Synthesis and Characterization of Leather Impregnated with Bismaleimide (BMI)–Jeffamine® Resins

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ABSTRACT: Leather/polymer composites were prepared by impregnating chrome-tanned cattlehide with a solution containing 1,1′-(methylenedi-4,1-phenylene)bismaleimide and Jeffamine® D-230. The mechanical properties in tension, glass transition temperatures, dynamic storage moduli, and moisture absorption of the composites were measured. Impregnated samples showed significant changes in tensile properties, such as the Young's modulus and strain at break, when compared with chrome-tanned cattlehide. In addition, impact energy increased significantly upon formation of the leather/polymer composite over that of the bismaleimide–Jeffamine® resin itself. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1019–1027, 1998

Key words: leather/polymer composite; interpenetrating polymer network (IPN); bismaleimide (BMI); dynamic mechanical analysis (DMA); cattlehide

INTRODUCTION

Natural fibers and other agricultural coproducts can be combined with synthetic polymers to form new composite materials and copolymers displaying remarkable technical, environmental, and economic advantages. Modification of natural fibers, such as wood and cotton, with synthetic polymers has been studied extensively for the several decades.[1–3] Similar approaches have yielded polymer-based leather products. These products have been termed radiation-modified leather,[4] polymer–collagen copolymers,[5] composites,[6–14] and leather interpenetrating polymer networks (IPNs).[7,15,16] In general, the preparation of these modified leathers involved the deposition of polymers onto coarse collagenous materials, for example, chrome-tanned cattlehides,[4,8–13] sheepskins,[5,7,16] and other kinds of chrome-tanned animal skins.[4,16] Graft polymerization was usually effected by solution or emulsion polymerization[4,7–14] by heat, radiation,[4,8] or initiators. Chrome-tanned leather shavings, buffing dust, or powder was added as a filler to a variety of resins.[6,13,14] Acrylate monomers were the monomers most often used in the studies described above.[4,5,9–14,16] Recently, composites based upon impregnating hide or leather with thermosetting resins have been reported.[17–19] For example, chrome-tanned cattlehide impregnated with epoxy resins has shown increased fracture toughness and higher impact energy when compared to the neat epoxy resins.*

Polymerization of bismaleimides (BMIs) resembles that of epoxy systems in that volatile products are not released during processing.[20,21] The double bonds in BMIs are electron-deficient due to the adjacent carbonyl groups and, hence, are capable of undergoing nucleophilic addition

* Requests for information regarding the licensing of this technology should be directed to the Kansas State University Research Foundation, Durland Hall, Kansas State University, Manhattan, KS 66506.
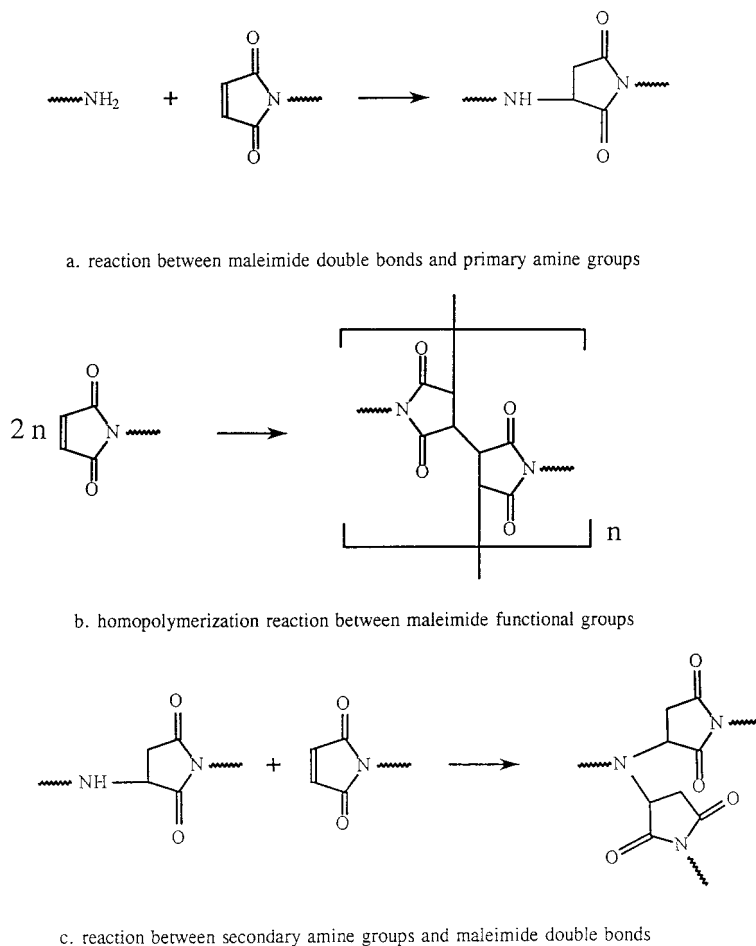
a. reaction between maleimide double bonds and primary amine groups

