

Effect of Diluents on Fusion Temperature of the Crystalline Regions in Plain and Tanned Cowhide

INTRODUCTION

In a recent publication by Garrett and Flory¹ it was demonstrated that tendon collagen containing ethylene glycol as a diluent exhibited a melting transition at a specific temperature and that this temperature decreased as the diluent content of the sample increased. This behavior was attributed to melting of crystallites in the tendon and indicated that collagen exhibits crystal-liquid transitions analogous to those in other polymeric substances. Since the crystalline areas of cowhide contain extended protein chains which contract on melting, it was thought that a simple shrinkage measurement might yield similar information and in addition provide an insight into the effect of tanning on the shrinkage phenomenon. This publication reports the effect of glycol, phenol, formamide, and water content on the shrinkage temperature of isoelectric acetone-dehydrated cowhide and some preliminary observations of the effect of water content on the shrinkage temperatures of vegetable- and formaldehyde-tanned leather.

EXPERIMENTAL

Preparation of Sample. The cowhide used in the experiments was depickled to pH 4.9, washed in running tap water, and dehydrated in acetone. The vegetable-tanned samples were of commercial upholstery leather which was analyzed for total hide substance by determination of nitrogen. The formaldehyde tanning was carried out in a 1% formaldehyde, 0.1 molar sodium bicarbonate solution to a final pH of 7.5. The leather was then washed free of unreacted tannin and air dried.

Specimens for the shrinkage measurements were cut from the hide in strips 2.5 inches long, 0.25 inch wide, and about 0.15 inch thick. The specimens were subsequently dried under vacuum at 50°C. Approximately seven hours was required for the sample to attain constant weight. The dried specimens were equilibrated in a vacuum desiccator over the diluent in the case of ethylene glycol and water. The glycol desiccator was heated to 60°C. to facilitate equilibrium, which required as long as six days in some cases. Although water vapor was readily absorbed from an atmosphere of nearly 100% relative humidity at room temperature for

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specimens containing up to 40% by weight of water, it was very difficult to obtain higher water contents by this technique. For the higher water contents the specimens were soaked three minutes in distilled water and then allowed to dry slowly in an atmosphere of about 100% relative humidity until the desired water content was attained. In preparing samples of varying phenol or formamide content it was necessary to soak the dry hide samples in absolute alcohol solutions of phenol or formamide. Varying amounts of these diluents were obtained in the specimens by changing the concentration or time of soaking. After soaking, the samples were conditioned in a vacuum desiccator containing desiccant for at least 24 hours. The diluent content of the cowhide samples reported here are based on the total weight of sample and diluent.

Melting (Shrinkage) Temperature Measurements. The instrument used in measuring the shrinkage temperatures of the samples has been described in a previous paper² and simply provides a means of measuring

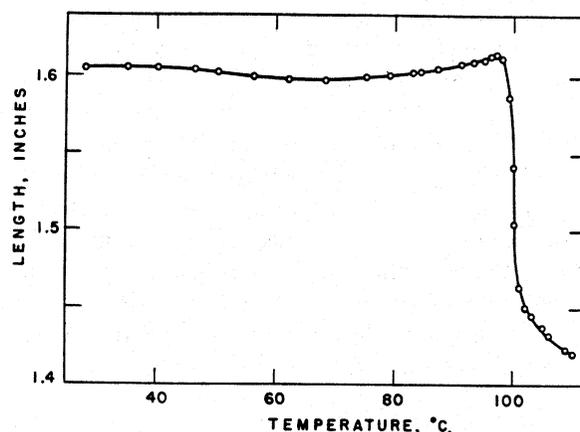


Fig. 1. Plot of length vs. temperature for plain cowhide containing 29.5% by weight of ethylene glycol.

changes in length with an accuracy of ± 0.001 inch. In determining the shrinkage temperature, a sample of known diluent content was immersed in a mercury bath to prevent loss of diluent during the test. The mercury bath was surrounded by a glycol bath in which a heater and stirrer were immersed. The temperature was measured by placing a thermometer in the mercury bath. As a result of numerous trial runs on rate of heating the following was adopted as most suitable and expedient. The sample was heated at a rate of 3°C. per minute up to approximately 10°C. below the shrinkage temperature on the basis of a trial run, then at a rate of 0.5°C. per minute through the shrinkage range. The shrinkage temperature was considered to be that at which a sharp change in slope occurred in the temperature *versus* length plot (Fig. 1). This temperature was reproducible to $\pm 1^{\circ}\text{C.}$ in separate runs.

