# DYNAMIC MECHANICAL PROPERTIES AND MICROSTRUCTURE OF SOME CARBONIZED HARDWOODS[1]

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ABSTRACT

Dynamic mechanical properties (DMP) from 100 to 400 K have been determined for black cherry, carbonized at temperatures from 593 to 1173 K in an inert atmosphere. The elastic modulus of a specimen carbonized at 593 K shows a marked decrease with heat treatment, but this trend appears to be reversed as the carbonization temperature is increased. Internal friction data suggest that there are relatively complex relaxations for all specimens. Scanning electron micrographs for carbonized black cherry, birch, ash, and white oak are presented. The amount of cellular integrity that remains after carbonization in an inert atmosphere is displayed. This form of specimen preparation appears to be a very useful method for investigating certain ultrastructural features of wood.

## INTRODUCTION

Dynamic mechanical spectroscopy is a particularly sensitive method for studying the behavior of graphites, carbons, and polymeric systems (Taylor et al. 1968; Taylor and Kline 1967; Woodward and Sauer 1965; Bernier and Kline 1968). This method of analysis is useful because it is nondestructive, requires relatively few specimens, and often offers some insight into molecular structure responsible for the behavior.

Carbonization of wood in the manufacture of charcoal is assumed complete between 673 to 873 K (Schaffer 1970). A recent article discussed the conversion of wood to charcoal and presents some micrographs of charcoal (McGinnes et al. 1971) prepared in a static atmosphere. The authors discuss the possible conversion of wood into graphite; however, this rearrangement into a long-range order of crystallites characteristic of graphite typically requires much high temperature ($>>$ 873 K) (Sinclair 1969), even for graphitizable material. From micrographs McGinnes et al. conclude that the microfibrillar orientation of the cell wall in wood changed into a smooth amorphous wall structure. On the other hand, upon heat treatment to 513 K in an inert atmosphere and near 550 K in air, Kollmann and Sachs (1967) found that the structure of certain xylem wood cells remained basically intact. The specimens

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TABLE 1. *Characteristics of uncarbonized black cherry specimens*

| Properties | Specimen A* |
|---|---|
| $l$ (cm) | 10.72 |
| $d$ (cm) | 0.61 |
| $wt$ (g) | 1.734 |
| $f_n$ (300 K, Hz) | 2178.4 |

* Heat treated to 400 K at a rate of 1 K/min prior to testing. The moisture content before testing was about 2%.

heated in air displayed evidence of material flow. Knudson and Williamson (1971) pyrolyzed Douglas-fir in an oven with oxygen present and found that various cell-wall components decomposed at rates related to their chemical composition.

Considerable interest has been generated recently in the use of filamentary composites. A reason for this is the desirability of obtaining a high modulus/density ratio. One of the important fillers in fiber-composites is carbon fiber with a strength/density ratio of $\sim 7 \times 10^6$ inches. These fibers are typically obtained by carbonizing polyacrylonitrile (PAN) or cellulose precursors. Presently a major drawback in the use of carbon fibers is their cost ($\sim$ \$100/lb). This has led to some speculation as to the possible use of carbonized wood as a filler for composite material. It is realized that carbonized wood composites may not obtain as high a strength/density ratio as systems using carbon fibers, but they may prove very useful in other ways.

Rate-carbonized wood in this paper is

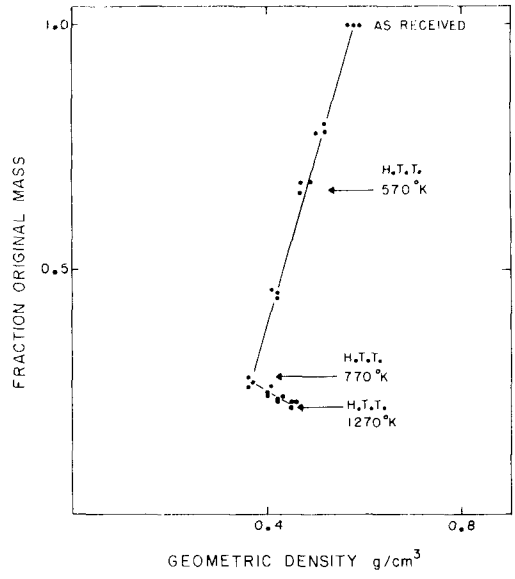


FIG. 1. Effect of heat treatment temperature on the residual mass versus geometric density.

wood that has been heat treated at a specified rate of temperature rise in an inert atmosphere. It is of interest because of its relation to the carbon-backbone polymers in wood. The dynamic mechanical properties and the microstructure of carbonized wood have been relatively unexplored. The primary purpose of this paper is to report on some results of the dynamic mechanical properties of carbonized black cherry and microstructure of carbonized black cherry, white oak, birch, and white ash for carbonization temperatures up to 1173 K.

TABLE 2. *Characteristics of carbonized black cherry specimens*

| Specimen | Before | | | After | | | |
|---|---|---|---|---|---|---|---|
| | $l$ (cm) | $d$ (cm) | wt (g) | $l$ (cm) | $d$ (cm) | wt (g) | wt % loss |
| (B)* HT 593 K | 11.40 | 0.60 | 2.010 | 11.33 | 0.58 | 1.253 | 38 |
| (C)** HT 873 K | 11.30 | 0.60 | 1.949 | 9.14 | 0.44 | 0.545 | 72 |
| (D)** HT 1173 K | 11.20 | 0.60 | 1.993 | 8.74 | 0.42 | 0.482 | 76 |

* Rate carbonization was conducted in an $N_2$ atmosphere. The rate was 6 K/min and the specimen was held for two hours at the reported temperature.

** Rate carbonization was conducted in an $N_2$ atmosphere. The rate was 3 K/min and the specimen was held for two hours at the reported temperature.

NOTE: DMP testing was carried out at a rate of — 1 K/min.