b. homopolymerization reaction between maleimide functional groups

c. reaction between secondary amine groups and maleimide double bonds

Figure 1 Polymerization reactions between BMI and Jeffamine® D-230.

reactions with primary and secondary amines.[21–24] In addition, BMI homopolymerization leads to chain growth and to formation of crosslinks between network chains (Fig. 1). BMI resins are important in applications where high service temperatures are required.[20] The temperatures required for the cure of BMI/aromatic amine and related systems usually are higher than those required for epoxy resins. The processing temperatures for BMIs can be substantially reduced by employing catalysts,[20] by utilizing a BMI without aromatic functional groups,[23] by reacting an aromatic BMI resin with a polyoxypropyleneamine such as a Jeffamine®,[24] or by adding reactive diluents such as divinylbenzene.[20] BMIs can be copolymerized with vinyl ester resins at temperatures well below 170°C.[25]

While the properties of polyimides make this family of polymers attractive as a component in leather/polymer composites, the processing temperatures are limited by decomposition of the leather. Leather composites impregnated with BMI–Jeffamine® systems are described herein (referred to as leather/BMI–Jeffamine® IPNs hereafter) which have been formulated to lower the processing temperatures. BMIs and their derivatives are a leading class of thermosetting polyimides and have received more and more attention over the past 20 years. They are prime candidates for diverse applications such as adhesives, coating, matrices in structural composites, and electronic applications.[20,26–32] The most important property of BMIs is that they can be polymerized thermally, with or without catalysts, to form thermosetting networks having service temperatures as high as 250°C, thereby bridging the temperature-performance gap between epoxies and polyimides.[28] BMI-based polymers have found popular use in the high-temperature polymer and composite markets mainly because of their low cost and ease of processing.[31]

The lack of volatile emissions during cure per-

mits BMIs to be processed easier than can condensation-type polyimides, which have a number of disadvantages as matrix resins for fiber-reinforced composites.[20,33] For example, BMI monomers are usually cured with hardeners by addition polymerization and crosslinking reactions via reactive terminal groups to give highly crosslinked and void-free thermoset structures. The thermosetting networks thus formed possess many desirable properties, such as excellent thermal and oxidative stability, low moisture absorption, almost constant electrical properties over a wide range of temperatures,[32] and nonflammability.

The present study reports the mechanical properties of leather/BMI–Jeffamine® IPNs as well as of those for the corresponding neat resins. Two different cure schedules were followed in preparing the samples. The effects of the reaction conditions on the mechanical properties of leather/ BMI–Jeffamine® IPNs and neat resins are discussed.

EXPERIMENTAL

Starting Materials

All samples were prepared from chrome-tanned cattlehide (IBP, inc., Garden City, KS). The BMI monomer chosen was 1,1′-(methylenedi-4,1-phenylene)bismaleimide (95% purity, Aldrich Chemical Co., Milwaukee, WI). Jeffamine® D-230 (with an approximate molecular weight of 230 g/mol) was supplied by Texaco Chemical Co. (Houston, TX). 1,4-Dioxane (99.9% purity, Fisher Scientific Co., Fair Lawn, NJ) served as the solvent. The chemical structures of the reagents are given in Figure 2.

