

Synthesis and Mechanical Properties of Leather–Epoxy Interpenetrating Polymer Networks

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Received 9 January 1997; accepted 20 January 2000

ABSTRACT: Leather–epoxy interpenetrating polymer networks (IPNs) were synthesized; these IPNs have an approximate epoxy concentration of 25 wt %. The flexural and tensile moduli of the IPNs prepared are equivalent to those of the epoxy resin. The Izod impact energy and fracture toughness measured for the IPNs, however, exceed those attained by the epoxy resin alone by at least a factor of 4. The glass transition of leather–epoxy IPNs occurs over a wide temperature range, thus indicating that the IPN is an intimate admixture of the epoxy resin throughout the collagen matrix of the hide. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1224–1232, 2000

Key words: leather; epoxy; interpenetrating polymer networks (IPNs)

INTRODUCTION

The unique physical properties of leather (strength, flexibility, and dyeability) make it ideally suited for the manufacture of a variety of products. It has been a useful material since prehistory with applications ranging from interior articles, such as cushions, ornaments, and book bindings, to war needs, such as slings and shields. With the advent of the Industrial Revolution, new applications, for example, belts and packings, came into being. Even today, leather remains a significant agricultural resource, having the potential for developing value-added materials with unique engineering properties. Current reviews on the raw materials, manufacture, and processing of leather were given by Bienkiewicz¹ and Bailey.²

As synthetic polymers have become available, products, for example, coated fabric and synthetic leather, have competed with traditional leather goods. While these synthetic materials provide superior properties in many applications, leather is often the material of choice because of its mechanical properties and its ability to transmit moisture. Even though a wide variety of leather-like materials has been developed over the past 40 years, synthetics have not been able to replace hide and leather in numerous applications.³ Hide and leather continue to be valuable agricultural coproducts with the potential for developing into value-added materials.

During the 1960s, polymeric precoatings were investigated for the purpose of increasing the leather's scuff resistance and improving its handling characteristics. These efforts centered on impregnation of the grain layer with acrylic and polyurethane resins.^{4–7} During the 1970s, the Eastern Regional Research Center of the USDA reported incorporation of vinyl, acrylic, and styrene monomers into leather with a patent being issued in 1974.^{8–10} These investigations, including both surface treatments and the incorporation of polymer beyond the grain layer, have continued

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Contract grant sponsor: Cooperative State Research Service, U.S. Department of Agriculture; contract grant number: 92-37500-7911.

Journal of Applied Polymer Science, Vol. 78, 1224–1232 (2000)
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through the efforts of several researchers at the Eastern Regional Research Center of the USDA.¹¹⁻¹⁴ The impregnation of the polymer beyond the grain layer-corium interface was aimed at preventing delamination at that interface upon folding of the leather and to improve the hardness of the grain layer so as to minimize scuffing.

As a consequence of the research activities mentioned above, extensive literature on hide impregnated with polymers exists which contains numerous data on moisture adsorption, system morphology, mechanical properties, and viscoelasticity. The Central Leather Research Institute (Madras, India) prepared collagen-vinyl copolymers as well. The formation of the copolymer was confirmed by infrared and UV spectroscopy and electron microscopy, as well as by the properties of the associated polymer solutions.^{15,16} The extent to which these polymers react to form graft copolymers with hide and leather was examined, but much remains to be clarified.^{17,18}

Prior studies on the polymer impregnation of leather have been limited in several respects. The vast majority of the resin systems studied were acrylates; the synthetic procedures are characterized by addition reactions involving double bonds. No information has been found in the literature emphasizing polymer systems based on condensation reactions, with the exception of the polyurethane systems patented by Neher and Vely¹⁹ and Lowell and Buechler.⁷ Prior studies emphasized the synthesis of a polymeric coating on the leather surface to increase the scuff resistance and to improve the handling characteristics of the product. While impregnation through the grain-corium interface is the focus of the majority of the literature, data on fully impregnated leathers are practically nonexistent. In the limited cases where full impregnation was mentioned, complete impregnation was not a major focus, and no discussion was given of the impact of full impregnation of the hide on the bulk mechanical properties of a leather-polymer composite system.