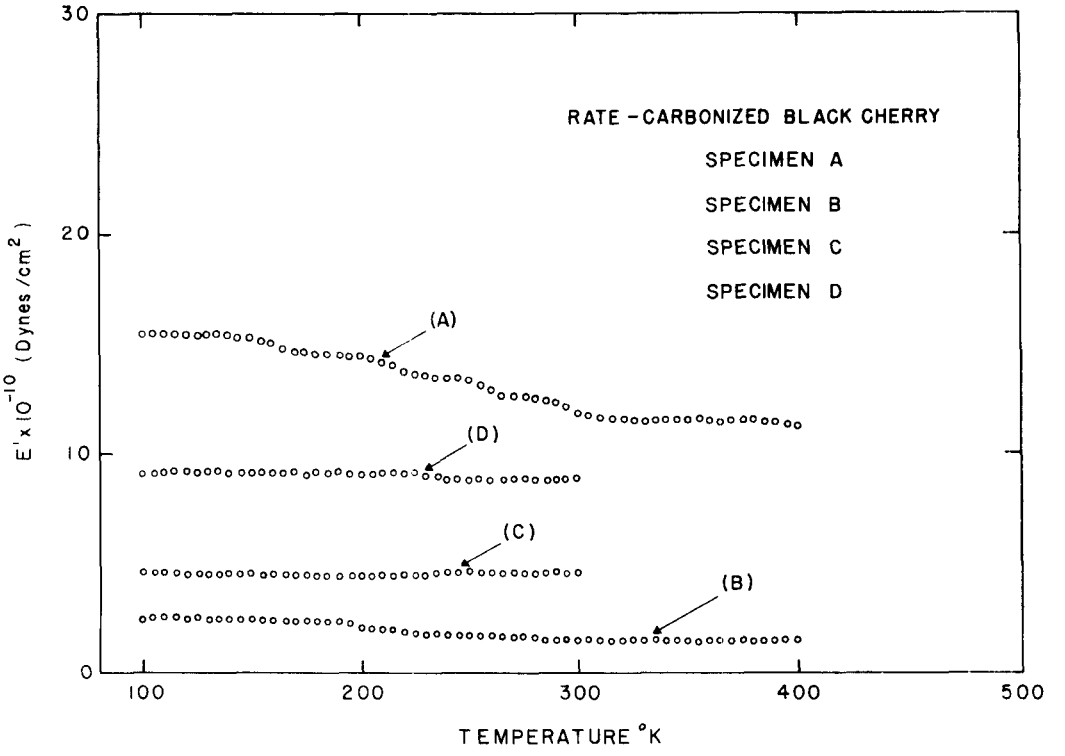


FIG. 2. Dynamic elastic modulus of rate-carbonized black cherry as a function of temperature.

## EXPERIMENTAL

### A. *Apparatus*

The dynamic elastic modulus and internal friction were measured as a function of temperature in a transverse dynamic mechanical properties (DMP) apparatus (Kline 1956) at audio frequencies. In this apparatus, a specimen is suspended horizontally by two strings near the nodes of the primary mode of transverse vibration. One string is attached to a magneto-strictive transducer used to excite the specimen while the other string is attached to the stylus of a piezoelectric crystal pickup cartridge used as a detector. Internal friction of specimens, $Q^{-1}$, is determined from the half power width, $\Delta f$, of the resonance curve and the resonant frequency, $f_o$; i.e., $Q^{-1} = \Delta f/f_o$. The dynamic elastic modulus, $E'$, is determined from the resonant frequency and the relationship

$$E' = \frac{1}{12.7}\frac{l^4\rho}{R^2} f_o^2 .$$

In this relationship, $E'$ is in dynes/cm$^2$, $l$ is

TABLE 3. *Dynamic mechanical properties for various specimens at 300 K*

| Specimen | Temp. of $Q^{-1}$ Peak (K) | $Q^{-1} \times 10^3$ at 300 K | $f_o$ at 300 K (Hz) | $E' \times 10^{-10}$ at 300 K (dyne/cm$^2$) |
|---|---|---|---|---|
| *A* | 250 | 15.9 | 2178.4 | 11.76 |
| *B* | 230 | 21.9 | 734.0 | 1.38 |
| *C* | 180 | 16.5 | 1799.0 | 4.30 |
| *D* | 130 | 7.1 | 2361.5 | 8.84 |

