Effects of Dehydration Methods on the Characteristics of Fibrous Networks from Un-tanned Hides

by

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Abstract

To improve prospective markets and to secure a viable future for the hides and leather industries, it is important to develop new uses and novel biobased products from hides. We hypothesize collagen fiber networks derived from untanned hides can be utilized to prepare high performance green composites and air filters, of which both have a great market potential. Collagen fiber networks were obtained from split hides that have been processed to remove the noncollagenous materials through liming, hair removal and bating steps. This study was devoted to understand the effects of a key processing step — dehydration on the morphology and physical properties of the resultant fiber networks, which will be the starting material for constructing air filters and green composites. Five dehydration methods were investigated and observation showed solvent- and freeze- drying yielded the lowest apparent density indicating a higher degree of separation in the fibrous networks that will be favorable for further processing into useful products. ESEM observations also confirmed the fibers were more separated from solvent- and freeze-drying than those from the other dehydration methods. Mechanical testing showed the lower apparent density led to lower tensile strength, greater elongation at break, lower Young's modulus, and higher toughness. The results of this research could be useful to the production of high quality fibrous products such as high efficiency air filters or fiber-reinforced green composites.

Resumen

Para mejorar los mercados de futuros y asegurar un futuro viable para las industrias de la piel y el cuero, es importante desarrollar nuevos usos y nuevos productos de base biológica a partir de las pieles. Planteamos la hipótesis de las redes de fibras de colágeno derivados de pieles sin curtir se puede utilizar para preparar compuestos ecológicos de alto rendimiento y filtros de aire, de los cuales ambos dos tienen un gran potencial de mercado. Las redes de fibras de colágeno se obtuvieron a partir de cueros divididos que han sido procesados para eliminar los materiales no colágenicos a través del pelambre, la eliminación del pelo y el proceso de rendido. Este estudio se dedica a comprender los efectos de un paso clave de procesamiento: la deshidratación en la morfología y las propiedades físicas de las redes de fibra resultante, que será el material de partida para la construcción de filtros de aire y los compuestos verdes. Cinco métodos de deshidratación fueron investigados y la observación mostró que el secado con solvente y por congelación resulta en la menor densidad aparente, que indica un mayor grado de separación de las redes de fibra lo que será favorable para su posterior transformación en productos útiles. Observaciones ESEM también confirmó que las fibras se separan más secados con solventes y por congelación que los de los otros métodos de deshidratación. Las pruebas mecánicas demostraron la menor densidad aparente llevó a una menor resistencia a la tracción, mayor alargamiento a la rotura, menor módulo de Young y una mayor dureza. Los resultados de esta investigación podrían ser útiles para la producción de productos de alta calidad de fibra, tales como filtros de aire de alta eficiencia o de compuestos verdes de fibras reforzadas.

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INTRODUCTION

The hides and leather industry has been facing a serious challenge in the disposal of solid wastes such as trimmings and lime-splits.[1,2] Most of these wastes are transported out of processing plants for landfills, not only incurring the expense of transportation but also creating environmental issues. One strategy to solve this problem is to convert these wastes into useful products such as air filters and green composites. Therefore research is needed to investigate the preparation of fibrous materials having adequate mechanical properties and optimal degree of fiber separation from waste hides. Thus, this research not only helps to develop new uses and novel biobased products from unwanted tannery waste but also could improve prospective markets and secure a viable future for the American hides and leather industries.

In recent years, increased emphasis has been placed on developing environmentally friendly biodegradable composites with the goal of protecting the environment.[3] Most petroleum-based polymer composites are difficult to recycle or incur substantial cost for disposal. Green composites use agricultural-based polymers and biodegradable bio-based fillers or fibers that are renewable and degradable.[4-6] Green composites can be used in nondurable applications, short-term products, or indoor applications. The most reported biodegradable polymer for preparing green composites is poly(lactic acid), PLA. It is a hydrophobic polymer prepared from renewable agriculture-based feedstocks, which are fermented to lactic acid, and then polymerized.[3] PLA is biodegradable in soil, compost or water, and the degradation products of PLA are non-toxic to the environment. The use of renewable and biodegradable fillers is desirable to provide cost-competitive polymer composites. Recently, sugar beet pulp, a coproduct of sugar refining, was blended with PLA to reduce the cost of raw materials.[7,8] Besides fillers, natural fibers were also blended with PLA to reinforce the mechanical strength of composites. It was reported that ramie/PLA biodegradable composites that were molded resulted in a fairly high tensile and bending strength as well as modulus values compared to other biodegradable molded composites.[9] Processing raw materials with consistent dimensions and properties that are comprised of natural fibers is probably the main challenge for preparing fiber-reinforced green composites.