This work describes interpenetrating polymer networks (IPNs) formed by polymerization of an epoxy resin within a leather (chrome-tanned cattlehide). These leather-epoxy IPNs and their preparation are described in detail in a U.S. patent.^{20,†} According to Sperling,²¹ an IPN com-

prises two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other. The network of crosslinked collagen fibers and fiber bundles has an inherent two-dimensional quality without requiring the formation of a woven or nonwoven fabric from fibers. Epoxy resins are relatively brittle thermosets with good dimensional stability and commonly serve as adhesives, coatings, and matrix materials in fiber-reinforced composites. The low molecular weight of the epoxy monomers facilitates complete impregnation of the leather. The epoxy-impregnated leather cures via condensation reactions without generating unwanted volatile by-products, which can lead to voids in the resulting IPNs.

The mechanical properties of the leather-epoxy IPNs formed were characterized by tensile tests, impact energy, fracture toughness, and dynamic mechanical analysis (DMA). For comparison, data were obtained on samples of the leather itself and the leather subjected to the same hot-press schedule as that of the cured epoxy and leather-epoxy IPNs.

EXPERIMENTAL

Starting Materials

Chrome-tanned cattlehide was the leather component chosen for this work; for simplicity, it will be referred to as leather hereafter. Diglycidyl ether of bisphenol A (DGEBA; Epon[®] Resin 825, Shell Chemical Co., Houston, TX) was the epoxy resin selected, and 1,3-phenylenediamine (mPDA; Aldrich Chemical Co., Milwaukee, WI) served as the curing agent. A variety of organic liquids is suitable as solvents with the criteria of compatibility with the epoxy resin and the curing agent. Methyl ethyl ketone (MEK) and dimethylformamide (DMF) are two such solvents. All components were used as received.

Sample Preparation

The leather samples were presoaked in the selected solvent for 2-4 h prior to impregnation by the polymer precursors. DGEBA paste and ground mPDA powder were mixed at a mass ratio of 100:14 (ref. 22) and subsequently dissolved in the solvent at room temperature. The presoaked leather samples were immersed in the DGEBA/mPDA solution for 2 h. The samples were blotted

[†]The Kansas State University Research Foundation, 1500 Hayes Dr., Manhattan, KS 66502-5068, should be contacted concerning licensing of the technology described in this patent.

dry upon removal from the solution. Polymerization was effected in an MTP-8 Press (Tetrahedron Associates, Inc.) under a load of 44.5 kPa. The cure schedule given below was followed.

- 4 h at 27°C
- 1.5 h at 79.5°C
- 1.5 h at 93°C
- 1.5 h at 107°C.

The leather–epoxy samples were cured inside a standard vacuum bag assembly.

Unimpregnated leather was treated in the hot press according to the temperature and pressure schedule for forming the leather–epoxy IPN. A sample of the neat DGEBA/mPDA polymer (termed cured epoxy hereafter) was prepared according to the hot-press conditions described above. In addition to the residence time in the hot press, the solution of DGEBA and mPDA was left at room temperature for 2 h, equal to the impregnation time during preparation of the leather–epoxy IPN. The DGEBA/mPDA polymer samples were cured in aluminum molds treated with Release-All 40 (Airtech International, Inc., Carson, CA).

Tensile Tests

Leather specimens were cut from various regions of a full-thickness chrome-tanned cattlehide with the long dimension perpendicular to the backbone according to type I tension-test specimens specified in ASTM standard test procedure D 638-90. The tensile-test specimens were divided into three groups, one for tensile test measurements of the leather as-received and the other two for subsequent preparation of hot-pressed leather and leather–epoxy IPN specimens. Specimens of epoxy with similar dimensions were cast in aluminum molds and cured in an oven.

The tensile tests were performed on an Instron 8500 test machine. A 2-in. extensometer (Instron 2620-824) measured the displacement up to 2.5% strain; the internal transducer of the testing machine measured higher strain values. The tensile properties were obtained for leather, hot-pressed leather, leather–epoxy IPN, and cured epoxy as specified in ASTM standard test procedure D 638-90 with a constant strain rate of 5.08 mm/min.