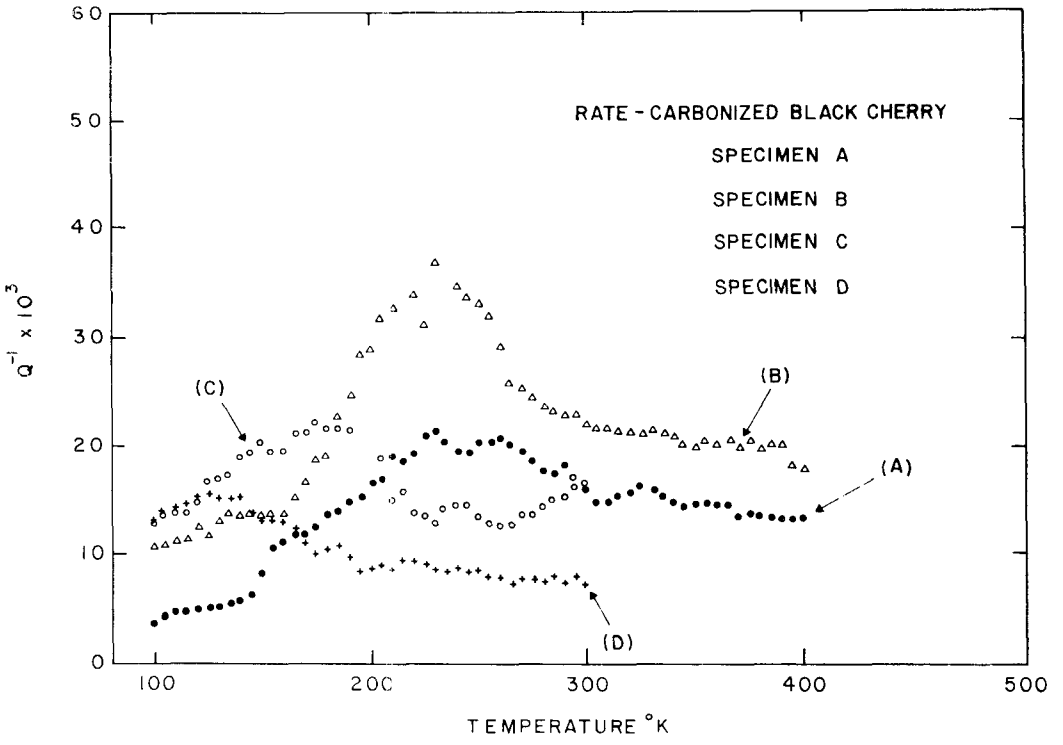


FIG. 3. Internal friction of rate-carbonized black cherry as a function of temperature.

the specimen length in cm, $\rho$ is the specimen density in g/cm$^3$ (obtained from mass and geometric dimensions prior to testing) and $R^2$ is the radius of gyration of the specimen cross section in cm$^3$. Since room temperature dimensions are employed in calculating $E'$, the values are only nominal. The temperature can be varied in the test chamber from 80 to 800 K. Typically, the temperature is steadily increased at a rate of about 1 K/min while nitrogen is slowly passed through the test chamber. The details of the use of DMP spectroscopy in the study of wood and the particular apparatus employed are discussed elsewhere (Blankenhorn 1972). The reference discusses errors and reproducibility in this method of measurement. It also presents extensive data on a series of specimens.

### B. *Specimens*

All the DMP specimens were machined in the form of a rod from black cherry in the longitudinal direction of the tree. The characteristics of uncarbonized specimen *A* are given in Table 1. Prior to the DMP test reported, this specimen was heated at a rate of about 1 K/min in a DMP test (not reported) until the temperature reached 400 K and was immediately cooled to room temperature. The characteristics and carbonization treatments of carbonized specimens *B*, *C* and *D* are given in Table 2. All the specimens were oven-dried prior to carbonization. Specimens *B*, *C*, and *D* were placed under vacuum overnight before testing. Table 3 lists the dynamic mechanical properties at 300 K for the various specimens reported.

Black cherry specimens were used to determine the effect of heat treatment temperature on the residual mass and the density that is determined from the specimen mass and geometric dimensions after carbonization. The specimens were oven-dried prior to carbonization. The plot of the

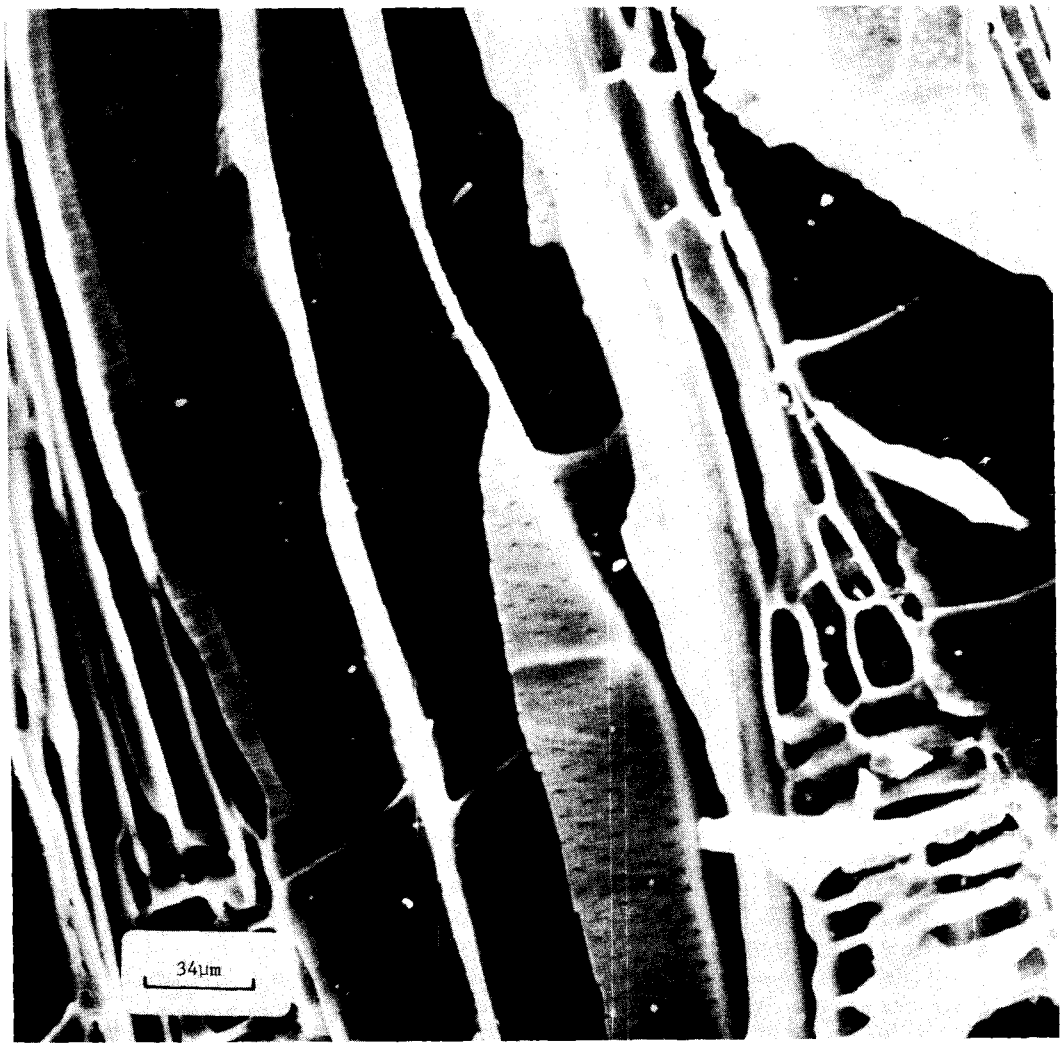


FIG. 4. Radial view of black cherry specimen *C*, which has been rate-carbonized to 873 K (scanning electron micrograph).

fraction original mass versus density for various heat treatment temperatures (HTT) is reproduced in Fig. 1.

