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VISCOELASTICITY OF CALF HIDE IMPREGNATED WITH RADIATION-POLYMERIZED
POLYHYDROXYETHYL METHACRYLATE

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INTRODUCTION

In order to combine the desirable properties of synthetic polymers (elasticity and water, chemical, and biological resistance) with those of animal hide (strength, flexibility, and dyability), composites can be formed between the two types of material. Actually, adding materials to hide has long been an aspect of traditional leathermaking, usually to increase thermal stability and to make the hide more hydrophobic. Newer uses for hide material require it to be stable but compatible with aqueous environments. Appropriate compositions can be formed from leather and hydrophilic polymers. Composites of collagen with poly(hydroxyethyl methacrylate) (polyHEMA or PHEMA) (1), with starch (2), or with polyacrylamide (3) have been described for surgical implants with blood compatibility and lack of tissue inflammatory reactions. Other uses for these compositions may be found as substrata for cells and enzymes in biotechnology.

The previously described composites were prepared from collagen fibers from comminuted skin, in which the strength of the original skin has been lost. Calfskin dermis, about 98% collagen, has a fibrous texture with a density of 0.5 g/cm^3 . Since collagen has a density of 1.4 g/cm^3 , there is a considerable amount of free space between and within the fibers. These have irregular cross sections about $5 \mu\text{m}$ thick and are

collected into bundles of various thicknesses, around 100 μm . The fibers are subdivided into fibrils with regular round cross sections of 100 nm diameter. The free space among the fibrils and among the fibers account for the flexibility of the material; it stretches with difficulty, however, because the fiber bundles are only slightly extensible. Note that if the voids are collapsed by air drying the skin or if they are filled with polymer, shear between fibers is restricted; the flexibility is lost; and a hard but very strong material results.

The 100nm fibrils are stable structures that persist in comminuted preparations even after treatment with dilute acid and base. The lowest level of fiber structure is that of the Type I or type III collagen molecule, about 1.5 μm thick and 300 μm long, packed together in regular array to make up these fibrils. When stained with phosphotungstate, regular bands appear along the fibrils, which reflect the regularity of the molecular packing, evidently a genetic adaptation of the collagen protein chain.

Consideration of these structures indicates that impregnation of animal skin should occur between fibers or fibrils, not between molecules, if the structure is not to fall apart. Insertion of polymer into the fibrils among the molecules would be expected to weaken the structure, which is held together by cooperative electrostatic and hydrophobic bonds. The desired structure is then a composite of the interpenetrating-network type with cocontinuous phases.

Electron micrographs published earlier (4) showed the disposition of polymethylmethacrylate (pMMA) introduced into leather by in-situ emulsion polymerization. The polymer entered the hide, coated the fibers and bundles, and filled the space among them. Very little polymer entered the spaces among the fibrils. The spaces within the fibers may be about the same size as or smaller than the micelles of the polymerization, inhibiting their diffusion. The result was a hard, strong composite, with few of the properties of leather. Here we have attempted to prepare structures with the polymer within the fibers, not between them, so that the deformation characteristics of the open, woven structure would be preserved, but with greater stability to chemical degradation and modified surface properties. For compatibility with aqueous systems and maximum capillary penetration of the collagen fibers, HEMA was used as monomer.

It has a surface tension of 40 dyne/cm, close to the critical surface tension of collagen (5). It can be shown theoretically that capillarity is a maximum when the penetrant has a critical surface tension slightly lower than that of the walls of the capillaries. We deposited HEMA from acetone solution into specimens of chrome tanned calf hide and polymerized it with γ -radiation. The paramagnetic Cr^{3+} ions, by relaxing all nearby protons from excited magnetic states, allowed us to analyze the spatial distribution of the polymer with respect to the Cr^{3+} -containing collagen fibrils. Our measurements show that pHEMA in the product penetrates into the 10- μm fissures. The dynamic mechanical properties of the pHEMA were imparted to the composite without loss of the flexibility of the open-fiber structure.

METHODS

HEMA WAS PURCHASED FROM Polysciences, Inc. (Warrington, PA)^{*} and used without further purification. It was observed to contain some polymer, which precipitated from water but not from acetone.

