THERMAL SOFTENING AND DEGRADATION OF WOOD AND BARK[1]

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ABSTRACT

A thermogravimetric analyzer was modified for the study of thermal softening of several Pacific Northwest woods and barks under constant load at a heating rate of 16 C/min.

Several stages of thermal softening were found in barks and wood. Regardless of species, oven-dry samples start to soften at 180 C, with termination at about 500 C. The maximum rate of softening occurred at 380 C with an additional softening at 280 C for bark and 320 C for wood of hardwood species. An increase of moisture content decreased the softening temperature. When the moisture content of either material was higher than 10%, a new maximum rate of softening appeared at 160 C, while the 280 C, 320 C and 380 C maxima were retained. The absolute softening of wood and bark at 160 C increased with increasing moisture content to a limit at about 30%.

In conjunction with results from infrared spectrum, X-ray diffraction and differential thermal analysis, the heating of oven-dry wood and bark was found to exhibit neither physical nor chemical changes at less than 200 C. The softening of wood and bark in the presence of water at temperature less than 200 C must occur only in the amorphous regions, with water serving as a plasticizer. Softening of wood and bark at more than 200 C is a combined response of physical and chemical degradations. These thermal responses of wood and bark, particularly bark, are expected to be important to the strength, dimensional stability, water resistance and fire-retardant properties of composite products.

INTRODUCTION

Bark is an abundant by-product of the forest-products industry. About 10 to 30% of log volume, depending on tree species and age, is bark. The production of bark in North America is at least 15 million tons per year (U.S.F.P.L. 1965). The disposal of this bark usually pollutes the environment. The effective utilization of bark in composite products will solve not only the environmental problem, but also increase economic gains.

Bark differs greatly from wood in morphological and chemical structures. The main wood chemical component is cellulose (about 50%), while the major constituent of bark is extractives, about 30 to 40%. Since bark has a 20 to 30% lignin content, the total content of phenolic materials, therefore, amounts to 50 to 70%. Because the extractives are amorphous and cellulose is mainly crystalline, the structural component of bark is expected to be more sensitive to temperature and pressure than that of wood. At room temperature, bark extractives are in a relatively stable solid form, but they may become flowing when heated under pressure. This thermal property would be important to the ultimate utilization of bark in board production.

Goring (1963, 1966) in recent years has extensively studied the thermal softening of isolated lignin, hemicellulose, and cellulose. His observations were made by the thermally induced collapse of a column of powdered samples under constant gravitational load. Softening temperatures of lignin were found to range from 127 to 193 C, while hemicellulose softened in the 167 to 181 C region, and cellulose softened at temperatures greater than 240 C. In wood the characteristics of these isolated materials did not fully appear. Wood tended to soften at more than 200 C. Goring attrib-
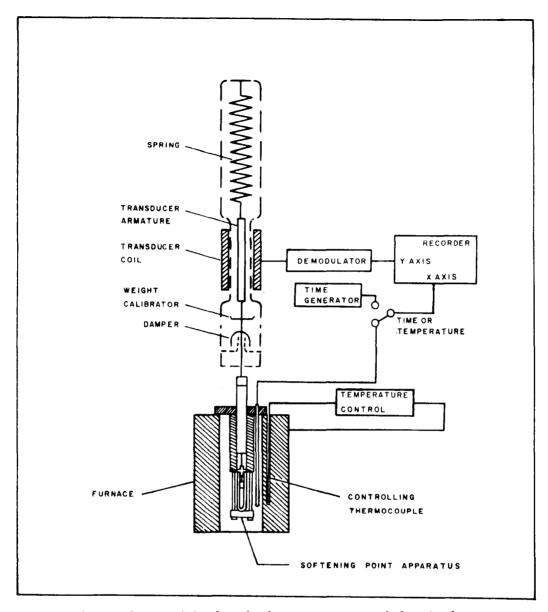
Fig. 1. Schematic diagram of the thermal softening apparatus attached to the thermogravimetric analysis system.

uted this softening phenomenon to the fact that wood is not a random mixture of cellulose, hemicellulose, and lignin. Wood softening is thus affected by morphological arrangement and chemical interconnection between wood components. By further experiments (1963, 1966) it was found that addition of moisture reduced softening temperature, and that the softening point of both dry and moist lignins or hemicelluloses correlated with the temperature at which a sample developed adhensive properties.

