

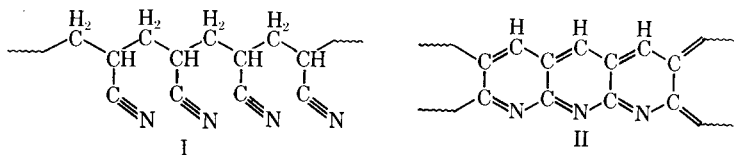
NOTES

Impervious Graphite by Radiation Polymerization of Acrylonitrile in Porous Graphite Followed by Thermal Cyclization

Recent technological interest in the development of impervious graphites with improved mechanical and physical properties, and especially low gas permeability, has led to the detailed evaluation of various organic impregnants in porous carbon and graphite.¹ The process reported here utilizes the radiation-induced polymerization of acrylonitrile absorbed in the porous carbon material, followed by the thermal cyclization of the occluded polymer.

Porous carbon/graphite (Grade 139, Stackpole Carbon Company) was vacuum impregnated with acrylonitrile and exposed to gamma radiation from a ⁶⁰Co source. A dose rate of about 1 Mrad/hr was used to polymerize the absorbed monomer. The size of the specimen was about 6 cm × 1.5 cm × 0.8 cm, and the porosity was calculated as 24% from the amount of acrylonitrile absorbed. By repeating the vacuum impregnation and irradiation steps with the same specimens, the porosity decreased to less than 0.5%, and the density correspondingly increased from 1.32 g/cm³ to 1.69 g/cm³. Compression tests were carried out in an Instron testing instrument, model TTCML, using 2.5 cm × 1.3 cm × 0.85 cm specimens at a rate of testing of 0.1 cm/min. It can be seen from Table I that the compressive strength increased considerably by the impregnation of porous graphite. A further significant increase was noted (see Table I) when the impregnated specimens were heated to 300°C for about 5 hr in an inert atmosphere. These specimens, however, reacted easily with concentrated nitric and perchloric acids, giving rise to immediate color change of the reagents. Further heating at 350°C for 10 hr increased the chemical inertness of the specimens to the same level as that of the original porous graphite, i.e., no apparent change was observed in the presence of 50% NaOH, and there was only a slow development of a pale-yellow color on long standing in concentrated perchloric and nitric acids.

In our experiments, the heating of graphite specimens impregnated with polyacrylonitrile was continued until a sample of polyacrylonitrile powder, included as a control, turned completely black. Pyrolysis of polyacrylonitrile (I) between 200° and 300°C is known² to lead to a ladder-type structure (II)³ via initial cyclization followed by dehydrogenation:



The pyrolyzed ladder polymer with the extensive conjugated system has an unusually high resistance to thermal decomposition⁴ and, as shown in this study, chemical resistance as well.

The chemical resistance of impervious graphite is limited by the characteristics of the impregnant employed, and, in addition, the resins currently in use permit a maximum working temperature of only 170°C.⁵ However, pyrolyzed polyacrylonitrile is said to be consumed only after 3 hr of heating at 900°C.⁴ It can be expected to withstand even more severe conditions when it is present in the pore structure of the graphite.

TABLE I
Compressive Properties of Polyacrylonitrile-Impregnated Carbon

Graphite	Strength, kg/cm ²	Modulus, kg/cm ²
Porous	835	21,700
Impregnated	1020	22,200
Impregnated and heated at 300°C	1160	22,600

A particularly favorable feature of using acrylonitrile is the low monomer viscosity which is maintained even during polymerization, since polyacrylonitrile is insoluble in the monomer and is precipitated out as a fluffy powder. This facilitates efficient penetration by the monomer of even extremely small pores in graphite.

Among other advantages of using gamma rays rather than conventional free-radical initiators, the following must be stressed. Graham and coworkers¹ found a diminution of polymerization efficiency with each successive impregnation while using the same catalyst concentration. Thus, only 25% of the impregnated monomer was polymerized in the fourth impregnation, compared to 75% efficiency in the first. For any further increase in efficiency in later impregnations, catalyst concentrations had to be increased drastically. These difficulties are clearly obviated when using gamma rays for initiation of polymerization.

While it is demonstrated here that an impervious graphite with increased density, strength, chemical inertness, and high temperature resistance is obtained by the gamma radiation-induced polymerization of acrylonitrile absorbed in porous graphite and subsequent heat treatment, the choice of the base stock, number of cycles of impregnation and polymerization, and pyrolysis conditions can be suitably varied according to the degree of permeability, strength, and chemical resistance of the desired product.

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