Dynamic Mechanical Properties of Polymer–Leather Composites

Synopsis

The effects of polymer impregnation, moisture, and lubricant oils on the complex modulus of the grain layer of leather have been studied. The impregnated materials were prepared by introducing a mixture of polyurethane oligomer and vinyl monomers into the grain layer and polymerizing by electron-beam irradiation. Synergism was observed in the interaction of the components of the system and analyzed in terms of the adhesion of the polymer to the collagen fibers.

INTRODUCTION

In recent years there has been an emphasis on emulsion polymerization of monomers within wet leather to form full-thickness polymer/leather composites. The process has been reviewed in detail and reported in this journal by Jordan et al.[1–4] Their findings of nonuniform deposition in cattlehide leather and the wasteful requirement for splitting away a portion of the product to obtain the desired thickness of the grain side for shoe uppers (its principal end use) has prompted an alternate approach of controlled partial impregnation of the grain layer and polymerization to a controlled depth by electron beams as suggested by Buechler.[5]

The grain split is a fibrous structure containing a grain layer, formed from the *corium minor* of the original dermis and a deeper *corium major* layer, made up of coarse collagen fiber bundles. The grain layer contains only fine collagen fiber bundles, usually about 0.001–0.003 mm thick, and is deeply penetrated by channels opening to the surface, which earlier contained hair follicles. The ratio of grain layer to *corium major* varies with the thickness of the grain split, but is usually less than 1.0. In creasing of the leathers, the coarse fiber structure in the *corium major* frequently dominates the fine fiber structure in the *corium minor* and leads to unsightly folds after multiple creasing, as occurs in the vamp of a shoe. Buechler[6] has shown that the way the leather creases when it is folded is greatly improved by impregnation of the *corium minor* with a penetrating low-modulus polymer prior to finishing with polymer coatings. This property is an important aspect of both the esthetics and the durability of the leather. Scuff resistance of the leather is greatly increased by this impregnation treatment. It is known that the impregnant should have a low glass tran-

sition temperature, high molecular weight, and compatibility with the fibrous component of the leather, the collagen fibers. The requirement of high molecular weight, which implies high viscosity, prevents satisfactory impregnation of preformed polymers into full-grain leathers, in which the dense grain layer is preserved intact.

Buffed leathers, in which the grain layer is not a barrier, have been predominant over the years, so that the process has been of large commercial value; but natural-looking full-grain leathers are now being emphasized. For this reason we have been developing a new system where, to impregnate a full-grain leather with a high molecular weight polymer, the impregnant is introduced into the grain layer as an oligomer diluted with vinyl monomers, to be polymerized *in situ* by electron-beam irradiation. Scholnick et al.[7] have described a series of polymeric surface coatings for leather which can be radiation cured in seconds with 100% utilization of starting reactants. However, the situation in *in situ* polymerization of impregnating mixtures to effect improvements in creasing properties and scuff resistance is much more complex and requires greater characterization to determine why some impregnating mixtures work and some do not. The impregnation system used in this present work was successful. It contained equal parts of a polyurethane oligomer, *N*-vinyl pyrrolidone, and 2-ethylhexyl acrylate. It penetrated the grain layer and improved the scuff resistance and crease appearance of the leather. We have investigated the interaction of this polymer system with the collagen of the leather, especially seeking possible synergistic mechanical effects. To study the interaction, we have determined the effects of moisture, oils, and impregnants on the dynamic mechanical properties of leather grain layer separated from tanned but unfinished leather.