RESULTS AND DISCUSSION

Melting Temperature Measurements on Plain and Tanned Cowhide-Diluent Systems. A typical example of a shrinkage temperature determination curve is shown in Figure 1, in which length is plotted against temperature for a sample of cowhide containing 29.5% by weight of ethylene glycol. Above 70°C. the sample length increased slowly with temperature until a temperature of 97°C. was reached, at which point the length of the specimen began to decrease rapidly with further increase in temperature. Contraction continued to take place over a wide temperature range.

In an experiment to determine the effect of heating rate on shrinkage temperature, a specimen of cowhide containing 39% moisture was heated rapidly up to a temperature 3°C. below the shrinkage temperature and then raised at a rate of 3°C. in four hours. The shrinkage temperature observed was the same within experimental error as that obtained by the method previously described. At the shrinkage temperature, the specimen shrank very slowly. The rate of shrinkage increased with increasing temperature. This increase in rate with increasing temperature would be expected if shrinkage were the result of a melting process. The melting of the crystallites in hide appears to occur abruptly at a reproducible temperature independent of the heating rate below a rate of 0.5°C. per minute.

The shrinkage temperatures (melting temperatures) of cowhide specimens containing 25.0, 29.5, 36.5, and 42.0% by weight of ethylene glycol are given in Table I. The shrinkage temperature decreases with increasing ethylene glycol content.

Flory³ has shown that the melting point of semicrystalline polymer systems is depressed by diluents as demanded by the relationships obtained by the application of thermodynamic equilibrium to phase transitions. The following expression, which relates the equilibrium melting temperature of a crystalline polymer-diluent system to the composition as represented by the volume fraction of the diluent was used in treating the experimental data:

$$1/T_m - 1/T_m^0 = (R/\Delta H_u) (V_u/V_1) (v_1 - \chi_1 v_1^2) \quad (1)$$

where T_m is the melting point of polymer-diluent system, T_m^0 is the melting point of pure polymer, v_1 is the volume fraction of diluent, V_u and V_1 are the molar volume of polymer and diluent, respectively, χ_1 is the interaction parameter, ΔH_u is the heat of fusion of the crystalline material, and R is the gas law constant.

A plot of the reciprocal of the absolute melting temperature against the volume fraction of ethylene glycol for samples of cowhide is shown in Figure 2. Also shown in the graph are similar data obtained by Garrett and Flory¹ with a dilatometer using collagen and ethylene glycol. Within the limits of experimental error the two experimental methods yield the same results. Thus the shrinkage temperature of hide is identical to the first-order transition temperature and therefore will be referred to hereafter as the melting temperature.

TABLE I
Effect of Diluents and Diluent Content on Melting Temperature (Shrinkage Temperature) of Plain and Tanned Cowhides

Plain Hide Diluent							
Glycol		Formamide		Phenol		Water	
Wt. %	t_m , °C.	wt. %	t_m , °C.	wt. %	t_m , °C.	wt. %	t_m , °C.
25.0	103	12.5	106	17.5	115	24.5	97
29.5	97	14.0	100	27.0	96	25.5	95
36.5	85	21.0	87	29.0	96	33.5	84
42.0	81	21.5	86	31.0	92	34.0	82
		23.5	84	34.0	88	35.5	78
		30.5	75	34.0	88	36.0	80
				43.5	78	39.0	77
						48.5	63
						62.5	56
						Immersed	56

Tanned Hide			
Vegetable ^a		Formaldehyde ^a	
% water	t_m , °C.	% water	t_m , °C.
0	120	26.0	98
11.5	97	29.0	94
16.5	89	30.5	92
19.5	85	35.5	83
24.0	84	Immersed	73
27.0	82		
35.5	79		
37.0	79		
Immersed	78		

^a Based on total weight of hide, tannin and water.

