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Mechanical relaxation processes due to sugars in cane (*Arundo donax* L.)

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Abstract The storage modulus and the mechanical loss tangent of untreated, extracted, and sugar- impregnated canes (*Arundo donax* L.) were measured over a temperature range of −150° to 0°C at low frequencies. Two relaxation processes, labeled α and β, were detected in the ranges −60° to 0°C and −120° to −100°C, respectively. The α and β processes shifted to lower temperatures with increasing moisture content. The α process was detected only in the canes containing sugar. The magnitude of its loss peak increased with an increase in sugar content. It was speculated that the α process was due to some interactive molecular motions of the adsorbed water and sugar. The β process, detected in all of the canes, was attributed to the motion of the adsorbed water in the amorphous cell wall substances.

Key words Relaxation process · *Arundo donax* · Storage modulus · Loss tangent · Extractives

Introduction

The cane (*Arundo donax* L.) used for the vibrating reed of woodwind instruments has a high water-soluble extractive content, mainly consisting of glucose, fructose, and sucrose.[1] The extractives increase the storage modulus (E') and the loss tangent (tanδ) of cane resulting in improved timbre of reed. Although this timbre is degraded by water extraction, it can be recovered by glucose-impregnation treatment.[2] From these results, it is speculated that the sugar in the cane induces a relaxation process that shifts to higher frequencies with an increase in moisture content. The aim of this study was to investigate the mechanism of the relaxation process due to the sugars in cane. For this purpose, the storage modulus and the loss tangent were measured at frequencies ranging from 0.05 to 110 Hz and over a temperature range of −150°C and 100°C in untreated, extracted, glucose-impregnated, and sucrose-impregnated cane.

Materials and methods

Materials

Specimens of 70 mm in the fiber direction by 4 mm in the radial direction by 1 mm in the tangential direction made from the inner part of cane (*Arundo donax* L.) were used. An untreated specimen was used as the control. One specimen was soaked in water at room temperature for 4 days to remove the water-soluble extractives. One water-extracted specimen each was soaked in 3%, 5%, 10%, and 15% glucose solution for 4 days. An additional water-extracted specimen was soaked in 10% sucrose solution for 4 days. These specimens were then dried in vacuo before being conditioned at room temperature (20°C) in desiccators containing various aqueous salt solutions.

Measurement of viscoelastic properties

After conditioning at 30%, 60%, 85%, and 90% relative humidity (RH), E' and tanδ of the untreated and extracted canes at 1, 3.5, 11, 33, and 110 Hz in the temperature range −150° to 0°C were measured while being heated at a programmed heating rate of 1°C/min using Orientec, Rheovibron DDV-25FP. The E' and tanδ of the sugar-impregnated canes were measured after conditioning at 20°C and 60% and 90% RH. Furthermore, the E' and tanδ at 0.05 Hz of untreated, extracted, and glucose-impregnated canes initially conditioned at 20°C and 100% RH were measured in the temperature range 20°–100°C. A programmed heating rate of 3°C/min was applied using Seiko-Denshi, TMA/SS-120.

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Differential scanning calorimetric analysis

Differential scanning calorimetric analysis (DSC) for pure water, isolated extractives, and glucose was carried out from −100° to 20°C with a programmed heating rate of 10°C/min using the TA instrument DSC2910. The samples were conditioned at 20°C and 60% and 90% RH prior to the measurements.

Results and discussion

Relaxation processes in cane

The relaxation processes in cane are analyzed in Figs. 1–4. The parameters under consideration were E' and $\tan\delta$ as a function of temperature under various experimental conditions at a constant measuring frequency of 11 Hz. Although the temperature location of loss peak shifted to a higher range with increasing testing frequency, the temperature dependence of E' and $\tan\delta$ exhibited similar trends irrespective of testing frequency. Figure 1 shows the temperature dependence of E' and $\tan\delta$ for the untreated cane with various moisture contents (MC). The E' decreased with increasing temperature. With respect to $\tan\delta$, two relaxation processes, labeled α and β, were observed at −60° to 0°C and −120° to −100°C, respectively. Both of these processes shifted to lower temperatures at higher MC. Figure 2 shows the temperature dependence of E' and $\tan\delta$ for the extracted cane. The α process was not recognized in the extracted cane. In addition, the E' values over the temperature range examined were reduced by water extraction. These results suggest that the extractives enhanced the E' of the cane and induced the α process. The β process was also detected in the extracted cane, but the amplitude of its loss peak was larger than that of the untreated cane.