Taylor et al. investigated the feasibility of preparing composites using gelatin, extracted from leather waste, as the matrix, and adding some fillers such as polyvinyl alcohol to enhance the composites.[10] The hides and leather program at the Eastern Regional Research Center (ERRC) recently started a new 5-year research project developing novel bio-based composite materials. The new composite will consist of a significant amount of collagen fibers thereby greatly improving the mechanical properties of resultant composites, which will have useful properties, such as high strength and stiffness. The new composites will be evaluated for their potential use in a variety of applications such as furniture, automobile dashboards, and construction material for home doors and walls.

Collagen fibrous materials have long been used in medical applications in sutures, artificial skin and tissue engineering.[11] These applications have high profit margins, but the markets are limited. An air filter is a device composed of fibrous materials that remove solid particulates such as dust, pollen, mold, and bacteria from the air. Worldwide market for air filters and filtration equipment was projected to exceed $7.1 billion in 2010, as stated in a report published by Global Industry Analysts (March 2008). In the current market, air filters are mostly made of synthetic polymeric nonwovens. There is a great interest in developing new air filters from renewable sources because of environmental concerns. Collagen fibers if well separated into single collagen fibrils, will be an ideal starting material for air filters. It has been reported that fiber bundles (20-200 μm) of leather are comprised of very fine element fibers (10 μm), which can further be divided into even finer fibrils (0.01-0.5 μm).[12,13] Because the fibrils (average diameter 150 nm) are much smaller than regular fibers (average diameter 10 μm or 10000 nm), a fabric made from them has more pores per square inch, allowing for higher dirt-holding capacity and lower pressure drop when compared to regular filter fabrics. Smaller diameter fibers will produce more uniform pore size distributions and have a greater surface area, improving a filter's overall quality and ability to capture and retain particles. As mentioned before, the collagen fibers are comprised of fibril bundles, several hundred micrometers in diameter, containing fibrils with an average diameter of 150 nm.[13] To develop air filters using collagen fibrils, the technical challenge will be the separation of collagen fibers into collagen fibrils, which are held together by glue-like noncollagenous proteins. Two methods known for achieving this goal have been demonstrated. Collagen dispersions, produced from fibrils recovered from milled bovine collagen, have shown promise in environmental remediation, in applications as settling aids, filtration aids, fractionation media, oil drop stabilizers, and water purification aids.[14] Although the initial processing involves a ball mill, the actual operation is more of an unraveling of the fiber to expose the fibrils, which have nanoscale dimensions. Research also has been done for the preparation of collagen nanofibers from collagen solutions by an electrospinning process.[15,16] Electrospinning is a fiber formation process that uses an electric field to spin fibers from collagen solutions to yield fiber diameters ranging from several microns down to 100 nm or less. Most recently, electrospinning was exploited to produce tissue-engineering scaffolds composed of collagen nanofibers that were spun from solutions of 5 wt. % calfskin type I collagen in 85 wt. % 1,1,1,3,3,3-Hexafluoro-2-propanol (HFP).[16] Both ball milling and electrospinning methods are far too expensive for the production of air filters, and consequently a better method for preparing collagen fibrils needs to be developed. In previous research projects, Brown et al. have investigated the mechanical effects of ultrasonic treatment on bovine hide collagen.[12] Scanning electron micrographs showed that low frequency, high power ultrasound (20 kHz) appeared to unravel the 50 - 100 nm fibrils, seen in ball-milled collagen, into smaller diameter fibrils. Although these smaller fibrils are more susceptible to attack by collagenase, the individual collagen molecules remained intact as demonstrated by SDS PAGE. Therefore ultrasonic treatment or a combination of ultrasonic treatment with results from predecessor research projects, using proteolytic enzymes, may be an economical alternative to separate the collagen fibers into fibrils.[17]