In addition to the DMP tests reported, a large series of DMP tests have been conducted on both uncarbonized and carbonized black cherry and white ash (Blankenhorn 1972; Kline et al. 1972). It is intended that detailed papers concerning these data will be published later. The data presented here are consistent with the unpublished data.

## RESULTS

The dynamic elastic modulus, $E'$, data as a function of temperature are presented in Fig. 2. Carbonization at 593 K resulted in a decrease in the overall level of $E'$ compared to specimen *A* (uncarbonized). Carbonization at higher temperatures (873 to 1173 K) appears to result in a reversal of this trend, and the overall level of the modulus increases as compared to specimen *B* carbonized at 593 K. Data for specimen *A* show the effects of a prominent relaxation


FIG. 5. Cross-sectional view of a multiple pore of black cherry specimen *D* which has been rate-carbonized to 1173 K (scanning electron micrograph).

centered near 250 K. The modulus for specimen *B* had a slight relaxation near 230 K and for specimen *C* near 190 K corresponding to internal friction peaks (Fig. 3) near these temperatures. The modulus data for specimen *D* were relatively flat over the temperature region.

Internal friction data ($Q^{-1}$) are presented in Fig. 3 and supplement the information on the relaxations. Specimen *A* had a broad internal friction peak centered near 250 K and a slight hump near 160 K. Specimen *B* had a higher internal friction level than specimen *A*, and the peak was centered near 230 K with a broader hump near 160 K. Upon heat treatment to 873 K (specimen *C*), there is a broad internal friction peak centered near 190 K and evidence of the hump near 160 K (evident in specimen *A*; also *B*) again appears. The mass of specimen *C* increased during DMP testing. With further heat treatment (1173 K for specimen *D*), the internal friction showed a slight hump near 130 K followed by gradually


FIG. 6. Radial view of a vessel of black cherry specimen *D*, which has been rate-carbonized to 1173 K (scanning electron micrograph).

decreasing values as the temperature increased. Table 3 is a summary of the internal friction and $E'$ values for the various specimens at 300 K.

In order to assist in the characterization and understanding of the carbonized wood, a large series of scanning electron micrographs (scanning electron microscope Type —JSM, Japan Electron Optics Lab Co., Ltd.) were taken of cherry and some other hardwoods. Some of these micrographs are presented in this article to display the excellent cellular integrity that remains upon carbonization in an inert atmosphere and to present the overall structure for the reader. Specimens carbonized to $\geq$ 873 K are sufficiently conductive that they were placed in the scanning electron microscope (SEM) without any special coating or preparation. The specimens were simply broken in the appropriate plane and mounted on the specimen holder. The SEM micrographs presented are characteristic of the complete specimen cross section.

