

Articles

Thermally Activated Phenolic Fibers

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The activation of phenolic fibers in air, at temperatures between 300 and 450 °C, was studied. Products with a surface area up to 500 m²/g and acceptable wear resistance were prepared. Treatment conditions for optimizing the surface area were defined, and the limits for time-temperature of activation established. Thermogravimetric analysis was used to simulate operating conditions such as temperature and time, in a given activation configuration. The activated phenolic fibers were characterized in terms of their chemical composition, density, wear resistance, and adsorption characteristics. Thus, activation at 450 °C, for 5 min, led to a product with 57% yield and 480 m²/g. The oxygen content in these products is as high as 30%, and a density of 1.571 g/mL is measured. Finally, the adsorption and retention of polar gases are favored in relation to nonpolar substances.

Introduction

High surface area carbons are a very important class of materials with extensive applications, such as purification of liquids and gases, filtration, catalysis, etc. Among these materials activated carbon fibers (ACF) produced from phenolic precursors^{1,2} deserve particular attention because of their unique textile configurations tailored for end uses. Thus, the availability of a sorptive material with surface area as high as 2000 m²/g, in a range of textile forms, greatly simplifies the design of pollution control devices and processes.³⁻⁶ The pore size distribution in ACF can be controlled as a result of the structural uniformity of the precursor network polymer. Due to their cross-linked structure, phenolic precursors are advantageous over the traditionally used rayon and poly(acrylonitrile) (PAN) fibers, as they facilitate pore formation and are comparatively easily activated not only to higher surface areas but also with better retention of the original textile properties. Furthermore, due to their conductivity, the ACF can be reactivated in situ by electrical resistance heating to 200 °C to recover 100% of their original activity, whereas conventional reactivation is accomplished by passing a high-temperature gas stream (800 °C) through the spent carbon. Today, ACF from phenolic precursors are produced commercially by direct activation at 800-1000 °C using the products of air combustion of liquified petroleum gas (LPG), i.e., a H₂O, CO₂, CO, H₂, C₃H₈, and N₂ mixture. Surface areas as high as 2000-3000 m²/g are reported, and a near-ideal monodispersed distribution of pore size, with a peak in the range 0.8-1.0 nm is claimed.^{7,8} However, a recognized disadvantage of the commercially available ACF is their low strength and brittleness. Also, weight losses of 70-90% are observed during activation, which

Table I. Reported Fiber Properties for Kynol 5092 Fabric

| | | | |
|----------------------------|-------|-----------------------|-----------|
| diam, m × 10 ⁻⁶ | 14-33 | tensile strength, GPa | 0.16-0.20 |
| denier | 2-10 | modulus, GPa | 3.4-4.5 |
| specific gravity | 1.27 | elongation, % | 20-60 |

greatly increases the cost of the ACF.

In the present study, an attempt was made to prepare high surface area phenolic fibers that might display much higher weight retention during activation, as well as significantly improved mechanical characteristics.

Phenolic woven fabrics were treated by heating in air, in the temperature range 300-450 °C. An earlier report⁵ indicated that such fibers display adsorption characteristics similar to ACF; however, no details were reported on their preparation and properties.

It seemed reasonable that APF, because of their potentially lower weight loss during activation, should have lower cost and display higher strength. Also, since adsorption activity is dependent on pore dimensions, surface area, and nature of the surface,⁵ it was expected that APF might yield distinctly different adsorption features compared to ACF.

Experimental Section

The phenolic fabric used was Kynol 5092, obtained from Nippon Kynol Inc., Osaka, Japan. Typical textile properties are presented in Table I. The fiber activation was carried out in a 2-L reactor vessel heated by a mantle or on an electrically heated aluminum plate. The reactor vessel was a typical flat-flange, cylindrical glass jar with wide neck and thick walls. In both cases the sample was mounted in a stainless steel frame and held in contact with the hot surface by gravity. The yield was determined as the percentage of residual mass of the fibers after the activation.

A Shimadzu TGA-50 thermogravimetric analyzer (TGA) was used, not only to determine the thermal stability characteristics of the raw material but also to simulate conditions in the activation equipment. The reported temperature conditions for the preparation of ACF⁷⁻⁹ describe the actual temperature of the heating gas, and little is known about the temperature variation at the fiber surface.