Impact Energy and Fracture Toughness

The specimens were cut from full-thickness plates of the leather–epoxy IPNs and 5-mm-thick plates

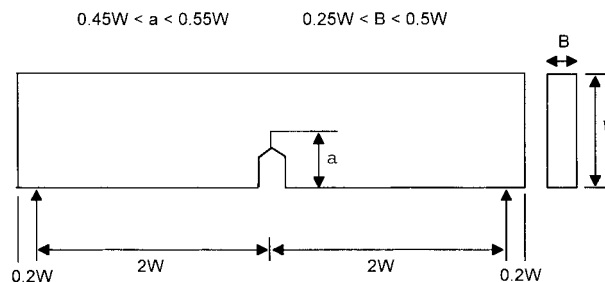


Figure 1 Geometry of a single-edge notch bend (SENB) specimen.

of cured epoxy. The long dimension of the leather–epoxy IPN specimens was chosen perpendicular to the backbone of the original hide.

The impact energy of the leather–epoxy IPNs and that of the cured epoxy were determined by an Izod impact tester with a capacity of 2 ft-lb_f. The machining procedures, dimensions for the Izod-type specimen, and the test procedure were as specified in ASTM standard test procedure D 256-90b. Six replicates were obtained for each material.

The fracture toughness of leather–epoxy IPNs and that of the cured epoxy were measured according to the *J*-integral approach.²³ The sample preparation and test were carried out according to ASTM standard test procedure D 5045-91. A diagram of the single-edge notch bend (SENB) specimen is illustrated in Figure 1. The specimens were notched with a band saw, and the resultant notches were sharpened by sliding a razor blade across the root of the machined notch. The data on the SENB specimens were obtained at room temperature with an Instron 8500 test machine at a crosshead speed of 10 mm/min. Deflection was measured with the internal transducer of the testing machine.

The *J*-integral was calculated as follows:

$$J = \frac{2U}{B(W - a_0)}$$

where *U* is the area under the load-deflection curve taken at the displacement of interest; *B*, the sample thickness; *W*, the sample width; and *a*₀, the notch length. The values of the *J*-integrals of leather–epoxy IPNs and cured epoxy were calculated utilizing the maximum on the load-deflection curve. An average *J*-integral for each material was calculated based upon measurements from five SENB specimens.

DMA

Leather specimens were cut from various regions of a chrome-tanned cattlehide with the long dimension perpendicular to the backbone of the original hide. The leather was sliced (with the grain side retained) to obtain rectangular DMA specimens having dimensions of approximately $25 \times 8.5 \times 2.5$ mm. These DMA specimens were divided into three groups, one for DMA tests and the other two for subsequent preparation of hot-pressed leather and leather-epoxy IPN specimens. For the cured epoxy samples, rectangular specimens having the dimensions of $25 \times 8.5 \times 1.6$ mm were cut from a cast sheet.

The storage moduli, the $\tan \delta$'s, and the loss moduli were measured with a Perkin-Elmer DMA System 7 equipped with a 3-point flexural assembly. Subambient data were obtained with a liquid nitrogen cryogenic attachment. Temperature scans were carried out under strain control at a frequency of 1 Hz; strain control (amplitude of oscillating relative deformation) was set at 3.2×10^{-4} .

RESULTS AND DISCUSSION

The porosity and fibrous features of the samples are easily discernible from the scanning electron micrographs (SEMs) (see Fig. 2). The epoxy resin distribution was essentially uniform, as seen from SEMs of a polished cross section of the leather-epoxy IPN (see Fig. 3). The resin contents of the leather-epoxy IPNs were determined on the basis of weight gain after cure; they ranged from 21 to 27 wt % for the samples studied. These values were approximately 10 wt % less than the uptake of epoxy resin determined prior to hot pressing the samples.