Calf skin was chrome tanned according to the USDA standard process (6), which involves removing epidermis and hair with basic sodium hydro-sulfide, swelling with limewater containing sodium sulfide, neutralizing to pH 8 and treating with trypsin, then treating with chromic sulfate and 6% sodium choride at pH 1.5, and neutralizing to form chromic carboxylate crosslinks in the collagen. The product contains 3.2 to 3.7% chromium as Cr_2O_3 , based on dry weight.

Undried tanned skin samples, about 5 x 5 x 0.5cm³, were extracted with water and then with acetone and then rolled in acetone solutions of HEMA for 8 hours. The acetone was evaporated, leaving the residual HEMA to penetrate the fibers of the leather. The samples, containing different amounts of HEMA, were sealed into a jar under N_2 and irradiated for 3 Mrad (5 hours) at room temperature, by means of the 0.67-MEV γ -radiation from ¹³⁷Cs. An 0.2-mm thick film of outgassed HEMA, contained between glass plates with spacers, was included in the jar.

^{*}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.

A measure of the interpenetration of synthetic polymers among the collagen fibrils of hide was sought through NMR studies of the polymer. The ^1H spin-lattice relaxation times of collagen crosslinked with chromic ions (tanned leather) are significantly shortened with respect to untanned collagen, 3 ms versus 600 ms. Consequently chrome tanned leather constitutes an ideal matrix for probing the spatial distribution of slower relaxing (T_1 ca. 100 ms) polymer protons through the induction of faster relaxation times in the polymer by contact with paramagnetic centers. A pulse sequence (7) previously devised to examine the phase homogeneity of pMMA in chrome tanned leather, (8) was used. This pulse sequence combines inversion-recovery of the protons (9) with cross-polarization (10) and interrupted ^1H decoupling (11) to measure the proton T_1 values of the polymer. The pulse sequence is illustrated in Fig. 1 along with the CP-MAS Fourier-transformed spectra of the 1:4 polymer:leather composite obtained at selected values of the pulse interval. The NMR studies were performed on a JEOL FX60QS spectrometer modified to carry out CP-MAS experiments. Instrument operating conditions were 5000 scans acquired in 2K memory using a 8 KHz spectral window; the cross-polarization contact time, 0.8 ms; the period of interrupted decoupling, 40 μs ; and the recycle delay, 0.5 s.

The real and imaginary parts of the complex modulus were determined at two frequencies (3.5 and 110 Hz) with a Rheovibron II (for the pHEMA film) or a Rheovibron III (for leather samples) dynamic viscoelastometer (Toyo Baldwin Co.)^{*}, operated at an oscillating relative deformation of 3.8×10^{-4} . The samples were mounted 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 $^\circ\text{C}/\text{min}$ with electric 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 leather sample were $50 \times 5 \times 3 \text{ mm}^3$; those of a pHEMA film sample, $50 \times 5 \times 0.1 \text{ mm}^3$. This instrument (12) measures the amplitudes of the harmonic force and amplitude signals and determines their phase, δ , by means of 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:

$$E^* = E' + iE'', \text{ with } \tan \delta = E''/E'.$$

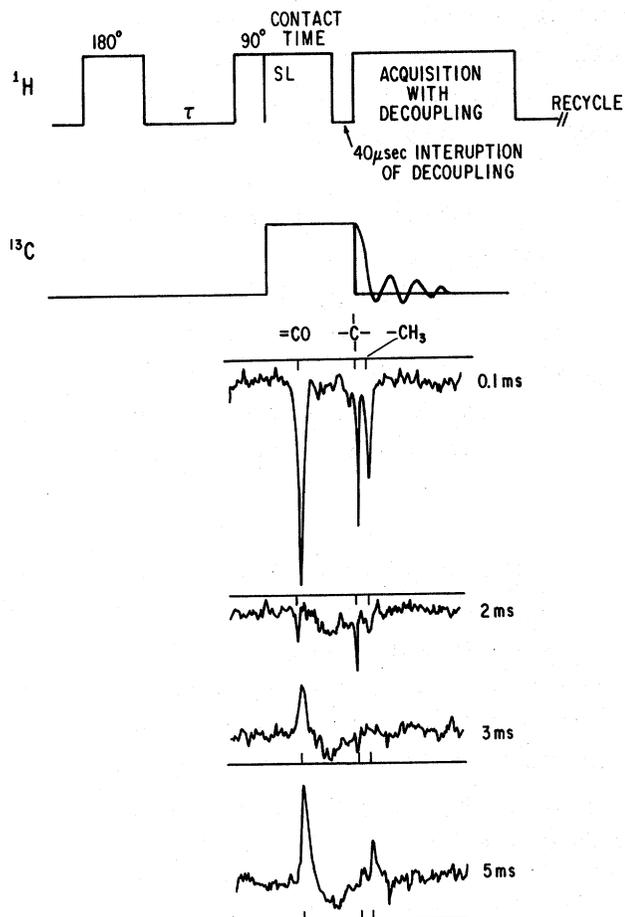


Fig. 1. Proton T_1 interrupted decoupling/inversion-recovery pulse sequence and spectra at selected time intervals for the hide-pHEMA composite containing 20% pHEMA.