In this research, the thermal softening of bark and wood was studied. The relationship between this property and thermal degradation of the materials was examined

in conjunction with their infrared spectrum, X-ray diffraction, and differential thermal analysis.

EXPERIMENTAL

Materials

Three softwoods—Douglas-fir [*Pseudotsuga menziessi* (Mirb.) Franco], western hemlock [*Tsuga heterophylla* (Raf.) Sarg.] and western red cedar (*Thuja plicata* Donn)—and three hardwoods—red alder (*Alnus rubra* Bong.), broadleaf maple (*Acer macrophyllum* Pursh) and western white birch [*Betula papyrifera* Marsh. var. *commutatal* (Regel) Fern.]—were used in this experiment.

The bark and sapwood samples were obtained from the campus of the University of British Columbia. The materials were dried in a forced-draft oven at 105 C for 6 hr. (It is admitted that some minor chemical changes may occur in samples.) They were then ground to pass a 120-mesh screen and were stored in a desiccator over P_2O_5 under vacuum for at least one week. Portions of the bark and wood powders of Douglas-fir and red alder were stored in four humidity-control rooms for three weeks. The percentage moisture contents measured were for Douglas-fir wood 0, 9, 14, 31, 39%; alder wood 0, 9, 13, 28, 31%; Douglas-fir bark 0, 10, 14, 29, 39%; alder bark 0, 9, 13, 31, 36%.

Softening temperature determination

A softening-temperature apparatus similar to that of Goring (1963) was used. Figure 1 illustrates the softening-temperature equipment attached to an Aminco thermal gravimetric analyzer.

The sample powder (20 to 25 mg) is tamped to a 10-mm height in a glass capillary of 3-mm diameter. The capillary, about 40-mm long and sealed at one end, rests in a machined indentation on the bottom plate. Inside the stainless-steel case is a stainless-steel weight resting on a 1/16-inch diameter rod passed through the steel holder, which holds the capillary securely in position. This small rod rests on a 3-mm diameter by 7-mm-long stainless-steel plunger, which

presses on sample powder inside the capillary tube with a constant pressure of 50 psi. The large stainless-steel weight protrudes above the case where it is attached to the constant temperature weighing spring of the Aminco thermal-gravimetric-analysis system. The softening equipment is placed inside an electric furnace and heated at a programmed rate of 16 C/min from room temperature to 600 C. The recorder pen traces movement of the plunger (Y-axis) as the sample powder collapses into a solid plug. The sample temperature, recorded on the X-axis of the recorder, is measured by a chromelalumel thermocouple that is encased in a glass tube closed at the bottom end. The softening temperature is also evaluated by use of a differentiator connected to the second pen of the X-YY recorder.

Differential thermal analysis (DTA)

The analyses were performed using the Aminco DTA instrument. Sample and reference material holders made of Inconel alloy were so designed that chromel-alumel thermocouples were in direct contact with the sample and reference material. Calcined alumina (Al_2O_3) was used as the reference material. The sample weight was 15 mg. The heating rate was 16 C/min under static air.

Infrared and X-ray analyses

The samples of wood and bark for these analyses were heated at different temperatures (25, 120, 200, 250, 300, 350, and 420 C) inside the tube of the thermal gravimetric analyzer at a heating rate of 16 C/min under static air. A 2-mg sample was pelletized with 300 mg of KBr powder for infrared analysis. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer from 4000 to 700 cm^{-1}.