The average stress-strain curves for chrome-tanned cattlehide, hot-pressed chrome-tanned cattlehide, leather-epoxy IPN, and cured epoxy are compared in Figure 4, with the mechanical properties summarized in Table I. Pressing the leather according to the temperature-pressure schedule described herein increased the Young's modulus of the leather. The modulus of the leather-epoxy IPN, however, was only slightly different from that of the cured epoxy. In addition, the breaking stress for the leather-epoxy IPN exceeded the average strength of the leather and hot-pressed leather and was 55% of the breaking strength measured for the cured epoxy. Signifi-

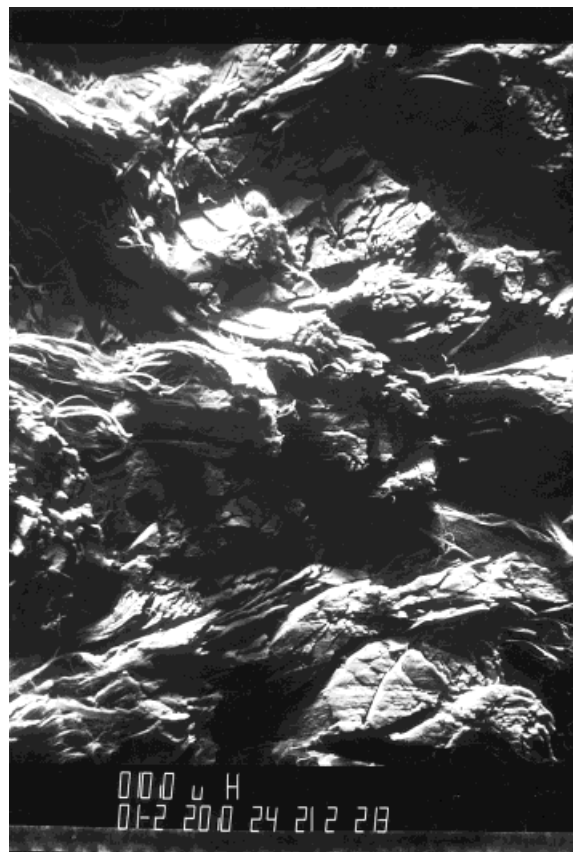


Figure 2 SEM of a cross section of chrome-tanned cattlehide prior to impregnation.

cant necking was observed during tensile tests of leather and hot-pressed leather; nevertheless, this was not the case for the leather-epoxy IPN and cured epoxy. Meanwhile, the variability of the mechanical properties of the leather was reduced both by hot pressing and by forming a leather-epoxy IPN.

Table I lists the average impact energies for the leather-epoxy IPNs and cured epoxy as well as their fracture toughness measurements based upon the J -integral approach. In the data, the point of maximum load on a load-deflection curve was selected to evaluate the J -integrals of the leather-epoxy IPNs and of the cured epoxy. The fracture toughness results as calculated by the J -integral method and the Izod impact data indicate the same trend. While the rate at which the load was applied to the sample was significantly different, both of these tests employed notched samples. The manner in which the load was applied to the sample was similar in both cases, resembling a Mode I geometry. It is not surprising that the results of these two tests are similar in

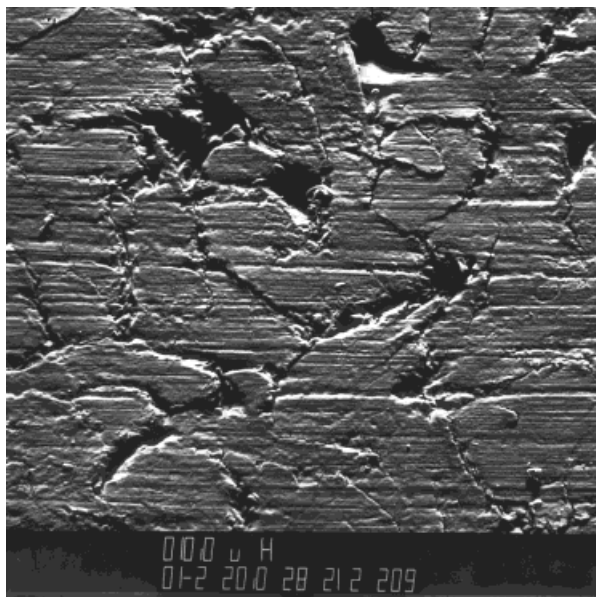


Figure 3 SEM of a polished cross section of a leather-epoxy IPN.

character and show trends that are different from toughness data acquired by integrating the tensile stress data.

