Absorption of Glycerol and Its Effects on the Physical Properties of a Collagen Material: Leather

Cheng-Kung Liu

Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, 600 East Mermaid Lane, Wyndmoor, Pennsylvania 19038-8598

ABSTRACT: An aqueous solution of glycerol was applied to a polymeric biomaterial, leather, to evaluate its effects on the physical properties of leather, particularly stiffness. The initial strain energy, Young's modulus, and acoustic-emission methods were used to characterize the stiffness of the resultant leather treated with these glycerol solutions. The measurements revealed that the glycerol treatment significantly reduced the stiffness of the dried leather, indicating the strong lubrication function of glycerol for leather. Experiments were also conducted to investigate the mechanism of glycerol adsorption into the leather matrix. Fick's second law of diffusion was employed to systematically derive a mathematical model for the absorption rate. The effect of temperature on the absorption rate was also included in the model by incorporation of the Arrhenius equation into Fick's second law of diffusion. The resultant model fits the experimental data very well. It not only depicts the mechanism of absorption but also predicts the absorption rate as a function of key variables. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1221–1231, 2003

Key words: adsorption; diffusion; stiffness; modeling

INTRODUCTION

Since the dawn of human civilization, collagen materials such as leather have been among the most dominant natural fibrous materials used by mankind, especially for clothing, upholstery, and shoes. Leather is economically significant because it is a major byproduct derived from the meat industry.[1] Fatliquoring is an oil-addition process by which the collagen fibers in leather are lubricated so that after drying they will be capable of slipping over one another, thereby imparting flexibility and compliance to leather.[2] The addition of surfactants to the lubricating oil (called fatliquor) is essential in decreasing the interfacial tension between oil and water to make the lubricating emulsion permanent.[3] The fatliquored leather, therefore, attains a greater softness and flexibility than imparted by the tannage alone. We have previously reported its pronounced effects on the drying rate and leather properties.[4,5] Our measurements have shown that the drying rate decreases as the fatliquor concentration increases by a factor of $(1 - f)^{1/2}$, where f is the fatliquor concentration fraction. Observations have also shown that the tensile strength, elongation, and toughness all increase steadily with an increased fatliquor concen-

tration, whereas Young's modulus decreases with an increased fatliquor concentration. Current methods for lubricating leather, however, employ oils and surfactants that are known to destabilize collagen fibers and to impair the physical properties of leather.[6,7] Therefore, we recently have explored the use of an aqueous solution of glycerol [$HOCH(CH_2OH)_2$] as a lubricant for leather. Because of its strong hydrophilic properties, glycerol easily dissolves in water without the need of surfactants to form a stable solution. Another advantage of glycerol is related to its moisture retention. Leather is a collagenous material; it can be overdried, becoming very brittle and weak. Glycerol is a well-known humectant and a key ingredient in skincare products. One may expect, therefore, that glycerol may improve the moisture retention of leather. The possibility of overdrying the leather will be greatly reduced because of the inherent nature of humectants, which is to promote the retention of water. Glycerol may also significantly increase the denaturation temperature of collagen.[8] Therefore, glycerol potentially may function as a heat-resistant agent for leather.

EXPERIMENTAL

Materials

Bovine leather, chrome-tanned from steer hides 2.4–2.6 mm thick, were obtained from Prime Tanning Co. (St. Joseph, MO). Rectangular samples (10 mm × 100 mm) were cut from the standard test area, as described in ASTM D 2813-91, with the long dimension

---

TABLE I
Experimental Plan

Run	Coded values			Actual value		
	X_1: concentration (%)	X_2: time (min)	X_3: temperature (°C)	X_1': concentration (%)	X_2': time (min)	X_3': temperature (°C)
1	−1	−1	−1	30	60	25
2	−1	−1	1	30	60	45
3	−1	1	−1	30	180	25
4	−1	1	1	30	180	45
5	1	−1	−1	70	60	25
6	1	−1	1	70	60	45
7	1	1	−1	70	180	25
8	1	1	1	70	180	45
9	−1.682	0	0	16.4	120	35
10	1.682	0	0	83.6	120	35
11	0	−1.682	0	50	19	35
12	0	1.682	0	50	221	35
13	0	0	−1.682	50	120	18
14	0	0	1.682	50	120	52
15	0	0	0	50	120	35
16	0	0	0	50	120	35
17	0	0	0	50	120	35
18	0	0	0	50	120	35
19	0	0	0	50	120	35
20	0	0	0	50	120	35
21	0	0	0	50	120	35
22	0	0	0	50	120	35
23	−2.5	0	0	0	120	35

perpendicular to the backbone. Each sample (average weight ~ 1.82 g and apparent density ~ 0.728 g/cm³) was immersed in a 125-mL flask of a glycerol solution prepared from analytical-grade glycerol (Fisher Scientific, Pittsburgh, PA) and distilled water. The solution was slowly stirred with a magnetic stir bar. The purpose of stirring was to maintain a uniform concentration of glycerol throughout the container; it was not to create a force diffusion of glycerol into leather, which would complicate the absorption rate measurements. The solutions were maintained at a constant temperature by the solution container being seated in a constant-temperature water bath. The treatment conditions, such as the glycerol concentration, solution temperature, and treatment time (duration), were arranged according to the experimental plan listed in Table I. The treated samples were then brought into open air and slowly dried at 21°C and 65% relative humidity for 1 week. They were stored in a physical property testing room and conditioned at 23°C and 50% relative humidity for another week before the mechanical property testing.

Measurements

The absorption rate (as listed in Table II) of glycerol was calculated for glycerol-treated samples as follows:

$$\psi = (M_t/W_o) \times 100/t \qquad (1)$$

where Ψ is the absorption rate (%/min based on the original weight of the samples), M_t denotes the amount of glycerol uptaken (absorbed) by the leather samples at time t, and W_o is the original weight of the samples. M_t was computed by the subtraction of W_o from W_b, the weight of the samples treated with glycerol. The samples for measuring W_o and W_b were dried in a vacuum oven (absolute pressure, 3.07 kPa) at 60°C for 5 h for the removal of water; therefore, the weight was taken on a moisture-free basis. Observations showed that water boiled and evaporated from the leather, whereas glycerol remained in the leather samples; glycerol boils at 290°C under normal atmospheric pressure. An analytical balance with accuracy of 0.001 g was used to weigh the samples.