The X-ray diffractions of samples were recorded by use of a Phillipe Eindhoven diffractometer from Bragg angle 5 to 35°. Powder samples were used directly for recording the diffraction patterns. The diffraction area of a sample was 2 × 1 cm^2. The crystallinity of samples was obtained

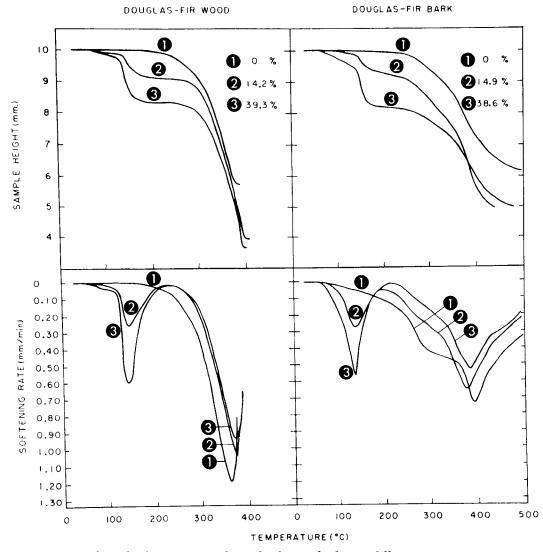DOUGLAS-FIR WOOD   DOUGLAS-FIR BARK

FIG. 2. Thermal softening curves of Douglas-fir samples having different moisture contents.

by use of the method devised by Jayme and Knolle (1964).

RESULTS AND DISCUSSION

Thermal softening

Wood and bark of different tree species have similar responses to thermal softening. As shown in Figs. 2 and 3 (curve 1), oven-dry bark and wood of Douglas-fir and red alder softened near 180 C with a maximum softening peak at 380 C. Additional maxima were found in the shoulder of the 380 C

peak, in the 250 to 280 C range for bark of both species, and at 320 C for red alder wood only.

In the presence of moisture (Figs. 2 and 3, curves 2 and 3), another softening peak appeared below 180 C. The higher the moisture content, the greater was the absolute softening and the lower the softening temperature. At moisture contents higher than 10%, the softening temperatures were somewhat constant, showing softening maxima at 160 ± 5 C for bark and wood of both
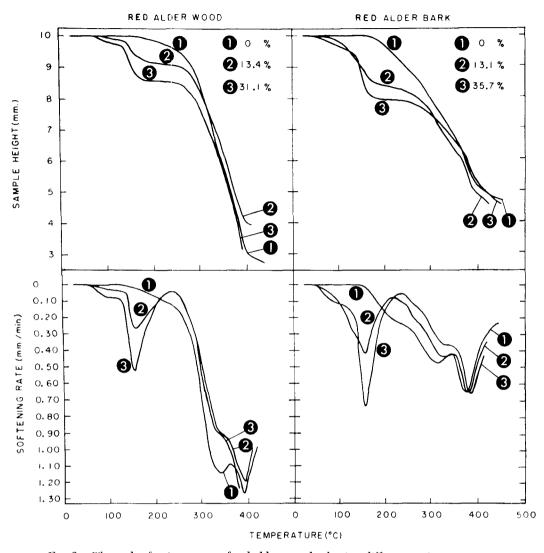
FIG. 3.   Thermal softening curves of red alder samples having different moisture contents.

species. The magnitude of softening, based on the percentage of original sample height, of Douglas-fir wood (Fig. 4) increased from 0% at oven dry to about 8% at 14% moisture content and then increased linearly with moisture content. At a moisture content of 39%, the softening was 17%. On the other hand, bark softened to a lesser amount than wood when the moisture content was below 15%. However, when the moisture content was greater than 15%, the softening of Douglas-fir bark was greater than that of wood. At 39% moisture content, the softening of Douglas-fir bark was 18%. Red alder bark and wood showed similar softening trends to Douglas-fir.