The sugar contents (C) and MC values of untreated and treated canes are shown in Table 1. Figures 3 and 4 show the temperature dependence of E' and $\tan\delta$ for the untreated and treated canes initially conditioned at 20°C and at 60% and 90% RH, respectively. After sugar impregnation, relaxation processes similar to the α process occurred, and the E' values increased slightly over the temperature range examined. These results suggested that the effects of the extractives were reproduced by the sugar introduced. The temperature location and the shape of the α loss peak for the untreated cane were similar to those for cane impregnated with glucose. The effect of extractives might be governed by that of glucose, the most abundant constituent of the extractives. Figure 5 represents the logarithmic frequency ($\log f$) plotted against the reciprocals of absolute

Table 1. Sugar and moisture contents of untreated and treated canes at 20°C

Condition	Sugar content (%)	Moisture content (%)	
		60% RH	90% RH
Untreated	14.0[a]	12.7	29.2
Extracted	0.0	8.9	17.8
Glucose-impregnated	18.3	12.1	28.8
Sucrose-impregnated	16.1	12.0	23.2

RH, relative humidity

[a] Mainly consisting of glucose, fructose, and sucrose

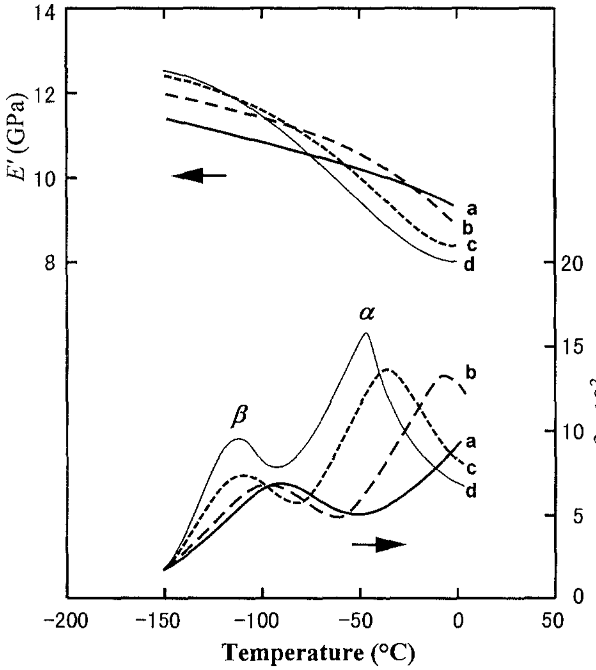


Fig. 1. Temperature dependence of storage modulus (E') and loss tangent ($\tan\delta$) at 11 Hz for untreated cane. Moisture content: *a*, 8.7%; *b*, 12.7%; *c*, 18.6%; *d*, 29.2%

