SOME PHYSICAL PROPERTIES OF BIRCH CARBONIZED IN A NITROGEN ATMOSPHERE[1]

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ABSTRACT

The dynamic mechanical properties, mass loss, and shrinkage data of birch carbonized in a nitrogen atmosphere to different temperatures from 473 to 973 K have been investigated. The dynamic elastic modulus data decreased as the heat treatment temperatures approached 673 K. Major mass loss and shrinkage accompanied the decrease in the modulus data. Treatments at higher temperatures (> 673 K) produced substantially less additional mass loss and shrinkage but produced increased rigidity in the char. The internal friction behavior of the char was complex.

Additional keywords: Betula sp., heat treatment, shrinkage, dynamic elastic modulus, internal friction, thermal degradation.

INTRODUCTION

The material produced by the relatively slow thermal degradation of wood in a nitrogen atmosphere has been shown to be a carbonaceous skeleton of the precursor (Blankenhorn et al. 1972; Beall et al. 1974). The structure and properties of this material over a range of treatment temperatures and for various species of precursors have not yet been well determined. Initial investigations (Blankenhorn et al. 1972) indicate, however, that this type of carbonized wood is a potentially useful composite material.

Considerable interest has been developed in regard to the dynamic mechanical properties (DMP) of carbonized wood, since this method of analysis has been used extensively in carbon and graphite work (Taylor and Kline 1967; Taylor et al. 1968). The measurement of dynamic properties is nondestructive, requires few specimens, and can offer some insight into the molecular structure of materials. Blankenhorn et al. (1972) reported the DMP as a function of temperature for black cherry (*Prunus serotina* Ehrh.) heat treated at temperatures from 593 to 1173 K. Heat treatment to 593 K produced a marked decrease in the dynamic modulus, while treatments at higher temperatures (873 K and above) restored some of the lost rigidity. Internal friction (Q^{-1}) behavior was rather complex, and was also dependent on heat treatment temperature.

It is the purpose of this paper to further characterize the dynamic mechanical properties of carbonized wood by examining birch treated at temperatures from 473 to 973 K. An examination of the mass losses
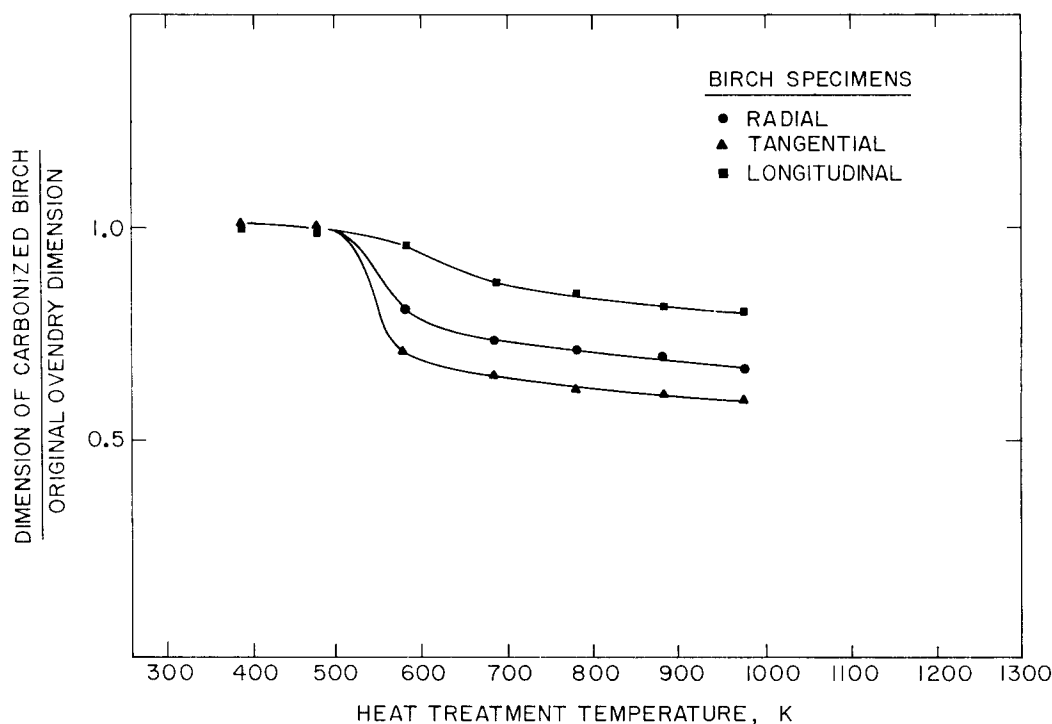
Fig. 1. Longitudinal, radial, and tangential dimensions of birch specimens as a function of heat treatment temperature.