Tensile tests were performed for glycerol-treated samples that had been conditioned in a test room at 21°C and 50% relative humidity for 1 week. Tensile property measurements included the tensile strength, Young's modulus, and initial strain energy. These properties were measured with a gauge length of 50 mm, and the strain rate (crosshead speed) was set at 50 mm/min. The *tensile strength* is defined as the maximum stress that a sample can sustain without fracture. *Young's modulus* is a physical quantity representing the stiffness of a material. It is determined by the measurement of the slope of a line tangent to the initial stress–strain curve. The *initial strain energy of*

leather is defined as the energy needed to stretch the leather to 10% strain.[9] This is the area under the stress–strain curve from 0–10% strain. If other material variables are equal, the initial strain energy of leather will be proportional to the volume of tested samples. For the comparison of different samples, the value of the initial strain energy for each test sample was divided by the volume of that sample to obtain the initial strain energy with the SI units of J/cm^3. An upgraded Instron mechanical property tester (model 1122, Instron Corp., Canton, MA) and Testworks 3.1 data-acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work.

To measure the degree of lubrication, we used our previously established acoustic-emission (AE) method.[10,11] Our studies have shown that the degree of lubrication has a direct link to the total acoustic hits (cumulative acoustic hits measured from the beginning of the tensile stretch up to the fracture of samples) measured by an acoustic analyzer.[11] In the tensile test, the leather sample was gripped between two jaws, subjected to a tensile force, and slowly stretched at a constant strain rate. Because of this tensile stretching, stress was created in the leather along with a rapid movement, relocation, or breaking of structural elements such as fibrils, fibers, and fiber bundles. As a result, sound waves were produced that could be detected by an acoustic transducer. The basic phenomenon may be defined as an AE event, which was translated by an AE analyzer as a hit. For the measurement of AE hits, a small piezoelectric transducer resonating at 150 kHz (model R15, Physical Acoustics Corp., Princeton, NJ), 10 mm in diameter, was clipped against the leather sample. AE signals emanating from this transducer when the Instron stretched the leather samples were processed with a model 1220A preamplifier and a LOCAN-AT model 3140 AE analyzer (Physical Acoustics Corp.). Each acoustic hit from an acoustic event in the sample caused a damped oscillation to be emitted by the transducer. The analyzer recorded the total number of hits as a function of time until the tensile tester fractured the sample.

Experimental design

For any systematic investigation, it will be very desirable to present the results in a mathematical form that precisely describes the relationship between the variables and responses. Therefore, we applied the statistical experimental design technique to establishing the regression models. As shown in Table I, a central composite design provided by SAS statistical software (version 8e) was used to arrange experimental conditions, thereby establishing regression models. This experimental design was developed by Box and Hunter[12] and is widely used for fitting a second-order model. A

TABLE II
Experimental Results

Run	Absorption rate (%/min)	Tensile strength (MPa)	Young's modulus (MPa)
1	0.49	19	5.7
2	0.74	16.4	4.4
3	0.19	21.1	5.6
4	0.26	14.9	3.4
5	0.82	20.8	4.3
6	1.21	15.5	2.8
7	0.36	19	2.8
8	0.44	16.4	1.7
9	0.23	15.9	5.8
10	0.64	16.6	2.4
11	1.73	19.2	6.4
12	0.23	19.8	4.1
13	0.51	15.5	2.5
14	0.54	16.2	3.5
15	0.40	19.4	4.4
16	0.44	21	4.6
17	0.47	18.5	4.4
18	0.41	20.9	4.2
19	0.47	19.2	4.2
20	0.49	18.3	4.3
21	0.55	16.1	3.2
22	0.41	20.9	4.6
23	0.00	14.8	10.7

comprehensive description for this type of experimental design was given by Cochran and Cox.[13] The three factors selected in this study were the glycerol concentration (X_1), treatment time (X_2), and bath temperature (X_3). A regression model was derived with the form of a polynomial equation in which the variables were presented as their linear and quadratic terms as well as their bifactorial cross-products (CPs), as shown in Table III.[13] The regression coefficients, along with an analysis of variance, were obtained readily with SAS software with a microcomputer. For the sake of easy calculation and simplification of the regression equations, the variables X_i were coded (transformed) from X_i' with original scales. The levels of the coded variables X_1, X_2, and X_3 were obtained by means of the following formulae: $X_1 = (X_1' - 50)/20$, $X_2 = (X_2' - 120)/60$, and $X_3 = (X_3' - 35)/10$, where X_1' (%), X_2' (min), and X_3' (°C) are the variables with original scales.

For a better understanding of the results of an investigation, it is extremely beneficial to visualize the relationship between the response (dependent variables) and factor (independent variables) levels geometrically. Response surfaces[14] (surface plots of the resultant property as a function of multiple independent variables) were constructed on the basis of the regression equation, as shown in Table III, with graphics and data analysis software (Axum, version 6) developed by MathSoft, Inc. (Cambridge, MA).

TABLE III
Equation of Response Surface and Statistical Analysis of Variance

	Equation of response surface	Analysis of variance p values	R^2
Absorption rate [eq. (2)]	$\psi = 0.455 + 0.131X_1 - 0.332X_2 + 0.061X_3 - 0.022\,X_1^2 + 0.165X_2^2 - 0.004X_3^2 - 0.057X_1X_2 + 0.020X_1X_3 - 0.062X_2X_3$	1st order 0.0001 2nd order 0.0011 CP[a] 0.3266 Model[b] 0.0001	0.93
Young's modulus	$Y = 4.058 - 1.208X_1 - 0.554X_2 - 0.324X_3 + 0.369X_1^2 + 0.262X_2^2 - 0.533X_3^2 - 0.188X_1X_2 + 0.112X_1X_3 - 0.062X_2X_3$	1st order 0.0001 2nd order 0.0306 CP 0.9276 Model 0.0007	0.84
Tensile strength	$Y = 19.210 + 0.034X_1 + 0.052X_2 - 1.136X_3 - 0.757X_1^2 + 0.232X_2^2 - 1.058X_3^2 - 0.188X_1X_2 + 0.112X_1X_3 - 0.112X_2X_3$	1st order 0.1440 2nd order 0.0483 CP 0.9862 Model 0.1455	0.57

[a] CP term.
[b] The whole regression equation.