Differential scanning calorimetry was carried out with a Perkin Elmer DSC instrument at a scanning rate of $10^\circ/\text{min}$ from 30° to 150° for hide-pHEMA or from 150° to 270° for neat radiation-polymerized pHEMA.

RESULTS

The pHEMA film prepared by irradiation was very highly crosslinked, swelling only to 25% in water. When pHEMA is prepared by chemical initiation, its swelling is not sensitive to the degree of crosslinking, usually swelling to 30-40% (13). The reduction of water uptake in these samples is therefore striking.

By means of a Du Nouy tensiometer, the surface tension of our HEMA reagent was determined to be 40 dyne/cm, matching the critical surface

tension reported for collagen (5). The ability of the HEMA to wet and penetrate the collagen fibers of the calf skin was obvious from the spreading behavior, with no measurable wetting angle, and from the dry appearance of the samples containing up to 40% monomer.

Carbon-13 resonances are observed in three well separated spectral regions: carbonyl, quaternary carbon, and methyl (Fig. 1). The carbonyl and methyl arise from carbons in both the collagen and polymer, while the remaining resonance has been demonstrated to arise only from quaternary carbons in pHEMA. The more rapid spin-lattice relaxation of the chrome treated collagen relative to the polymer is also evident in these spectra, the carbonyl resonance being partially recovered at 3 ms while the polymer peak remains inverted.

Spin-lattice relaxation times of pHEMA were obtained by measuring the intensities of the quaternary-carbon signals. Attempts to fit the data to a single relaxation time were unsuccessful; it was therefore decided to assume that spin-lattice relaxation was occurring in the polymer at two different rates, a fast one for polymer penetrating among the chrome treated fibrils, and a slow one for polymer segregated among the fiber bundles. The relaxation of the quaternary carbon signal intensity $a(t)$ would be described by the following equation (1):

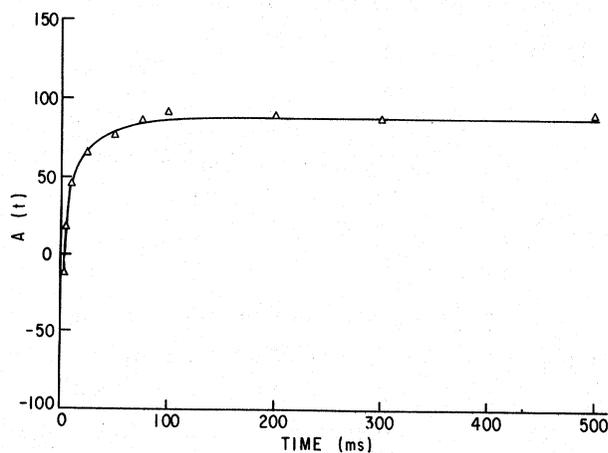


Fig. 2. Relaxation of quaternary protons in the hide-pHEMA-leather composite containing 20% pHEMA.

TABLE I

Wgt. % pHEMA	p_f	T_f (ms)	p_s	T_s (ms)
20	0.72 (± 0.07)	3.55	0.28 (± 0.07)	30.55
33	0.66 (± 0.16)	3.55	0.37 (± 0.15)	30.55
37	0.58 (± 0.14)	3.55	0.48 (± 0.11)	30.55
52	0.32 (± 0.04)	3.55	0.68 (± 0.07)	30.55

$$a(t) = p_f [1 - 2\exp(-R_f t)] - p_s [1 - 2\exp(-R_s t)] \quad (1)$$

where p_f and p_s are the fast and slowly relaxing fractions of the polymer, and R_f and R_s are their respective rates (relaxation times are inverses of the rates). Intensity data were fitted to the above equation using a least-squares computer program. While the long relaxation time might be expected to equal that of neat polymer, 102 ms, a better fit to the data for all the samples was obtained when it was shorter; 30.6 ms (Fig. 2).