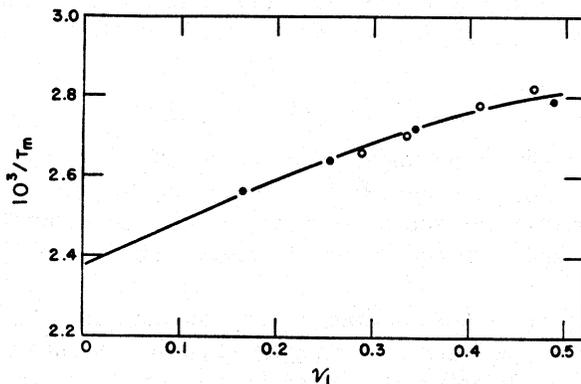


Fig. 2. Plot of reciprocal melting temperature *vs.* volume fraction of diluent, v_1 , for the ethylene glycol-cowhide system (O), and for the ethylene glycol-collagen system (●).¹

Extrapolation of the curve of Figure 2 to zero diluent content yields a value of about 145° for the melting point of the crystallites in undiluted cowhide, the same as reported¹ for unswollen collagen. No real melting of the crystallites of dried cowhide could be detected experimentally.

Even when the specimen was heated 20°C. above the anticipated melting point, it showed only a slight amount of contraction and this occurred over a wide temperature range.

The values of melting temperature, t_m , for cowhide containing water, phenol, and formamide as diluents are listed in Table I. Like the ethylene glycol system, these showed a decrease in the melting point of the crystallites as the diluent concentration increased. For example, the cowhide specimen containing 24.5% water contracted at 97°C. while the one containing 62.5% water contracted at 56°C. The latter temperature was the same as that obtained when the specimen of hide was completely immersed in water. Although the melting temperatures of cowhide containing ethylene glycol, water, formamide, and phenol show the same general dependence on the diluent concentration, the individual values obtained at the same diluent concentration (weight per cent) are different. When the values of melting temperature and diluent content were treated in the same manner as the glycol data shown in Figure 2, extrapolation of the curves to zero diluent content gave about the same t_m^0 value (145°C.) in all cases.

A preliminary investigation of the melting-point depression in cowhide specimens which had been tanned with a vegetable tannin in one instance and with formaldehyde in another was then undertaken to determine the effect of tanning. Water was the only diluent used with the tanned specimens. Like the plain cowhide, the vegetable- and formaldehyde-tanned leathers melted at lower temperatures as their content of diluent (water) was increased (Table I).

Comparison of Plain and Tanned Cowhide-Diluent Systems. Comparing the melting temperature of a formaldehyde-tanned specimen with that of untanned hide at similar moisture contents, 26 and 25.5% respectively, it may be noted that the t_m values are about the same (98 and 95°C., respectively). However, when immersed in water the hide shrank at 56°C. and the formaldehyde-tanned leather at 73°C. These results indicate that, when fully hydrated, the formaldehyde-tanned leather would contain approximately 40% (effective) water by weight based on hide content only, compared with 62.5% for plain hide in the hydrated state. This indicates that in the specimens tested, formaldehyde tanning reduces the availability of the amorphous regions to water either through a type of crosslinking and/or a reduction in the number of active sites. Since the amount of water available to act as a diluent is much less in the tanned specimen than in plain hide, the shrinkage temperature of the former is elevated. The melting temperature of dry formaldehyde-tanned leather obtained by extrapolation of the experimental data was 151°C., about 6°C. higher than that of plain cowhide. This indicates that formaldehyde tanning produces an increase in the stability of the crystallites. If formaldehyde acts as a crosslinking agent in the ordered regions, this result is to be expected. The effect of formaldehyde on the disordered region is shown below. With the formaldehyde-tanned leather, as with the untanned cowhide, no real melting, of the crystallites could be detected experimentally in a dry specimen.