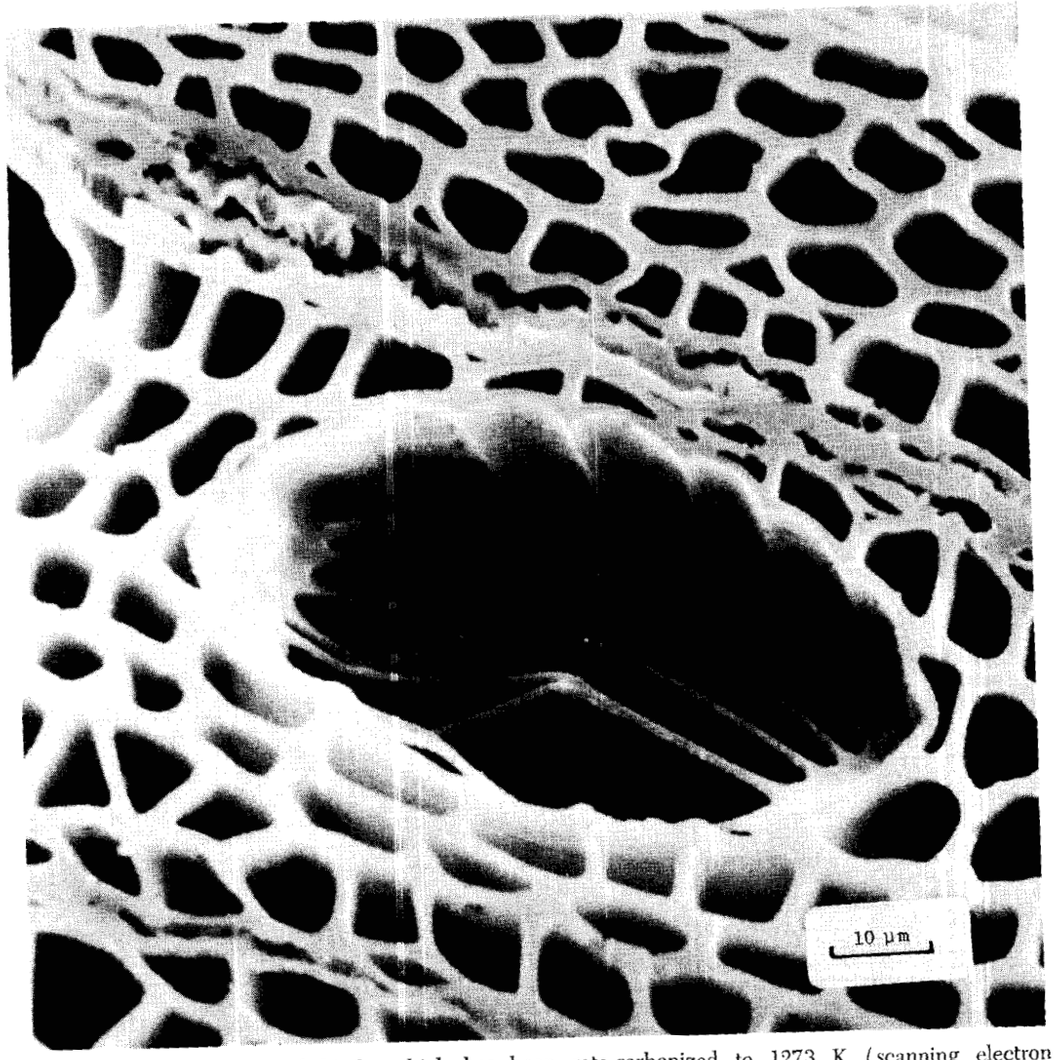


FIG. 7. Cross section of birch, which has been rate-carbonized to 1273 K (scanning electron micrograph).

Figure 4 is a view of a radial section of a piece of specimen *C*. The depth of field of the SEM assists in revealing the cellular integrity that remains after carbonization. In this figure, one can see both the upright and procumbent ray cells. Fibers, longitudinal parenchyma, helical thickening, simple perforation plates, and vessel pits are evident.

Figure 5 and 6 are micrographs of specimen *D*. In Fig. 5 (cross section), the carbon skeleton and intervessel pitting between multiple pores are evident. Figure 6 is a radial view of contiguous vessel elements with a ray field behind them. The pit membrane has disappeared and the aperture has been enlarged to varying degrees after this heat treatment, but the basic form of the structure remains intact. Helical thickening and a simple perforation are clearly displayed.

Different species of wood were investigated with the SEM after carbonization. A few of these micrographs are presented

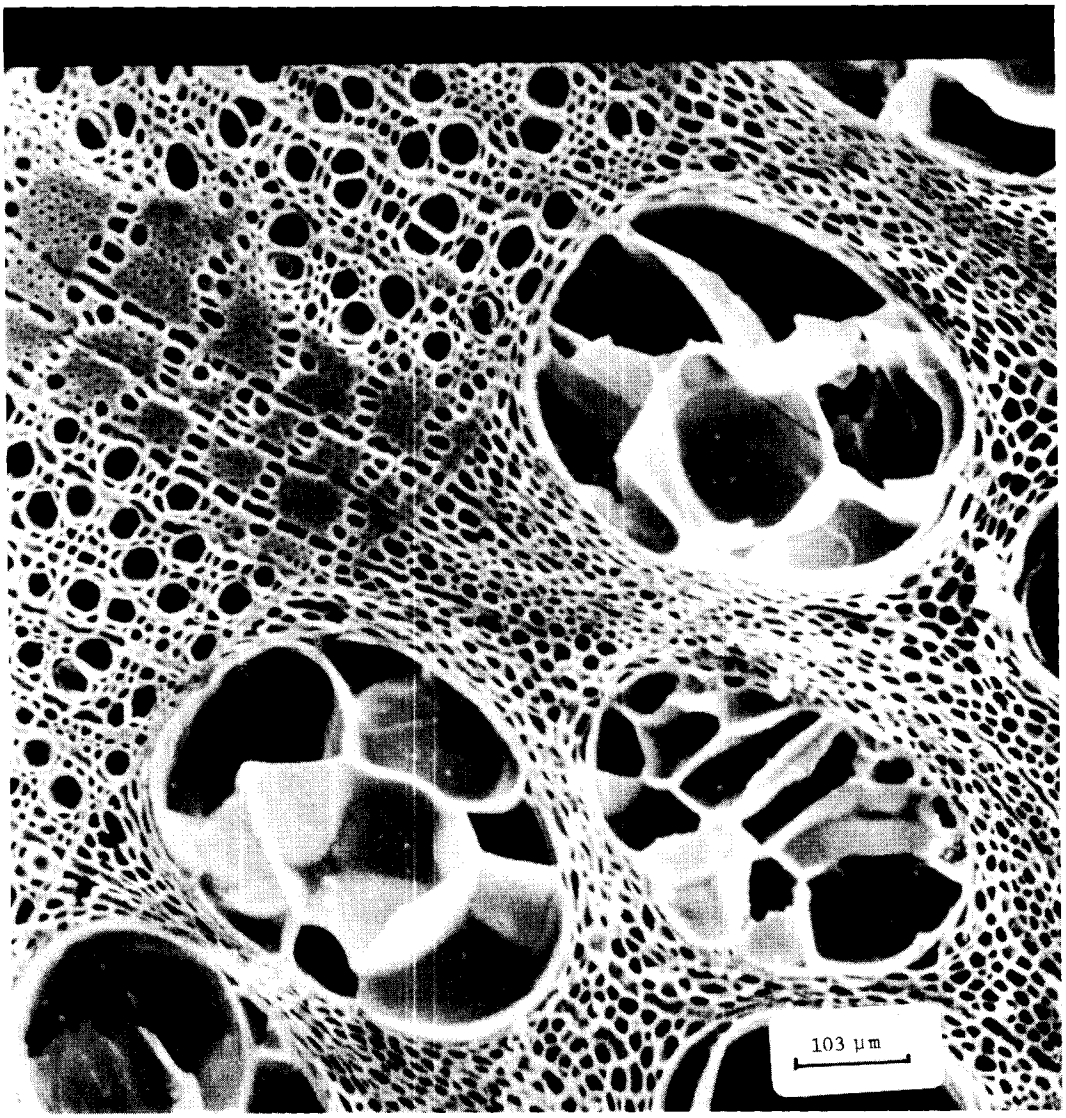


FIG. 8. Cross section of white oak, which has been rate-carbonized to 873 K (scanning electron micrograph).

to emphasize some of the uses of carbonization and the SEM in investigating the microstructure of wood. Figure 7 is a micrograph of birch heat treated to 1273 K in which a scalariform perforation plate is clearly visible. Figures 8 and 9 are cross-sectional views of white oak heat treated to 873 K. Fibers, longitudinal parenchyma, uniseriate rays, vessels, and tyloses are clearly visible in Fig. 8. Figure 9 shows intertylosic and tylosic pitting. Figure 10 is a tangential view of ash heat treated to 873 K. End-wall pitting and intercellular spaces are clearly evident in this figure.