(1) Economy, J.; Lin, R. Y. *Appl. Polym. Symp.* 1976, 29, 199.

(2) Lin, R. Y.; Economy, J. *Appl. Polym. Symp.* 1973, 21, 143.

(3) Economy, J.; Lin, R. Y. U.S. Patent 3,769,144, 1973.

(4) Economy, J.; Lin, R. Y. U.S. Patent 3,831,760, 1974.

(5) Economy, J. *CHEMTECH* 1980, 10, 240.

(6) Economy, J. *Chemist* 1988, 1, 1.

(7) Kasaoka, S.; et al. *Int. Chem. Eng.* 1989, 29, 101.

(8) Hayes, J. S., Jr. *1985 Nonwoven Symp.* 1985, Apr., 257.

(9) Kasaoka, S.; et al. *Int. Chem. Eng.* 1989, 29, 734.

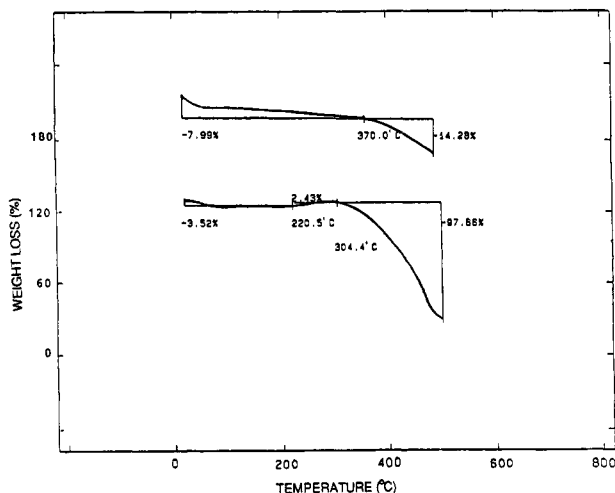


Figure 1. TGA scans for Kynol 5092 in N_2 and in air (upper and lower curves, respectively).

In a typical TGA experiment the temperature was raised at a maximum rate of $50\text{ }^\circ\text{C}/\text{min}$ to a specific point within the range $300\text{--}450\text{ }^\circ\text{C}$, and the weight loss as a function of heating time was recorded. The TGA crucible was a platinum pan, 5 mm in diameter and 2 mm in height. The weight of samples varied from 5 to 10 mg.

The chemical composition of the APF was determined by elemental microanalysis and FTIR using a Perkin-Elmer 1600 instrument. The density of the untreated and activated fibers was measured by using CCl_4/EtOH mixtures, and the wear resistance was determined according to the AATCC (American Association of Textile Chemists and Colorists) test method 93-1989, using an accelerator fitted with an abrasive liner no. 180, at a speed of 1500 rpm for 1 min, using square specimens 1×1 in.

The determination of surface area was carried out in a nitrogen adsorption instrument (ASAP 2400, Micromeritics) by using BET and Langmuir equations. The adsorption characteristics of the APF were evaluated by using TGA. The procedure, which is described in detail elsewhere,¹⁰ depends on the fluxing of the desired gas through the measuring chamber, and thus the initial and equilibrium gas uptake can be recorded. Measurements were made at $25\text{ }^\circ\text{C}$, and the partial pressure of the gas was 0.2 atm.

Results and Discussion

The thermal stability of the phenolic fibers, can be evaluated from the curves presented in Figure 1 (upper and lower curve, respectively). It is evident that the apparent decomposition in N_2 starts at about $370\text{ }^\circ\text{C}$, whereas oxidative reaction in air appears to start at about $200\text{ }^\circ\text{C}$. It should be noted that the weight increase in the range $220\text{--}305\text{ }^\circ\text{C}$ (lower curve) can be attributed to oxygen pickup. Scanning of this area in more detail showed a weight increase of 7.65% in 55 min at $200\text{ }^\circ\text{C}$. Studies on the oxidation of phenolic resins, in air at $200\text{ }^\circ\text{C}$ showed a rapid formation of carbonyl groups.¹¹ Subsequent increases in aldehyde and acid groups were found. Since hydroxyl content does not decrease until much later, an initial degradation process was proposed in which methylene carbon is oxidized sequentially to the carbonyl, aldehyde, and acid derivatives before chain scission occurs.¹² On the other hand, oxidation of poly(acrylonitrile) in air at $250\text{ }^\circ\text{C}$ develops cross-linking with increasing oxygen content.¹³

(10) Jung, H.; Economy, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1990, 31, 574.