METHODS

Impregnation of Leather

The leather (A. C. Lawrence Co.†) was of the type used for shoe uppers: 1.8 mm full-grain cattlehide tanned with chromium and lightly retanned with quebracho. To reduce cohesion of the fibers when the leather is dried and to reduce interfiber friction and excessive orientation when it is later stretched, an oil-in-water emulsion was added during manufacture. The oil, which comprised 12.3 wt % of the leather after drying, is typically a mixture of sulfated oil, raw neatsfoot oil, and a nonionic detergent. This material, referred to as "fatliquor," was removed from some samples by sequential extraction in a Soxhlet apparatus with dichloromethane, 1:1 dichloromethane:acetone, and petroleum ether (60°C fraction).‡

The depth of polymer impregnation was determined histochemically. The polymer in impregnated material was stained by an adaptation of the water

† Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

‡ Precautions derived from manufacturer's material safety data sheets were taken when using all chemicals. After the experiments were completed, it was learned that EHA may be tumorigenic; we found that isodecyl acrylate can be substituted.

soluble basic dyes used by Lowell and Buechler.[8] HCl was substituted for acetic acid in the preparation of their dye solution number one (Sandocryl Brilliant Red B-4G). The staining time was also increased from 0.5 h to 2 h at ambient temperatures. Auramine O (dye solution no. 2) was used as described, but the dye bath was kept at ambient temperature. The sections were mounted from glycerin jelly. The depth of the impregnation should be measured or photographed within several hours because in some leathers the colors fade with time.

Impregnation of the leather was effected by hand application of the oligomer–monomer solution using a swab covered with commercial plush fabric, which was thoroughly wet with the solution. The samples absorbed the mixtures readily, but the swab was then wiped semidry and used to level the leather surface before radiation with electron beams. The electron beam experiments were conducted at Energy Sciences, Incorporated (Woburn, Mass.), using their CB 250/30/20 irradiation unit. The usual dose employed was 2.5 Mrads, beam current at 2.5 mA, and terminal voltages of 160–200 kV. All EB experiments were carried out under inert gas (O_2 < 500 ppm) to avoid formation of ozone.

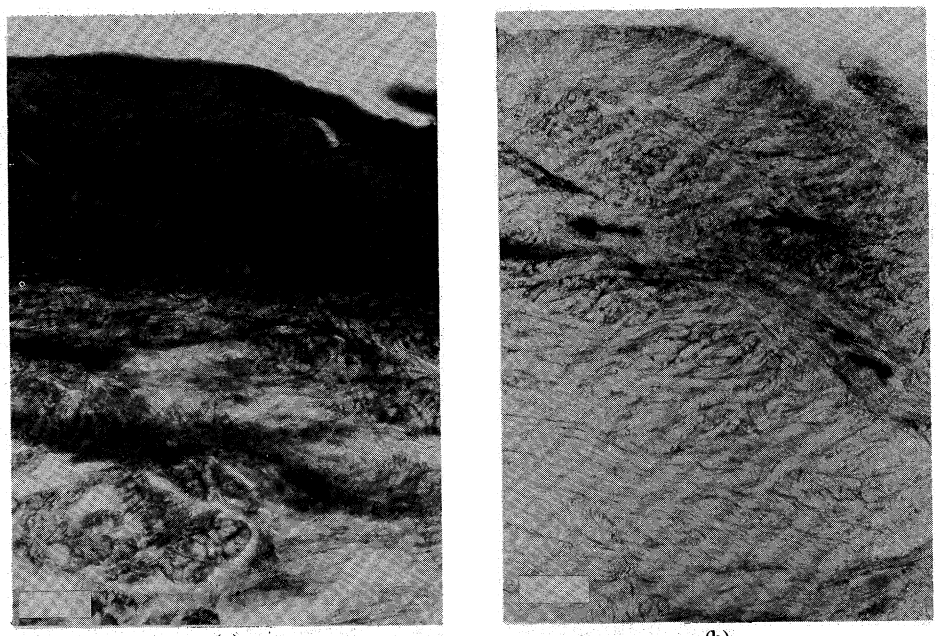
To prepare films containing polymer alone, the oligomer–monomer solution, sensitized with 2% diethyoxyacetophenone, was drawn down on glass plates and cured with ultraviolet light. Ultraviolet irradiation was carried out using a Fusion Systems Corporation (Rockville, Md.) conveyorized Model F 440 system. It includes two electrodeless, microwave activated, 300 W/in. lamps, 10 in. in length which were operated in series, with principal radiation at 210–270 nm. The conveyorized system was employed at a belt speed of 30 ft/min.