The melting temperature of plain hide containing 25.5% water was 13°C. higher than that of vegetable-tanned cowhide containing 27% water. However, when both were immersed in water, the vegetable-tanned leather contracted at a temperature 22°C. higher than the hide. This would seem to indicate that the vegetable-tanned sample, when immersed in water, would contain only about 40% effective water. This is less than the effective water content of plain hide, 62.5%, indicating that vegetable tanning, like formaldehyde tanning, has reduced the number of effective polar sites. The value of t_m^0 for vegetable-tanned hide obtained by extrapolation of the experimental data was 120°C., about 25°C. lower than that for hide. Unlike plain hide and formaldehyde-tanned hide this value was verified experimentally. A dry vegetable-tanned specimen showed an unmistakable shrinkage at about 120°C. This evidence for a decrease in crystalline stability indicates that vegetable tannin acts as a diluent for hide behaving in a manner similar to that of a copolymer consisting of units which crystallize and other units which do not. Thus the melting behavior of dry vegetable-tanned hide appears to be opposite that of dry formaldehyde-tanned hide. This indicates that the vegetable tanning agent employed does not crosslink hide to the same extent or in the same manner as formaldehyde. Its manner of attachment might be such that it acts as an internal plasticizer to some extent. Because of the relatively large size of the vegetable tannin molecule (molecular weight 1000–2000),⁴ a reduction in the interaction between protein chains might be expected.

If this is true, tanning would produce effects in the amorphous regions which should be quite different in the two cases. In order to measure these effects the torsional modulus of elasticity was measured on the same specimens before and after tanning. The samples were equilibrated at 73°F. and 50% relative humidity before testing. The modulus in torsion of the hide specimens increased by a factor of 5 after formaldehyde tanning while that of the vegetable-tanned specimens increased by a factor of only 1.5. This marked increase in modulus in the case of the formaldehyde-tanned specimens indicates the conventional type of crosslinking. That the vegetable tanning produced no marked over-all change in flexibility is to be expected in view of the above discussion.

In general, these observations indicate that tanning reduces the availability of the amorphous regions to diluents either through a type of crosslinking and/or a reduction in the number of active sites. This accounts for the observed elevation of the commonly measured shrinkage temperature of hide specimens after tanning. Thus any substance incorporated in such manner should produce an increase in the shrinkage temperature of the hide material. In addition, the same substance can markedly modify the mechanical properties of the amorphous regions by acting as a plasticizer or stiffening agent depending on such characteristics as its size and mode of attachment. It should be possible with these points in mind to modify the properties of hide substance as desired.

Heats of Fusion of Plain and Tanned Cowhide. The values of ΔH_u .

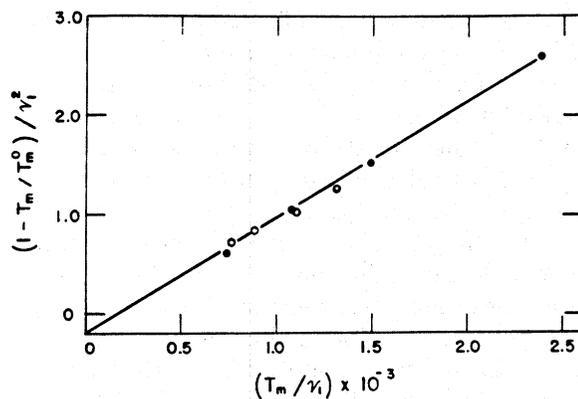


Fig. 3. A plot of $(1 - T_m/T_m^0)/v_1^2$ against T_m/v_1 for the ethylene glycol-cowhide system (O), and for the ethylene glycol-collagen system (●).¹

the heat of fusion of the crystallites, and χ_1 , the interaction parameter, were obtained as described⁵ by rearranging equation (1) as follows:

$$(1 - T_m/T_m^0)/v_1^2 = (T_m/v_1) (RV_u/\Delta H_u V_1) - (RT_m \chi_1/\Delta H_u)(V_u/V_1) \quad (2)$$

and plotting $(1 - T_m/T_m^0)/v_1^2$ against T_m/v_1 . As illustrated in Figure 3, a linear relationship is obtained for the ethylene glycol-cowhide systems and for all the other cowhide-diluent systems reported below. The value for ΔH_u , was calculated from the slope of the line. The density of cowhide was taken to be 1.35 g./cc. and the average molecular weight of the structural unit, 94 g./mole. The volume fraction of diluent, v_1 , was obtained by converting both hide and diluent weight to volumes using the following diluent densities: water, 1.0; glycol, 1.12; formamide, 1.13; and phenol, 1.07. The corresponding value for ΔS_u , the entropy of fusion of the crystallites, was calculated from the relationship $\Delta S_u = \Delta H_u/T_m^0$. The interaction parameter, χ_1 , was obtained from the intercept; however, since it has been more common to refer to energy of interaction, the former was converted into energy of interaction, B , by means of the relationship $B = \chi_1 RT/V_1$.