Sample Preparation

Leather/BMI–Jeffamine® IPNs

Chrome-tanned cattlehide (referred to as leather hereafter) was presoaked in acetone for 12–20 h and subsequently dried under ambient conditions. The presoaked, dehydrated leather sample was dried further at 90°C for up to 4 h in a vacuum oven (at a gauge pressure of less than −90 kPa) to remove all traces of moisture. The initial weight (W_0) and approximate area of the leather sample were recorded.

The impregnating solution was prepared by dissolving 10 g of the BMI monomer in 25–40 mL of 1,4-dioxane. Jeffamine® D-230 was added to this solution to achieve a 1 : 1 molar ratio of BMI to Jeffamine® D-230. The leather sample was completely immersed in this solution for approximately 2 days. Upon removal from the solution, the sample was blotted to remove excess solution from the leather surface. The solvent in the impregnated sample was removed by evaporation at ambient conditions for 1–2 days. The sample subsequently was placed in a vacuum oven at room temperature for several hours at a pressure less than −50 kPa to further remove any solvent. The vacuum was reduced to less than −70 kPa for an additional 24–36 h to complete the solvent removal. Elimination of the solvent at ambient temperature minimizes cure of the resin during processing.

The sample was sealed in Teflon bagging film and heated in a hot press (MTP-8 Press, Tetrahedron Associates, Inc., San Diego, CA) according to one of the temperature–pressure schedules outlined below. All pressures are gauge pressures.

Schedule I

- 95°C at 16 kPa for 1 h
- 150°C at 16 kPa for 4 h
- 49°C at 16 kPa for 1 h

Schedule II

- 95°C at 16 kPa for 1 h
- 150°C at 16 kPa for 4 h
- 160°C at 26 kPa for 24 h
- 49°C at 16 kPa for 1 h

At the conclusion of each cure schedule, the pressure was released and the sample was removed.

Preparation of Neat Resins

Samples of neat resin were cured at atmospheric pressure according to the temperature schedules below.

Schedule I

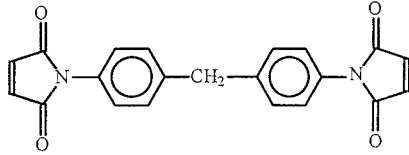- 95°C for 1 h
- 150°C for 4 h

Schedule II

- 95°C for 1 h

Chemical Name	Chemical Structure
1,1'-(methylenedi-4,1-phenylene) bismaleimide	
Jeffamine® D-230 (a polyoxypropylenediamine)	$H_2NCHCH_2-[OCH_2CH]_x-NH_2$ with CH_3 groups; $(X=2\text{-}3)$
1,4-dioxane	

Figure 2 Chemical structures of reagents of this study.

- 150°C for 4 h
- 160°C for 24 h

Preparation of Hot-pressed Cattlehide

Samples of chrome-tanned cattlehide were placed in the hot press and processed according to the temperature–pressure schedules employed in preparing the leather/BMI–Jeffamine® IPNs.

Property Measurements

Estimation of the Resin Content of the Leather/ BMI–Jeffamine® IPNs

Resin contents of the leather/BMI–Jeffamine® IPNs were calculated as

$$\{\% \text{ Polymer loading}\} = \{(W - W_0)/W_0\} \times 100\%$$

where W_0 is the weight of the leather dried via the vacuum oven as described previously. With the leather/BMI–Jeffamine® IPN prepared according to schedule I, W is the weight of the IPN immediately following preparation of the sample. For the leather/BMI–Jeffamine® IPN prepared according to schedule II, W is the weight of the

IPN sample after being dried at 90°C for up to 4 h at a vacuum less than −90 kPa.

Density Measurements

The room-temperature density was measured with a density gradient column containing an *m*-xylene/tetrachloroethylene solution.[34] Measurements were taken 24 h after placing the sample in the column.