After impregnation, an 0.05-cm layer was split off from the grain surface with a leather splitting machine (Fortuna Werke AG, Stuttgart), which utilizes a travelling-band knife, to obtain slices of uniform thickness. The thickness chosen included only the impregnated grain layer (Fig. 1).

Samples of the split grain were conditioned at 23°C over sodium chloride solution or dry calcium chloride at 55% or 0% relative humidity, respectively, for several days immediately before mechanical measurements, placed in the dry nitrogen of the measurement chamber and rapidly cooled to the lowest temperature of the measurement. It required only a few minutes of cooling to reduce the vapor pressure of water in the sample to less than 10% of the room vapor pressure, so there was no time for the samples to dry out. The water contents of the two types of sample, measured by the loss of weight when they were heated at 150 torr and 110°C, were 18% and 3.5%, respectively.

Dynamic Mechanical Properties

The real and imaginary parts of the complex modulus were determined at three frequencies (3.5, 11, and 110 Hz) with a Rheovibron II dynamic viscoelastometer (Toyo Baldwin Co.)[9] operated at an oscillating relative deformation of 3.8×10^{-4}. The samples were cooled in a chamber within an insulated copper block. The chamber was rapidly cooled to −100°C with boiling liquid nitrogen and then warmed at a rate of 2–3°C/min with electric



(a) (b)

Fig. 1. Photomicrograph of cross section of full-thickness leather, stained with brilliant red to reveal the polymeric impregnant: (a) Leather-impregnated and electron-beam cured; (b) untreated control. The dark regions are stained polymer.

heaters in contact with the copper block. The temperature was measured with a thermocouple inside the chamber very close to the sample. Temperature uniformity within the chamber was achieved by a flow of precooled dry nitrogen. Dimensions of a typical sample were 6.5 cm × 0.5 cm × 0.05 cm. This instrument measures the amplitudes of the harmonic force and amplitude signals and determines their phase, δ, with a phase meter of high precision. The phase data, together with the force and deformation amplitude signals, give the real and imaginary parts, E' and E'', of the complex modulus: $E^* = E' + iE''$, with $\tan \delta = E''/E'$.

RESULTS

The elastic modulus E' of the dry solvent extracted grain layer decreases by only 27% between −90°C and 53°C (Fig. 2). A very slight increase is observed above 5°C at all frequencies. The hysteresis, measured by tan δ, is small and almost constant over this temperature range. The loss modulus E'', unlike tan δ, is parallel to the elastic modulus at the lower frequencies and temperatures, but has a shallow maximum at −60°C at 110 Hz.

The extracted grain layer was also studied after it was conditioned at 50% relative humidity (Fig. 3). Again, the elastic modulus varies little with temperature below 35°C. Above this temperature, however, it increases with a slight tendency of the hydrated sample to shrink. E'' is again parallel to E' at low temperatures, but also shows a relaxation centered at 0°C, due to the presence of water, which also appears in tan δ at 25°C. The magnitude of tan δ below this relaxation peak is similar to that in the dehydrated