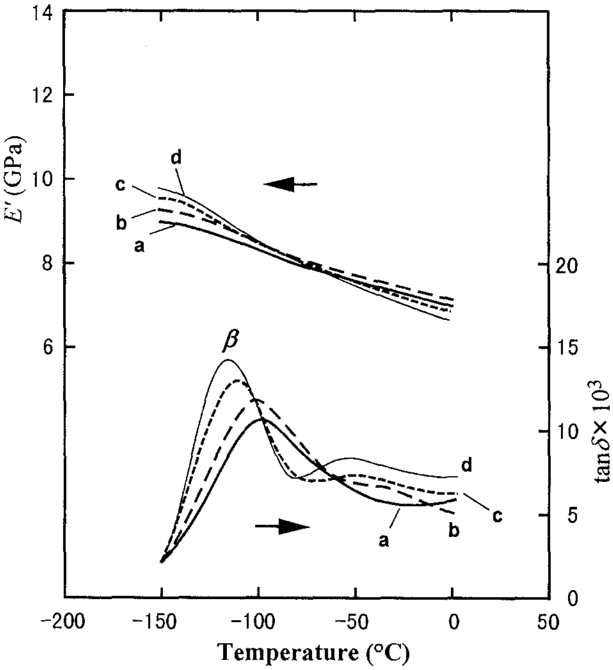


Fig. 2. Temperature dependence of storage modulus (E') and loss tangent ($\tan\delta$) at 11 Hz for extracted cane. Moisture content: *a*, 6.5%; *b*, 8.9%; *c*, 13.3%; *d*, 17.8%

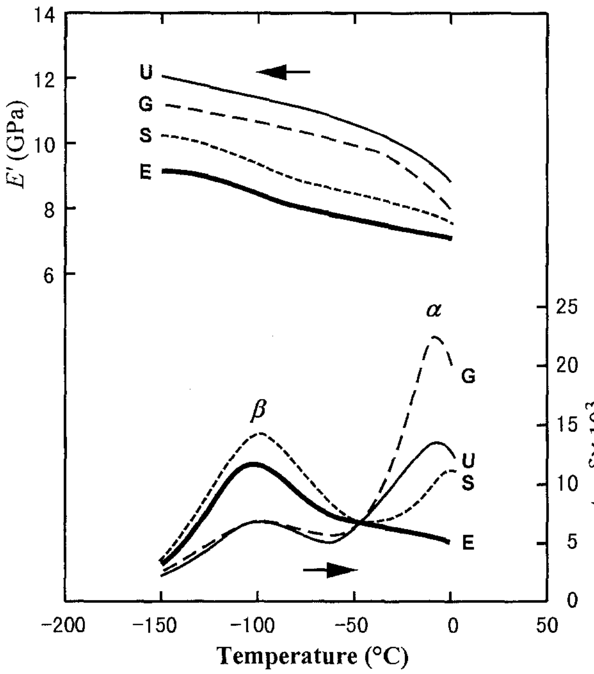


Fig. 3. Temperature dependence of storage modulus (E') and loss tangent (tanδ) at 11 Hz for untreated (U), extracted (E), glucose-impregnated (G), and sucrose-impregnated (S) canes initially conditioned at 20°C and 60% relative humidity (RH). The sugar and moisture contents of the canes are listed in Table 1