The rates of softening, expressed by the first derivative of the softening curves at 160 C, were also calculated. The softening rate of Douglas-fir wood was 0.14 mm/min at 9% moisture content and increased greatly at more than 10% moisture content. At 14% and 39% moisture content the rates were 0.26 and 0.59 mm/min respectively. The
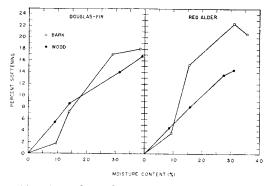
FIG. 4. Relationship between moisture content and percent softening of wood and bark at 160 C.

bark of Douglas-fir, on the other hand, produced a relatively lower rate of softening at moisture contents below 15% and also increased greatly above this moisture content. At 39% moisture content, the softening rate of Douglas-fir bark was 0.57 mm/min. The trends of softening rates of red alder wood and bark with increasing moisture content were comparable to those of Douglas-fir wood and bark, with the rates of bark softening being greater than wood at all moisture contents.

The softening of wood and bark of the two species below 180 C did not relate to the deformation of crystalline structure of cellulose. The softening occurring at 160 C in the presence of moisture is attributed to the moisture plasticization of the substrates (Goring 1966). Because the majority of the components of bark are amorphous extractives and lignin, the moisture plasticization is much more effective than in wood, as indicated by the greater softening at 160 C (Fig. 4). The plasticization effect is very important to pressing schedules for bark composite products.

DTA thermogram

The DTA thermogram of Douglas-fir and red alder woods are shown by curves 1 and 3 in Fig. 5. The major difference between the softwood and hardwood DTA thermograms was in the relative intensity between the 360 and 395 C endothermic peaks. The intensity of the 360 C peak in Douglas-fir (also western red cedar and western hem-
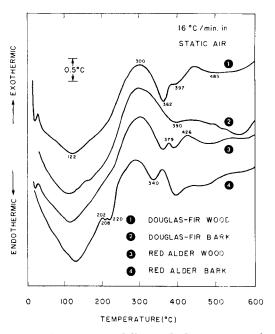

FIG. 5. Dynamic differential thermograms of wood and bark samples.

lock) was much stronger than the 395 C peak, whereas the intensity of the former peak was slightly greater than or equal to the latter peak intensity in the alder wood (also western white birch and broadleaf maple).

The thermograms of the barks for softwood and hardwood species were shown to differ greatly as shown by curves 2 and 4 in Fig. 5. The major differences between the softwood and hardwood bark thermograms were in the presence of a strong endothermic peak at 340 C and several small but clear exthothermic peaks at 202 C and 215 C, and endothermic peaks at 208 C and 220 C in the thermogram of red alder bark.

There are many arguments for the assignment of peaks in the DTA curve of cellulose (MacKay 1967) and wood (Beall and Eickner 1970). In general, the endothermic peak at 110 to 130 C region is well accepted as the heat absorption of water in a sample. However, the explanation for the formation of the small exothermic peak in the temperature range of 170 to 210 C is inconsistent (Arseneau 1971; MacKay 1967). According
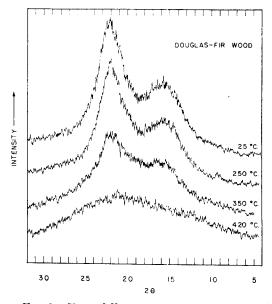
FIG. 6. X-ray diffraction pattern of Douglas-fir wood (powder) with increasing temperature treatment.

FIG. 7. X-ray diffraction pattern of Douglas-fir bark (powder).

to a recent study, Arseneau (1967) associated this exothermic reaction with the heat of formation of anhydrocellulose in cellulosic substances. Domburg et al. (1969), experimenting with birch wood at a heating rate of 10 to 12 C/min, assigned the exothermic temperature range of 180 to 200 C to the primary condensation of the macromolecules of wood components in the course of thermal dehydration. The exothermic peak at 220 C was explained as the cleavage of the glucosidic linkage of xylan, while the endothermic peak at 240 C was assigned as the cleavage of the short-chain lignins to vanillin. The relatively poor resolution of these peaks (180 to 240 C) in the wood thermogram was considered to be because of the concealing effect of the subsequent exothermic processes.