and shrinkages that accompany carbonization at various temperatures is also included in this study.

EXPERIMENTAL

Testing apparatus

The dynamic elastic modulus (E') and internal friction (Q^{-1}) were measured from 100 to 300 K on a transverse dynamic mechanical properties apparatus developed by Kline (1956), and later used by Blankenhorn et al. (1972) for examining carbonized black cherry. Details regarding the use of this apparatus are discussed by Blankenhorn (1972).

Specimens

Specimens used to determine mass losses and shrinkages were machined into cylinders with a radius of approximately 19 mm and a length of approximately 13 mm from defect-free commercial birch (*Betula* sp.) dowel stock. The nominal oven-dry density of the specimens was about 0.65 gm/cm³. The grain direction was that of the specimen length. DMP specimens were machined into rods having a radius of approximately 6 mm. Straight grain stock was chosen, but in some cases, warpage later occurred as a result of heat treatment. Because of this, samples 150 mm in length were carbonized and the straightest 100-mm portion was used for the specimen.

Carbonization

Carbonization was performed in a flowing nitrogen atmosphere at temperatures from 473 to 973 K at 100 K intervals. The rate of temperature increase during heating was 4 K per min and the desired final temperature was held for 2 h. Cooling occurred without programming in a static nitrogen atmosphere. Because of the hygroscopic nature of the chars, all specimens were dried in a vacuum oven at 60 C (333 K) for 24 h prior to testing.
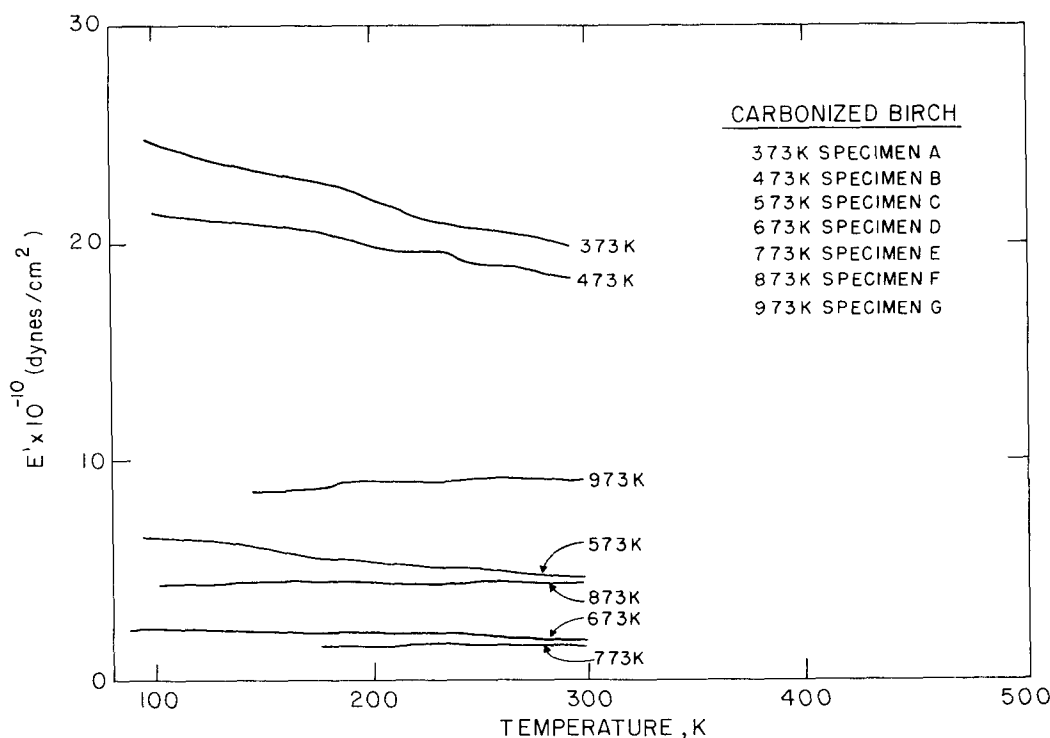
Fig. 2. Dynamic elastic modulus of carbonized birch as a function of temperature.

