

CARBON COMPOSITES FROM PRE-ACTIVATED CARBON FIBERS

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INTRODUCTION

In previous presentations we have described the formation and characteristics of rigid activated carbon composites¹⁻⁴. These materials are formed by filtration from dilute water slurries of chopped isotropic carbon fibers and resin binder. The green composites are then dried, cured, carbonized and subsequently steam activated at temperatures up to 870°C. The products are highly permeable, strong and can be easily machined. The pore structure developed by steam activation is predominantly microporous, with a narrow unimodal pore size distribution. Depending on the extent of activation (degree of carbon burn off) surface areas up to 2000 m²g⁻¹ are developed.

Numerous potential applications of these adsorbents are envisaged. A recent paper⁴ described the performance of the composites in the separation of methane and carbon dioxide.

Although we have shown that the process of steam activation can generate uniform porosity in pieces of moderate size (dimensions up to 120x40x15 mm, and variation in surface area of less than ± 5%), there will clearly be difficulties in uniformly activating larger artifacts. For this reason, we have investigated an alternative method for producing the activated composite, in which the fibers are activated prior to forming. In this case, the "green" form is processed only by drying and curing. In addition to addressing the problem of uniform activation, this procedure also offers the potential for lower cost processing. The results of studies of the fabrication process, and the properties and performance of the resulting composites are presented and discussed.

EXPERIMENTAL

The chopped carbon fibers used in this study were P400 grade (Ashland Oil) of median length 700 μm and 17.5 μm mean diameter. They were activated by reaction in a tubular furnace at 830°C for 1 to 3 hours in an atmosphere of steam and nitrogen (approximately 50:50), to burn-offs between 12 and 50 wt %.

Samples of the fibers were taken for characterization, and the remainder were used for composite fabrication. The fibers were slurried in water with a phenolic resin (median diameter 17 μm); the amount of resin binder was between 9 and 43% of the weight of fibers.

Cylindrical composites of nominally 27 mm diameter were formed by filtration. Details of the forming process will not be given here. The filter cake was blown with air to remove most of the water, and the composite was then dried and cured in air by heating at a rate of 5°C/min to 200°C.

The cured composites were weighed, their dimensions measured, and their densities determined. The N₂ BET surface areas of the pre-activated fibers and of the composites were measured using an Omnisorb 610. The ability of the composites to separate a 75%:25% methane and carbon dioxide mixture was measured as described previously⁴.

RESULTS AND DISCUSSION

Dimensional Stability

When using both raw and pre-activated fibers the diameter of the cured composite is very close to that of the mold in which it was made. However, only in the case of the pre-activated composite is this the final product diameter. When raw fibers are used the subsequent activation causes substantial volume shrinkage, particularly at high burn offs⁴. For example binder carbonization causes the composite diameter to reduce by only 1.5% whereas 44% burn off during activation results in a diameter reduction of 7% (equivalent to 20% volume). It has been shown that the fiber length changes, during activation but it is not known whether its diameter changes by the same percentage. As there is some preferred orientation of the fibers during composite formation, the extent depending on the precise forming condition used, the consequent linear shrinkage may not be the same in all directions; this combined with any variation in extent of burn off throughout a large composite block can result in weakening, distortion and even cracking of the composite. The pre-activated composites do not suffer these disadvantages.

Composite Strength

A composite's strength is dependent upon several parameters e.g. fiber size and strength and binder content. Activation of the fibers reduces the strength of a composite regardless of when the fibers are activated, e.g. the bend strength is roughly halved for a 20% burn off. This indicates that the fiber strength is of major importance.

Composite Density

The densities of various composites are shown in Figure 1. It has previously been noted that these fiber networks can accommodate an equal mass of small binder particles before the fiber network is expanded⁴. The composite density is thus the fiber network density enhanced by the mass of binder incorporated; this mass will obviously be reduced slightly during curing, and more if treated to higher temperatures (e.g. carbonisation to 800°C gives a binder yield of about 60%).

The densities of preactivated fiber networks have been calculated to be around 160 kg/m³ at 15% burn off and 120 kg/m³ for 50% burn off compared with the raw fiber network density of 170-180 kg/m³. These density reductions are similar to those which are observed when a composite is post activated; they are less than the weight loss due to the overall composite volume reduction caused by the fiber contraction already mentioned.