The exothermic reactions at 270 C and at 315 to 325 C of western white birch wood DTA curves were separately attributed to the basic decomposition of hemicellulose and the cleavage of the glucosidic linkages of cellulose by the same authors (Domburg et al. 1969). They noted the compensating effect of the exothermic condensation of the
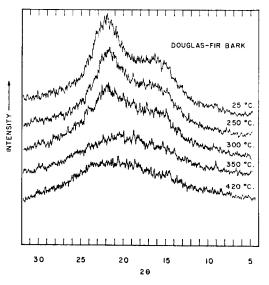
products from xylan decomposition and of the endothermic bond breaking in lignin macromolecules at 340 C which were not reflected in the wood DTA curve. The endothermic peak at 360 to 375 C was attributed to the decomposition of the subsequent condensation products of xylan (360 C) and lignin (365 to 375 C). Temperatures at 370, 400 to 420 C and 465 to 520 C were assigned to the condensation and recombination of celluloses, the destruction of lignin, and the cellulose decomposition, respectively. The assignments of the thermal peaks in the DTA curve of bark are also expected to be as complicated as those of wood. Much work remains to be done to define the nature of the bark thermograms.

X-ray diffraction

The X-ray diffraction patterns of Douglas-fir wood and bark were similar (Figs. 6 and 7). However, the diffraction pattern of red alder bark (Fig. 8) differed greatly from that of red alder wood, the latter being similar to that of Douglas-fir wood and bark. As shown in Fig. 8, in addition to the relatively poorly resolved (002) plane diffraction at 22 degrees and ($101 + 10\bar{1}$) plane diffraction at 15 to 16 degrees, red
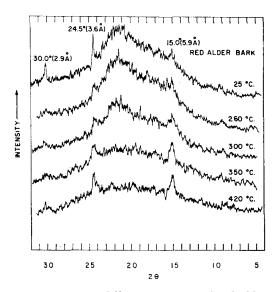
Fig. 8. X-ray diffraction pattern of red alder bark (powder).

alder bark gives sharp X-ray diffractions at 15, 24.5 and 30 degrees, equivalent to d spacings of 5.9, 3.6 and 2.9 Å, respectively. These diffractions did not disappear when the bark was heated to 420 C. Since at this temperature the known cellulose diffractions at 22 and 15 degrees had nearly disappeared (Figs. 6 and 7), the diffractions at these spacings are considered to be inorganic crystalline materials. The diffraction pattern of the bark of the other hardwoods (western white birch and broadleaf maple) was similar to that of red alder.
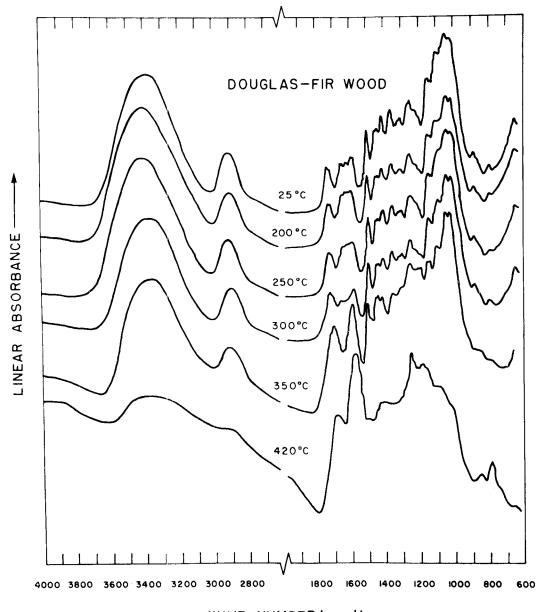
The calculated crystallinity of Douglas-fir wood and bark powder at room temperature was 41 and 30%, respectively, while the crystallinity for red alder wood and bark was 37 and 20%. The inorganic crystalline diffraction of bark was not included in the calculation. Thus, hardwood bark is very low in cellulose crystallinity. In practice, hardwood bark may be considered as a completely amorphous substance. Upon heat treatment of wood and bark, the crystallinity starts to decrease at a temperature of about 200 C, this temperature coinciding with the observed small exothermic reaction in the DTA curve and the initial softening temperature of the substances. This sug-