Water Uptake and Moisture Gain

The samples of cattlehides, leather/BMI–Jeffamine® IPNs, and neat BMI–Jeffamine® resins were dried in an oven for 1.5–4 h at a vacuum less than −90 kPa and at a temperature of 90°C with the individual sample weight, W_0, being determined immediately upon removal from the oven. The samples were immersed in water for 4 days at room temperature. Upon retrieval from the water, the samples were blotted to remove excess surface water, and the weight of each wet sample, W_1, was determined. The method is similar to others reported for measuring the water absorption of leather–polymer composites.[13,14] No attempt was made to control the sample size and geometry.

Table I   Density Data

Samples	True Density (mg/m^3)
Dry cattlehide	1.420 ± 0.010
Hot-pressed cattlehide	1.422 ± 0.007
Neat BMI–Jeffamine® resin	
Cure schedule I	1.223 ± 0.003
Cure schedule II	1.263 ± 0.003
Leather/BMI–Jeffamine® IPN	
Cure schedule I	1.345 ± 0.011
Cure schedule II	1.350 ± 0.006

$\pm$: 95% confidence interval.

The wet samples were left at ambient conditions for 10 days, at which time the weight of each air-dried sample, W_2, was obtained. No attempt was made to control the relative humidity of the ambient conditions. Percent water uptake and percent moisture gain were calculated from the formulas below

$$\text{Water uptake } \% = \{(W_1 - W_0)/W_0\} \times 100\%$$

$$\text{Moisture gain } \% = \{(W_2 - W_0)/W_0\} \times 100\%$$

Tensile Properties and Impact Resistance Tests

Tensile tests were performed according to ASTM Standard Test Procedure D-638-90. Tensile properties were measured at room temperature (23 $\pm$ 2°C) with an Instron 8500 test machine. The crosshead speeds were 5 mm min^{-1} for neat resins and IPNs and 200 mm min^{-1} for leather samples. The overall specimen length was 115 mm, with the gauge region being approximately 33-mm long and 6-mm wide. The sample thickness varied between 1 and 4 mm. The initial grip separation was 64 mm for all specimens.

The Izod impact energy was measured according to ASTM Standard Test Method D-256-90b. The Izod impact tester had a capacity of 2 ft-lb$_f$ and the data were obtained at ambient conditions. The impact energies reported were the average of five specimens.

Dynamic Mechanical Analysis (DMA)

Viscoelastic data were obtained from a Perkin–Elmer DMA-7 dynamic mechanical analyzer operating at a frequency of 1 Hz. A temperature range from 20 to 200°C was studied at a heating rate of 2°C per minute. The storage modulus (E'), the loss modulus (E''), and the loss tangent (tan δ) were measured with a three-point flexural accessory under ambient conditions. The sample length was approximately 25 mm, and the distance between supports was 20 mm. The system was operated under strain control (0.016% for cattlehides and IPNs and 0.008% for neat resins). The cattlehide and IPN samples had length-to-thickness ratios of approximately 25 : 3; samples of neat resins had length-to-thickness ratios of approximately 25 : 1.

RESULTS AND DISCUSSION

The polymer contents of the leather/BMI–Jeffamine® IPN samples prepared according to cure schedules I and II were 36 and 44 wt %, respectively. As can be seen in Table I, the true density of the pressed cattlehide is the same as that of the as-received cattlehide. As expected, the true

Table II   Representative Moisture Absorption Data

| Sample	Moisture Adsorption Immersion in Water for 4 Days Water Uptake %	Atmospheric Conditions Moisture Gain %
Dry cattlehide	106.7 ± 8.1	8.8 ± 2.0
Hot-pressed cattlehide (both schedules)	85.0 ± 1.2	13.1 ± 3.9
Neat BMI–Jeffamine® resin		
Cure schedule I	9.6 ± 1.7	4.0 ± 3.3
Cure schedule II	3.3 ± 0.3	0.4 ± 0.2
Leather/BMI–Jeffamine® IPN		
Cure schedule I	49.2 ± 3.1	10.0 ± 1.9
Cure schedule II	34.3 ± 2.6	6.2 ± 2.6