(11) Conley, R. T.; Bieron, F. T.; Perch, P. *Coat. Plast. Prepr. Pap. Meet. (Am. Chem. Soc., Div. Org. Coat. Plast. Chem.)* 1960, 20(2), 244.

(12) Keutgen, W. A. Phenolic Resins. In *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1969; Vol. 10, p 47.

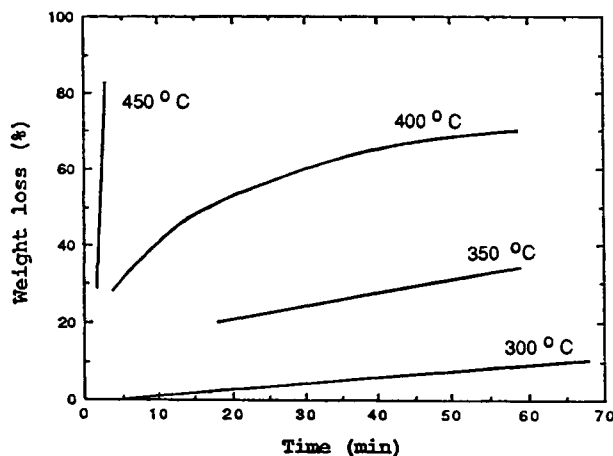


Figure 2. Weight loss as a function of time in TGA.

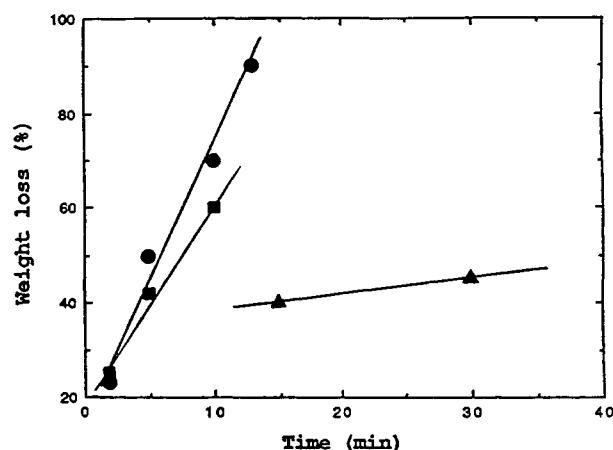


Figure 3. Weight loss versus time for different heating conditions: ■, hot plate ($450\text{ }^\circ\text{C}$); ●, ▲, reactor vessel ($450, 350\text{ }^\circ\text{C}$).

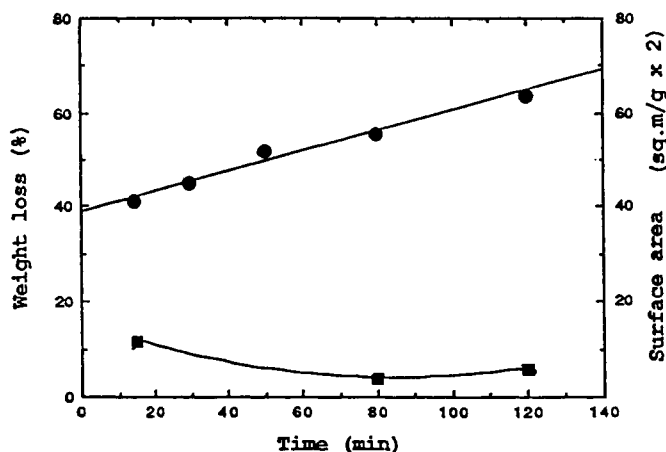


Figure 4. Treatment in reactor vessel, at $350\text{ }^\circ\text{C}$: ● weight loss (%); ■, BET surface area.