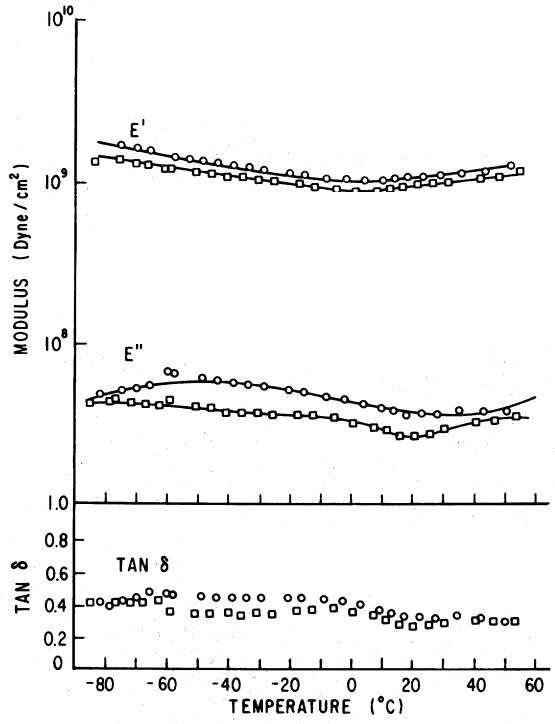


Fig. 2. Dynamic mechanical properties of dessicated leather grain layer after solvent extraction to remove fatliquor oil: (○) 110 Hz; (□) 3.5 Hz.

grain layer (Fig. 2). The minimum in E' is not reversible on temperature cycling in dry nitrogen, does not appear in the dehydrated sample of Figure 2, and is accompanied by shrinkage; it is clear that it is caused by dehydration when the temperature of the sample in dry nitrogen is raised above 35°C.

The elastic modulus of leather containing 30% fatliquor (Fig. 4) and conditioned at 55% relative humidity is much more temperature-dependent than that of the dry or hydrated extracted materials, increasing by an order of magnitude between 35°C and −100°C. The loss modulus E'' is strictly parallel to the elastic modulus down to −85°C, where there is a maximum. Like the hydrated extracted leather (Fig. 3), tan δ in the hydrated leather with fatliquor has a low, broad, but clearly resolved maximum at 25°C.

Even at temperatures away from its maximum, tan δ of the fatliquored sample is twice that of the extracted sample. The increases in E' and E'' between 35°C and 55°C were accompanied by a tendency of the sample to shrink, although it was held at constant length. These increases are not reversible with temperature cycling, and so are probably due to dehydration above 35°C. Thus, lubrication of the fibrils by fatliquor occurs mostly around room temperature; below −60°C, it actually increases the elastic modulus. It also increases the level of the tan δ—the relative contribution of the internal friction to the stiffness—at all temperatures.

For impregnating the grain layer, polyurethane (PU) oligomer (CMD 6700 UV/EB Curable Resin, Celanese Plastics and Specialties Co.) was diluted

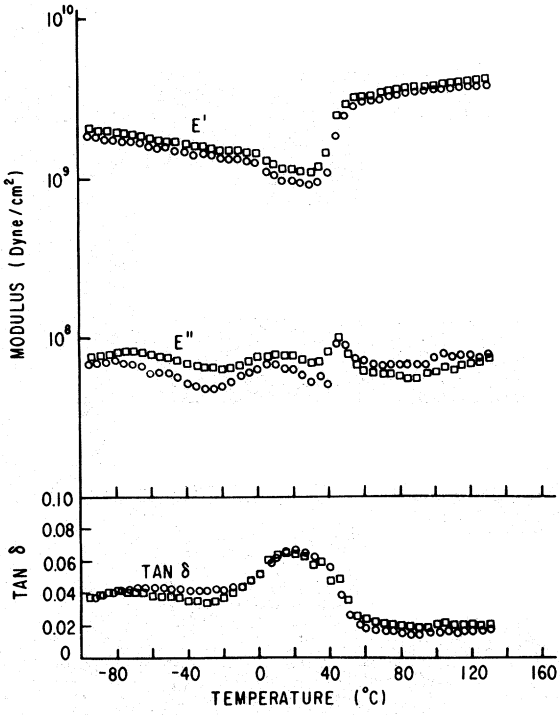


Fig. 3. Dynamic mechanical properties of leather grain layer after extraction to remove fatliquor oil and hydration at 55% relative humidity: (□) 110 Hz; (○) 3.5 Hz.