The shorter value might be due to the proximity of a portion of the interfibrillar polymer to the surfaces of the Cr^{+3} bearing fibers. The data for each sample was therefore fitted to equation (1) with $R_s = 1/30.6 \text{ ms}^{-1}$ and $R_f = 1/3.6 \text{ ms}^{-1}$ to obtain fractions, p_f , for the polymer in the faster relaxing regions (Table I).

The table shows that, at low pHEMA content, the fractions of fast-relaxing polymer protons are high, most of the polymer being in the proximity of Cr^{+3} in the collagen fibrils. As the content increases above 37%, the proportion of slowly relaxing polymer protons increases rapidly, as all the added polymer enters regions of the composite distant from the Cr^{+3} -containing collagen. Therefore, the NMR data show that the capacity of the collagen for the pHEMA is about 37%, above which the value of p_f decreases rapidly. The end point does not appear to be sharp.

The dynamic mechanical properties of the pHEMA film are shown in Fig. 3. The main transition is a strong one, with a large maximum of $\tan \delta$. The temperature of the transition, 140°C , is much higher than that at 1 Hz reported for pHEMA prepared by chemical initiation, 109°C (14). This might be expected from the high degree of crosslinking which we infer from the low degree of swelling. Above 200°C , a rubbery region

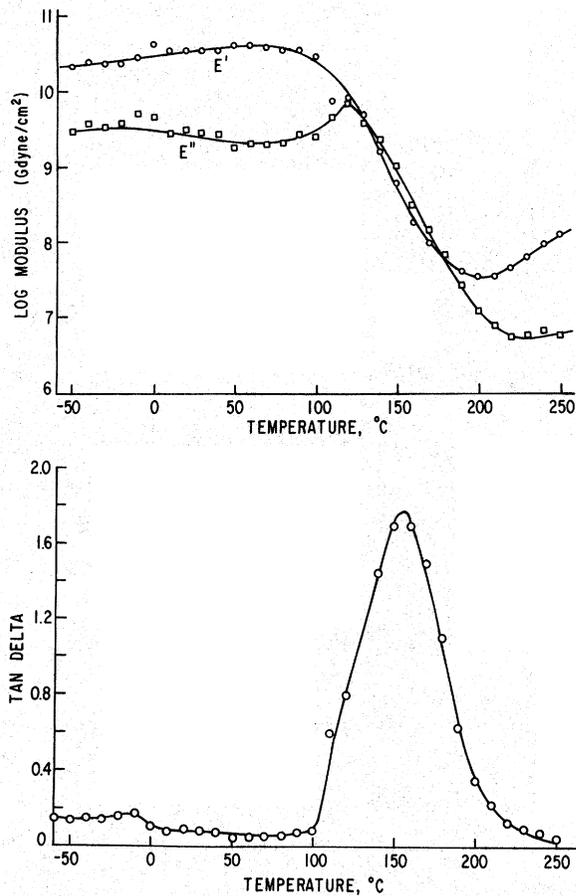


Fig. 3. Dynamic mechanical properties of radiation-polymerized pHEMA film.

appears, E' increasing with temperature as expected from rubber elasticity theory. The molecular weight between crosslinks calculated from the slope of E' vs. temperature in this region by means of the classical equation $M_c = RTp/(\text{slope})$, however, equals only 250 Daltons ($\rho = \text{density}$). This is below the range of validity of the equation, but we have already mentioned the small swelling in water, confirming a high crosslinking density. Chemical reaction during the measurement, progressively introducing substantial numbers of crosslinks (more than 1 per 1000 residues) at the high temperatures at which the positive slope of the modulus-temperature curve is observed, is unlikely, since the material gave no exotherm