$\pm$: 95% confidence interval.
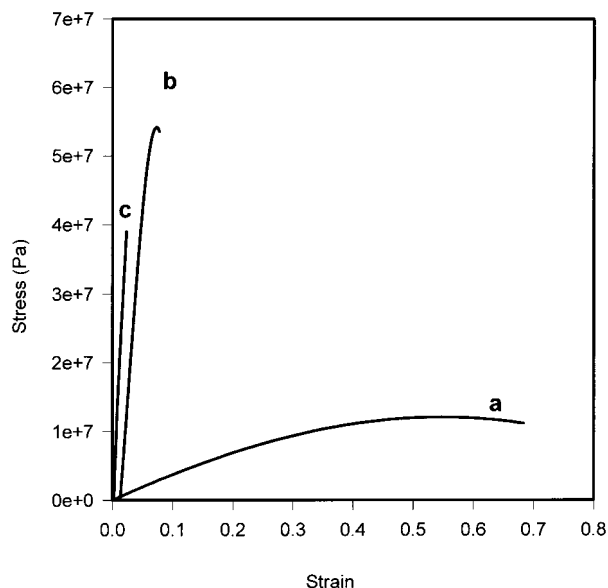
Figure 3   Tensile test data for (a) cattlehide, (b) neat BMI–Jeffamine® resin (cure schedule II), and (c) leather/BMI–Jeffamine® IPN (cure schedule II).

densities of the leather/BMI–Jeffamine® IPNs are intermediate between those of the chrome-tanned cattlehide and the neat BMI–Jeffamine® resins.

Representative data for moisture absorption based upon water immersion and exposure to ambient atmospheric conditions (moisture gain) are given in Table II. Tensile test data for the dry cattlehide, neat BMI–Jeffamine® resin, and leather/BMI–Jeffamine® IPN are shown in Figure 3 with the characteristic mechanical properties of these samples provided in Table III. The tensile behavior of the leather/BMI–Jeffamine® IPN exhibits features similar to that of the neat BMI–Jeffamine® resins; however, the IPN has a smaller percent elongation at failure. The IPN formed via cure schedule II resulted in a material which had tensile and breaking strengths approximately two-thirds of those of the neat BMI–Jeffamine® resin. The yield strength of the IPNs exceeded that of the neat resin prepared from cure schedule II by at least a factor of two. IPNs prepared from both cure schedules exhibited enhanced Izod impact energies over the neat resins alone.

Figures 4 and 5 present typical dynamic storage moduli and tan δ data, respectively, for the neat BMI–Jeffamine® resins prepared according to cure schedules I and II. These data show that the glass transition temperature (T_g) for the sample prepared from cure schedule I is 33°C. T_g in-

