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Activated Carbon Fiber and Fabric Achieved by Pyrolysis and Activation of Phenolic Precursors

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ABSTRACT

Phenolic textiles (fiber or fabric) were pyrolyzed in a nitrogen atmosphere at 500°C for up to 4 hr. One hour of pyrolysis gave optimum carbonization based on weight loss. The resulting carbon textiles were activated at 900°C in a carbon dioxide atmosphere for up to 3½ hr. The level of activity attained was determined routinely by carbon tetrachloride vapor sorption. Surface area, pore diameter, and pore volume determinations were conducted on representative samples. Surface areas as high as about 2800 m²/g were attained.

KEYWORDS

Carbon. Activated carbon. Fibers. Fabric. Carbon fibers. Carbon fabric. Activated carbon fibers. Activated carbon fabric. Sorption. Pyrolysis. Activation. Kynol. Phenolic fibers. Phenolic fabric. Phenolic precursor.

Introduction

Efforts to prepare textiles capable of neutralizing high levels of toxic chemicals have previously been directed toward impregnation of materials with a detoxicant or a sorbent. Certain protective clothing items produced with these impregnated materials have been tested in military clothing but have been found to reduce the wearer's efficiency due to high physiological heat stress. Such heat stress is the result of several factors including moisture vapor transport, air permeability, weight, and thickness. An investigation of activated carbon fiber and fabric was undertaken to reduce the effect of heat stress, yet retain protective capability by attaining a highly sorbent textile material which is thin and light and has a high air permeability and rate of moisture vapor transport. An initial stage of this work is reported here and concerns the pyrolysis and activation of

a new phenolic textile material, available in fiber and fabric form, being marketed under the trademark Kynol.¹

Generally, activated carbon fiber and fabric can be prepared from textile polymer precursors in similar form by pyrolysis to carbon in an inert atmosphere, followed by activation (pore and surface area formation) at a higher temperature in an oxidizing gas atmosphere of air, flue gas, oxygen, carbon dioxide, or superheated steam. This is the same basic principle that has been used for years in the manufacture of powdered and granular activated carbon. However, a special pre-

¹ Kynol is a product and trademark of the Carborundum Company, Sanborn, N. Y. This trademark is for a generic type of fiber, for which the Federal Trade Commission has established the temporary generic designation "CA-0001." The generic description specifies a cross-linked novolac fiber. Citation of this and subsequent trade names does not constitute an official endorsement by the U. S. Army Natick Laboratories.

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requisite is that the textile precursor carbonize without melting [9]. It thereby retains its textile morphology and does not become stiff due to fiber and/or yarn bonding. If the activated material is to be suitable for gas sorption, then a dense noncrumbling carbon fiber must be developed during pyrolysis, and a proper pore structure consisting of a distribution of macropores, transitional pores, and micropores [3] must be achieved during activation.

Perhaps the two best known examples of textile polymer precursors used to make activated carbon textiles to date are viscose [2] and acetate [11]. Viscose is the precursor of one commercially available activated carbon fiber [10]. Other precursors, such as phenolics, have been used to obtain glassy carbon fibers [1, 6] and vitreous carbon thin discs, annuli and unspecified forms [1, 5, 8]. Phenol-formaldehyde resins have been used to produce carbons [4] and activated charcoals using steam activation [7]. However, until now the activation of phenolic fibers has not been reported.²

Experimental

The phenolic precursor fiber used for this study was a 1½-in. staple, with an average diameter of 14 microns (1.7 denier), a wooly texture, and a golden hue. The phenolic fabric precursor was a plain weave with starch sizing, weighing 4.80 oz/sq yd, and having a yarn count of 46 in the warp and 32 in the filling. Before use, this fabric was desized with a diastatic amyolytic enzyme.

The fiber pyrolysis and activation procedures were carried out in a laboratory muffle furnace having a quartz tube inserted loosely to permit delivery of 140 cc/min of an inert or oxidizing gas, i.e., nitrogen or carbon dioxide. In the pyrolysis study, preweighed samples were placed in covered porcelain crucibles and individually pyrolyzed at 500°C in a nitrogen atmosphere for periods of ¼ to 4 hr. In the activation study, duplicate carbon fiber samples were simultaneously pyrolyzed for 1 hr under the same conditions and then activated in the same crucibles, without covers, at 900°C in a carbon dioxide atmosphere for up to 3½ hr. Upon removal from the furnace, the samples were quickly covered to prevent ignition. After both pyrolysis and activation steps, the samples were allowed to cool under ambient conditions and then weighed.