gests that the exothermic reaction takes place not only in the amorphous region, but also in the crystalline region of the cellulose. When heated to higher temperature, all woods and barks lost almost all crystallinity and produced an amorphous diffraction at 420 C and 350 C, respectively.

The glass transition temperature for ovendry wood and bark polymers occurs in the vicinity of 180 to 200 C. At this temperature, the thermal expansion coefficient of material undergoes a discontinuity (Ferry 1961), while the configurational rearrangement of polymer chain backbones takes place. At temperatures higher than the transition temperature, the free volume of a material increases and its heat capacity and compressibility change (Okano et al. 1963). This 180 to 200 C transitional temperature is thus meaningful for setting suitable conditions for wood and bark composite-board production.

Infrared spectra

The infrared spectra of wood and bark heated at different temperatures are shown in Figs. 9 to 11. On heating to 260 C, the infrared spectra of softwood and hardwood species showed essentially the same spectra as at room temperature (Figs. 9 and 10). However, at 300 C hardwood spectra indicated a large reduction in the 1730 cm^{-1} band intensity and a shift of the peak maximum to 1720 cm^{-1}. The 1630 cm^{-1} band, a major absorption of carbonyl or polyphenol and flavonoid compounds, either decreased (softwood) or disappeared (hardwood). At 350 C, the infrared spectrum of wood showed a major change, the 1730 cm^{-1} carbonyl band shifting to 1700 cm^{-1} and 1630 cm^{-1} band (softwood) disappearing; the 1600 cm^{-1} aromatic or double bond intensified and band shape sharpened.

At 350 C, both softwood and hardwood spectra showed improved resolution in comparison with spectra of samples heated to 300 C. But the relative intensity between 1020 and 1060 cm^{-1} bands reversed from the 25 C sample. The improvement of general resolution may be due to decrease of the molecular weight of carbohydrate that
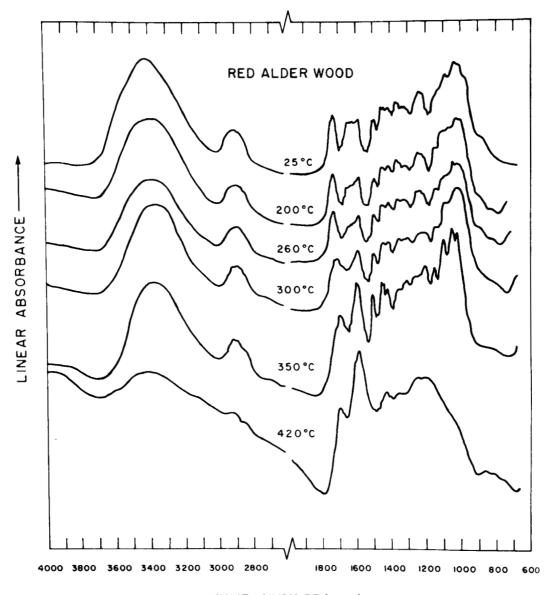
FIG. 9. Infrared spectra of Douglas-fir wood heated to different temperatures.

permits more freedom for vibrational modes. At 420 C, the major carbohydrate characteristics of both softwoods and hardwoods disappeared. The infrared spectra showed major bands at 1690, 1580, 1430, 1260, and 800 cm⁻¹. The spectra indicated essentially an aromatic, double bond or some levoglucosan absorption.