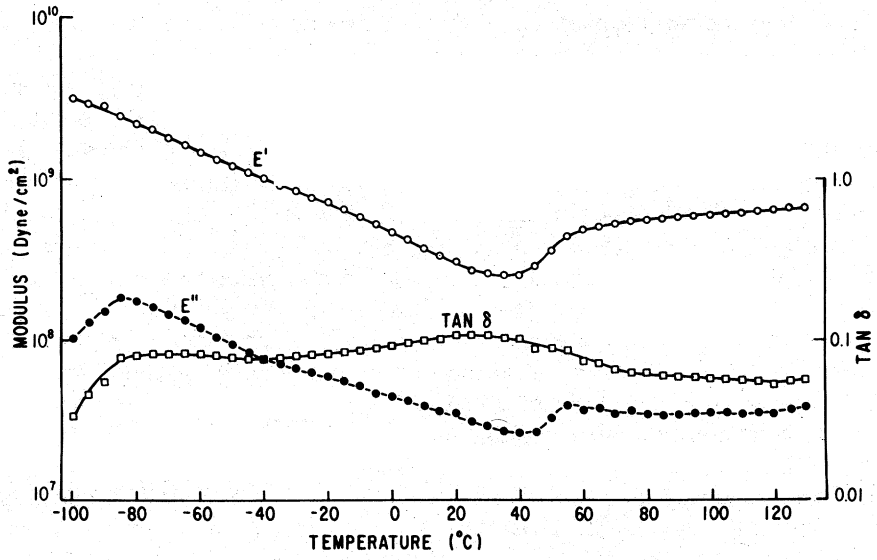


Fig. 4. Dynamic mechanical properties of leather grain layer conditioned at 55% relative humidity and containing 30% fatliquor oil.

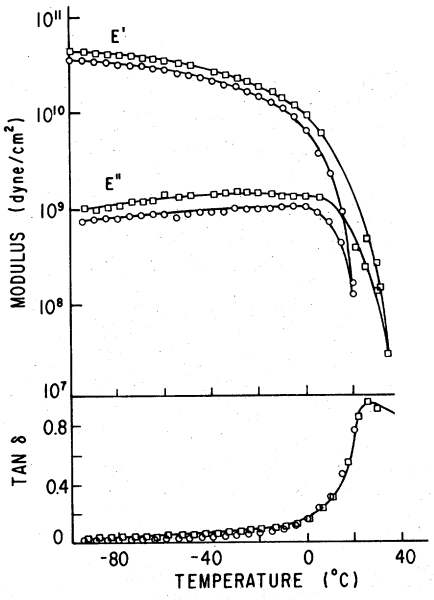


Fig. 5. Dynamic mechanical properties of a film of PU/NVP/EHA 1:1:1 cast on glass with sensitizer and cured with ultraviolet light. Film dimensions are 4.49 × 0.42 × 0.017 cm³: (□) 110 Hz; (○) 3.5 Hz.

with *N*-vinyl-2-pyrrolidone (NVP) (GAF) to reduce its viscosity, and further diluted with 2-ethylhexylacrylate (EHA) (Rohm and Haas) to lower the glass transition temperature of the polymeric product below room temperature. To study this polymer, we spread a solution of (PU/NVP/EHA) (1/1/1) containing 2% diethoxyacetophenone (Upjohn Corp.) onto a glass plate and polymerized it by illuminating it with ultraviolet light as described in Methods. The dynamic mechanical properties of the film product at two frequencies are shown in Figure 5. It has a well-defined glass transition temperature at 10°C, with a sharp peak in tan δ, but the modulus decreases over a broad temperature range. The loss modulus E'' is unusually flat below T_g and shows only a low, broad maximum centered at −15°C, perhaps reflecting a tendency of the components of the copolymer mixture to segregate. The film, however, was clear.

To prepare the composite, the leather grain layer described in Figure 4 was impregnated with the (PU/NVP/EHA) (1/1/1) and irradiated with high-energy electrons as described in Methods. A micrograph of this impregnated grain layer, stained as described in Methods, is shown in Figure 1, compared with an untreated control. A sample impregnated with the monomer–oligomer mixture without curing stained like the control, demonstrating that our staining technique reveals only polymerized impregnate. The polymer extends uniformly through the thickness of the grain layer.