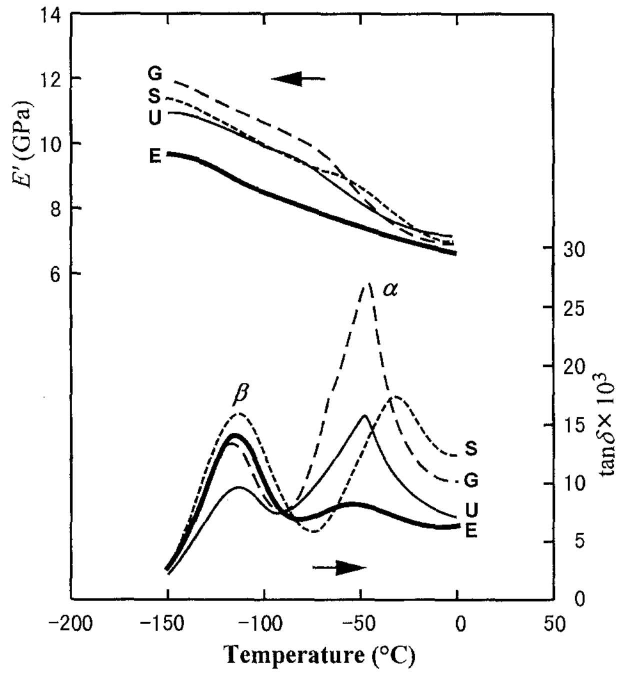
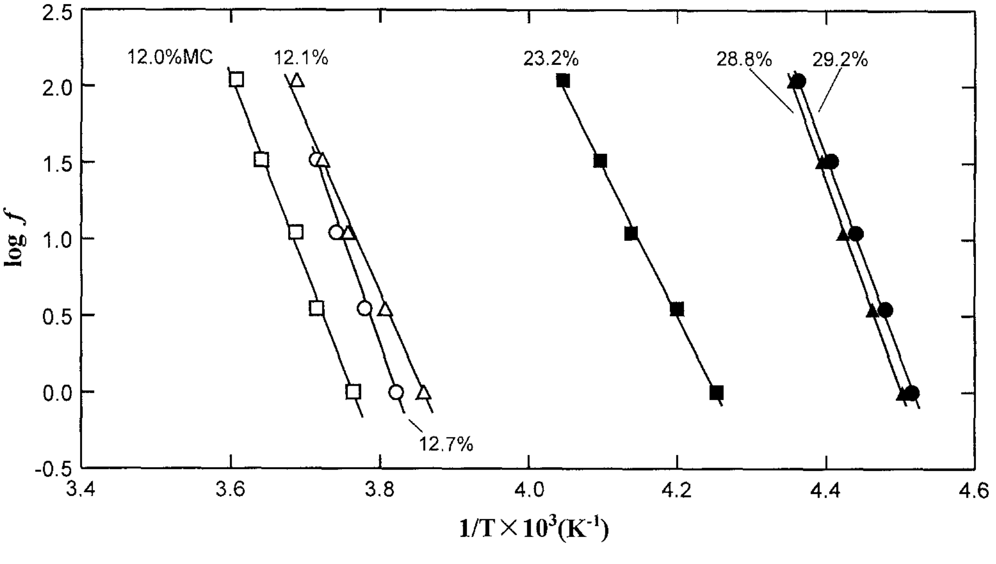


Fig. 4. Temperature dependence of storage modulus (E') and loss tangent (tanδ) at 11 Hz for untreated (U), extracted (E), glucose-impregnated (G), and sucrose-impregnated (S) canes initially conditioned at 20°C and 90% RH. The sugar and moisture contents of the canes are listed in Table 1

Fig. 5. Logarithmic frequency (log*f*) plotted against the reciprocal of absolute temperature (1/T) for the α loss peaks at indicated moisture content (MC). *Circles*, untreated cane; *triangles*, glucose-impregnated cane; *squares*, sucrose-impregnated cane; *open symbols*, initially conditioned at 20°C and 60% RH; *filled symbols*, initially conditioned at 20°C and 90% RH



temperature (1/T) for the α loss peaks of cane. The apparent activation energies (ΔE) of the α process given by the plot of log*f* versus 1/T ranged from 45 to 67 kcal/mol. These ΔE values were distinguished from those of the β process, which ranged from 8 to 14 kcal/mol.

Assignment of the β process

The β process was detected in all of the canes examined. With increasing MC it shifted to lower temperatures, and the magnitude of its loss peak increased. Similar relaxation processes have been detected in wood,[3,4] cellulose,[5] and some synthetic high polymers.[6-8] Analogous dielectric relaxation processes have also been observed in wood.[9,10] Several researchers have concluded that these relaxation processes are due to segmental motions of amorphous cell wall substances associated with the adsorbed water because they occurred on methanol adsorption as well as water adsorption.[6,9] However, this can hardly explain the disappearance of relaxation processes on absolute drying irrespective of measuring methods.