RESULTS AND DISCUSSION

Absorption rate

Rate measurements are important for any process investigation because they provide insight into the mechanism underlying a process. A second-order regression model can be expressed as follows:

$$\psi = 0.455 + 0.131X_1 - 0.332X_2 + 0.061X_3 - 0.022X_1^2 + 0.165X_2^2 - 0.004X_3^2 - 0.057X_1X_2 + 0.020X_1X_3 - 0.062X_2X_3 \quad (2)$$

With a coefficient of multiple determination[15] (R^2) of 0.93, it is evident that the quadratic model fits the data very well. As indicated in Table III, the analysis of variance shows that the regression coefficients for the first-order and second-order terms are highly significant with p values of 0.0001 and 0.0011, respectively. The p value indicates the probability that effects originate from noises (instead of the factor itself); therefore, a smaller value of p indicates a greater significance of effects. The value of 0.1 (or 10%) is a commonly used cutoff p value for significance. The p value for the CP terms for eq. (2), however, is greater than 0.10; therefore the effects of the CP terms are not statistically significant. This indicates very little interaction between the factors; for example, the change in the glycerol concentration does not affect how the treatment time influences the absorption rate. Figure 1 presents a three-dimensional plot of the response surface of the absorption rate as a function of the glycerol concentration and temperature simultaneously, according to eq. (2), for a leather sample with a treatment time of 2 h. The absorption rate increases steadily with increasing temperature or glycerol concentration. Figure 2, however, presents a three-dimensional plot of the response surface as a function of the treatment time and glycerol concentration, with the treatment temperature fixed at 35°C. As shown in this figure, the absorption rate is not constant; instead, it decreases as the treatment proceeds. This behavior implies that there is limited space in the leather for accommodating the penetration of glycerol. The absorption rate slows down as less space is available for glycerol to occupy.

Absorption rate model

The model presented as eq. (2) gives an integral and quantitative description of how the absorption rate changes with three major variables: time, temperature, and concentration. This polynomial equation is adequate for predicting the absorption rate, but it reveals very little about what makes the absorption rate behave in the way it does. Therefore, an effort has been made to establish a mechanistic model that produces a basic understanding of the physical process involved in glycerol absorption.

There is no evidence that glycerol reacts chemically with collagen. The absorption is mainly driven by the concentration gradient of glycerol. Therefore, Fick's diffusion law may govern the absorption process. However, absorption rate measurements, as shown in Figure 2, reveal that glycerol diffusion into leather is an unsteady-state problem. Therefore, a model of the sorption rate may be based on Fick's second diffusion law. For a linear, one-dimensional system, the equation for the diffusion of glycerol into a sheet of leather can be written as follows:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial X^2}\right) \quad (3a)$$

where C denotes the concentration of glycerol at point X in the leather sheet at time t. D denotes the diffusion
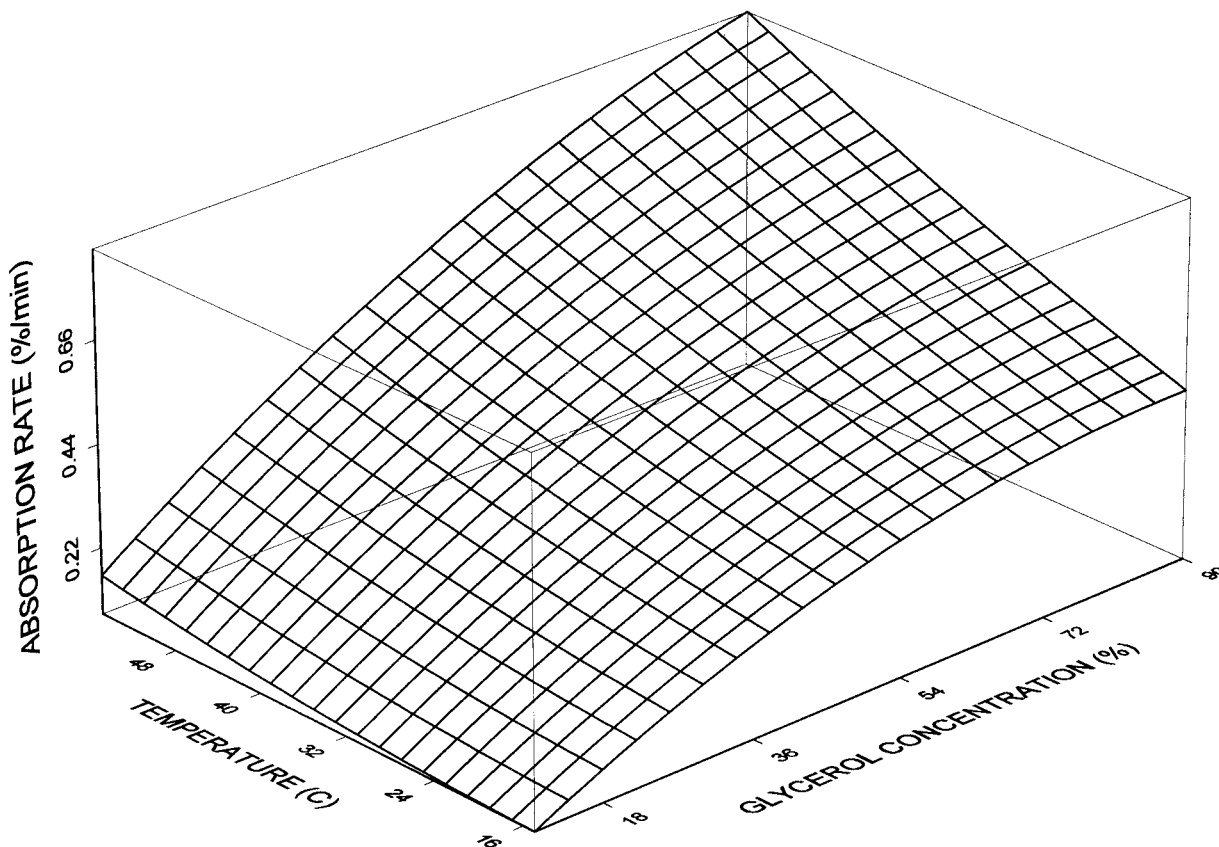
Figure 1 Absorption rate as a function of the glycerol concentration and temperature.

coefficient in the leather sheet with a thickness of d. X is the distance in the direction of glycerol diffusion. At $t < 0$, $C = 0$ for all X, whereas at $t > 0$, the surfaces of the leather sheet at $X = 0$ (the top position) and d (the bottom position) assume the value C_∞. After enough time, C_∞ is the value achieved for all X, that is, the equilibrium concentration of glycerol. If M_t denotes the total amount of glycerol that has entered the leather sheet at time t and M_∞ denotes the amount at equilibrium ($M_\infty = AdC_\infty$, where A denotes the area of the leather sheet), then the solution to eq. (3a) for these boundary conditions is[16]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^2 (t/d^2)} \quad (3b)$$

It is difficult to manipulate eq. (3b), which is typical of solutions to Fick's second law. If diffusion has not proceeded for too long, the equation can be simplified as follows:[17]

$$M_t = 4M_\infty \left(\frac{Dt}{\pi d^2}\right)^{1/2} \quad 0 < \frac{M_t}{M_\infty} < 0.6 \quad (4)$$

We also know that

$$M_t = \psi W_o \frac{t}{100} \quad (5)$$

where W_o denotes the original weight of the leather samples (the weight without water and glycerol).