RESULTS AND DISCUSSION

Mass loss and shrinkage

The mass loss that occurred as a result of heat treatment is shown in Table 1. Very little change was noted for treatments up to approximately 500 K. However, between 473 and 573 K over 50% of the original mass was lost. From 573 to 773 K, there was a gradual decrease in the rate of mass loss, followed by a leveling off to a value of approximately 77% for the 973 K treatment.

The 76% mass loss found for the birch specimens carbonized to 873 K is in fairly close agreement with the 80% reported by Beall et al. (1974) for yellow poplar (*Liriodendron tulipifera* L.) carbonized to that temperature. This undoubtedly reflects some of the constitutional similarities of the two hardwoods.

The longitudinal, radial, and tangential shrinkages that arose from heat treatment are shown in Table 2. The shrinkage in each direction appeared to follow a trend similar

to that of the mass loss; most of the shrinkage occurred in the 473 to 673 K region and the shrinkage in each direction appeared to level off somewhat at higher heat treatment temperatures. Shrinkage was uniform and produced no noticeable checking because of the small specimen size.

Examination of Fig. 1 shows that a large portion of the shrinkage in the tangential and radial directions occurred for heat treatments between 473 and 673 K. The longitudinal shrinkage behaved somewhat differently; while 45% of the total tangential shrinkage observed and 58% of the total radial shrinkage observed had occurred by the 573 K treatment, only 19% of the total longitudinal shrinkage observed had occurred. Similar effects were reported by Beall et al. (1974) for yellow poplar.

In spite of the possible large-scale rearrangements that could accompany the large mass loss, the least shrinkage occurred in the longitudinal direction. This is
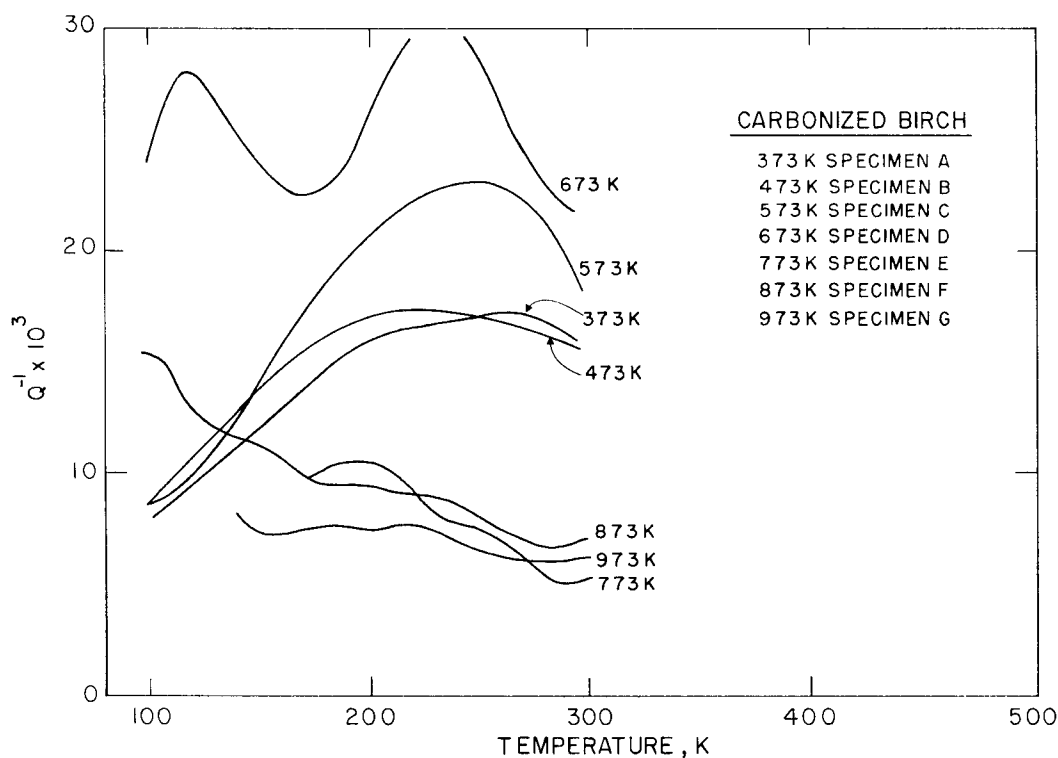
Fig. 3. Internal friction of carbonized birch as a function of temperature.