Table III   Mechanical Property Data

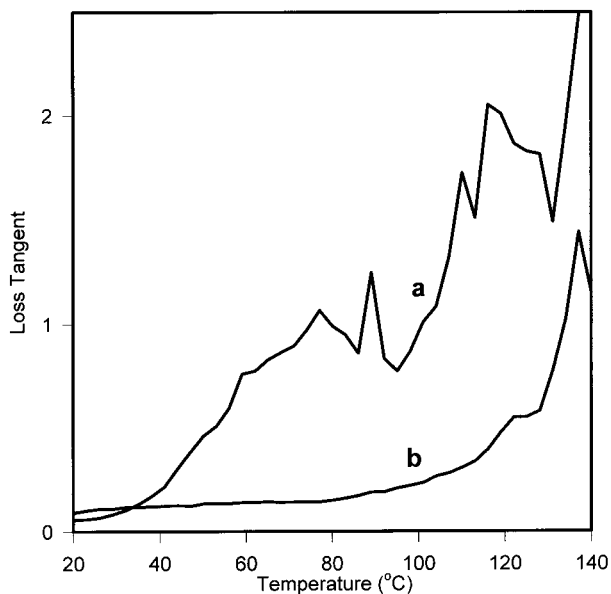| Sample	Resin Content (wt %)	Young's Modulus (GPa)	Tensile Strength (Mpa)	Breaking Strength (MPa)	0.2% Yield Strength (MPa)	% Elongation at Break (%)	Energy to Break Point (J)	Izod Impact Energy (J/m)
Dry cattlehide	N/A	0.32 ± 0.26	17.2 ± 3.1	17.0 ± 2.7	0.65 ± 0.10	77.7 ± 33.8	4.0 ± 1.7	N/A
Leather/BMI–Jeffamine® IPNs								
Cure schedule I	44%	1.75 ± 0.21	27.2 ± 9.7	27.2 ± 9.7	15.3 ± 3.3	2.29 ± 0.52	0.21 ± 0.15	139 ± 9
Cure schedule II	36%	1.67 ± 0.34	39.2 ± 3.7	39.2 ± 3.7	19.1 ± 5.5	2.31 ± 0.17	0.37 ± 0.08	219 ± 34
Neat BMI–Jeffamine® resins								
Cure schedule I	N/A	—	—	—	—	—	—	101 ± 38
Cure schedule II	N/A	1.56 ± 0.22	62.8 ± 6.2	60.3 ± 4.6	6.8 ± 2.2	7.38 ± 0.74	0.59 ± 0.10	69 ± 30

N/A: not applicable; ±: 95% confidence interval.
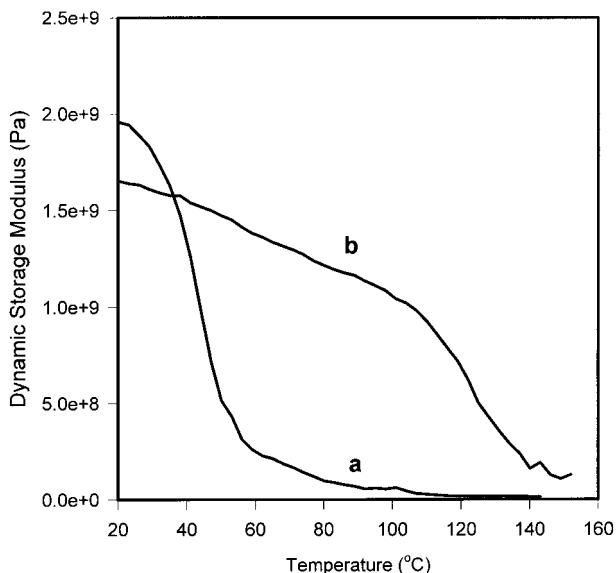
Figure 4 Dynamic storage moduli (E') for the neat BMI–Jeffamine® resins prepared according to (a) cure schedule I and (b) cure schedule II.
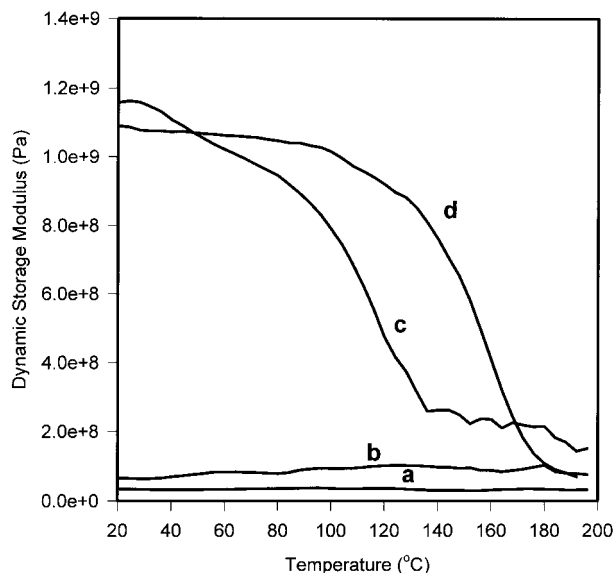
Figure 6 Dynamic storage moduli (E') for (a) cattlehide, (b) hot-pressed cattlehide (cure schedule I), (c) leather/BMI–Jeffamine® IPN (cure schedule I), and (d) leather/BMI–Jeffamine® IPN (cure schedule II).