Therefore, eq. (4) can be transformed into

$$\psi = 4M_\infty \left(\frac{D}{\pi}\right)^{1/2} \left(\frac{1}{t}\right)^{1/2} \left(\frac{1}{d}\right) \left(\frac{100}{W_o}\right) \quad (6)$$

The effects of the temperature on the diffusion coefficient may follow the Arrhenius relationship:[18]

$$D = D_0 \, e^{\frac{-E_a}{RT}} \quad (7)$$

where D_0 denotes the pre-exponential factor determined from the plot of $\log(D)$ versus $(1/T)$, which is independent of temperature, and E_a is the activation energy of diffusion, generally about 10 kcal/mol; R is a gas constant [8.314 J/(K mol)]; and T denotes the temperature (K). Inserting eq. (7) into the absorption rate equation , we obtain

$$\psi = 4M_\infty \left(D_0 \frac{(e^{-E_a/RT})}{\pi}\right)^{1/2} \left(\frac{1}{t}\right)^{1/2} \left(\frac{1}{d}\right) \left(\frac{100}{W_0}\right) \quad (8)$$
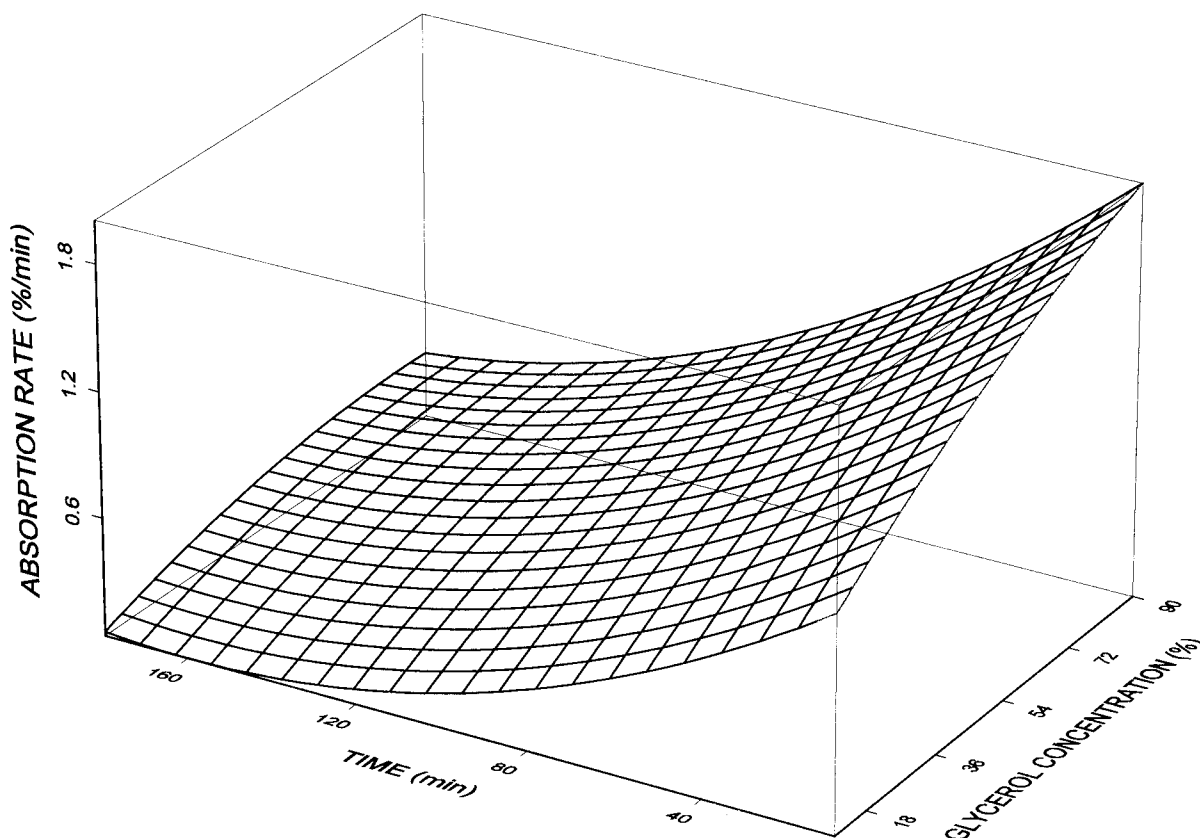
Figure 2 Absorption rate as a function of the time and glycerol concentration.

The results of the experimental data for the absorption rate fit eq. (8) very well and are demonstrated in Figure 3. We obtained a value of 15.38 for D_0 from curve fitting and assumed a value of 10 kcal/mol for E_a. The correlation coefficient of 0.96 was observed for the correlation between the experimental data and theoretical data based on eq. (8). For a natural material such as leather with many intrinsic variations between samples, this is indeed a very strong correlation. The rate equation derived here is easily understood. It indicates that absorption does not proceed at a constant rate but decreases as time increases. As with many diffusion-controlled processes, the absorption rate increases as temperature rises, following the Arrhenius relationship. In addition, eq. (8) also indicates that the absorption rate is proportional to M_∞, which is directly linked to the concentration of glycerol in the bath. In addition to giving a clear picture of how factors affect the absorption, eq. (8) is useful for predicting the absorption rate and, subsequently, the amount of glycerol added to the leather by the completion of the treatment cycle.

Tensile strength

The tensile strength is one of the most important qualities of a material and strongly governs its end use.

Figure 4 presents a three-dimensional plot of the response surface of the tensile strength as a function of the glycerol concentration and time simultaneously according to the regression equation listed in Table III. It demonstrates that the tensile strength of leather increases steadily as the glycerol concentration increases. This may be attributed to glycerol functioning as a lubricant. It promotes the movement of fibers and decreases the frictional resistance of fibers when leather is subjected to a tensile force. The reduction of friction leads to a more uniform stress distribution in the stretched leather, which results in an increase in the tensile strength. Figure 4 also demonstrates that the tensile strength increases with an increase in the treatment time. This is attributable to more glycerol being added to the leather, thereby increasing the tensile strength.