Fabric pyrolysis and activation procedures were somewhat different from those for fibers. The material was sandwiched between two circles of asbestos covered wire gauze in an empty 16 mm film can and covered with glass beads to assure a flat configuration. The assembly with the can lid in place was heated at 500°C

in a nitrogen atmosphere for 1 hr of pyrolysis. After cooling, the glass beads and top layer of asbestos covered wire gauze were then replaced with sand (standard Ottawa) and the assembly reheated without the cover at 900°C in a carbon dioxide atmosphere for ¼ hr of activation. The sand was intended to promote uniform gas diffusion and prevent sample ignition after removal from the furnace.

Carbon tetrachloride vapor sorption tests were used as a screening tool to measure the approximate extent of activation. A desiccator, containing 1 liter of carbon tetrachloride, was partially immersed in a constant temperature bath so that the CCl₄ vapor temperature was maintained at 25°C. Selected carbon textile samples were allowed to sorb the saturated solvent vapor until an equilibrium was achieved; that is, until they reached a maximum constant weight. Upon sample removal from the desiccator, it was necessary to obtain weighings rapidly with a torsion balance to eliminate desorption errors. The percent weight increase was then calculated.

Surface area measurements were obtained with a BET apparatus for two representative samples selected from among the most activated fiber and fabric forms, as determined by carbon tetrachloride screening. The apparatus used was an Orr surface-area pore-volume analyzer.³

Pore size data were obtained for the most activated fabric sample using a mercury porosimeter³ which measures a minimum effective pore diameter of 35 angstroms, and has a 50,000 psi rating.

Results and Discussion

Initial pyrolysis experiments at 500°C with the golden phenolic material in fiber form resulted in soft black fibers. Considerable weight loss was observed and some activation occurred, each depending on the pyrolysis time, as shown in Figures 1 and 2, respectively.

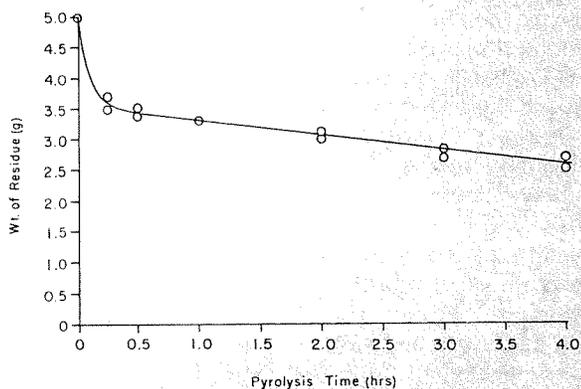


FIG. 1. Weight retention of phenolic fibers after pyrolysis at 500°C.

² Such an achievement was recently announced as a winner in the IR-100 series; i.e., it is one of the 100 most significant new products of 1971 (*Industrial Research*, September 15, 1971, page 34).

³ The Orr analyzer was Model 2100A and the mercury porosimeter was Model 905, both of which are manufactured by the Micromeritics Instrument Corp., Norcross, Ga.

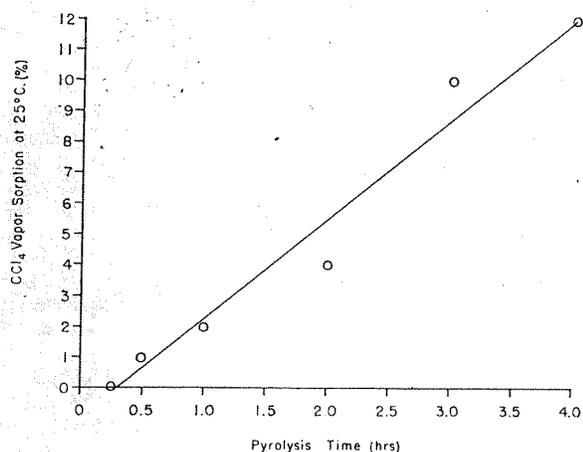


FIG. 2. Average CCl₄ vapor sorption of phenolic fibers after pyrolysis at 500°C.

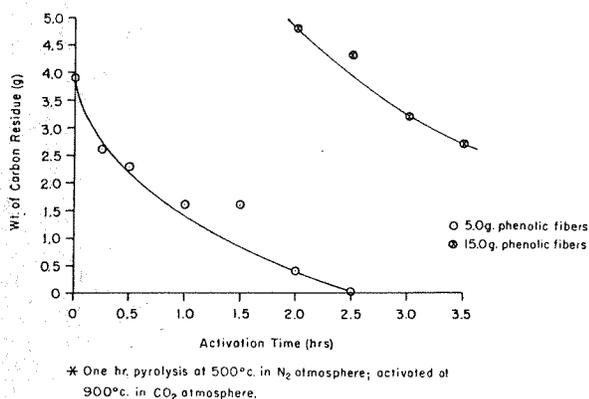


FIG. 3. Average weight retention of phenolic fibers after pyrolysis and activation.