## DISCUSSION

The internal friction peak observed here for uncarbonized black cherry (specimen *A*) near 250 K is similar to the peak in birch reported by Bernier and Kline (1968). This

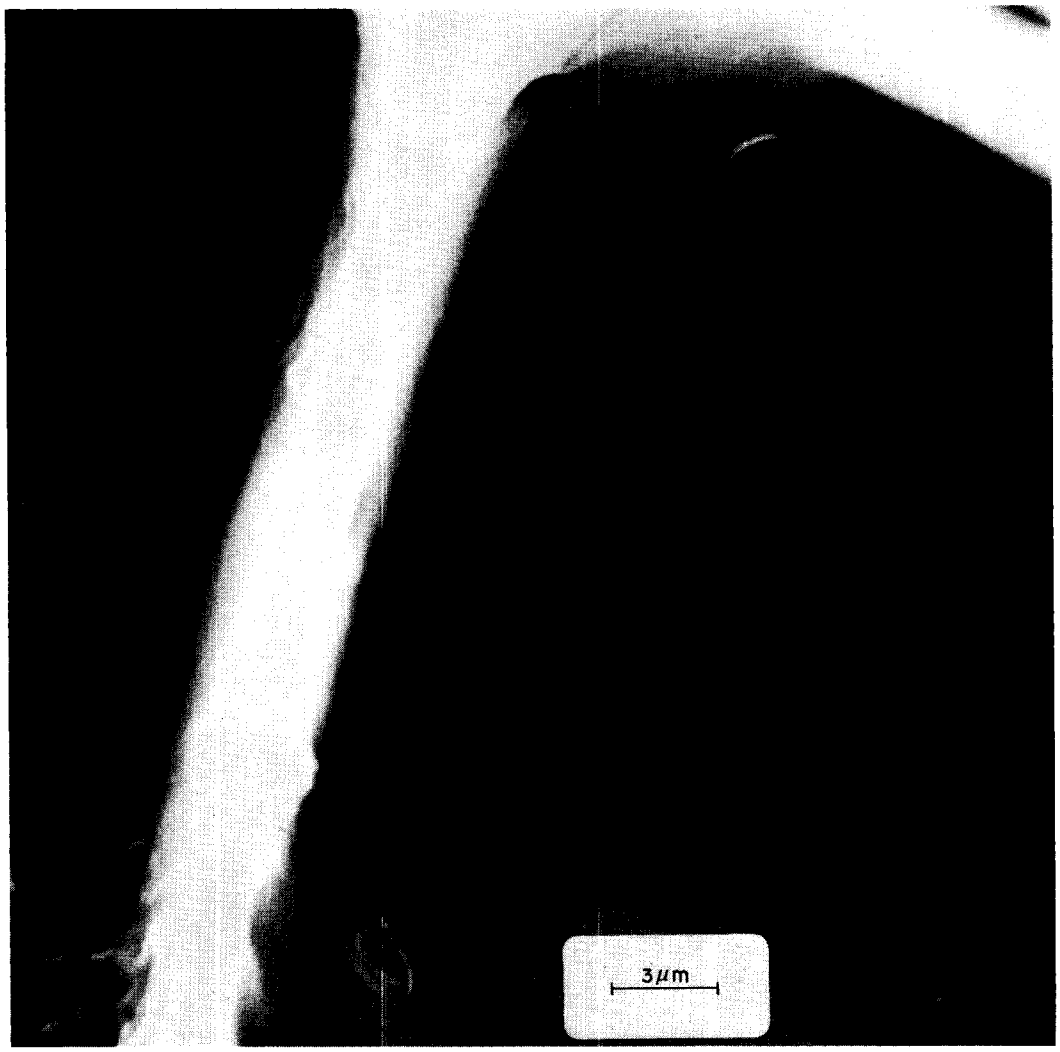


FIG. 9. Cross-sectional view of a white oak tyloses, which has been rate-carbonized to 873 K (scanning electron micrograph).

peak appears to be characteristic of at least several types of completely dry wood (Blankenhorn 1972; Kline et al. 1972). Research is presently being conducted in order to characterize this peak better. The reported modulus values are higher than reported for cherry in static tests and are not inconsistent with static moduli comparisons reported elsewhere (Jayne 1959; John and Lal 1964). John and Lal (1964) state that static and dynamic values may differ because static modulus is an isothermal modulus while the dynamic modulus is an adiabatic modulus. In static tests the values often differ because of the change in rate of loading and the increased stress levels. Little if any static modulus values are available for the complete temperature range.