Stiffness

Adequate pliability is a very important quality requirement for certain leather products, particularly garments, upholstery, and footwear. It provides comfort and a good "hand feel" to the user. The quantitative assessment of pliability or its reverse term stiffness can be based on measurements of the resistance to a small deformation by tensile stress. The resistance
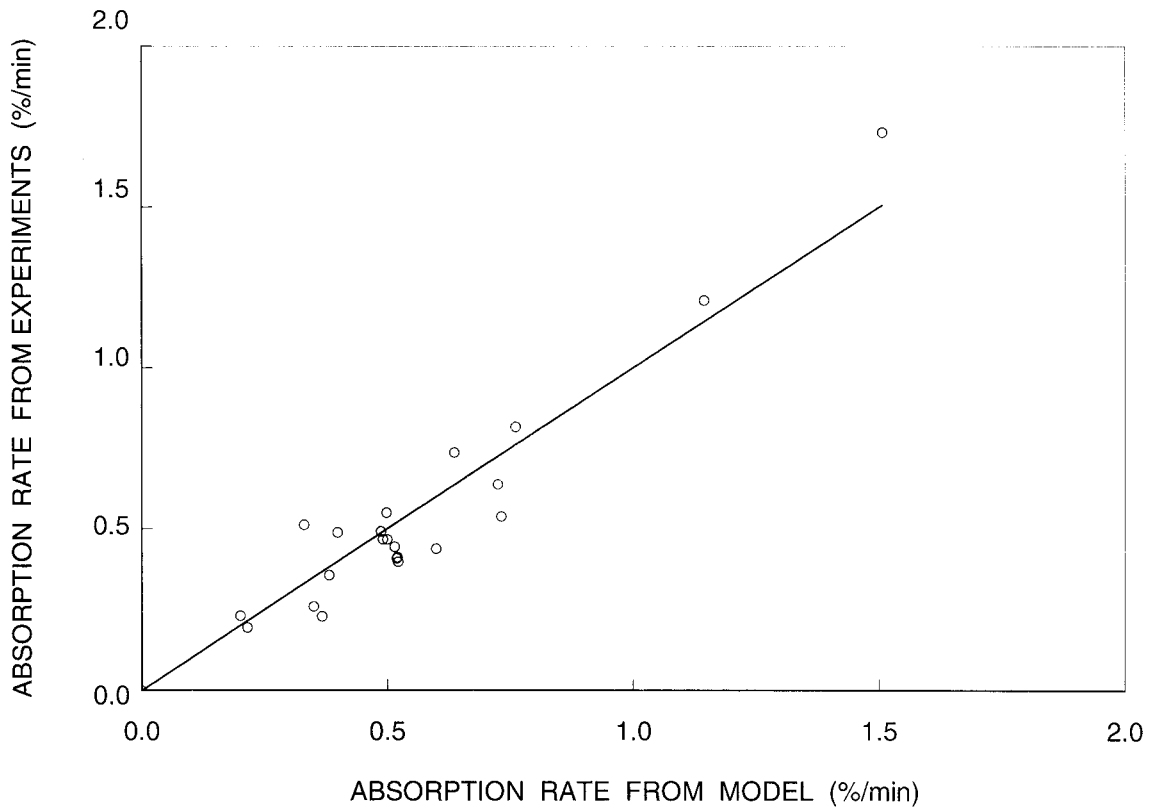
Figure 3 Absorption model.

may be quantitatively represented best by the initial slope of the load-displacement curves or the stress–strain curves in the elastic deformation region, that is, Young's modulus. It expresses the resistance of leather subjected to a small tensile deformation. It is commonly known that the higher Young's modulus is, the
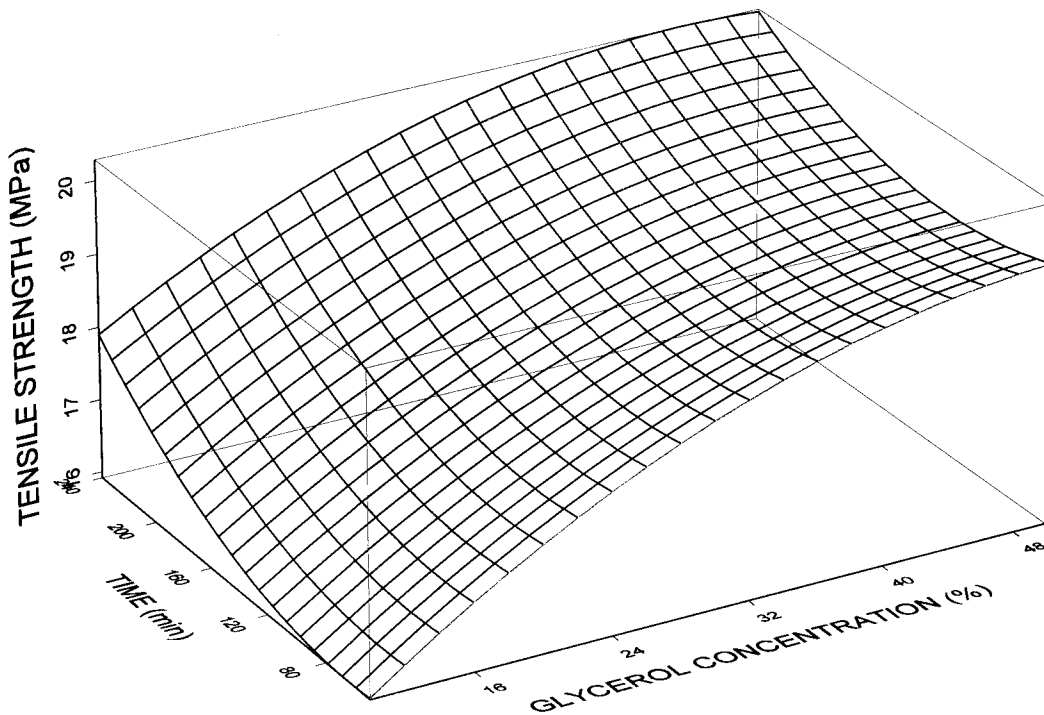