It is generally accepted that water molecules in the vicinity of a polymer behave somewhat differently from normal water because of their interaction with the polymer.[11] This anomalous water is not freezable below 0°C; thus it is often called "nonfreezing" or "bound," being distinguished from normal "bulk" water. It has been suggested that the small amount of water adsorbed on collagen forms an amorphous state, and its glass transition occurs near −120°C.[12] The temperature location of the β process at relatively high MC was comparable to the glass transition point of nonfreezing water adsorbed on collagen. An analogous concept was proposed to explain the dielectric behavior of wood with various moisture contents.[10] Although there is controversy regarding the behavior of water molecules, the β process is thought to be caused by the motion of the adsorbed water itself.

As shown in Fig. 2, the E' of cane increased with increasing MC in the temperatures below which the β process occurred, whereas a reverse trend was observed at temperatures above which the process occurred. This trend was essentially the same as that in wood.[13] It was considered that the adsorbed water stiffened the cell wall of cane below the transitional temperature of the adsorbed water, whereas it plasticized the cell wall above that temperature.

Assignment of the α process

The α process was recognized only in the cane containing extractives or related sugars. Figure 6 shows the temperature dependence of E' and tanδ at 0.05 Hz for the untreated, extracted, and glucose-impregnated canes at 100% RH. The viscoelastic profile of the cane was similar to that of wood. In general, wood and its amorphous constituents exhibit a glass–rubber transition in the temperature range 0°–100°C when they are swollen with water.[14–16] Because the chemical components of cane are essentially the same as those of wood,[17] the apparent transition detected at 90°C was attributed to the glass transition of the amorphous cell wall substances. If the α process was related to the glass transition of the cell wall, the loss peaks at 90°C should disappear or change markedly in the presence of extractives or sugars. The peak remained unchanged for all of the treatments. Thus the α process was independent of the glass transition of the amorphous cell wall substances.

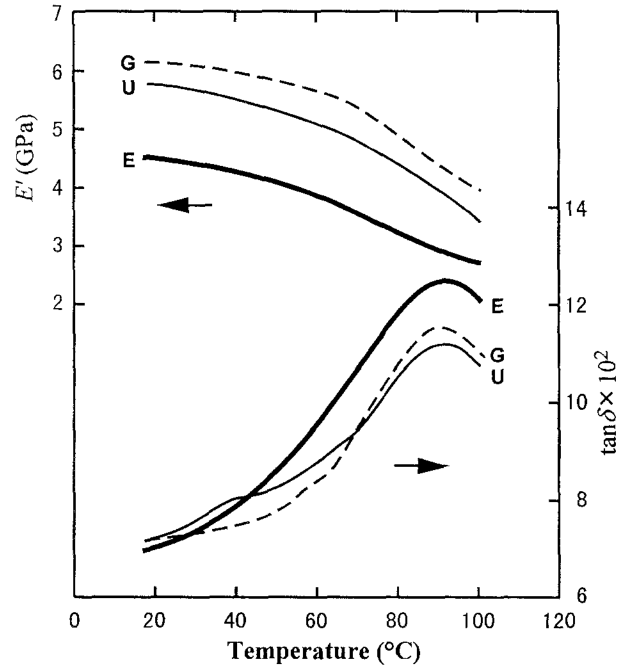


Fig. 6. Temperature dependence of storage modulus (E') and loss tangent (tanδ) at 0.05 Hz for untreated (U), extracted (E), and glucose-impregnated (G) canes under 100% RH