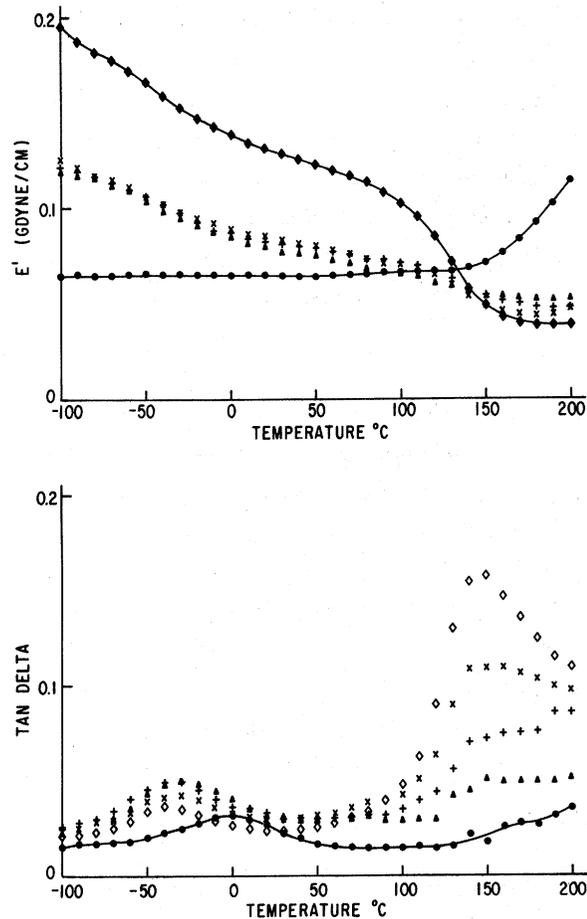


Fig. 4. Dynamic mechanical properties of pHEMA-hide composites. % pHEMA from bottom: 0, 8, 20, 33, and 37.

or endotherm (less than 0.05 kcal/mol) in differential scanning calorimetry. It should be observed that, although the degree of crosslinking is very high, the polymer, which imbibes water up to 25% of final volume, still hydrates to a hydrogel as defined by Wichterle and Lim (13).

The data for the polymer were obtained at two frequencies, 110 and 3.5 Hz, and can be used to calculate a heat of activation of 17 kcal/mole for deformation.

The mechanical behavior of the composites is shown in Fig. 4. The compositions with up to 37% polymer, which had nearly homogeneous polymer protons as indicated by the ^{13}C spectra, have nearly identical E' behavior.

The polymer stiffens the assembly below the glass transition and softens it above in all compositions, the softening increasing with the amount of polymer present. The increase in E' of the unimpregnated collagen above 120°C is unexplained, but may be due to dehydration, as observed before (15). The mechanical relaxation of the pHEMA is clear, with a large maximum in $\tan \delta$ at exactly the same temperature as observed in the neat polymer (Fig. 3). As in the case of E' , increasing the polymer content alters the mechanical loss only above temperatures where the polymer is glassy.

The height of the main loss peak increases with the polymer content of the composite. That of the low-temperature peak, usually named the γ peak, decreases with polymer content. Since this peak is not present in the loss curves of the leather or of the dry polymer film, this behavior of the composite cannot be understood by superposing the properties of the components. It has been reported that the γ loss peak of pHEMA is suppressed by small amounts of low molecular-weight material, such as water. The small decrease of the γ peak might be due to the water content increasing slightly with polymer content. The water content must be small, since the position of the main transition is the same for all the compositions.

Another surprising feature of the data at low temperatures is the small increase in modulus of these composites over that of leather, considering the relatively large amount of polymer (over 30%) with its modulus over 100 times as great as that of the leather. Above 37% polymer the modulus does not increase regularly, and segregated aggregates of polymer are seen in the impregnate. The behavior is not that of a composite of two continuous phases, but rather that of a continuous collagen phase containing discontinuous bodies of polymer held among the fibrils.

At high polymer contents, above 37%, pHEMA was observed to segregate into interstices among the fibers. We could see this clearly by fluorescent staining with Sandocryl Brilliant Red by the method of Lowell and Buechler, but omitting their counterstain (16). Observed under a fluorescence microscope, samples containing 37% pHEMA or less showed dimly fluorescent fibers demarcated by dark lines corresponding to the interstitial regions; those containing more than this amount were brightly fluorescent between the fibers. As the polymer becomes less evenly dispersed, the

transition temperature moves upward, so that a sample with 50% polymer had a transition at 160°C. Samples with more than 52% polymer had deposits of polymer that were observable without a microscope and had poorly reproducible dynamic mechanical properties.