Simulation of the activation in air at 300, 350, 400, and $450\text{ }^\circ\text{C}$ was carried out using TGA, and the results, in terms of weight loss versus time, are shown in Figure 2. For temperatures lower than $400\text{ }^\circ\text{C}$ it is clear that the weight loss during activation is rather slow, whereas at $450\text{ }^\circ\text{C}$ the oxidative etching rate is very fast. Thus, the temperature range $400\text{--}450\text{ }^\circ\text{C}$ seemed most suitable, in terms of an optimized process of oxidative activation of the phenolic fibers. It also should be noted that, due to the

(13) Timmons, W. D. 1983 TAPPI Nonwoven Symposium Notes 1983, 73.

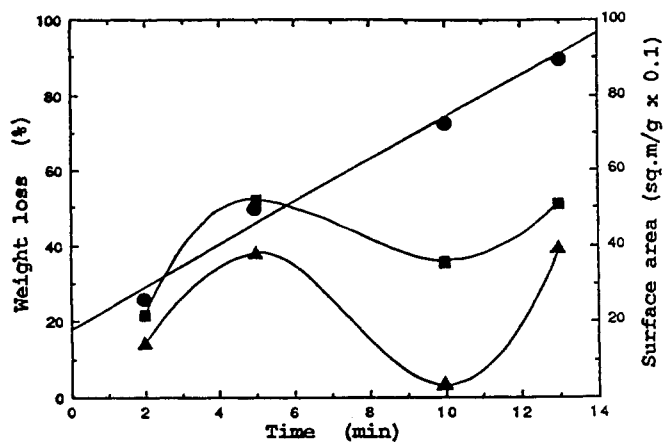


Figure 5. Treatment in reactor vessel, at 450 °C: ●, weight loss (%); ■, Langmuir surface area; ▲, BET surface area.

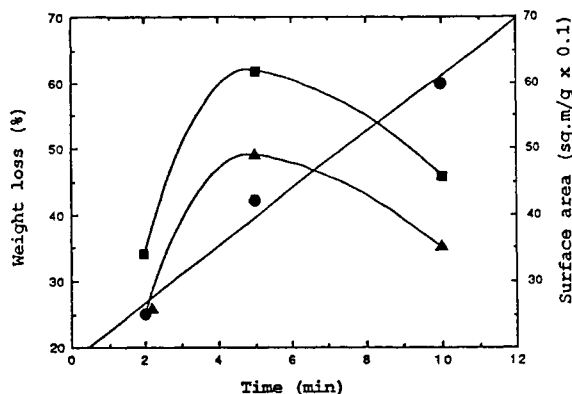


Figure 6. Heating in hot plate, at 450 °C: ●, weight loss (%); ■, Langmuir surface area; ▲, BET surface area.

small size of the sample, the above-mentioned temperatures are the actual fiber temperatures (measured by a thermocouple placed just below the TGA pan) and not the setting temperature of a heating device (e.g., a furnace).

In Figure 3 the weight loss versus time is plotted by using different apparatuses for etching. Thus, correlation of the curves of Figure 3 with those of Figure 2 provides a direct comparison as to the temperature deviations between the activation apparatus and the TGA. As a matter of fact, the actual fiber temperature seems to be lower than the setting temperature of the activation apparatuses, since a lower rate of weight loss is displayed.

The weight loss during heating and the effect on surface area are plotted versus time of treatment in Figures 4–6. In all cases the reported temperature is that of the surface in contact with the fiber (i.e., glass wall or hot plate). The curves in Figures 4–6 indicate that the weight loss has a linear dependence on the activation time. On the other hand, activation time (or weight loss) influences the creation of pores in a nonlinear way. As a matter of fact, the surface area reaches a maximum and then it decreases, probably as a result of the collapse of pores. This kind of collapse of pores with temperature has also been observed in the carbonization of coal.¹⁴ As shown in Figure 5, the development of higher surface as the activation time increases beyond 10 min is consistent with the above hypothesis. The differences in results between the two techniques presented in Figures 5 and 6 can be attributed to the different thermal environment provided by the two apparatuses. In the reactor vessel weight loss proceeds

Table II. Characteristics of the APF (Yield 57%) Compared to ACF

| property | sample | | |
|-------------------------------------|--------|---------------------|---------------------|
| | APF | ACF-15 ^a | ACF-25 ^b |
| density, g/mL | 1.5718 | <i>c</i> | 2.09 |
| wear resistance, % wt loss | 22.1 | 43.8 | 70.4 |
| surface area BET, m ² /g | 480 | 1500 | 2500 |
| chemical compn, % | | | |
| C | 68 | 92.2 | 94.3 |
| O | 29.8 | 7.3 | 5 |
| H | 2 | 0.5 | 0.7 |
| N | 0.2 | 0.03 | 0.03 |

^{a,b} Activated carbon fibers from phenolic precursors with surface area 1500 and 2500 m²/g, respectively. ^c Not determined.