approximately the average alignment direction of most of the cellulose occurring in the cell wall (the S2 fibril angle [Harada 1965] is about 5 to 10°). However by 650 K (the temperature at which cellulose is largely degraded), only about half of the longitudinal shrinkage that was to occur in an 873 K treatment had occurred. It appears that the longitudinal shrinkage of wood is an unlikely indicator of overall percentage of cellulose degradation.

Shrinkage in the tangential direction was greater than in the radial direction. The ratio of tangential shrinkage to radial shrinkage (T/R) was approximately 1.3 for heat treatments above 573 K. Beall et al. (1974) found a T/R of 1.23 for yellow poplar treated at 873 K. McGinnes et al. (1971) observed a T/R of 1.73 for white oak (*Quercus alba* L.) after conversion in a charcoal oven (T ≤ 673 K). The large T/R value obtained by McGinnes et al. (1971) for white oak, although obtained from car-

bonization in the corrosive atmosphere of a charcoal oven, may indicate that the rays play an influential role in determining the difference between the radial and tangential shrinkages.

Dynamic mechanical properties

The dynamic elastic modulus as a function of temperature is shown in Fig. 2. Specimen A represents birch in the uncarbonized oven-dry state. Heat treatment at 673 K resulted in a drastic reduction in the value of E' at all temperatures from 100 to 300 K. Carbonization at higher temperatures (873 to 973 K) resulted in a gradual increase in the value of E' with increasing heat treatment temperature. Specimens treated at 673 K and above showed much less dependence of E' on temperature from approximately 160 to 300 K than those heat treated at lower temperatures.