TABLE II

Melting Temperatures, Heats and Entropies of Fusion, and Energies of Interaction of Plain and Tanned Cowhide

System	t_m^0 , °C.	ΔH_u , cal./mole	ΔS_u		B , cal./cc.
			cal./ deg./ mole	cal./ deg./ bond	
Plain cowhide-glycol.	145	2200	5.3	2.6	4.6
Plain cowhide-formamide.	145	1600	3.8	1.9	16.0
Plain cowhide-phenol.	145	1800	4.4	2.2	-1.5
Plain cowhide-water.	145	7200	17.0	8.5	2.0
Vegetable-tanned cowhide- water.	120	7200	18.4	9.2	35
Formaldehyde-tanned cow- hide-water.	151	8000	19.0	9.5	-8.6

Comparison of the ΔH_u values for the various plain cowhide systems as given in Table II shows similar values for formamide and phenol as diluents, 1600 and 1800 cal./mole, respectively. These are slightly less than the value, 2200 cal./mole, obtained for the glycol system. On the other hand, a value of 7200 cal./mole was obtained for the hide-water system. This latter value is the one to be expected if one hydrogen bond were broken per residue. However, the reason for the spread in ΔH_u values for the various systems is not apparent. According to the method, heats of fusion obtained using different solvents should be the same. If the dielectric constant of the diluent affects the strength of the linkages involved in shrinkage (fusion), it is not obvious from the results. Formamide and water, diluents with high dielectric constants, differed by a factor of more than four in their value for the heat of fusion. On the other hand, phenol with a low dielectric constant yielded a heat of fusion similar to that of the formamide system.

The value obtained for ΔH_u of vegetable-tanned cowhide using water as the diluent was 7200 cal./mole, the same as that found for the plain cowhide-water system. The formaldehyde-tanned cowhide-water system yielded a slightly greater value, 8000 cal./mole. This latter observation points to the stabilizing effect of the crosslinks introduced by formaldehyde on the crystallites.

Entropies of Fusion of Plain and Tanned Cowhide. The corresponding values for the entropy of fusion, ΔS_u , ranged from 3.8 cal./deg./mole for the formamide system to 17.0 for the water system (Table II). These values should be the same if the number of configurational arrangements of the chain segments on melting were identical in the systems investigated. The entropies of fusion for most of the polymers reported³ are in the range from 1.5 to 2.0 cal./deg./bond. A value of 2.6 was reported¹ for the collagen-glycol system, assuming that two bonds per residue were freed on melting. On the same assumption the glycol-, formamide-, and phenol-cowhide systems yielded 2.6, 1.9, and 2.2 cal./deg./bond, respectively. The water system, however, yielded a value of 8.5. Values similar to the latter were also obtained for the two tanned cowhide-water systems. In order to reduce the entropy of fusion values for the water systems to approximately those of the other systems it would be necessary to assume that eight bonds per residue are freed on melting. Why four times as many bonds would be involved per residue in the melting of crystallites of the water systems is not apparent.

Energies of Interaction for Plain and Tanned Hide-Diluent Systems. The values of B , the energy of interaction, for the untanned hide-diluent systems ranged from -1.5 cal./cc. for the phenol-cowhide system to 16.0 for the formamide-cowhide system (Table II). According to theory a positive B value would indicate a poor solvent, but this is certainly not true for formamide as evidenced by the relatively low melting temperatures obtained. Similarly it is difficult to explain the large positive value, 35, obtained for the vegetable-tanned cowhide-water system in contrast to the negative value, -8.6 , obtained with the formaldehyde-tanned cowhide water system. The application of thermodynamic equilibrium to the phase transitions that take place in the cowhide systems investigated is in

general satisfactory. However, there are a few discrepancies, particularly the variations in the heats of fusion and the energies of interaction observed with the different solvents, which cannot be explained at the present time without further refinements.