The dynamic properties of the uncured impregnate are shown in Figure 6. The experiment is analogous to an impregnated-braid test, with leather grain substituted for glass fibers. As the oligomer–monomer mixture hard-

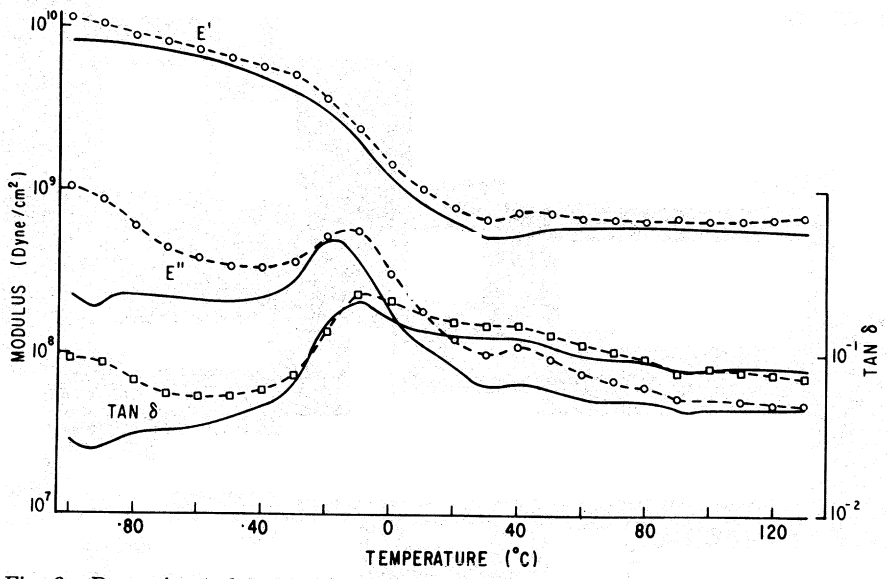


Fig. 6. Dynamic mechanical properties of leather grain layer containing fatliquor oils, impregnated with uncured oligomer–monomer mixture. and hydrated at 55% relative humidity: (——) 3.5 Hz; (- - -) 110 Hz.

ens below room temperature, it passes through a frequency-dependent glass transition, with peaks in E' and tan δ at -19°C and -10°C for 3.5 Hz and 110 Hz, respectively. Removal of fatliquor before impregnation did not affect the dynamic mechanical properties, showing a lack of interaction of the impregnant with this part of the system. Further, substitution of chrome alum-retanned grain layer without fatliquor for the vegetable-retanned and fatliquored leather also had no effect on the transition.

The properties of the cured composite at two frequencies are shown in Figure 7. It shows the separate features of the leather and polymer components. The properties of the composite above 35°C are almost identical to those of the leather, especially the hydration-caused minimum. Below T_g of the polymer, the behavior is controlled by the polymer, but the actual values of E', E'', and tan δ depend on all the components. In the impregnated system the dynamic mechanical properties are strongly frequency-dependent. The tan δ peak for the composite is much broader than that of the polymer film on glass, reflecting the mechanical interaction between the polymer and fiber structure.

DISCUSSION

Leather grain layer containing 3.5% water is essentially an elastic material between -90°C and 60°C (Fig. 2). There is a small but measurable mechanical loss and frequency dependence of moduli, but the constant level of tan δ does not suggest a molecular relaxation as the mechanism. We suggest that E'' is determined by the frictional resistance of fibers sliding over one another. This resistance would depend on the forces pressing the fibers together, which, in the fibrous leather, would be derived from the elastic deformation when it is elongated. In such a system, one would expect