Dehydration is a process to remove water from products and by which fibrous materials can acquire their final texture, consistency and flexibility, and is one of the most important operations in the manufacturing of collagen fibrous products. Most methods of dehydration involve convective and conductive processes such as air drying and vacuum drying. Radiation drying, including radio frequency drying and microwave drying, has not gained popularity due to a high capital cost. The most common phenomenon involved in the drying process is shrinkage. The shrinkage of hydrophilic materials after removal of water is a well known behavior. During water removal, the space originally occupied by water is slowly squeezed and decreased driven by an internal pressure release causing the materials to shrink. There are various drying methods currently being used today in manufacturing. To make quality fibrous products, it is imperative to understand the effects of different drying methods on the physical characteristics of these fibrous products. This study was devoted to understand the effects of dehydration on the morphology and physical properties of resultant fiber networks, which will be the starting materials for constructing green composites and air filters. Five commonly used dehydration methods were investigated, including air-, vacuum-, freeze and vacuum-, and freeze drying. The results of this research could lead to the production of high quality fibrous products such as high efficiency air filters or fiber-reinforced green composites.

Experimental

Materials and Procedures

Bovine hides were processed through the bating step and then washed. The bated hides were then split to approximately 0.48 cm using a Fortuna SAS splitter (Stuttgart, Germany) in order to remove the excess flesh. Samples, 7.62- x 1.27-cm, were cut out parallel to the backbone as described in ASTM D2813. The samples were then either air-dried, vacuum-dried, frozen then vacuum-dried, solvent-dried, or freeze-dried (lyophilized). The air-dried samples were placed in an open petri dish and set in a fume hood to dry at room temperature. The frozen samples were placed in a petri dish in a refrigerator freezer overnight and then placed in individual test tubes (1.6 cm in diameter, 15 cm long) along with the vacuum-dried only samples into a vacuum oven (Thermo-Scientific Model 3608-5, Dubuque, IA) set at room temperature (~21°C) and -98 kPa pressure for 24 h. The solvent-dried samples were placed in acetone, and the acetone was replaced periodically until the specific gravity of the float was the same as that of acetone, and no further water could be removed. Freeze-drying (also known as lyophilization) is a dehydration process by freezing the material and then reducing the surrounding pressure to allow the frozen water in the material to sublime directly from the solid phase to the gas phase. The freeze-dried samples were placed individually in test tubes (1.6 cm in diameter x 15 cm long) and then distilled water was added so the water level was approximately 2.5 cm above the sample. The test tubes were covered with filter paper, secured with a rubber band and then partially immersed in dry ice and acetone to freeze the water surrounding the samples. Once the water in all of the tubes was completely frozen, the test tubes were placed in a flask and then connected to a freeze drier (Labconco, Model number 7740021, Kansas City, MO) until the samples were dry.

Mechanical Property Evaluations

Apparent density was measured for each of the dehydrated samples, which is defined as the weight per unit volume of a material including voids inherent in the material as tested. The final weight of the dehydrated samples was measured with an Adventure Pro scale (Ohaus Corp., Pine Brook, NJ). A standard ruler and caliper were used to measure the length, width and thickness. Mechanical property measurements included tensile strength, elongation at break, Young's modulus and toughness. Tensile strength is the stress in tension that is required to fracture the samples. The percentage of the original sample length to the sample length at break is defined as the Elongation. Young's Modulus is a measure of the stiffness of a material and is determined from a tangent line at the beginning of the stress-strain curve. Toughness is determined by the energy needed to fracture the samples. These properties were measured with a grip separation of 3.5 cm and a 5 cm/min strain rate (crosshead speed). An Insight 5 mechanical property tester and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on five samples to obtain an average value.