The authors wish to thank D. R. Killen for the melting temperature measurements.

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Synopsis

Melting (shrinkage) phenomena in plain cowhide were investigated by measuring the temperature at which contraction first occurred in specimens containing varying amounts of ethylene glycol, formamide, phenol, and water as diluents. Similar measurements were made on cowhide specimens which had been tanned with formaldehyde and with a vegetable tannin and contained water as the diluent. In all cases the temperature at which contraction first occurred was found to increase as the diluent concentration was decreased in general accord with the theory of melting-point depression. The melting temperature of the crystallites in undiluted cowhide was found, by extrapolation of the data of each system to zero diluent content to be about 145°C. The melting temperatures of undiluted tanned cowhide, however, depended on the tanning agent employed. A value of 120°C. was obtained for the vegetable-tanned cowhide, and 151° for formaldehyde-tanned cowhide. The former value was verified experimentally by direct measurement. This evidence for a decrease in crystallite stability indicates that vegetable tannin acts as a diluent. The observations indicate that tanning reduces the availability of the amorphous regions to diluents either through a type of crosslinking and/or a reduction in the number of active sites. This accounts for the observed elevation of the commonly measured shrinkage temperature of hide specimens after tanning. In addition, the tanning agents can markedly modify the mechanical properties of the amorphous regions by acting as a plasticizer or stiffening agent. The heats of fusion, ΔH_u , for cowhide diluted with glycol, formamide, and phenol were 2200, 1600, and 1800 cal./mole, respectively. However, with water as diluent for plain hide, ΔH_u was 7200 cal./mole. Similar values were obtained with the tanned hide. Entropies of fusion, ΔS_u , for cowhide diluted with glycol, formamide, and phenol (assuming two bonds per residue freed on melting) were 2.6, 1.9, and 2.2 cal./deg./bond, respectively, while for plain hide, vegetable-tanned hide, and formaldehyde-tanned hide diluted with water, the values were 8.5, 9.2, and 9.5 cal./deg./bond. In order to bring the entropy values for the water systems into agreement with the other diluent systems it is necessary to assume that eight bonds per residue are freed on melting.

Résumé

Des phénomènes de rétrécissement du cuir de vache ont été étudiés en mesurant la température à laquelle la première contraction se manifeste dans des échantillons contenant des quantités variables d'éthylène glycol, de formamide de phénol, et d'eau comme diluants. Des mesures semblables ont été faites sur des échantillons qui avaient été tannés au formaldéhyde et au moyen d'un tannin végétal, et qui contenaient de l'eau comme diluant. Dans tous les cas la température, à laquelle la première contraction se passe, croît avec une diminution de la concentration en diluant, ce qui est en accord avec la théorie de l'abaissement du point de fusion. La température du fusion des cristallites dans le cuir de vache non-dilué a été trouvé environ égal à 145°C. par extrapolation des résultats de chaque système jusqu'à teneur en diluant nulle. Les tempéra-

tures de fusion de cuir de vache non-dilué et tanné dépendent toutefois de l'agent de tannage utilisé. On obtient ainsi une valeur de 120°C. pour un cuir de vache traité au tannin végétal, 151°C. s'il a été tanné au formol. La première valeur a été vérifiée expérimentalement par mesure directe. La diminution de stabilité des cristallites indiquent que le tannin végétal agit comme diluant. Ces observations indiquent que le tannage réduit la disponibilité des régions amorphes à l'égard des diluants soit par un mécanisme de cross-linking soit par une diminution du nombre de centres actifs. Ceci rend compte de l'augmentation de la température de rétrécissement généralement mesurée pour les échantillons de peaux après tannage. De plus, les agents tannants pourraient modifier considérablement les propriétés mécaniques des régions amorphes par suit de leur action plastifiante ou durcissante. Les chaleurs de fusion, ΔH_u , pour le cuir de vache dilué au glycol, formamide, et le phénol s'élevaient respectivement à 2200, 1600 et 1800 cal/mole, toutefois dans le cas de l'eau comme diluant, ΔH_u s'élevait à 7200 cal/mole. Des valeurs semblables ont été obtenues avec le cuir tanné. Les entropies de fusion; ΔS_u , pour le cuir de vache dilué au glucol, le formamide, et le phénol s'élevaient respectivement à 2,6, 1,9 et 2,2 cal/deg (en admetant la mise en liberté de deux liaisons par résidu lors de la fusion). Par contre pour le cuir plein, les peaux tannées aux végétaux et les peaux tannées au formol diluées d'eau, des valeurs de 8,5, 9,2 et 9,3 sont notées; afin de faire accorder les valeurs de l'entropie mesurées pour les systèmes aqueux avec les autres systèmes à diluant il est nécessaire d'assumer que 8 liaisons par fragment soient libérés par fusion.