Internal friction results are shown in Fig. 3. Specimen A had a broad peak centered
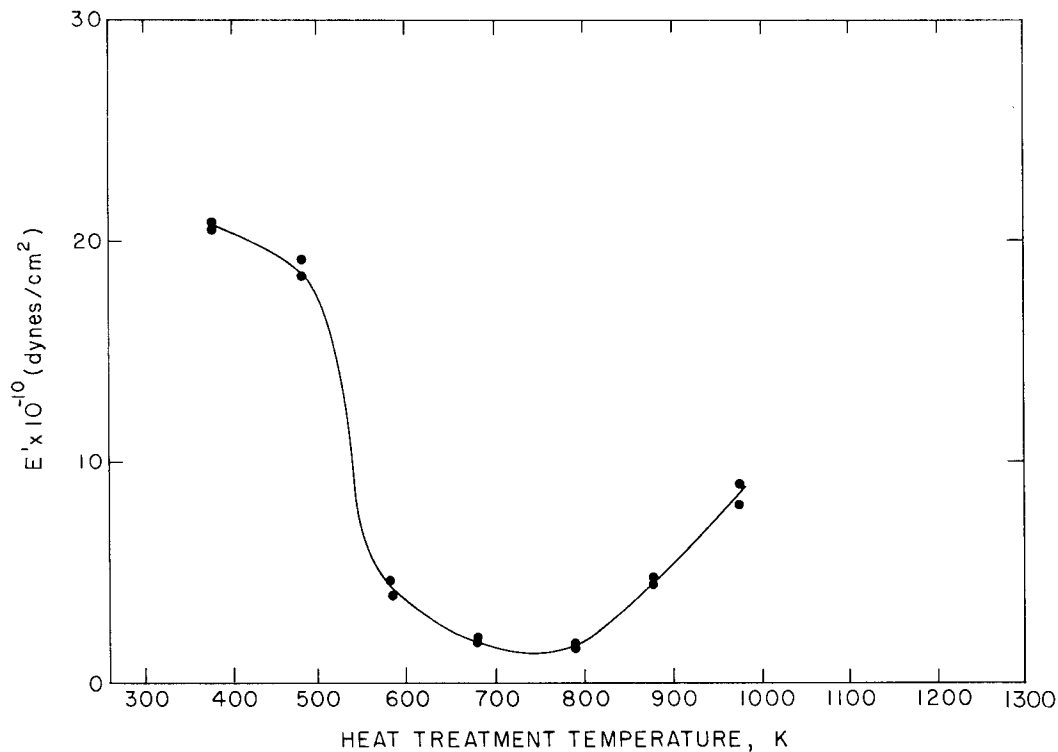
Fig. 4. Dynamic elastic modulus of carbonized birch at 300 K as a function of heat treatment temperature.

around 240 K. This is in accord with the results reported by Bernier and Kline (1968) for oven-dry birch. Q^{-1} results for the 473 K treatment (Specimen B) were similar to those for Specimen A. Specimen C had a higher internal friction level than Specimen A or B, with a peak centering around 250 K. Specimen D, heat treated to 673 K, displayed the highest internal friction levels noted in the present work, with values typically in the 25×10^{-3} range from 100 to 300 K. Heat treatments at 773 K and above produced substantially lower Q^{-1} levels (in the 8×10^{-3} range) having much less temperature dependence than the specimens heat treated at lower temperatures.

Considerable difficulty was encountered with regard to measuring the dynamic properties of specimens carbonized at temperatures from 773 to 973 K. Specimens heat treated in this range appeared to have poor resistance to thermal shock. Many suffered

damage when cooled to 100 K. It was not difficult to detect an indication of this damage. Internal friction values became erratic and resonance curves developed irregular, jagged peaks. A drastic change in resonant frequency also accompanied the damage.

In order to minimize these temperature shock effects, the susceptible specimens were cooled at much slower rates and to temperatures that were around 150 K instead of 100 K. The internal friction and resonant frequency of each specimen were measured at 300 K before and after low temperature runs; if these values were in agreement, it was assumed that the specimen had not been damaged by the cooling and subsequent heating.

In the present work, the greatest decrease in modulus values at 300 K (Fig. 4) was found to occur for the heat treatments at from 573 to 773 K. The modulus subse-

TABLE 1. *Mass loss due to heat treatment of birch*

Heat Treatment Temperature	Number of Specimens	Average Mass Loss* % original
473K	5	0.04 ($\sigma < 0.01$)
573K	10	0.49 ($\sigma < 0.01$)
673K	10	0.71 ($\sigma < 0.01$)
773K	10	0.74 ($\sigma < 0.01$)
873K	10	0.76 ($\sigma < 0.01$)
973K	10	0.77 ($\sigma < 0.01$)

*The original oven-dry mass of the precursor was used as the base figure.
σ = standard deviation.

quently increased for treatments above approximately 800 K. Blankenhorn et al. (1972 and 1973) found similar behavior for the modulus of black cherry specimens at 300 K. In the present study, DMP results for the uncarbonized oven-dry birch were similar to those found by Bernier and Kline (1968) for oven-dry birch.