Upon carbonizing in a nitrogen atmosphere to 593 K, the modulus values drop considerably and there is some loss of mass. This would appear to be consistent with the breakdown of some of the wood structures including groups from the celluloses known

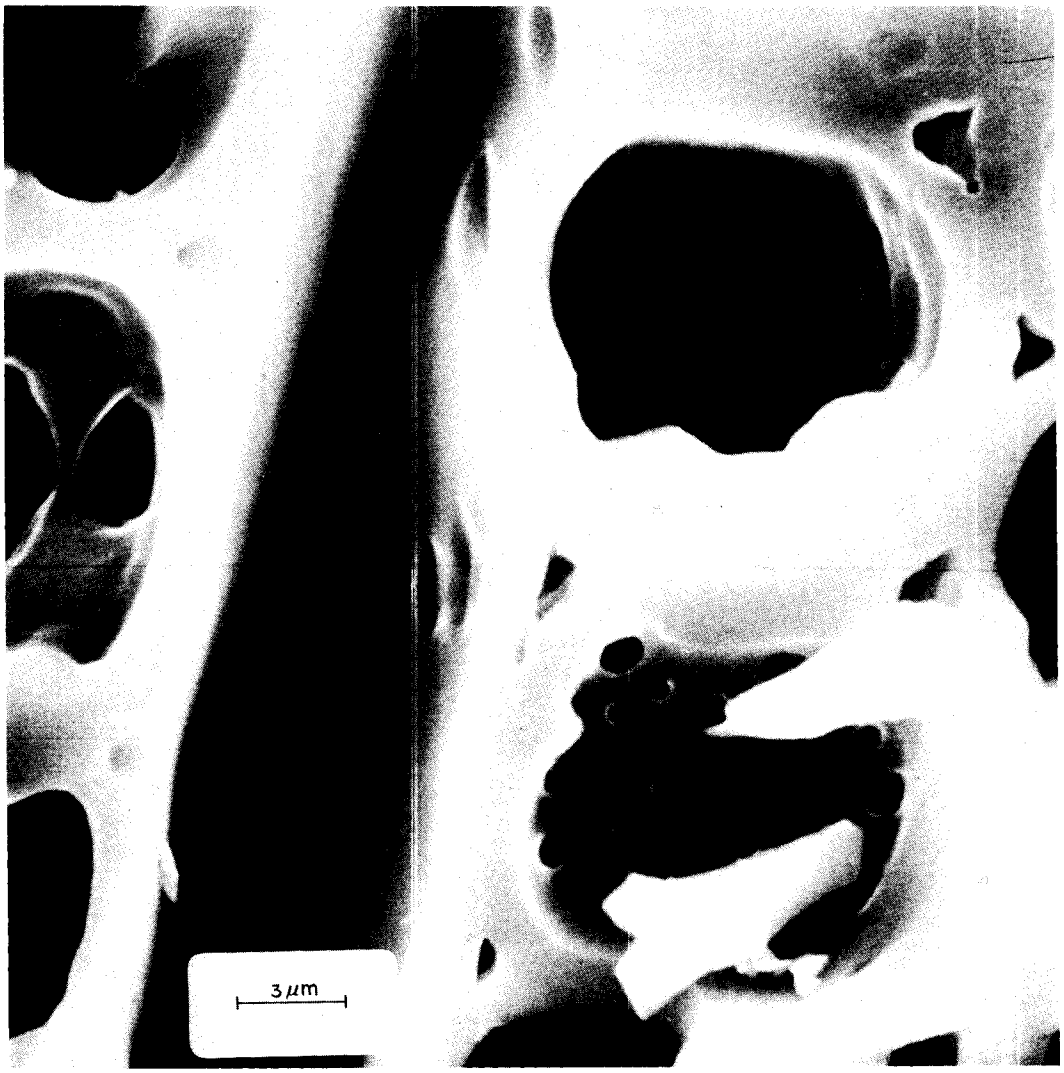


FIG. 10. Tangential view of white ash, which has been rate-carbonized to 873 K (scanning electron micrograph).

to occur in this temperature region (Beall and Eickner 1970). Most of the products are probably carried off by the flowing nitrogen atmosphere preventing large scale secondary reactions. The cause of the internal friction peak near 250 K in specimen *A* is uncertain. A peak that is larger occurs at a lower temperature in specimen *B* treated to 593 K. Carbonization alters the structure, but if these are related it would appear that barriers to movement of segments responsible for the relaxation are reduced by the heat treatment. The high internal friction values of specimen *B* are not inconsistent with the results of Kanagawa and Yamada (1970).

Upon heating to 873 K, data for the cherry (*C*) exhibit a rise in overall modulus compared to specimen *B*. The modulus is also less temperature-dependent. The weight loss in this case amounts to about 72% and much of the remaining structure is carbon on a weight basis. Presumably shrinkage accompanied by carbon-carbon

bond formation is responsible for the increased modulus. An internal friction peak is centered near 180 to 190 K. The small area of the peak compared to that of *B* suggests that fewer segments are participating compared to previous specimens while the lower temperature location suggests a relatively low activation energy.

Specimen *D* (heat treated to 1173 K) data for the modulus exhibit a rather remarkable rise in the modulus compared to specimens *B* and *C* and the temperature dependence of the values is very slight. The slight temperature dependence is similar to that observed in a glassy carbon (Taylor and Kline 1967). The internal friction peak now observed near 125 K is somewhat smaller than those for specimens *A*, *B*, and *C*. The reason for this is not clear.

A process that may be similar to the progressive changes occurring in carbonized wood was observed recently (Jenkins and Kawamura 1971) in the carbonization of phenolic resins to produce glassy carbon. Changes in structure were followed by high resolution electron microscopy and monitored by various physical techniques. It was concluded that there were three distinct pyrolysis regimes in the progress from polymer precursor to pyropolymer to defective carbon to fully annealed glassy carbon. These were:

a) Between 573 and 773 K, oxygen was removed largely in steam leaving loosely bound bundles of graphitelike ribbons clothed in hydrogen. This was accompanied by large weight loss, a corresponding lowering of density, and deterioration in mechanical properties.

b) Between 773 and 1273 K, the hydrogen was progressively eliminated and crosslinks were formed between ribbons that came together to form a mass of randomly oriented fibrils. There was a slight weight loss appropriate to the low atomic weight of hydrogen, but the density increased and the mechanical properties improved enormously.

c) Between 1273 and 3272 K, grown-in defects were removed to leave regions of parallel ribbons in each fibril. The mechanical properties showed some deterioration as the interlamellar cohesion was reduced.