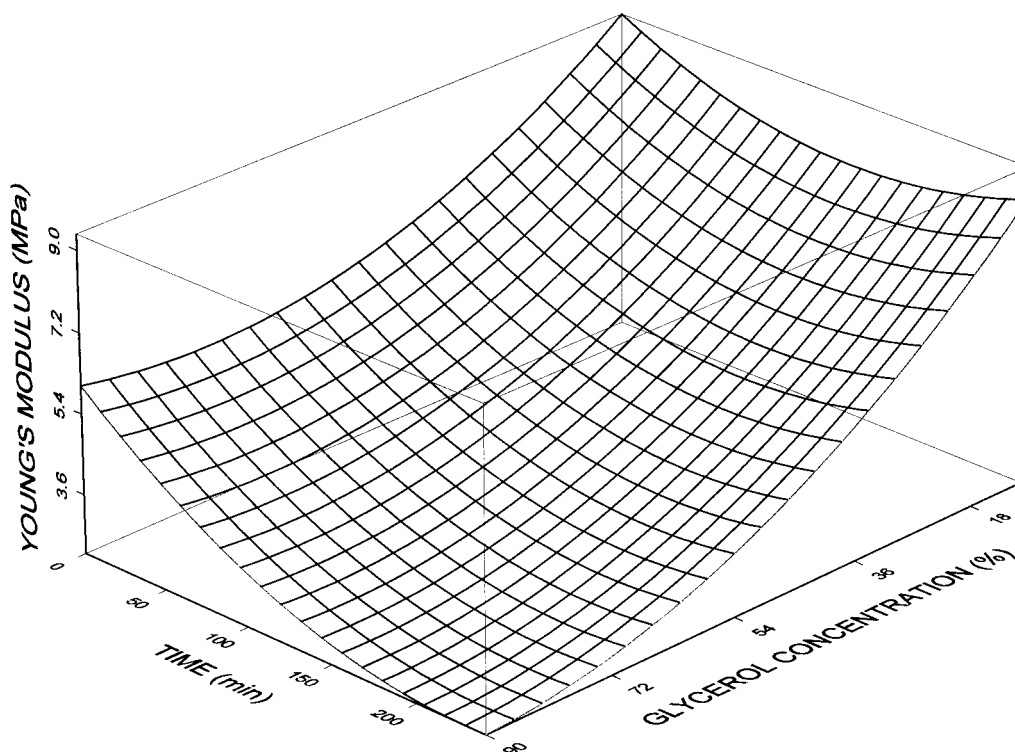**Figure 4** Tensile strength as a function of the time and glycerol concentration.

Figure 5 Young's modulus as a function of the time and glycerol concentration.

stiffer the leather is. This physical quantity has been associated with leather softness, temper, and handle.[19,20] Its reciprocal is commonly named *compliance*.[21]

The main purpose of using lubricants (fatliquors) in the leather-making processes is to provide flexibility and compliance. The significant effect of glycerol on the stiffness or pliability of leather can be seen in Figure 5. It presents a three-dimensional plot of the response surface of Young's modulus as a function of the glycerol concentration and time simultaneously according to the regression equation listed in Table III. The stiffness of leather decreases as the glycerol concentration increases. Figure 5 also shows that the stiffness increases as the treatment time increases. An increase in either the glycerol concentration or treatment time leads to the diffusion of more glycerol into the leather. Because of the lubrication function of glycerol, Young's modulus decreases as the treatment time and glycerol concentration increase.

The profound effect of glycerol on stiffness is clearly demonstrated in Figure 6. Young's modulus decreases linearly with increasing glycerol content. A linear regression analysis gave the following equation with an R^2 value of 0.88. Variance analysis showed that the p value is less than 0.001, confirming that this linear model is highly justifiable:

As shown in the previous section, the traditional method of determining the stiffness is based on measuring the slope of the initial portion of the stress–strain curve. This initial curve, however, is not always linear for most organic materials. Reports have shown the initial strain energy method may also be useful for measuring the stiffness of a polymeric material.[22] Because of the complex structure, leather is a nonlinear viscoelastic material even at a small deformation. This creates difficulties; to measure Young's modulus, one has to draw a tangent line to estimate the value, which is very time-consuming. Our previous investigation established the initial energy method for characterizing the stiffness of leather while taking into account the nonlinear viscoelasticity of leather.[9] The profound effect of glycerol on the stiffness or pliability of leather can be seen in Figure 7. It shows that the initial strain energy of leather decreases linearly as the glycerol content increases. Linear regression analysis showed the following equation with an R^2 value of 0.91, which indicates an increased effectiveness of the linear regression model in comparison with that of Young's modulus. Variance analysis showed that the p value is less than 0.001, confirming that this linear model is highly justifiable:

$$\text{Young's modulus (MPa)} = 9.20 - 0.095$$
$$\times \text{Glycerol content (\%)} \quad (9)$$

$$\text{Initial strain energy (J/cm}^3) = 5.352 - 0.0625$$
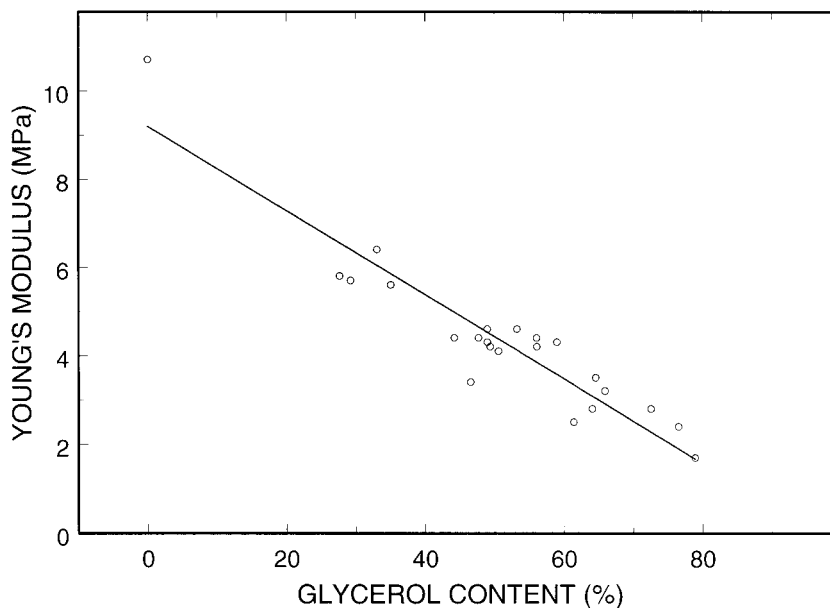$$\times \text{Glycerol content (\%)} \quad (10)$$

Figure 6 Correlation between the glycerol content and Young's modulus.