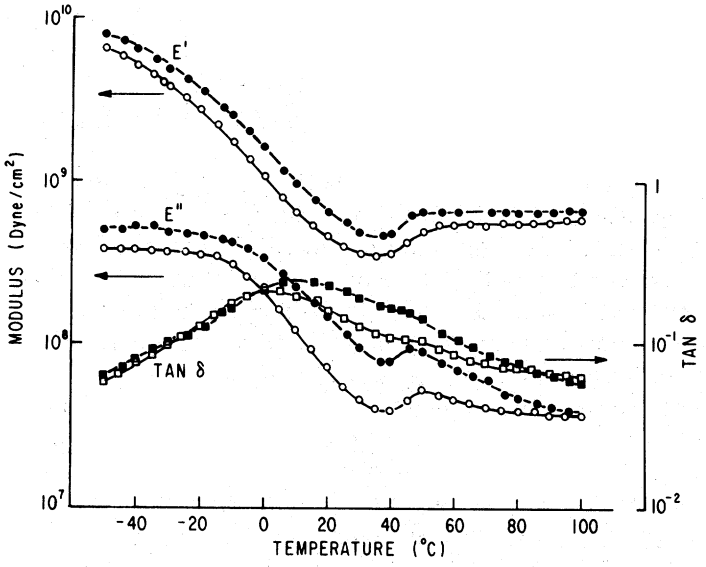


Fig. 7. Dynamic mechanical properties of leather grain layer containing fatliquor oils, impregnated with electron-beam-cured PU/NVP/EHA 1:1:1 polymer and conditioned at 55% relative humidity: Solid symbols, 110 Hz; open symbols, 3.5 Hz.

the interfibrillar frictional force to increase with elastic modulus, so that E'' increases with E'. The effect is seen more clearly in the fatliquored leather (Fig. 4), in which the two moduli are strictly and clearly parallel.

Introducing moisture at 55% RH has little effect on the moduli E' and E'' below room temperature (Fig. 3), although E' is then slightly more sensitive to temperature. It does result in a relaxation mechanism centered at 20°C, as seen in the tan δ data. The 35°C modulus plateau, which was reported previously[10] for reconstituted collagen, is observed only on the rising part of any temperature cycle and accompanies dehydration. This behavior is not often observed at 35°C because it requires a dehydrating environment. The previous observation on purified collagen[10] shows that the effect is due to the collagen and water, and not to the tanning of the leather. The maximum in tan δ between −20°C and 60°C is also found in hydrated purified collagen[10] and is also intrinsic to the collagen–water system. It is accompanied by enhanced temperature dependence of E' below 0°C, and so is due to bound (nonmelting) water. The decrease in tan δ at temperatures above the maximum is probably due to dehydration.

Although showing the same features, the dynamic mechanical properties of the fatliquored leather grain are much more sensitive to temperature than are the extracted grains (Fig. 4). The E' and E'' curves for the fatliquored material cross those of the extracted at about −50°C, so the fatliquored material is actually stiffer than the extracted at low temperatures. Further, the relative loss, tan δ, is double that of the extracted material at all temperatures. The elevated tan δ and lower elastic modulus at room temperature mean that above −50°C the fatliquored leather is less elastic and springy than solvent-dried leather at ordinary temperatures. Nevertheless, the values of E'' become considerably smaller on fatliquoring, con-

sistent with a reduction of interfibrillar friction. The data suggest that the lubrication effect of the fatliquor also reduces the elastic modulus by giving the collagen fibers more freedom to deform by bending instead of having to stretch. The result is the "leathery" consistency which is the purpose of the additive.

The structure of the impregnated leather resembles that of a fiber-reinforced composite. Halpin and Tsai described such systems comprising unidirectionally oriented elastic components.[11] Their equation is identical to a relation derived earlier by Takayanagi et al. for microheterogeneous polymer blends.[12] Both analyses treat linear models and consider the relative amounts of the components and the mechanical interaction between them. This interaction arises from the adhesion of the matrix to the fibers, preventing each component from deforming independently or homogeneously. The equations can be applied to impregnated leather, in which both components are viscoelastic, by use of the correspondence principle, which permits substituting the complex modulus E^* for the elastic modulus E. Explicit equations for E'_c and E''_c are[13]

$$E'_c = E'_L A/C - E''_L B/C$$
$$E''_c = E''_L A/C + E'_L B/C$$

where

$$A = (1 - \phi)(1 + q\phi)(E'^2_L + E''^2_L) + (1 - \phi)(q + \phi)q(E'^2_P + E''^2_P) + [(1 - \phi)^2 q + (q + \phi)(1 + q\phi)](E'_L E'_P + E''_L E''_P)$$