The large aromatic content of bark substance was revealed in the strong and sharp C-H stretching absorption in the infrared spectra at 2920 cm⁻¹, in comparison with
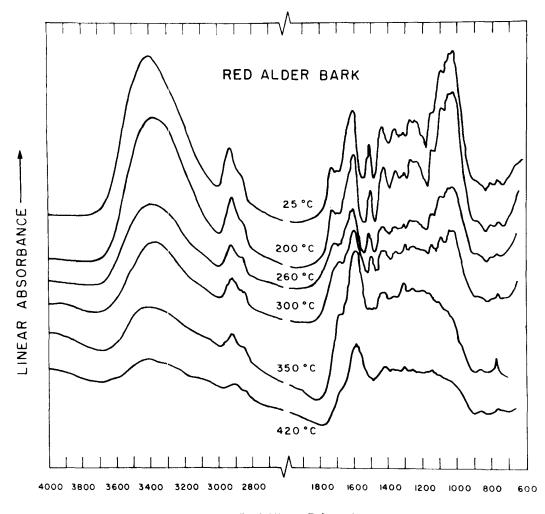
FIG. 10.   Infrared spectra of red alder wood heated to different temperatures.

the carbohydrate C-H absorption at 2850 cm⁻¹. This was also shown in the strong 1580 cm⁻¹ absorption of aromatic skeletal vibration. As the bark spectra of softwoods and hardwoods are very similar, only the red alder bark spectra are shown in Fig. 11. Upon heating to 200 C, the infrared spectra of both hardwood and softwood barks were essentially the same as at room temperature. At 260 C major changes occurred in both softwood and hardwood spectra. The 1735 cm⁻¹ band of softwood was split into 1730 cm⁻¹ and 1710 cm⁻¹ bands, while the 1730 cm⁻¹ band intensity of hardwood decreased slightly and band maxima shifted about 10 cm⁻¹ lower. The 1430 cm⁻¹ (methylol

RED ALDER BARK

25 °C

200 °C

260 °C

300 °C

350 °C

420 °C

LINEAR ABSORBANCE

4000 3800 3600 3400 3200 3000 2800   1800 1600 1400 1200 1000 800 600

WAVE NUMBER (cm⁻¹)

FIG. 11.   Infrared spectra of red alder bark heated to different temperatures.

or methoxyl) and 1270 cm⁻¹ (phenolic hydroxyl) absorption band intensities decreased in respect to the 1500 cm⁻¹ band in hardwood. The 1600 cm⁻¹ band intensity increased, being especially pronounced in the hardwood spectra. On further heating to 300 C, the weak 1710 cm⁻¹ band became the only absorption of carbonyl and the carbohydrate band at 1020 cm⁻¹ was greatly weakened. At 350 C, the carbohydrate characteristic of the spectra still remained, but the signal was very weak. At 420 C, the spectrum showed that essentially only

the aromatic and double-bond structure remained.

The spectral changes of heated woods and barks also can be observed from the shift of band maxima for hydroxyl and carbonyl absorptions. In all cases examined, wood and bark hydroxyl absorbed at about 3390 to 3400 cm⁻¹ at 25 C. These bands shifted to a lower wave number after 200 C. The bark hydroxyl maxima shifted about 20 to 30 cm⁻¹, while in wood the absorption band shifted about 10 cm⁻¹. At 300 C, both

bark and wood absorption maxima were at 3350 to 3360 cm^{-1}. It is well known that the infrared band at 3000 to 3600 cm^{-1} of wood is the superposition of many hydroxyl groups absorbing at different states of hydrogen bonding. The 3400 cm^{-1} absorption was assigned to the intermolecular hydrogen-bonded hydroxyl groups in the 10$\bar{1}$ plane, while the 3350 cm^{-1} band is the absorption of intra-molecular hydrogen-bonded hydroxyl groups in cellulose (Liang and Marchessault 1959). Therefore, the shift of the hydroxyl absorption maxima to a lower wave number may indicate the loss of intermolecularly bonded hydroxyl groups to form anhydrocellulose or the other macromolecular components of wood (Domburg et al. 1969). On further heating of the wood and bark to temperatures higher than 300 C, the loss of the overall hydroxyl band intensity suggests degradation of intramolecular-bonded hydroxyl groups. This agrees with the results of X-ray crystallinity data as shown in Figs. 6 to 8.