Acoustic Emission (AE)

To achieve a better understanding of stress-strain behavior for a fibrous material in this study, we simultaneously performed AE measurements and tensile stress-strain tests for the samples previously described. Hides are a fibrous material and as the hides are squeezed, torn or stretched by an external force, it is accompanied by a rapid movement, relocation, or breaking of structural elements such as fibrils, fibers and/or fiber bundles. As a result, sound waves are produced that can be detected by an acoustic transducer and converted into electronic signals. When the transducer detects a signal over a certain threshold (40 dB), an AE event is recorded, and this AE event is then translated by an AE analyzer as a "hit." A small piezoelectric transducer was clipped against the sample and this transducer resonates at 150 kHz (Model R15, Physical Acoustics Corp., Princeton Junction, NJ). AE signals emanating from the samples were amplified in a 40 dB preamplifier and then processed into an 18 bit 40 x 10^6 samples/sec analog to digital PCI board and analyzed using the software AE WIN (Physical Acoustics Corp, Princeton Jct., NJ). This AE system has been used for studying the deformation and fracture mechanisms of fabrics, leather and bio-composites, in which the typical test samples are dumbbell or rectangular in shape with a thickness less than 3 mm.

Microscopic observations

A field-emission environmental scanning electron microscope (ESEM) was used to compare the structural difference between fibrous materials prepared with various dehydration methods. The ESEM is advantageous over conventional scanning electron microscopy (SEM) because a relatively high vacuum in the specimen chamber is not needed, which prevents atmospheric interference with primary or secondary electrons; an ESEM may be operated with a poor vacuum (up to 10 Torr of vapor pressure, or one seventy-sixth of an atmosphere) in the specimen chamber. The ESEM was operated at low vacuum (0.3 Torr) with the voltage set at 15 kV, spot size 5.0 and working distance of approximately 10 mm. Samples were uncoated, thus preserving the original characteristics of the samples.