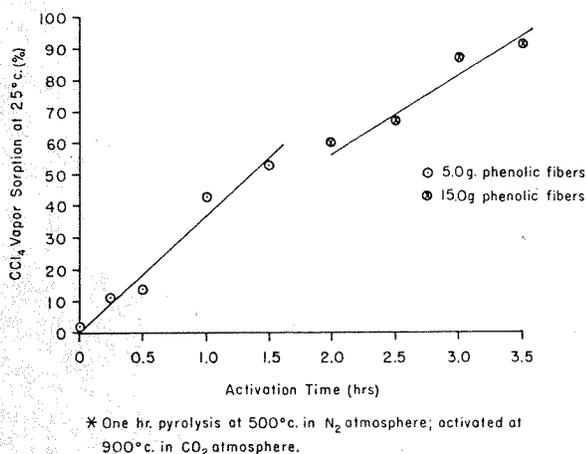


FIG. 4. Average CCl₄ vapor sorption of pyrolyzed and activated phenolic fibers.

Activation appeared to increase at a constant rate during pyrolysis but did not exceed 12% CCl₄ sorption after 4 hr at 500°C. However, weight loss was significant, initially increasing at a high rate and then tapering off to a constant lower rate. The optimum pyrolysis time thus appeared to be about 1 hr. At this time the material had a CCl₄ sorption level of 2%.

The results in Figure 3 of activation experiments performed on the pyrolyzed fibers were similar to those of the pyrolysis step except that the activity of the product increased markedly. The maximum activity obtained for an individual sample was 104% CCl₄ sorption after 3½ hr activation at 900°C. This sample had an extraordinarily high surface area of 2804 m²/g. The average rate of activation remained constant throughout the heating period, as indicated in Figure 4. During activation, as during pyrolysis, the initial rate of weight loss was relatively high probably because volatiles and/or reaction products were being removed (see Fig. 3). If activation continued long enough, the 5 g sample was entirely consumed. Therefore, the sample size was increased to 15 g to permit sufficient residue for accurate sorption tests at the longer activation times. However, even with larger samples, at the level of about 100% CCl₄ sorption, only 6% of the original weight of fiber remained, indicating a low yield of usable highly activated fibrous material.

Pyrolysis and activation of phenolic fabric gave results which paralleled those for the above phenolic fibers. One hour of pyrolysis followed by ¼ hr of activation resulted in flexible carbon fabrics having CCl₄ vapor sorption values in the 47 to 57% by weight range. The fabric exhibiting the 57% sorption value had a surface area of 245 m²/g (BET method) and a fiber pore volume of 0.26 cc/g (mercury porosimeter method). The latter includes pore sizes down to 35 angstroms diameter and agrees in order of magnitude with the volume, 0.36 cc/g, calculated from the weight of CCl₄ sorbed. However, the actual difference, a 38% greater pore volume with CCl₄, is significant because it indicates the presence of a large number of micropores smaller than 35 angstroms which the 6.4 angstrom diameter CCl₄ molecule can penetrate. Such micropores are typical of gas and vapor sorbents.

The CCl₄ vapor sorption data also correlates to a degree with surface area measurements as expected, i.e., the higher the CCl₄ sorption the higher the surface area. This appears to fit a common pattern for other precursor systems activated to different levels by a similar process. For example, commercially pyrolyzed viscose fabrics having CCl₄ vapor sorption values of 15 and 31% had surface areas of 250 and 450 m²/g respectively.

The strength of the activated carbon fibers and fabrics prepared was obviously much lower than the original phenolic material. Presumably, such strength loss was caused by bond rupture, rearrangement and

pore formation. An accompanying cause of strength reduction was a decrease in fiber diameter; e.g., activated fibers with 87 and 104% CCl_4 sorption had average fiber diameters of 12 and 11 microns, respectively, whereas their original diameter was 14 microns. Related fiber length changes could not be accurately determined since fiber breakage during handling introduced errors.

Summary

Fibrous phenolic polymer materials have potential as precursors for the production of highly activated carbon fibers and fabrics as indicated by the levels of carbon tetrachloride vapor sorption, surface area, and pore volume attained. By control of pyrolysis conditions and the activation procedure, still higher orders of sorption might be achieved. However, for many practical purposes, a compromise among activity, yield, and strength would undoubtedly have to be reached. Further study is in progress to improve pyrolysis and activation conditions and to elucidate properties such as tensile strength and elongation.

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