The average storage moduli as measured by the DMA experiments over a temperature range from -120 to 225°C are compared in Figure 5 for the leather, hot-pressed leather, leather-epoxy IPN, and cured epoxy. Pressing the leather according to the temperature-pressure schedule described herein increased its storage modulus by nearly a factor of 10 throughout the temperature range studied. At temperatures significantly below 50°C , the storage modulus of the leather-epoxy IPN was only slightly less than that of the cured epoxy. At temperatures above 120°C , the storage moduli of the leather-epoxy IPN and hot-pressed leather were the same within experimental error.

Figure 6 presents the average loss tangent ($\tan \delta$) data for temperatures between -120 and 225°C . The β -transition was observed in the data for hot-pressed leather, leather-epoxy IPN, and cured epoxy at transition temperatures of -57 , -81 , and -73°C , respectively. A relative maximum in $\tan \delta$ for leather was observed at 122°C ; this maximum was not present in the DMA data of the hot-pressed leather. This transition is most likely related to the presence of moisture in the leather and, therefore, would not be present once the leather was heated during the hot-pressing operation. The glass transition temperature of

the cured epoxy was 100°C . The glass transition temperature of the leather-epoxy IPN shifted to 84°C ; this transition occurred over a wider temperature range compared to the cured epoxy.

Values for the Young's modulus, breaking stress, and breaking strain for leather from the literature are 34.5 MPa, 27.6 MPa, and 40%, respectively.² For mPDA-cured DGEBA resin, these properties have values of 2483 MPa, 89.66 MPa, and 4.8%, respectively.²⁴ In the light of the known variability in the mechanical properties of leather and the fact that the epoxy samples were prepared according to different cure schedules, the data in Table I are in good agreement with the values cited. The differences observed in the case of leather may be a consequence of having followed the test standard for plastics instead of the ASTM standard test procedure for leather.

The general shape of the stress-strain curve for leather agrees well with the one discussed by Bienkiewicz.¹ Three steps can be distinguished when the network of fibers in leather is stressed; they include stretching of the network in the direction of the force applied, elongation of the fi-

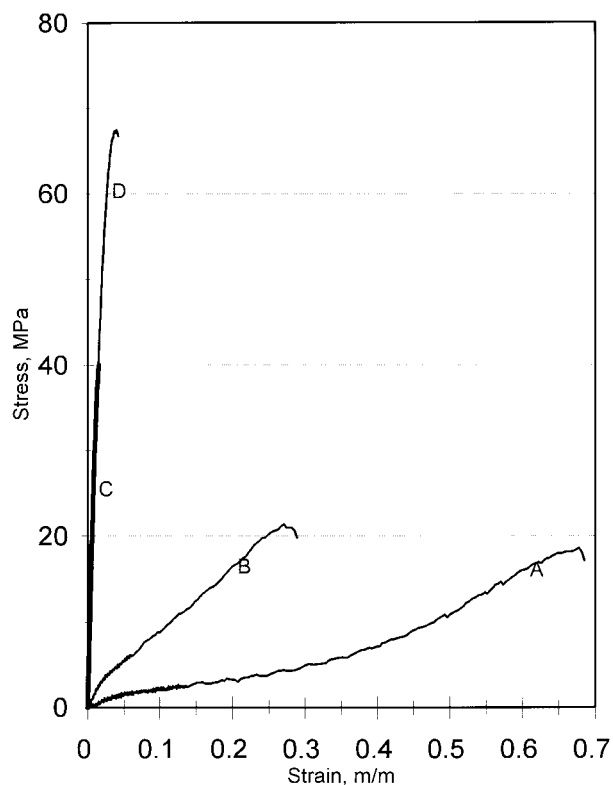


Figure 4 Stress-strain data for (A) chrome-tanned cattlehide, (B) hot-pressed chrome-tanned cattlehide, (C) leather-epoxy IPN, and (D) cured epoxy.