DISCUSSION

We have previously described leather grain impregnated with a polymer prepared *in situ* from a urethane oligomer and vinyl monomers (15). By staining and microscopy the polymer was located in the interstices of the fibrous matrix; the dynamic mechanical properties could be described by suitable averaging of the properties of the two components. The particular average used was that of the Takayanagi model (17), which combines the two viscoelastic components partly in parallel and partly in series. There was no evidence for chemical or local interaction between the two components, but there was mechanical interaction which prevented description of the system either as an assembly of parallel rods of the two components or as a series of sheets piled transverse to the deformation.

The intimacy of polymer-fiber interaction in the present system was examined with an NMR technique used previously (8) to explore composites of leather with hydrophobic polymers prepared from emulsions. Those systems also contained Cr^{+3} ion bound intimately to the protein of the fibrous matrix, which caused the protons of the protein and nearby polymer to relax rapidly. They, however, could contain only about 2% polymer closely enough associated with the collagen to be relaxed by the chromium. The protons of polymer in excess of that amount relaxed much more slowly, showing that the excess polymer was not located in intimate contact with the chromium-protein complex. Since all the protein in the composite is packed into fibers, most of the polymer must have been located between rather than within these fibers.

In the present work, the polymer was chosen so that it would spread spontaneously into the pores between collagen fibrils. The surface tension of the polymer was considerably higher than those of the polymers used previously (4,8,15), about 40 dyne/cm, which matched that of collagen (5). Unlike the nonpolar monomers, HEMA could penetrate the fibers to the level of the fibrils. Since it does not disturb the mechanical

integrity of the hide or even soften it, as water does, it must be inferred that there is no penetration to the molecular level within fibrils. Again, since the interfibrillar polymer did not affect the elastic modulus much, interfibrillar friction is not of great importance in determining the resistance to deformation.

The NMR results show that the first monomer added to the hide penetrates the fibers and that this can rise to about 37% of the total mass. This material when polymerized has less effect on the storage modulus E' than has polymer in excess of that. It is concluded that the effects of impregnant on the modulus of leather that are usually reported (4, 15) are mostly on the interfiber level, since only this excess polymer raises the storage modulus substantially. The loss modulus maximum increases uniformly with increased pHEMA content. Unlike in the system that we reported earlier (15), E'' of the present type of composite does not run parallel to E' as the temperature is varied, but instead has maxima at the mechanical transition temperatures of the neat polymer, with rather large maximal values of $\tan \delta$. This is to say that here E'' is controlled by the properties of the interfibrillar polymer, which dominates the interfiber adhesion or friction. The pHEMA acts as a plasticizer at high temperature and stiffens the structure at low temperature without increasing the interfiber friction.

Unlike the hydrophobic ethylhexyl acrylate/vinyl pyrrolidone/ oligourethane mixture impregnated into leather grain described in the previous paper (15), radiation-polymerized pHEMA in a composite with leather behaves like that polymerized as a film. Its effect on the leather is to protect it from chemically induced stiffening above 150°C, while only slightly stiffening it at lower temperatures. The polymer does penetrate between the fibrils, to the penultimate level of the fibrous structure, as shown by proton relaxation of the polymer by the collagen-bound chromium. The temperature of the transition of pHEMA is sensitive to its water content. The presented data describes samples which we tried to keep dry, but they must have contained very small amounts of water that were difficult to remove.

It is shown that it is possible, by choosing monomers with high surface tension, to impregnate the fibers of hide to the level of the fibrils. The result, even when a glassy polymer is used with a strong

transition and a very high modulus at low temperature, is a composite with the mechanical properties little different from those of the starting leather at all temperatures. Composites were also prepared similar to those discussed here using untanned calfskin. The polymer does raise the denaturation temperature of the collagen in these by 10 C as determined by differential scanning calorimetry, probably by stabilizing the fibrils, which in turn stabilize the cooperative forces among the molecules. It should be mentioned that the radiation itself lowered the denaturation temperature of the hide by that much judging from the control, so the dose of 3 Mrad was apparently excessive, even for polymerization. Interfibrillar pHEMA should permit small molecular-weight materials to diffuse to the collagen and vapors to diffuse among the fibers, while, we believe, still preventing microbial degradation of the protein.