In wood heat treated to 700 K, one of the products eliminated is water. It is known also that cellulose by itself forms glassy carbon and carbon fibers by pyrolysis (MacKay 1967; Sinclair 1969). In Fig. 5 some of the structure of the cell wall appears to be converted into carbon fibers by the carbonization of the wood in an inert atmosphere. The pyrolysis mechanisms would seem, therefore, to be similar to those observed in phenolic resins, and wood char belongs to the same general chars of other "polymeric carbons."

In terms of a molecular picture for thermal degradation, the initial decrease in modulus and increase in damping with heat treatment must be ascribed to the production of a loosely bound network of carbon ribbons. The subsequent modulus rise, the lowering of damping, and the migration of the damping peak with temperature to lower temperatures must be ascribed to the progressive coalescence of this loose network with elimination of hydrogen. The migration to lower temperatures does not generally seem to be compatible with tightening of the structure.

It is striking that the modulus values of the wood, heat treated under a nitrogen atmosphere, appear first to decrease with temperature of heat treatment and then rise. More will be published later illustrating this in detail. Physically, the material is relatively strong compared to the fragile nature of charcoal-like material. It is also striking, as observed from the SEM photos, that the character of the wood structure remains almost completely intact, although contracted. Kinking in some specimens is observed to emphasize that the shrinkage is not uniform in all structures. Kinking was usually not observed when clear, straight-grained material was carbonized. The entire process is clearly suggestive of the formation of glassy carbon structures that are hard and relatively strong compared to regular charcoal, which is probably loosened up by oxidation. It is also probable that the usefulness of the product is very different

and in many ways improved. For instance, if the strength is adequate, the usefulness as a filler may be greatly increased compared to other products.

## SUMMARY

Dynamic mechanical properties data for black cherry carbonized in an inert atmosphere have been presented. The structure after heat treatment to 593 K displayed substantially reduced rigidity, but upon higher heat treatments, much of the rigidity of the original system appears to return. A complex relaxation behavior between 100–300 K is evident for all specimens.

Scanning electron micrographs of the microstructure of carbonized wood are presented. This form of specimen preparation offers a unique method for investigating the structure of wood because much of the ultra-structure integrity remains after carbonization in an inert atmosphere.

Research in the area of mechanical properties and microstructure of carbonized wood is continuing to improve the characterization of this material and to improve its usefulness as a composite material.

## REFERENCES

BEALL, F. C., AND H. W. EICKNER. 1970. Thermal degradation of wood components: a review of the literature. U.S.D.A. Forest Service Research Paper. FPL 130.

BERNIER, G. A., AND D. E. KLINE. 1968. Dynamic mechanical behavior of birch compared with methyl methacrylate impregnated birch from 90° to 475°K. For. Prod. J. **18**(4):79–82.

BLANKENHORN, P. R. 1972. Dynamic mechanical behavior of black cherry (*Prunus serotina* Ehrh.). Ph.D. thesis, the Pennsylvania State University, University Park, Pennsylvania.

JAMES, W. L. 1961. Internal friction and speed of sound in Douglas fir. For. Prod. J. **11**(9): 383–390.

JAYNE, B. A. 1959. Indices of quality . . . vibrational properties of wood. For. Prod. J. **9**(11):413–416.

JENKINS, G. M., AND K. KAWAMURA. 1971. Structure of glassy carbon. Nature **231**:175–176.

JOHN, W. J., AND M. M. LAL. 1964. Dynamic elastic modulus and damping coefficient of some Indian timbers. Ind. J. Physics **38**: 401–408.

KANAGAWA, Y., AND T. YAMADA. 1970. Influence of carbonization (400°C) on water sorption hysteresis of wood. J. Japan Wood Res. Soc. **16**(3):126–129.

KLINE, D. E. 1956. A recording apparatus for measuring the dynamic mechanical properties of polymers. J. Polymer Sci. **22**:449–454.

KLINE, D. E., R. P. KREAHLING, AND P. R. BLANKENHORN. 1972. Dynamic mechanical properties and structure of white ash (*Fraxinus americana* L.) wood. Advances in Polymer Sci. Eng. Plenum Press, New York: 185–205.

KNUDSON, R. M., AND R. B. WILLIAMSON. 1971. Influence of temperature and time upon pyrolysis of untreated and fire retardant treated wood. Wood Sci. Technol. **5**(3):176–189.

KOLLMANN, F. F. P., AND J. B. SACHS. 1967. The effects of elevated temperature on certain wood cells. Wood Sci. Technol. **1**(1):14–25.

MACKAY, G. D. M. 1967. Mechanism of thermal degradation of cellulose: a review of the literature. Canada Department of Forestry and Rural Development, Forestry Department Publication No. 1201, O.D.C. 813.4:1–20.

MCGINNES, E. A., JR., S. A. KANDEEL, AND P. S. SZOPA. 1971. Some structural changes observed in the transformation of wood into charcoal. Wood and Fiber **3**(2):77–83.

SCHAFFER, E. L. 1970. Elevated temperature effect on the longitudinal mechanical properties of wood. Ph.D. thesis, University of Wisconsin, Madison, Wisconsin.

SINCLAIR, P. M. 1969. Composites: designers work and contemplate. Ind. Res. Oct.: 59–79.

TAYLOR, R. E., AND D. E. KLINE. 1967. Internal friction and elastic modulus behavior of vitreous carbon from 4°K to 570°K. Carbon **5**:607–612.

TAYLOR, R. E., D. E. KLINE, AND P. L. WALKER, JR. 1968. The dynamic mechanical behavior of graphites. Carbon **6**:333–347.

WOODWARD, A. E., AND J. A. SAUER. 1965. Mechanical relaxation phenomena, p. 637–723. *In* D. Fox, M. M. Labes and A. Weissberger (eds.), Physics and chemistry of the organic solid state. Interscience Publishers, New York.