Table I Summary of Mechanical Properties

	Young's Modulus (MPa)	Breaking Stress (MPa)	% Strain at Failure	Tensile Toughness (MPa)	Izod Impact Energy (J/mm)	J Integral (kJ/mm ²)
Chrome-tanned cattlehide	80 (81)	20.4 (7.4)	64.7 (25.3)	4.9 (1.2)	Not applicable	Not applicable
Hot-pressed chrome-tanned cattlehide	81 (6)	25.5 (3.5)	29.9	4.4 (0.8)	Not applicable	Not applicable
Leather-epoxy IPN	3166 (317)	35.6 (4.6)	1.5 (0.1)	0.29 (0.07)	0.0945	15.28
Cured epoxy ^a	3003 (101)	63.6 (6.2)	3.3 (0.7)	1.34 (0.46)	0.0112	1.97

Values in parentheses represent 1 standard deviation for the data acquired.

^a cured mPDA- DGEBA.

bers themselves, and breaking of the fibers. Eventually, disruption occurs, and the material is destroyed. The breaking strain and tensile toughness reported in Table I show that the leather-epoxy IPN is more brittle than is the cured epoxy. This is contrary to the expectation that leather will provide improved toughness upon combination with brittle epoxy, thereby yielding materials

similar to rubber-toughened plastics. The seemingly anomalous behavior may be attributable to suppression of creep and flow within an IPN, which is different from simple polymer blends and copolymers. While bulk leather is relatively flexible, collagen fibers themselves may be very stiff. The presence of the epoxy matrix serves to

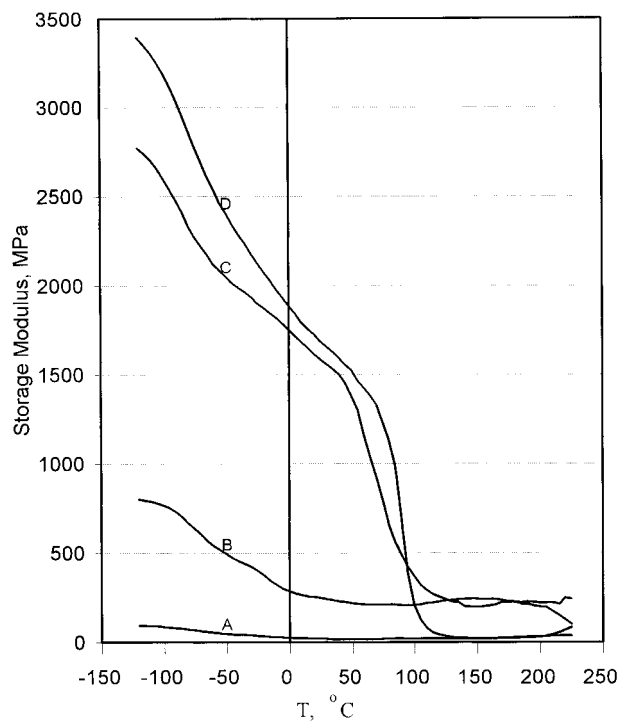


Figure 5 Storage moduli obtained from dynamic mechanical analysis of (A) chrome-tanned cattlehide, (B) hot-pressed chrome-tanned cattlehide, (C) leather-epoxy IPN, and (D) cured epoxy.

