their molecular sieve properties is an interesting question.

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Structural Isotropy in Glassy Carbon Monofilament

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A NUMBER of studies[1, 2] have been made in recent years on filamentous materials, particularly fiber reinforced composites which are useful in space and aeronautical applications as well as in several other fields.[3] For filamentous materials, properties of low specific gravity, high tensile strength and high modulus, and sometimes high thermostability, are generally of requisite importance. Also desirable for a filament is to be isotropic in its structure.

Recently, we have succeeded in preparing a monofilament of glassy carbon (named "glassy carbon fiber"—GCF) from a mixture consisting of resole, novolak and furan resin, 7:1:2 or 8:1:1 by weight, by spinning through a die followed by quenching, curing and carbonizing. Filament diameter covers a range of 6 to 25 microns, which is dependent upon the spinning condition. For example, a filament of $8 \cdot 1 \pm 1.0$ microns in diameter was obtained by using a die of diameter of $0 \cdot 25$ mm and an average draft-ratio of 450. The shape of cross section is oval and without creases as shown in Fig. 1. This process was the first successful spinning of a carbonaceous filament directly from a thermosetting resin-mixture.[4, 5] The filament thus obtained is expected from various properties of glassy carbons[6] to have an isotropic structure. The electrical resistivity of glassy carbon, for instance, has been found to be highly isotropic.[7]

To obtain structural information, an X-ray diffraction pattern is considered to be informative. In fact, the diffraction patterns have shown that cellulose carbon fibers possess an anisotropic tendency; the graphitic layers developed from cellulose chains are oriented along the length of the fiber.[8–10] In Fig. 2, a series of diffraction patterns obtained from (A) a raw filament of GCF prior to carbonization, (B) GCF carbonized at 1000°C, and (C) GCF graphitized at 2500°C is compared with (D) a diffraction pattern of a normal graphite fiber derived from polyacrylonitrile (PAN) graphitized at 2700°C.

No crystalline pattern showing orientational anisotropy was observed either in the raw filament or in the carbonized GCF. Even in the graphitized GCF, anisotropy was found to be very small in contradistinction to a large anisotropy observed in the carbon fiber from PAN source, for which an oriented crystalline pattern appeared even in a sample heated up only to 900°C. Further heat-treatment enhances the anisotropic features of PAN fiber remarkably, quite similarly to the case of cellulose,[6] which shows also a highly oriented structure. It is believed that the anisotropy is brought about by the rearrangements occurring during the carbonization. The observations here reported demonstrated the correctness of our expectation that glassy carbon fibers are highly isotropic in its structure. Before this finding, the "model-filament"[6] of cellulose fiber has been, to our knowledge, the only example of isotropic carbon filament which appeared in the literature.

An electron micrograph illustrating a broken surface of GCF prepared at 1000°C is presented in Fig. 3. It is seen that GCF possesses a glass-like structure, which is also quite similar to that of usual glassy carbon, but which is obviously different from that of cellulose carbon fiber.[11] The representative values for tensile strength and Young's modulus of GCF were found to be 150×10^3 psi and 10×10^6 psi, respectively.

microphotographs as well as in permitting their publication.

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Recovery of the Basal Plane Electrical Resistivity in Electron-Irradiated Pyrolytic Graphite

SINCE AUSTERMAN and HOVE[1] found that the recovery of electron irradiated graphite takes place in the temperature range from 80 to 300°K, the recovery of several physical properties has been studied by REYNOLDS and GOGGIN[2-4] and others.[5, 6] Although some interesting results have been obtained, the detailed structure of recovery stages is still uncertain. An experiment was therefore performed to clarify the structure of recovery stages in electron irradiated graphite by measuring the basal plane electrical resistivity changes.

Samples were cut from the pyrolytic graphite heat-treated at 3000°C for 2 hr in the purification atmosphere of Cl_2-Freon gas. The thickness of samples is 0.13 ± 0.01 mm. Current-carrying leads and potential-probes were soldered to nickel-plated tips.

The source of high energy electrons was an H.V.E.C. 2 MeV Van de Graaff Accelerator. The energy of electron beam was 0·7 and 1·4 MeV. During irradiation the beam current was adjusted so as to keep the temperature of the sample near 80°K.

After irradiation, isochronal and isothermal pulse annealing experiments were carried out. The changes in the basal plane electrical resistivity were measured at 77°K during each step of thermal treatments.

The details of experimental apparatus and procedure will be given elsewhere.

Figure 1 shows typical results of isochronal annealing of the resistivity increase by both 0·7 and 1·4 MeV electron bombardments. The total integrated flux was 1·4 and $9·1 \times 10^{17}$ electrons/cm² in the case of 0·7 MeV, and 2·5 and $21·1 \times 10^{17}$ electrons/cm² in the case of 1·4 MeV. The defect concentration is estimated from the known values of displacement cross section to be 1·3, 8·4, 3·0 and 25·3 ppm, respectively.[7] As the recovery hardly takes place below 80°K,[1] defects produced by the electron irradiation at 80°K consist mainly of Frenkel defects. The ordinate is the ratio of the resistivity increment remaining after annealing, $\Delta\rho$, to the initial resistivity increment due to irradiation, $\Delta\rho_0$. $\Delta\rho_0$ corresponds to the defect resistivity of $a(5·5 \pm 0·5)$ mΩ cm/at. % of Frenkel pairs[7] where a is about $3·0 \pm 0·5$. a is the ratio of the defect production rate at 80°K to that at 285°K. The abscissa is the annealing temperature, and the holding time at each temperature was 10·5 min. Temperature intervals were about 5°K below 280°K and about 10°K or larger than it above 280°K. Figure 2 presents a simple numerical derivative with respect to temperature of the isochronal recovery curve of Fig. 1 in the case of 1·4 MeV to show clearly the recovery features.

The following conclusions are obtained from Figs. 1 and 2: (1) The same reverse annealing as obtained by AUSTERMAN and HOVE is observed around 100°K; (2) Additional reverse annealing is found between 120 and 180°K; (3) The recovery