A statistical analysis showed an excellent correlation coefficient of 0.96 between these two physical quantities. Figure 8 demonstrates a close relationship between the initial strain energy and Young's modulus. Although the methods used to determine these two physical quantities are different, both may serve the same function of measuring the stiffness of leather. However, the initial strain energy method takes the nonlinear viscoelasticity of leather into account and is easier to measure and define, as mentioned earlier.

AE

For some years now in our research center, we have recognized AE as a useful method for characterizing leather properties. We have studied the sounds emit-
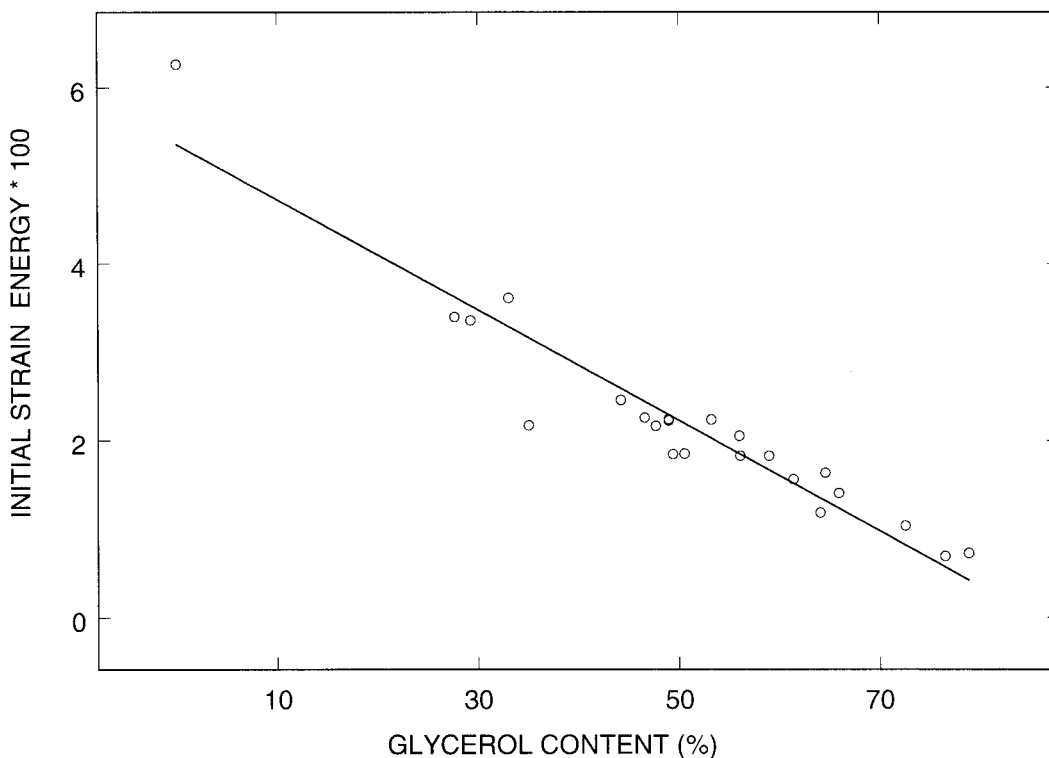

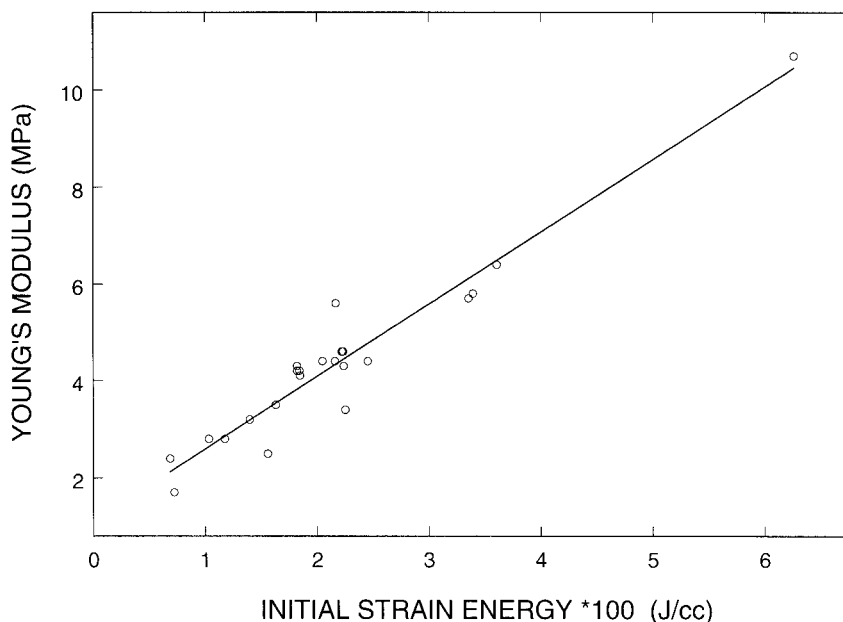**Figure 7** Correlation between the initial strain energy and glycerol content.

Figure 8 Relationship between the initial strain energy and Young's modulus.

ted by leather when it is stretched (in a tensile test) and examined the relationship between the tensile strength and AE quantities.[23,24] Our observations have shown an excellent correlation between the tensile strength of leather and the corresponding acoustic cumulative energy at break, as read from an AE analyzer. In addition to the tensile strength, one of the other important mechanical properties required for leather products, particularly those used for upholstery, is the ability to withstand tearing. Recently, an effort was made to use the AE method to gain insight into the reason for tear failure.[25] In a tongue-tear test, chrome-tanned leather samples were brought into contact with an acoustic sensor to collect various acoustic quantities. Measurements showed that the samples stronger in tear strength gave a significantly lower acoustic count. In contrast, the samples with poor tear strength generated much more frequent sound waves, that is, more acoustic counts. Our observations have also shown that harsh drying conditions or a thin corium could lead to a brittle structure, which consequently yields poor tear resistance.[26] In an AE test, this can be reflected in high acoustic counts due to frequent fiber breaking and friction associated with the brittle structure. More recently, we applied AE technology to measure the degree of *opening up* (a term used in the leather industry to express the extent of splitting and separation between collagen fibers) of the leather structure.[27] We have demonstrated that a history plot of AE counts could detect a change in the degree of opening up of the fiber structure associated with an increase in the liming time.