The shift of the 1730 cm^{-1} to 1700 cm^{-1} carbonyl absorption of bark and wood of all species was also observed. At 200 C, bark shifted about 5 cm^{-1} while wood remained unchanged. At 250 C, wood shifted 5 cm^{-1} while bark shifted about 20 cm^{-1}. When the samples were heated to 300 C, the absorption was at 1690 to 1700 cm^{-1}. The shift of peak maxima suggested the occurrence of deacetylation and carboxylation at lower temperatures (less than 200 C). At higher temperatures, either the formation of a new carbonyl of carboxyl or the destruction of crystalline lattice reduced the steric hindrance that caused absorption at the lower wave number.

The infrared data indicated that the major chemical change of wood and bark started at a temperature greater than the temperature of crystalline degradation and, also, after the first exothermic reaction at about 180 C. The major chemical change of the bark occurred at 250 C, which is about 50 and 100 C lower than the major woods, respectively. These results relate

well to the observed additional softening maxima of bark at 280 C and 320 C for hardwood and the major softening maximum at 380 C for all materials as shown in Figs. 2 and 3.

To sum up the observations, thermal softening of moistened wood and bark at temperatures below 180 C is more physical than chemical in nature. The softening can be attributed to the plasticization by water, thereby accelerating the reduction of hydrogen bonding and promoting the rearrangement of the chemical components under pressure. These thermal motions, therefore, may not relate to crystalline structure but to the relative motions of the mass in the amorphous region of materials. Since bark contains a greater amount of amorphous region than wood, the percentage softening of bark will be greater than wood in the presence of sufficient moisture.

The thermal reaction of wood and bark at more than the 180 C transition may be classified in two ways. One is the degradation reaction that caused depolymerization or modification of the chemical components. The degradation may include reactions, such as the dehydration of macromolecules, and conversion of heat-sensitive functional groups. Further, degradation of the crystallinity, shortening of the chain length of cellulosic materials, and formation of levoglucosan may also occur. On the other hand, there is another reaction more advantageous to bark utilization. This reaction is the possible polymerization of the extractives and lignin in bark. Since the bark consists of 30 to 40% of extractives and 20 to 30% of lignin, the polymerization products would exhibit a strong adhesive nature, which will give strength and dimensional stability (water resistance) to bark products, somewhat similar to the function of phenolic resin. In addition, the polymerization reactions produce a higher molecular-weight phenolic compound and this may add to fire-retardant properties of the products. Further experiments are underway to study the fire-retardant properties and moisture resistance of bark products.

CONCLUSION

Wood and bark of both softwood and hardwood species were found to have similar responses on thermal softening. The initial softening of oven-dry materials was about 180 C and reached a maximum at 380 C. Additional minor softening maxima at 280 C and 320 C were shown in the samples of bark and wood of hardwoods, respectively.

Addition of moisture to materials induced a new softening peak at 160 C. The critical moisture content for wood and bark, where greater softening occurs, is at about 15%. Softening at this temperature (160 C) is caused by moisture plasticization.

Supported by dynamic differential thermal, infrared and X-ray analysis of oven-dry samples, the thermal reactions of wood and bark after the 180 C transition were considered to be of two general types, the depolymerization degradations of carbohydrates and the polymerization of extractives and lignin components. The polymerization reaction is expected to be important to the moisture resistant, fire retardant, and strength properties of bark composite products.

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