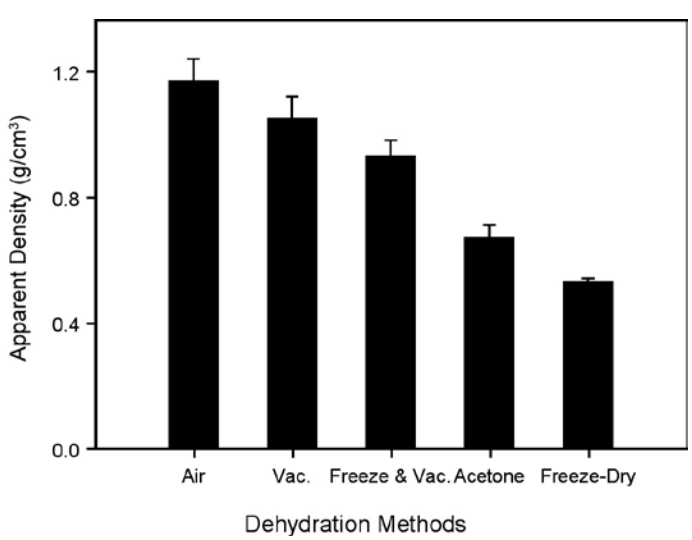


Figure 1. Apparent density vs. dehydration methods

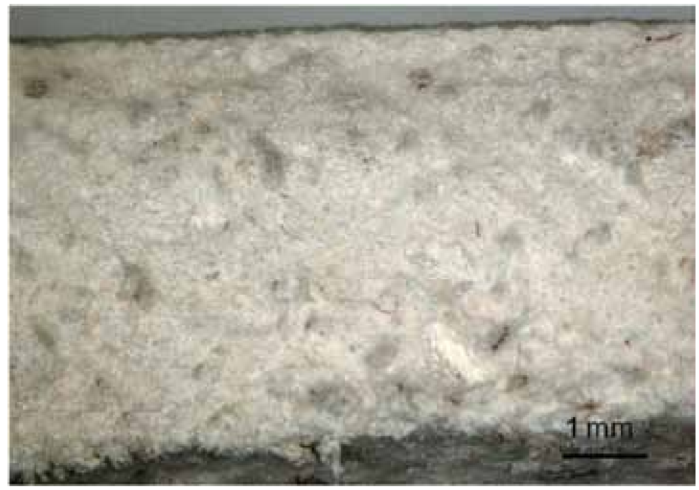


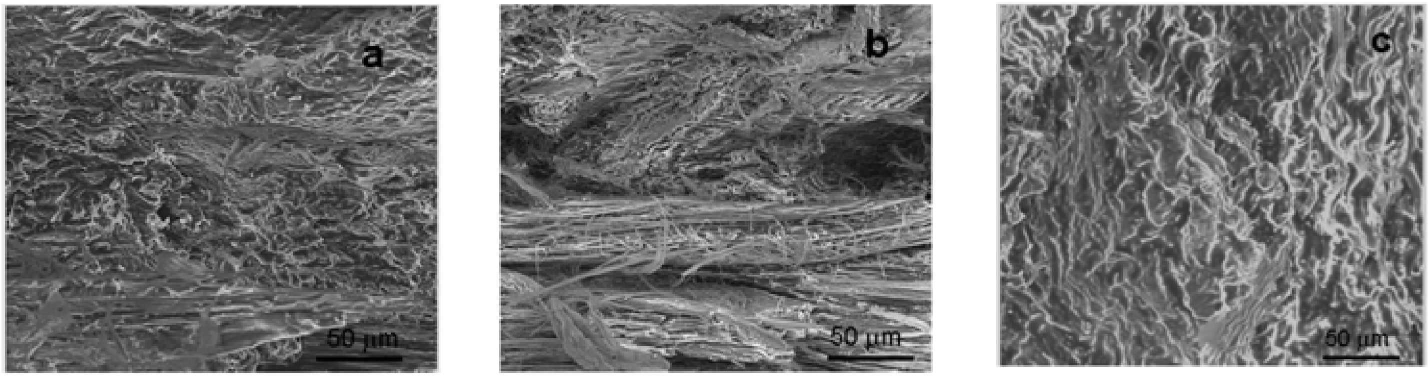
Figure 2. Stereo-micrograph of cross-section of a fibrous sample after freeze-drying

RESULTS AND DISCUSSION

The degree of fiber separation is one of the most important properties in a fibrous structure, which commonly is determined by measuring its apparent density. This data provides insight into the effect of dehydration methods on the fibrous structure. For the sake of achieving better fiber separation, obviously the lower the apparent density the more desirable the fibrous structure will be. Figure 1 demonstrates that the freeze-dried samples yielded the lowest apparent density, indicating this dehydration method provided the most open structure compared to the other four methods. Leather's typical apparent density ranges from 0.60 to 0.90 g/cm^3. Apparent densities measured from both solvent- and freeze-dried samples are below this range, implying those fibrous materials have a more open fiber structure than regular leather. As illustrated in Figure 2, a stereo-micrograph of a cross-sectional view of a freeze-dried sample shows a felt-like fibrous structure with very fine fibers interwoven together.

The dehydration methods greatly affect the morphology of the fibrous material as demonstrated in ESEM micrographs in Figure 3. The samples dried by air (Figure 3a) show a very compact structure, there is no individual fiber to be observed. On the other hand, samples dried by other methods such as vacuum (b), freeze/vacuum (c), solvent (d), freeze-drying (e) all show a certain degree of fiber separation, particularly the last two methods solvent and freeze-drying.

Figure 4 demonstrates a fibrous structure from a stereo-microscopic observation. The structure does not show any fusion. The fiber bundles are well separated from each other, and therefore result in a low apparent density.