We are now reporting another use for AE technology in associating it with the lubrication of leather. As a natural fibrous material, leather emits sound waves induced by a sudden stress accompanied by significant fiber movement or fiber deformation, including breakage. From an analysis of emitted sound waves during the tensile tests of leather treated with various amounts of lubricants, one may gain a correlation between AE quantities and the degree of lubrication. All the reported AE data are within the ultrasonic range, 50–200 kHz, thereby preventing the problems of noise produced by the testing machine or environment. Figure 9 plots the total hits (the cumulative hits read off as the sample fractured) as a function of the glycerol content in the leather samples. The total hits decrease drastically as the glycerol content increases. The statistical analysis showed a coefficient of correlation of -0.83. The total hits of a leather sample are closely associated with the flexibility of leather. The more flexible the leather is, the fewer the acoustic hits are emitted in a tensile test.

CONCLUSIONS

This investigation has demonstrated that treating leather with glycerol solutions significantly reduces the stiffness of leather, indicating the strong lubrication function of glycerol for leather. Studies on the absorption rate of glycerol have revealed that the rate of absorption is not constant; therefore, Fick's second law of unsteady-state diffusion has been employed to derive a mathematical model for the absorption rate. The effect of temperature on the absorption rate is also included in the model by the incorporation of the Arrhenius equation into Fick's diffusion equation. The resultant model fits the experimental data very well. It
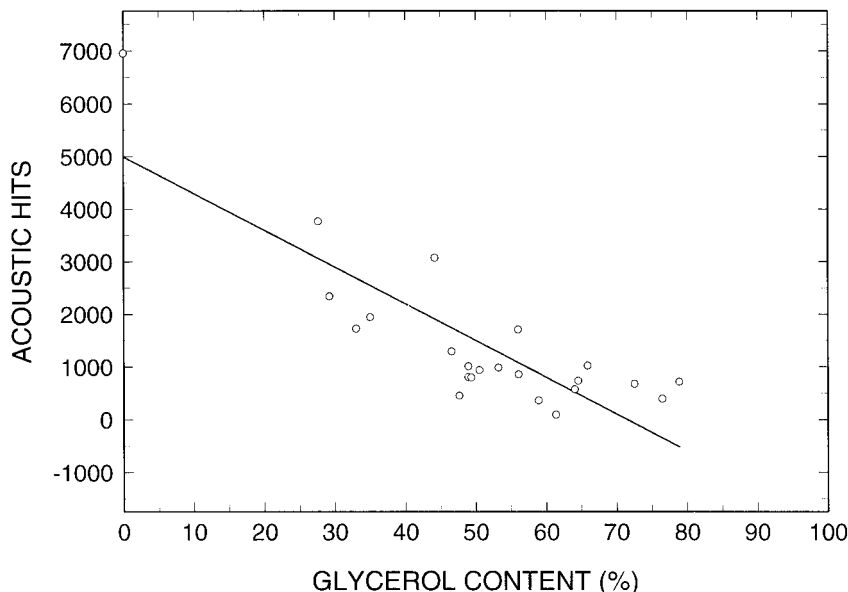
Figure 9 Correlation between the AE hits and glycerol content.

not only depicts the mechanism of absorption but also predicts the absorption rate as a function of key variables. This implies that glycerol sorption is an unsteady-state-diffusion-controlled mass-transfer process conforming to Fick's second law of diffusion.

References

1. Marmer, W. N. J Am Leather Chem Assoc 2001, 96, 88.
2. Leather Facts, 3rd ed.; New England Tanners Club: Peabody, MA, 1994; p 19.
3. Thorstensen, T. C. Practical Leather Technology, 3rd ed.; Krieger: Malabar, FL, 1985; p 190.
4. Liu, C.-K.; Latona, N. P.; Dimaio, G. L. J Am Leather Chem Assoc 2002, 97, 284.
5. Liu, C.-K.; Latona, N. P.; Dimaio, G. L. J Am Leather Chem Assoc 2002, 97, 329.
6. Kronick, P. L. J Am Leather Chem Assoc 1996, 91, 246.
7. Kronick, P. L. J Polym Sci Part B: Polym Phys 1998, 36, 805.
8. Heidemann, E. Fundamentals of Leather Manufacturing; Roether: Darmstadt, Germany, 1993; p 113.
9. Liu, C.-K.; McClintick, M. D. J Am Leather Chem Assoc 1997, 92, 157.
10. Liu, C.-K.; Latona, N. P.; Dimaio, G. L. J Am Leather Chem Assoc 2001, 96, 367.
11. Liu, C.-K.; Latona, N. P. J Mater Sci 2002, 37(18), 3827.
12. Box, G. E. P.; Hunter, J. S. Ann Math Stat 1957, 28, 195.
13. Cochran, W. G.; Cox, G. M. Experimental Designs, 2nd ed.; Wiley: New York, 1957; p 343.
14. Box, G. E. P.; Wilson, K. B. J R Stat Soc B 1951, 13, 1.
15. Montgomery, D. C. Design and Analysis of Experiments; Wiley: New York, 1978; p 334.
16. Crank, J.; Park, G. S. Diffusion in Polymers; Academic: New York, 1968; p 16.
17. Paul, D. R. In Applied Polymer Science, 2nd ed.; Tess, R. W.; Poehlein, G. W., Eds.; ACS Symposium Series 285; American Chemical Society: Washington, DC, 1985; p 257.
18. Barrer, R. M. Nature (London) 1937, 140, 106.
19. Guy, R. BLMRA J UK 1972, 15(3), 65.
20. Diebschlag, W. Das Leder, Germany 1975, 26(1), 7.
21. Morton, W. E.; Hearle, J. W. S. Physical Properties of Textile Fibers; Textile Institute: Manchester, 1978; p 272.
22. Liu, C.-K.; Brewer, J. U.S. Pat. 5,217,485 (1993).
23. Kronick, P. L.; Thayer, P. J Am Leather Chem Assoc 1989, 84, 257.
24. Liu, C.-K.; Mcclintick, M. D. J Am Leather Chem Assoc 1999, 94, 8.
25. Liu, C.-K.; Dimaio, G. L. J Am Leather Chem Assoc 2000, 95, 170.
26. Liu, C.-K.; Dimaio, G. L. J Am Leather Chem Assoc 2001, 96, 243.
27. Liu, C.-K.; Latona, N. P.; Dimaio, G. L. J Am Leather Chem Assoc 2001, 96, 367.