Further clarification of the effect of heat treatment on birch may also be obtained by considering the low temperature behavior of the internal friction. The internal friction results for Specimens A and B were similar. Since the 473 K treatment had little effect on the modulus and caused little visible change in the specimens, the mechanisms responsible for the Q^{-1} results for Specimens A and B (Fig. 3) were probably very similar. Heat treatments at 573 and 673 K resulted in increasing the magnitude of the loss peaks occurring around 240 K. It seems rather certain that the mechanisms involved with these peaks are associated with the degradation processes.

An interesting aspect to note is the drastic change that occurred in the internal friction

between treatments at 673 and 773 K. Between these two treatment temperatures, the mechanisms causing very high internal friction were apparently altered. For treatments ranging from 773 to 973 K, Q^{-1} was comparatively low, with no large loss peaks appearing in the 100 to 300 K region. This is consistent with results reported for white ash (*Fraxinus americana* L.) by Kline et al. (1972), for black cherry by Blankenhorn et al. (1972 and 1973), and for glassy carbon by Taylor and Kline (1967).

Since the char is believed to be predominantly lignin and hemicellulose residue (Beall et al. 1974), the char properties might be somehow related to these two precursors. The structure of these two polymers under given carbonization conditions is not well known and undoubtedly changes with treatment temperature. The case for wood is complicated by the fact that the degree of interaction of the various constituents and the effects of the cellulose residue are unknown. Blankenhorn et al. (1972) proposed that the pyrolysis of wood and particularly lignin may be similar to that observed by Jenkins and Kawamura (1971) in the formation of glassy carbon from phenolic resins. This process for phenolic resin (Jenkins and Kawamura 1971) was suggested to involve three stages. From 573 to 773 K, loosely bound bundles of graphite-like material are formed; it is during this stage that a large mass loss and decline in mechanical properties occur. Between 773 and 1273 K crosslinks are formed between the graphitelike material, hydrogen is lost, and a mass of randomly oriented fibrils is formed; there is only a slight mass loss at

TABLE 2. *Shrinkages due to heat treatment of birch*

Heat Treatment Temperature	Number of Specimens	Average % Shrinkage*		
		Radial	Tangential	Longitudinal
473K	5	0.01 ($\sigma < 0.01$)	0.01 ($\sigma < 0.01$)	0.00 ($\sigma < 0.01$)
573K	10	0.19 ($\sigma < 0.01$)	0.18 ($\sigma < 0.01$)	0.04 ($\sigma < 0.01$)
673K	10	0.26 ($\sigma < 0.01$)	0.34 ($\sigma < 0.01$)	0.13 ($\sigma < 0.01$)
773K	10	0.29 ($\sigma < 0.02$)	0.37 ($\sigma < 0.01$)	0.16 ($\sigma < 0.01$)
873K	10	0.30 ($\sigma < 0.02$)	0.39 ($\sigma < 0.02$)	0.18 ($\sigma < 0.02$)
973K	10	0.33 ($\sigma < 0.02$)	0.40 ($\sigma < 0.03$)	0.21 ($\sigma < 0.02$)

*The original oven-dry dimension of the precursor was used as the base figure.
σ = standard deviation.

this stage, but the mechanical properties improve greatly. Between 1273 and 2973 K defects are annealed out in each fibril. Table 1 and Fig. 4 show a large mass loss in wood and a decrease in the elastic modulus values for heat treatment up to 773 K. In Fig. 4, the dynamic elastic modulus values begin to increase above 773 K. This increase in E' seems to coincide with the improvement of mechanical properties proposed in the model by Jenkins and Kawamura (1971). To some extent, wood appears to follow the Jenkins and Kawamura model.

SUMMARY

The dynamic mechanical properties, mass loss, and shrinkage data of birch heat treated in a nitrogen atmosphere at temperatures from 473 to 973 K were presented. A substantial decrease in rigidity accompanied by a major mass loss and shrinkage occurred near the 573 and 673 K heat treatments. Treatments at higher temperatures produced substantially less additional mass loss and shrinkage, but also produced increased rigidity in the char. The internal friction behavior was complex, but was similar to that reported previously by Blankenhorn et al. (1972) for carbonized black cherry.

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