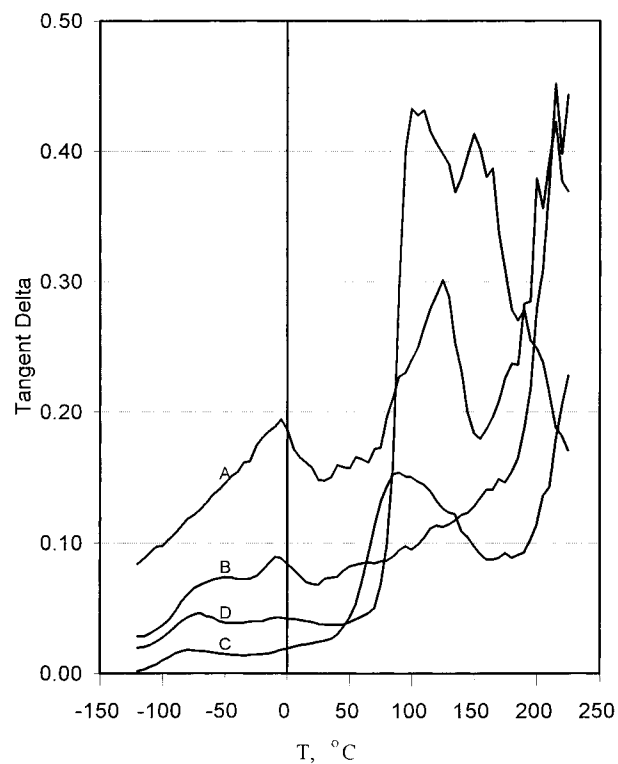


Figure 6 Loss tangent data obtained from DMA of (A) chrome-tanned cattlehide, (B) hot pressed chrome-tanned cattlehide, (C) leather-epoxy IPN, and (D) cured epoxy.

constrain relative motion between the collagen fibers; thus, when stress is applied to the leather–epoxy IPN, the flexural behavior is dominated by the epoxy matrix. The deformability and flexibility inherent in leather are reduced since a brittle polymer fills the void spaces within the hide.

An impact energy of 0.5 ft-lb_f/in. for mPDA-cured DGEBA was reported in the literature,²⁴ which is in reasonable agreement with the data reported herein. Corrections with respect to the initial values when the full swing of the pendulum is achieved should be considered to be a consequence of the energy losses that occur within the Izod impact tester during a measurement. The energy absorbed by the specimens is small (0.35 ft-lb_f) compared with the instrument capacity of 2 ft-lb_f, thus suggesting that the error estimated by simplified correction factors should be negligible.

Although the energy absorbed in a tensile test of the leather–epoxy IPN is much lower than that in a tensile test of the cured epoxy, the measured Izod impact energy of the former is actually much higher than that of the latter (see Table I). Similar discrepancies between these measures of toughness have been reported in other systems, and a rationale for these observations was discussed by Wyatt and Dew-Hughes²⁵ and Yee.²⁶ Many materials, tough in tension, fail at relatively low values in notched flexed-beam impact tests. The most important factor seems to be the concentration of triaxial stress immediately below the root of the notch, instead of either the differences in loading rate or the specimen being tested in a flexural rather than in a tensile mode. In the tensile mode, failure occurs by molecular elongation and bond breaking; however, when a crack propagates in the presence of a notch, other factors, for example, shear yielding and crack tip blunting, are also important, especially in heterogeneous systems such as rubber-toughened plastics and metallic alloys.

In contrast to the impact energy, fracture toughness of a solid polymer is measured under better defined experimental conditions. According to Moskala²⁷ and the references cited therein, crack growth in most materials is initiated shortly after the onset of nonlinearity on the load-deflection curves. On the other hand, Begley and Landes²⁸ pointed out that crack initiation is unambiguously defined by a drop in load. Consequently, if any point between the onset of nonlinearity and the maximum load on a load-deflection curve is chosen to calculate the fracture tough-

ness, the resulting J -integral value should serve as an estimate of the toughness of a material. For this reason, the maximum load point on the load-deflection curve was selected to evaluate the J -integral values for the leather–epoxy IPN and cured epoxy. Even though it may not be as accurate as J_{Ic} , this simple method is appropriate for comparing the fracture toughness of materials when the data are not intended as part of specific structural design calculations. The J -integral values for the leather–epoxy IPN and cured epoxy in Table I support the results of the Izod impact tests.

In summary, the limited elongation observed in the tensile mode for the hide–epoxy composite would not be expected to increase the toughness as measured by the area under the stress–strain curve. In fact, the presence of two phases and the defects that would arise in forming the IPN should lead to decreased toughness over that of the epoxy itself. When impact and J_{Ic} measurements are considered, different mechanisms for toughness must be considered. Here, crack propagation in the presence of a notch should dominate the behavior. The collagen fibers of the hide will act to blunt and deflect the cracks as they propagate through the sample. The increased energy required for crack propagation in this situation will enhance the fracture toughness observed.