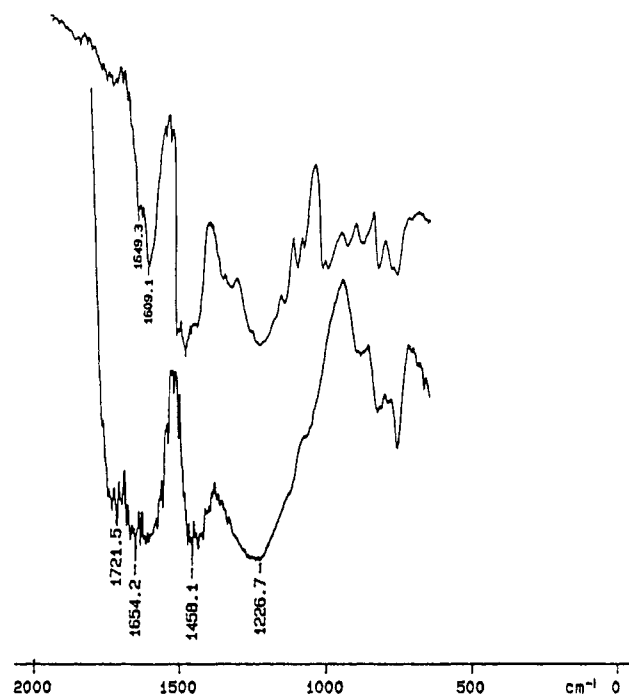


Figure 7. FTIR patterns for Kynol 5092 and the activated fabric with 57% yield (upper and lower curves, respectively).

faster and collapse of the pores is more enhanced.

These results are important for the ultimate optimization of a process leading to a high surface area fiber with high product yield. Thus, 5 min of heating on a hot plate (Figure 6) provides a surface area of 480 m²/g and a yield of 57%. The reproducibility of this technique was tested by preparing and evaluating 20 samples. The variation was $\pm 6\%$ for surface area and $\pm 1\%$ for yield.

The characteristics of the APF, in comparison to commercial ACF derived from the same fabric, are shown in Table II. From the values listed in this table it can be seen that the fabric density is considerably increased, indicating the absence of closed-cell pores in the fibers.

The wear resistance is significantly improved compared to that of the commercially available ACF-15. As a result of the oxidative activation, it is interesting to note that the oxygen content has doubled with respect to the starting material. The nature of the oxygen bonding was explored by FTIR analysis, which indicated enhanced adsorption in the range 1700–1670 cm⁻¹ (presumably quinones and carboxylic groups). Significant adsorption in the range 1260–1180 cm⁻¹ is also observed, indicating the retention of some phenolic hydroxyl groups (Figure 7). TGA of the APF up to 500 °C showed an increased rate of weight loss at 430 °C suggesting the possibility of decarboxylation (Figure 8).

(14) Singla, P. K.; et al. *Fuel* 1983, 62, 645.

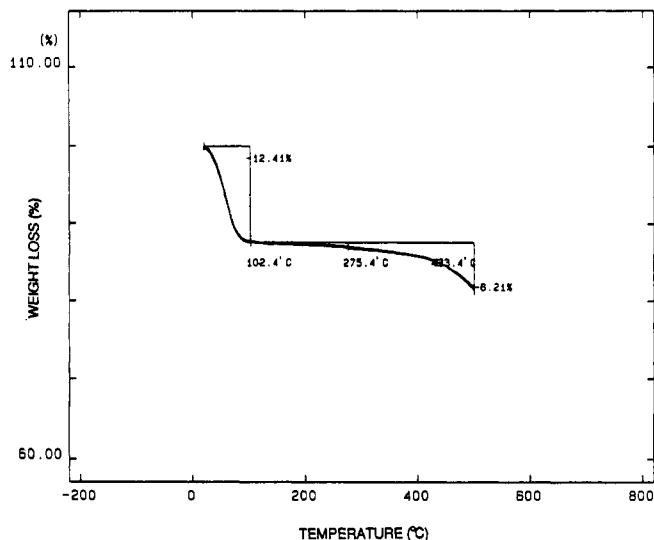


Figure 8. TGA for the activated fiber (yield 57%).