Figure 7 shows the temperature dependence of tanδ for the glucose-impregnated canes with various glucose contents. Irrespective of the MC levels, the α loss peak increased in magnitude with an increase in glucose content, whereas its temperature location remained almost unchanged. These facts indicated that the α process was caused by the glucose. However, it is not logical to attribute the apparent relaxation processes to the extractives and sugars because small molecules such as glucose and sucrose cannot induce a marked relaxation process in this temperature region by their own segmental motions. Consequently, the behavior of water should be taken into consideration. The anomalous "nonfreezing" water adsorbed on polymers induces the relaxation process corresponding to the β process. Ikada et al. suggested that another type of anomalous water exists in the vicinity of mucopolysaccharide.[18] The DSC measurement confirms the presence of this anomalous water, as indicated by the decrease of endothermic DSC peak due to the melting of bulk water. Figure 8 shows the DSC curves of extractives and glucose. At high RH levels, much water aggregates around the extractives with the deliquescence of extractives.[17] Although the DSC curves of the extractives and glucose at low MC levels showed no peak in the temperature range examined, those at high MC levels exhibited marked peaks at around −5°C owing to the melting of bulk water. Because the melting point of bulk water was evidently higher than the temperature location of the α process, the α process is independent of the melting of bulk water. On the other hand, the DSC peak detected at around −5°C was smaller in magnitude than that of pure water, with a broad shoulder in the lower temperature region. In addition, slight endothermic peaks were detected at around −50°C. These observations are similar to those for an aqueous solution of mucopolysaccharides. Thus the extractives and glucose at high MC levels seemed to be surrounded by one type of "nonfreezing" water molecule. Because the temperature locations of the slight endothermic peaks corresponded to those of the α process at high MC levels, the α process could be related to the motion of nonfreezing water at a limited high MC level.

The endothermic peak or shoulder below 0°C has frequently been attributed to the melting of nonfreezing water. However, "melting" is not an adequate term to account for the α process because its temperature location evidently depends on the measuring frequency, as shown in Fig. 5. Moreover, the α process evidently appears at relatively low MC levels, whereas no peak appears in the DSC curves of