The increase in the storage modulus becoming noticeable in the DMA data at 170°C can be attributed to the degradation of the leather component, which is in good agreement with the cited values in the range, 160–165°C, for leather without any moisture.² The β -transition typically is associated with secondary viscoelastic mechanisms observed in the glassy state of the system being studied. Very often, these mechanisms are associated with local molecular motions, such as those typical of pendant side groups. The β -transition shifts to lower temperatures and broadens significantly upon the formation of a leather–epoxy network.

The maximum in $\tan \delta$ (with the concomitant decrease in storage modulus), usually associated with the glass transition temperature, occurred at -10 and -5°C for hot-pressed leather and leather, respectively. The concept of a glass transition temperature may not be strictly applicable to leather. Nonetheless, the glass transition temperature with its associated increase in $\tan \delta$ is often associated with molecular motion involving 10–50 bonds within the polymer.²⁹ This interpre-

tation would be appropriate for the leather and leather-epoxy IPNs studied in this work.

The maximum in the $\tan \delta$ data, indicative of the glass transition for the leather-epoxy IPN, is broader than is the corresponding maxima in the $\tan \delta$ data for either of the two pure component systems, particularly the pure epoxy sample (Fig. 6). Broadening of the glass transition was reported for other IPN systems and was explained by two proposed mechanisms. The broadening of the loss peak upon the mixing of incompatible resins has been proposed. The explanation given is that the incompatibility of the resins leads to the formation of heterogeneities on the length scale of 10–50 Å. The resulting localized fluctuations in the concentrations led to a corresponding range of relaxation behavior, thus broadening the maxima observed in the loss modulus and $\tan \delta$ data.³⁰ Alternately, the existence of local concentration fluctuations in the phase boundary region of IPNs on a length scale of 50–100 Å has been proposed.^{31,32} At this length scale, the entire material would exhibit a single average relaxation time characterized by a single average T_g , which then would be expected to demonstrate broadening with respect to the pure component materials as a consequence of the localized concentration fluctuations. Either interpretation of the DMA data of the leather-epoxy IPNs suggests the formation of an intimate admixture of the epoxy resin throughout the collagen network; the motion of the polymer molecules is affected on a length scale of 10–50 bonds. If the two polymer systems did not interact, the $\tan \delta$ data would be simply the superposition of the pure component data. The changes observed in the β -transition upon the formation of the IPN suggest that crosslinked collagen fibers affect the molecular motion within the epoxy matrix over length scales on the order of 10 atoms or less. While it is convenient to consider the leather-epoxy IPN as a composite material, the DMA data suggest that it is more appropriate to regard the leather-epoxy product as an IPN.

CONCLUSIONS

An IPN was synthesized by polymerization of an epoxy resin within chrome-tanned hide; it was characterized by tensile tests, impact energy, fracture toughness, and DMA. Leather-epoxy IPNs were consistently fabricated with an epoxy content of approximately 25 wt %. They attained flexural and tensile moduli equivalent to those of cured epoxy; tensile strengths typically were

slightly lower than the average strength of leather or cured epoxy. Meanwhile, reproducibility of the mechanical properties was improved compared to unmodified leather. Although the toughness of leather-epoxy IPNs as measured by a tensile test was much lower than that of cured epoxy, the measured Izod impact energy and fracture toughness of the IPNs were actually much higher than those of the cured epoxy. The glass transition of leather-epoxy IPNs occurred over a wide temperature range; therefore, the epoxy resin was considered to be intimately mixed with the collagen network throughout the IPN.

This material is based upon work supported by the Cooperative State Research Service, U.S. Department of Agriculture, under Agreement No. 92-37500-7911. In addition, the authors gratefully acknowledge the assistance of IBP, Inc., in supplying chrome-tanned cattlehide for these studies. Lastly, the assistance of Dr. Hugh Walker of the Department of Mechanical Engineering, Kansas State University, was invaluable in obtaining the tensile test and J -integral data.

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