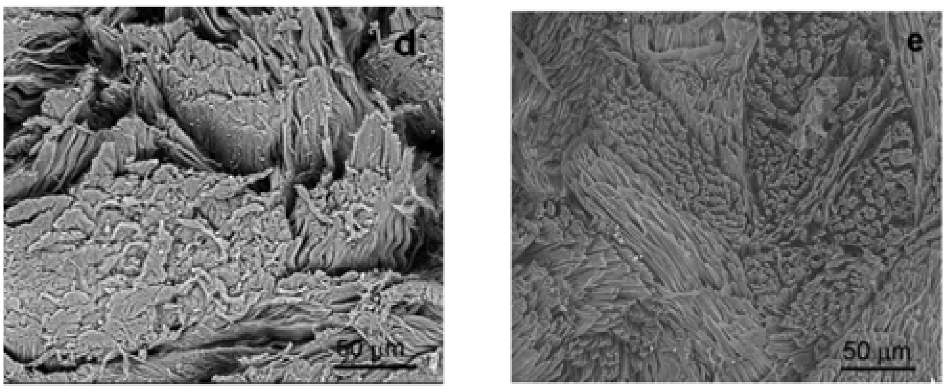


Figure 3. Micrographs show the fibrous structure (a) air- (b) vacuum- (c) freeze/vacuum- (d), solvent-, and (e) freeze-dried samples.

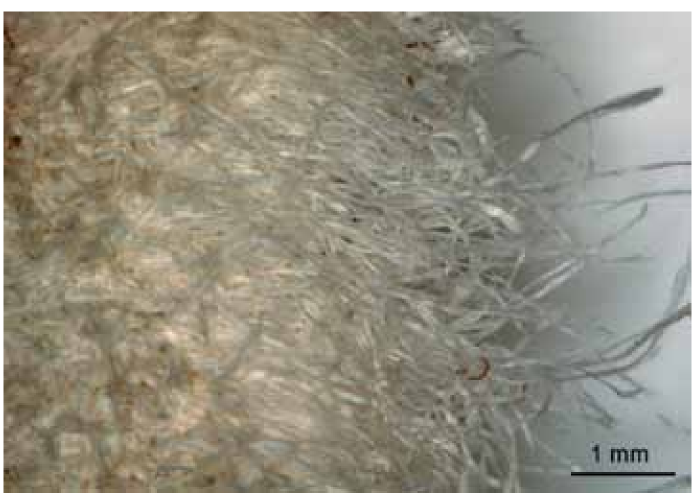


Figure 4. Stereo-micrograph of a fibrous sample after freeze-drying.

Mechanical Properties

Tensile strength is one of the most important mechanical properties of a material. It is an indication of the maximum tensile stress a material can sustain until fracture. Elongation is another physical property closely associated with a fibrous materials quality. As the name indicates, elongation refers to the ability of a material to lengthen, or stretch, when tensile stress is applied to it and indicates the maximum extent to which the material can be stretched until fracture. Figure 5 displays the resultant mechanical properties of samples dried with various dehydration methods. Measurements show air-dried samples yield the highest tensile strength, however lowest elongation at break. Freeze-dried samples, on the other hand, show the lowest tensile strength and highest elongation at break. Furthermore, the close relationship is clearly demonstrated in Figure 6, which reveals the denser structure produces the better tensile strength. The higher apparent density indicates increased concentration of load-bearing collagen fibers, thereby yielding greater tensile strength.

Figure 7a presents the effects of dehydration methods on the stiffness of the samples. Stiffness is quantified by measuring the Young's modulus, which is the initial slope of the stress-strain curve. As expected the air-dried samples yielded the highest stiffness, whereas the freeze-died samples produced the softest samples. Besides stiffness, toughness is also an important mechanical property for fibrous materials. Toughness has been described in a previous report as a quantity associated with the product of tensile strength and elongation.[18] Good toughness reflects a superior balance of strength and flexibility with good deformability, thereby minimizing the stress concentration and yielding a better tearing strength. Toughness was characterized by measuring the energy needed to fracture a sample, which is obtained by integrating the area under the stress-strain curve. As shown in Figure 7b, the solvent-dried and freeze-dried samples have