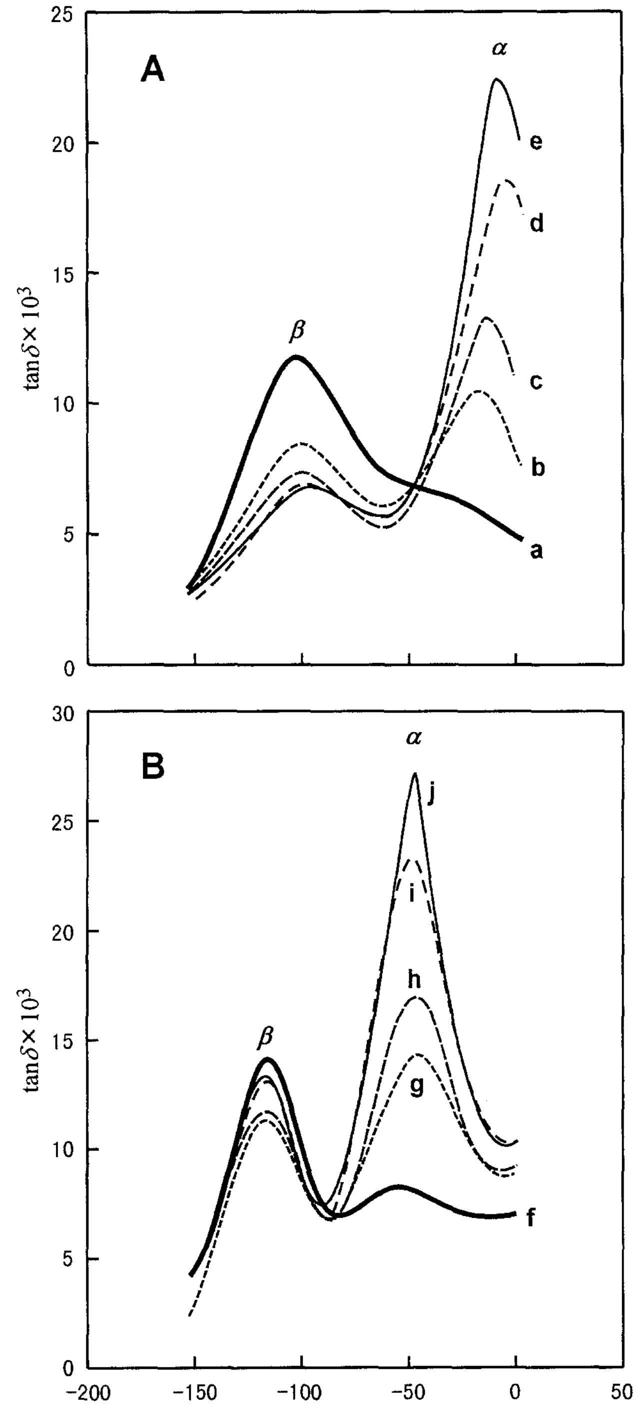


Fig. 7. Temperature dependence of loss tangent (tanδ) at 11 Hz for glucose-impregnated canes with various glucose contents initially conditioned at 20°C and 60% RH (**A**) or initially conditioned at 20°C and 90% RH (**B**). *a*, 0% glucose content (8.9% MC); *b*, 6.4% (11.9% MC); *c*, 9.8% (11.4% MC); *d*, 13.3 (9.7% MC); *e*, 18.3 (12.1% MC); *f*, 0% (17.8% MC); *g*, 6.4% (17.7% MC); *h*, 9.8% (21.1% MC); *i*, 13.3 (23.9% MC); *j*, 18.3 (28.8% MC)

the extractives and glucose at low MC levels. It is thought that the α process is due to some interactive molecular motion of nonfreezing water and sugar.

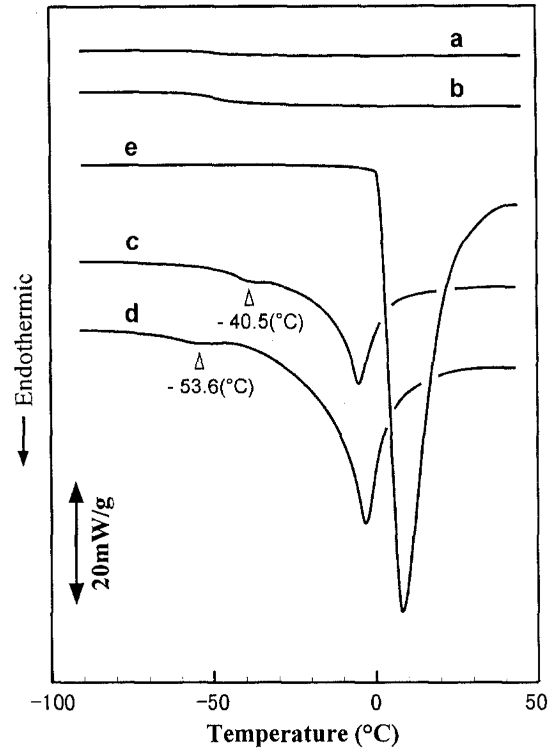


Fig. 8. Differential scanning calorimetric analysis (DSC) curves of pure water, extractives, and glucose. *a*, glucose (1.0% MC); *b*, extractives (24.4% MC); *c*, glucose (63.6% MC); *d*, extractives (142.8% MC); *e*, pure water

Based on these results, it is thought that the adsorbed water in cane consists of two types of anomalous "nonfreezing" water: W_α and W_β. In the absence of sugar, most of the adsorbed water consisting of W_β induces only the β process (Fig. 2). However, in the presence of sugar, a part of the adsorbed water surrounding the sugar, W_α, might contribute to the α process but not to the β process. Consequently, the β loss peaks decrease in magnitude with sugar impregnation because the amount of W_β decreases whereas the total amount of adsorbed water ($W_\alpha + W_\beta$) increases slightly in the presence of sugar (Figs. 3, 4, 7).

Conclusion

The cane had two mechanical relaxation processes, α and β, in the ranges −60° to 0°C and −120° to −100°C, respectively. The β process detected in untreated, extracted, and sugar-impregnated canes was attributed to the motion of adsorbed water in the amorphous cell wall substances. The α process was detected in the canes containing sugar, and its loss peak increased in magnitude with increasing sugar content. The temperature location of the α process depended on the testing frequency. The α process was independent of the glass transition of the amorphous cell wall substances. It was speculated that the α process was due to some interactive molecular motions of adsorbed water and sugar.

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