Zusammenfassung

Schmelz-(Schrinkungs)-Vorgänge in einfachem Kuhleder wurden durch Messung der Temperatur, bei welcher die Kontraktion zuerst auftrat, in Proben untersucht, die variierende Mengen von Äthylenglykol, Formamid, Phenol und Wasser als Verdünnungsmittel enthalten. Ähnliche Messungen wurden an Kuhlederproben ausgeführt, die mit Formaldehyd und mit einem Pflanzentannin tanniert worden waren und Wasser als Verdünnungsmittel enthielten. In allen Fällen wurde gefunden, dass die Temperatur, bei der die Kontraktion zuerst auftrat, mit Abnahme der Verdünnungsmittel-Konzentration zunahm, was in allgemeiner Übereinstimmung mit der Theorie der Schmelzpunktniedrigung steht. Durch Extrapolierung der Daten jedes Systemes zu Verdünnungsmittelgehalt Null wurde gefunden, dass die Schmelztemperatur der Kristallite in verdünntem Kuhleder ungefähr 145° ist. Die Schmelztemperaturen von verdünntem tanniertem Kuhleder sind jedoch vom verwendeten Tannierungsmittel abhängig. Für das Pflanzen-tannierte Kuhleder wurde ein Wert von 120°C erhalten und für das Formaldehyd-tannierte 151°. Der esstere Wert wurde experimentell durch direkte Messung geprüft. Dieses Anzeichen einer Abnahme der Kristallit-Beständigkeit zeigt, dass Pflanzentannin als Verdünnungsmittel wirkt. Diese Beobachtungen zeigen an, dass Tannin die Erreichbarkeit der amorphen Gegenden für Verdünnungsmittel entweder durch eine Art Querverbindung und/oder eine Reduktion der Anzahl aktiver Stellen herabsetzt. Dies trägt der beobachteten Erhöhung der allgemein gemessenen Schrinkingtemperatur von Lederproben nach Tannierung Rechnung. Ausserdem können die Tannierungsmittel die mechanischen Eigenschaften der amorphen Gegenden erheblich ändern, indem sie als Weichmacher oder Steifungsmittel wirken. Die Schmelzwärmen ΔH_u für mit Glykol, Formamid, und Phenol verdünntes Kuhleder waren 2200, 1600 beziehungsweise 1800 kal./Mol. Mit Wasser als Verdünnungsmittel für einfaches Leder war ΔH_u jedoch 7200 kcal./Mol. Mit tanniertem Leder wurden ähnliche Werte erhalten. Schmelzentropien ΔS_u für mit Glykol, Formamid und Phenol verdünntes Kuhleder (unter der Voraussetzung, dass zwei Bindungen pro Rückstand durch Schmelzen befreit wurden) waren 2,6, 1,9 beziehungsweise 2,2 kal./Grad/Bindung, während die Werte für einfaches Leder, Pflanzen-tannierte Leder und Formaldehyd-tannierte Leder, die mit Wasser verdünnt waren, 8,5, 9,2 beziehungsweise 9,5 kal./Grad/Bindung waren. Um die Entropiewerte für die Wassersysteme mit anderen Verdünnungsmittelsystemen in Übereinstimmung zu bringen ist die Annahme nötig, dass acht Bindungen pro Rückstand durch Schmelzen befreit werden.

Received January 11, 1957