

PORE ANALYSIS OF CARBON FABRIC BY
DENSITY GRADIENT TECHNIQUE

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1. Introduction

All polymeric carbon fibers have an internal pore structure. The size, shape and open or closed nature of these pores are instrumental factors which determine the effective fiber density within a composite. Since composite thermoset resins can penetrate into these pores the technique of measuring effective fiber density must utilize an excellent penetrating test fluid and be capable of providing very precise density values. A density gradient technique, which utilizes benzene as the penetrating fluid, was developed to meet these requirements [1]. If the carbons atom spatial arrangement of all polymeric carbon fibers is similar, the measurement of fiber density is in reality a study of the internal pore structure [2]. Commercial carbon fabric CCA3-1641B, produced by the Hitco Corporation, Gardena, California was used to study the relationship of the pore structure and fiber density. This paper analyzes the effect of fabric oxidation and residual moisture on fiber density values as determined by the density gradient technique.

2. Experimental

Oxidation and absorption specimens were 2" squares placed into tared aluminum dishes for handling. All specimens were pre-dried for 16 hours at 105°C under vacuum to remove residual fiber moisture. The specimens were quickly removed from the oven and weighed to obtain the initial specimen weight. After weighing, the specimens were returned directly to the vacuum oven. Oxidation specimens were moved directly from the vacuum oven to a large muffle furnace previously stabilized at 450°C. At 5 minute intervals the specimens were removed from furnace, weighed immediately and returned to the vacuum oven. A test chamber for moisture absorption study was prepared by filling a desiccator jar, to within 2 cm of the base plate, with distilled water. Specimens were moved directly into the desiccator from the vacuum oven and were left in this approx. 100% R.H. environment for 25 hours. Each specimen was removed individually from the desiccator and placed on the balance pan. The specimen was allowed to desorb by evaporation until the desired pre-determined absorption value was reached. At this point disc specimens were introduced into a beaker of pure benzene. The beaker was then exposed to 5 minutes ultrasonic agitation and the specimens introduced directly into the density gradient column.

3. Discussion

The objective of this study was to determine factors which could induce carbon fabric density variability and subsequently effect the final product composite density. A BET surface area and pore size study by E. B. Stuart, and T. Ising of the University of Pittsburgh indicated the presence of type 1 isotherm micropores which are constricted or capillary connected voids [3,4]. The open or closed nature of these voids to a penetrating composite resin could significantly affect the composite structure density. To analyse the nature of the internal pore structure, specimens were oxidized up to 4% and fiber density measurements made by the density gradient technique. Figure 1 presents the fiber oxidation effect on density. The density values presented are all based on 30 minute exposure time in the gradient column. The initial portion of the "S" curve is interpreted as a closed pore skin layer which is removed by about 0.88% oxidation at point "A". This relates to the removal of 300A of skin carbon structure. After removal of this "skin" the internal pore structure is penetrated by the intruding fluid and the apparent fiber density increases accordingly. The density effect of oxidation, in excess of point "B" is much less than the A to B rate and appears to be asymptotic. The dramatic oxidation effect in fiber density demonstrates the importance of oxygen free HTHT. Our fiber density acceptance limit is 1.490 gms/cc. This can be exceeded by 0.7% oxidation and would require 0.3 to 0.6 ft.³ air per yard of fabric depending upon the fabric weight and CO or CO₂ reaction.

The effect of residual moisture on fiber density was determined by pre-filling the internal pore structure with measured weight % water and measuring the apparent fiber density. The technique employed ensures the residual fiber moisture is not surface moisture but molecules of water trapped within the constricted internal pore structures. The experimental data is compared to theoretical calculations in Figure 2. The theoretical line is based on a wt.% addition to the initial fiber density i.e. the apparent fiber density with 1% by wt. water is $1.458 + 0.015 = 1.473$ gms/cc. This assumes no net volume change associated with the 1% wt. addition. The small slope variance of experimental and theoretical data can be associated with a slight fiber swelling effect which would increase pore penetration or experimental error. The slope change of experimental data at 4% residual moisture indicates pore saturation.

The rayon based carbon fiber we have studied has received sufficient HTHT to partially close the pyrolysis pore structure. Jenkins and Kawamura have recently speculated that all carbon fibers are related to glassy carbon in structure and pore development [2]. Our study on cellulose based fiber is in agreement, however the temperature range of pore closure for cellulose carbon occurs in the 1,200°C to 1,700°C range as compared to 700°C to 1,200°C range for conventional glassy carbon [5].

Conclusions

The carbon fibers tested have a semi-permeable skin about 300Å thick and porous interior core. The skin pore structure is permeable to the small water molecules and impermeable to the much larger molecules of benzene or thermoset resin.

References

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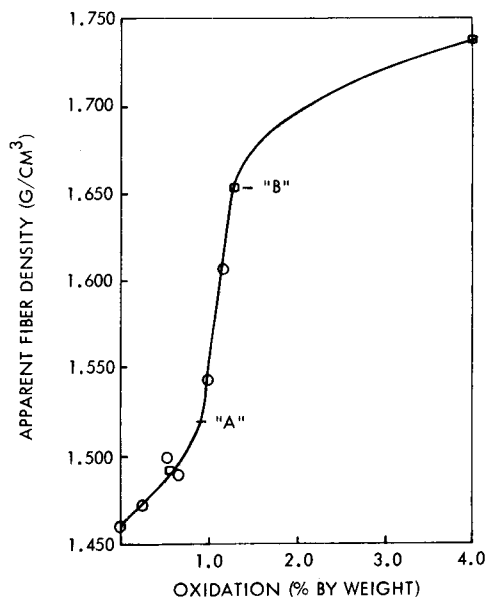


Figure 1

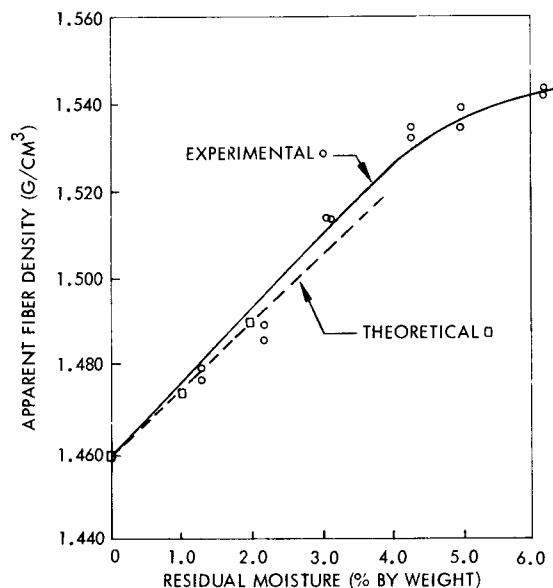


Figure 2