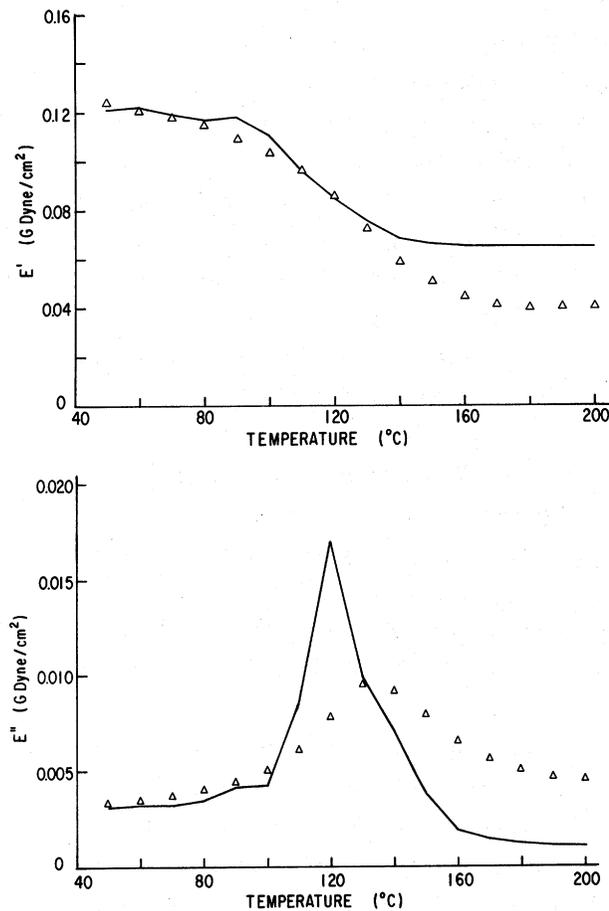


Fig. 5. Takayanagi model fitted to 37%-pHEMA composite with $\phi=0.37$ and $q = 0$ and 0.1 . Points, experimental; dotted line, $q = 0$; solid line, $q = 0.1$.

Attempts were made to model these composites by using the Takayanagi model (17). This calculation defines E^* of the composite as a weighted average of those of the components. The weights take into account geometric effects found when the spaces within a non-parallel assembly of fibers are filled with a continuous phase, so that the two components of the composite are arranged spatially neither completely in parallel nor in series. The geometry is accounted for by a parameter q , which would be zero in the case of a parallel assembly. The model as formulated is not appropriate for this system, because it assumes that all the volume of the material is occupied by one or the other component. These composites with amounts of polymer less than 37% contain empty spaces among the fibers. Because of this feature of the fibrous structure the modulus of the unimpregnated leather is orders of magnitude smaller than that of dry collagen or even gelatine. It should be observed, however, that the geometry of the pHEMA phase is the same as that of the collagen, since it shares the same space within the fibers, so an assembly of pHEMA fibers identical to that of the collagen fibers in the leather would be expected to have a modulus reduced by the same amount from that of the neat polymer film. Therefore, to account for the fibrous structure with its free space in the model, we divided the values of E' and E'' of the pHEMA (Fig. 3) by 100 and used these values with those of unimpregnated leather to represent the properties of the separate components. This is equivalent to introducing a different geometrical factor into the original calculations of the moduli from the experimental data.

Another difficulty with modeling this system is the large increase in E' of the unimpregnated leather at temperatures above 150°C, which is absent in the samples containing polymer. Since the polymer seems to interact with the collagen to prevent this effect, we artificially suppressed it in the calculations by holding the moduli of collagen, E' and E'' , constant above 140°C at their values at this temperature.

The composite containing 37% polymer has the smallest amount of free space within its fibers, while the spaces between the fibers are open, as described above. Its dynamic moduli are compared with those calculated by means of the Takayanagi series-parallel scheme in Fig. 5. Our working equations were shown previously (15), but here the parameter ϕ is the volume fraction of the polymer, instead of the ratio of polymer to collagen. The best fit was obtained with $q = 0.1$, a rather small value, and

even $q = 0$ was acceptable. Deviations are the lower values of E' for the sample at temperatures above the transition (where we held the moduli of the leather constant) and its higher transition temperature than found in the model. The low values of the moduli suggest a failure of the model to account for plasticization by the softened polymer, as suggested above. The elevated transition temperature of the sample may not be significant; both 120°C and 140°C are within the transition ranges of the sample and of the polymer, respectively. Aside from these two reservations, it must be concluded that the system behaves as an assembly of fibers of PHEMA and collagen, the two types of fibers lying almost parallel to each other with little mechanical interaction. This behavior reflects a geometry of collagen fibrils lying parallel to each other in fibers, with PHEMA lying in the long interstices among and parallel to the fibrils.

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