Thus, as illustrated in Figure 1, the differences in composite density between pre and post-activated composites are due primarily to the fact that in the former the resin binder has only been heat treated to 200 °C.

Surface Area

The surface area, as measured by N_2 adsorption at 77°K, for fibers and composites are shown in Table 1. About 80% of the surface area is retained in the composite. This is encouraging since it was thought possible that components of the resin might block off a larger proportion of the pore network.

It should be noted that obtaining uniform activation throughout a normal carbon composite is difficult to achieve even though the composite has high permeability that assists diffusion. Pre-activation of the fiber circumvents this problem.

Methane Carbon Dioxide Separation

The results of passing a 75% CH_4 , 25% CO_2 mixture through pre and postactivated composites are illustrated in Figure 2. The volumes of concentrated methane obtained have been corrected for any cured resin present. Most of the molecular sieving activity has been retained but it does appear that the lower binder content preactivated composites had the better capacity for gas separation. This suggests that some of narrow pores which presumably are causing the molecular sieving effect are being blocked by components of the resin.

CONCLUSIONS

Most of the surface area and molecular sieving performance of the preactivated carbon fibers is retained during processing into a composite.

This route for making active carbon fiber composites has potential advantages dimensional stability, even activation throughout the composite regardless of size, and cheaper processing.

REFERENCES

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TABLE 1. SURFACE AREAS AND PORE WIDTHS OF PRE-ACTIVATED FIBERS AND COMPOSITES

PRE-ACTIVATED FIBERS				COMPOSITES					
Code	Burn Off %	Surface Area m^2/g	Pore Width Nm	Code	Binder Content %	SURFACE AREA		Retained %	Pore Width Nm
						m^2/g	Resin Free m^2/g		
SA152	15	530	0.71	F 87 F 105	22 9	330 370	420 410	79 85	0.75 0.69
SA186	15	530	0.64	F 159 F 163	22 11	300 370	390 420	73 79	0.99 1.00
SA187	12	480	0.67	F 164	22	310	400	83	1.02
SA188	34	990	0.82	F 161	43	510	890	90	0.96
SA154	50	1190	0.91	F 104	14	860	1000	84	0.99

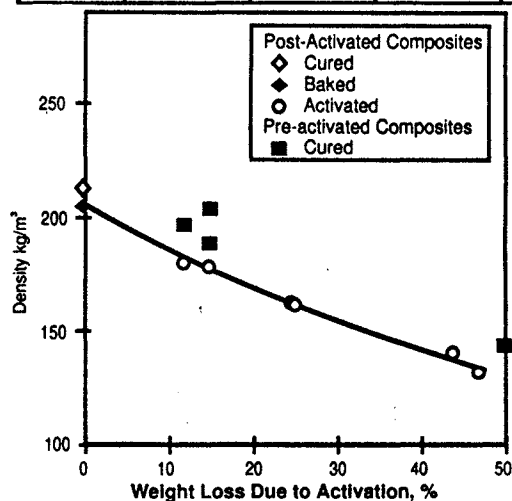


Figure 1. Density of Composites

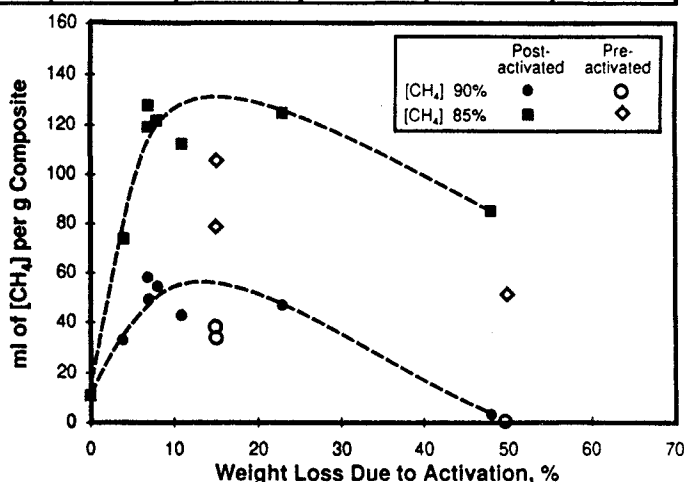


Figure 2. Methane Carbon Dioxide Separation