creases to 110°C when cure schedule II is employed. Both values for T_g indicated above were determined by the tangent-intercept method based upon dynamic storage modulus data. The increase in noise of the tan δ data observed in some cases at temperatures in excess of the glass transition temperature for neat resins most likely

is a consequence of the difficulty in maintaining strain control as the specimen softens. Figure 6 shows the temperature dependence of the dynamic storage moduli of unpressed dry cattlehide, hot-pressed cattlehide, and leather/BMI–Jeffamine® IPNs; Figure 7 presents typical tan δ data
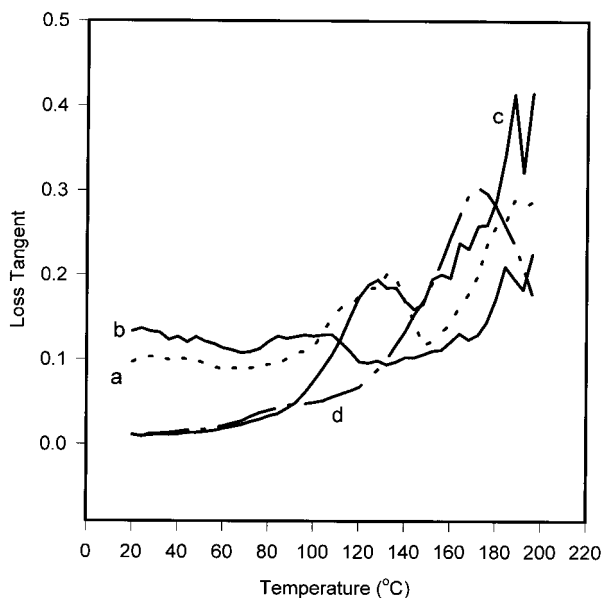
Figure 5 Loss tangent (tan δ) data for the neat BMI–Jeffamine® resins prepared according to (a) cure schedule I and (b) cure schedule II.

Figure 7 Loss tangent (tan δ) data for (a) cattlehide, (b) hot-pressed cattlehide (cure schedule I), (c) leather/BMI–Jeffamine® IPN (cure schedule I), and (d) leather/BMI–Jeffamine® IPN (cure schedule II).

for these samples. Leather/BMI–Jeffamine® IPNs from both cure schedules exhibit higher dynamic storage moduli than does cattlehide for temperatures less than 170°C. T_g's calculated by the tangent-intercept method for the leather/ BMI–Jeffamine® IPNs occur at 100 and 134°C for cure schedules I and II, respectively, indicating that the glass transition temperatures of the IPNs are higher than those of their respective neat resins.

Collagen, which is an essential component of hide or leather, contains amine functional groups. The question naturally arises as to whether these species are available to react with the BMI monomer. Preliminary differential scanning calorimetry studies suggest that only a limited reaction occurs between wet-blue cattlehide and epoxies. Tanning agents provide crosslinks between collagen molecules. Such crosslinks would limit the reaction of the amine functional groups with monomers such as epoxies or BMIs.

CONCLUSIONS

The processing temperatures required for polyimides limit the leather/polyimide IPNs that can be prepared without decomposition of the leather. Leather/BMI–Jeffamine® IPNs, however, have been prepared by *in situ* polymerization of 1,1′-(methylenedi-4,1-phenylene)bismaleimide in the presence of a polyoxypropylenediamine (Jeffamine® D-230). The resulting IPN (cure schedule II) retains the Young's modulus, tensile strength, and breaking strength typical of the similarly prepared neat resin. The yield strength and Izod impact energy of the IPNs are significantly greater than those measured for the similarly prepared neat resins. The IPNs have higher glass transition temperatures than those of the corresponding neat resins as well. These IPNs should be able to take advantage of the low moisture adsorption, electrical properties, and nonflammability of BMI resins and extend the performance of leather/epoxy IPNs.

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