$$B = (q + 1)^2 \phi(E''_P E'_L - E''_L E'_P)$$

$$C = (1 + q\phi)^2(E'^2_L + E''^2_L) + (1 - \phi)^2 q^2(E'^2_P + E''^2_P) + 2(1 + q\phi) \times (1 - \phi)q(E'_P E'_L + E''_P E$$

where E'_c and E''_c are moduli of the composite, E'_P and E''_P are moduli of the polymer, E'_L and E''_L are moduli of the leather, ϕ is the ratio of the volume of the polymer to that of collagen, and q is the parameter for the mechanical interaction described above. When leather is impregnated, the volume does not increase significantly: The polymer enters interstices between the fibers. For this reason, the composite contains as much fiber component as an unimpregnated sample with the same dimensions. Because the volumes of the components are thus not additive, we have redefined the parameter ϕ to be the ratios of the volumes of the components instead of the usual volume fraction of the polymer. This definition of ϕ, although different from that of Takayanagi et al.,[12] is still consistent with his because of the way we calculate the modulus E^*_L of the leather component, based on its

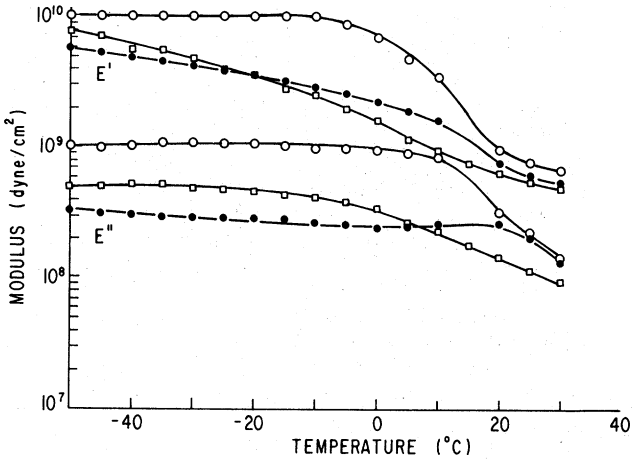


Fig. 8. Comparison of Takayanagi models [eq. (1)] of polymer–leather composites with electron-beam-cured, polymer-impregnated sample measured at 110 Hz from Figure 7. Dynamic mechanical properties of components are taken from the 110-Hz data of Figures 4 and 5: (○) model with no mechanical interaction between components $\phi = 0.40$, $q = 0.0$; (●) model with mechanical interaction between components $\phi = 0.40$, $q = 0.35$; (□) electron-beam-cured composite, experimental points.

total expanded cross section rather than on the area of the constituent fibers alone.

The above equations, although originally derived for mixtures and blends of polymers, are identical to the Halpin–Tsai equations, developed for composites with reinforcing particles of various shapes, in which $1/q$ is "a parameter which reflects reinforcement geometry and modulus influences on the elastic coefficients" of the composite.[11] In some structures it was shown to be simply related to the width-to-thickness ratios of the reinforcing fibers.

The dynamic moduli of the electron-beam cured composite are compared in Figure 8 with those calculated from the moduli of the components, using the analytically determined value of ϕ, 0.40, and with two different values of q. The calculated curves for $q = 0$, parallel noninteracting phases, deviate greatly from the experimental results, showing that the fibers and the polymer are not just acting as parallel elements. The optimum fit between experimental and calculated curves requires $q = 0.35$. The fit is good if it is considered that the model does not account for interfiber friction or anisotropy and that the pure polymer was polymerized under different conditions than the composite, and the same parameters must describe two different properties, E' and E''. We suggest that the value of q, which measures mechanical interaction between the collagen fibers and the impregnant, relates to the conformations of the collagen and polymer regions of the grain layers of these impregnated leathers, and to the improvement of their properties from the impregnation treatment.[6]

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