Table III. Adsorption of Various Gases by APF (Yield 57%)^a

| gas | uptake, % w/w | |
|----------------------------------|-------------------|------------------|
| | init ^b | ads ^c |
| NH ₃ | 13.9 | 6.3 |
| CCl ₂ CF ₂ | 16.1 | 5.4 |
| CH ₄ | 1.1 | 0.0 |
| C ₂ H ₆ | 2.7 | 0.1 |
| C ₃ H ₈ | 5.7 | 1.0 |

^a At 25 °C and 0.2 atm of gas partial pressure. ^b In the presence of gas. ^c Retained after gas flow is terminated.

The adsorption of various gases by APF is listed in Table III, and a typical adsorption-desorption curve, obtained using TGA, is shown in Figure 9. In Figure 9, the initially adsorbed weight is recorded as well as that which remains after purging of the sample with nitrogen. The remaining amount of adsorbed gas, which probably is present as a monolayer, is readily evolved by heating the sample between 100 and 200 °C. The values presented in Table III indicate that higher percentages are held in the case of polar gases (NH₃, CCl₂F₂), whereas the adsorption of alkanes seems to increase with molecular weight. This fact is probably related to the reduction of volatility as the molecular size increases. On the other hand, preferential adsorption of polar molecules suggests the potential for stronger interactions with the more highly polar surface.

As a matter of fact, the effect of carbon surface chemistry on its affinity with chemical substances has been already reported.^{15,16} Thus, the oxygen-rich surface, which

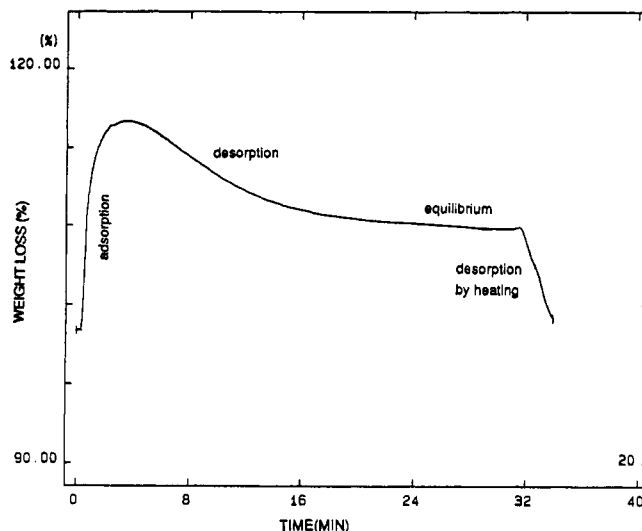


Figure 9. Typical adsorption-desorption curve for CCl₂F₂ (at 25 °C and 0.2 atm of gas partial pressure).

has a high polarity, should display increased affinity to polar gases such as NH₃.

Conclusions

Heating of phenolic fibers in air at temperatures of 400–450 °C provides a simple reproducible process for activating phenolic fibers with surface areas up to 500 m²/g. The wear resistance of APF is significantly better than that of ACF.

The APF display excellent gas adsorption characteristics with polar gases, probably because of the oxygen-rich surface.

An optimal activation process can be identified, on the basis of the data generated from the surface area-activation time curves.

TGA measurements provide a useful means both for simulation of activation conditions and also in characterizing the adsorption behavior of the APF with various gases.

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Registry No. NH₃, 7664-41-7; CCl₂CF₂, 79-35-6; CH₄, 74-82-8; C₂H₆, 74-84-0; C₃H₈, 74-98-6.

(15) Leonhard, J. Dissertation, Technical University of Aachen, Germany, 1980.

(16) Simitzis, J.; Sfyarakis, J. *Angew. Makrom. Chem.* 1988, 162, 47.