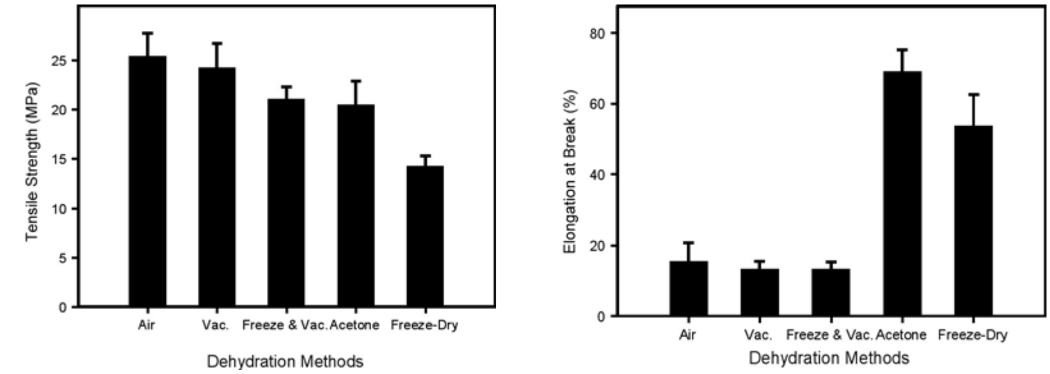


Figure 5. (a) Tensile strength; (b) elongation

better toughness values than those of the other dehydration methods. This is ascribed to the high degree of fiber separation in the fibrous structure produced from these dehydration methods. This leads to a more even stress sharing and results in a higher energy required to fracture the samples.

AE Studies

Acoustic emission (AE) has been used for characterizing the properties of fibrous materials such as wool fabric, leather, and fiber-reinforced composites.[19-23] In the present study, we performed the AE tests simultaneously with the tensile tests because we believe AE results may reveal some structural information that the other methods cannot offer. Figure 8 displays the chronological course of the test, demonstrating the hits rate vs. time profiles during tensile testing of the samples. As demonstrated in Figure 8, samples a, b, and c produce twin peaks in the hits rate (hits/sec) vs. time (sec) curve. The first peak signifies a partially fractured sample; with some unbroken fiber bundles still holding the sample together. The second peak shown on the figure is probably due to the subsequent breakage of those remaining fiber bundles. In contrast, the solvent- and freeze-dry samples as shown in Figure 8d and 8e yield only one major peak. Twin-peaks as shown in Figure 8a-c imply the existence of non-uniform stress sharing and a premature fracture in the structure. In contrast, a single peak as shown in Figure 8d-e, indicates that the fibrous structure uniformly shares the tensile stress without premature breakage or fracture. A fibrous structure is a necessity for the energetic acoustic activities demonstrated in Figures 8. In other words, the acoustic hits profiles demonstrated previously are a unique phenomenon for a fibrous structure. These samples consist of collagen fibers with a very complex structure, a network of interwoven fiber bundles with large spaces unevenly distributed among them. Fiber movements produce the mechanical waves when a fibrous material is stressed. In contrast, a non-fibrous structure

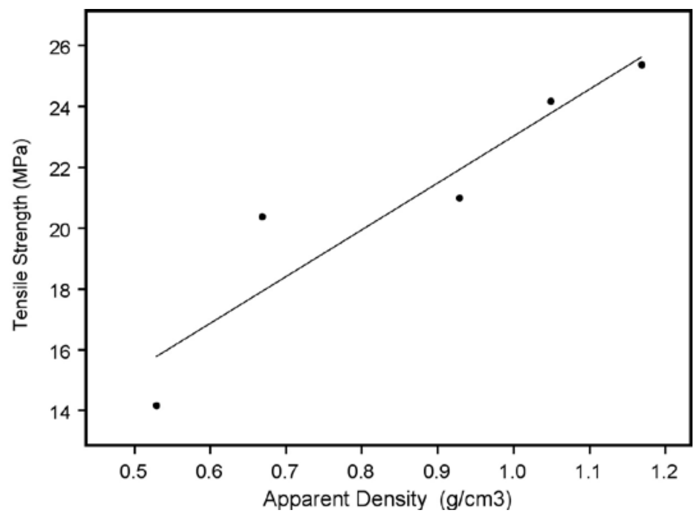


Figure 6. Tensile strength vs. apparent density

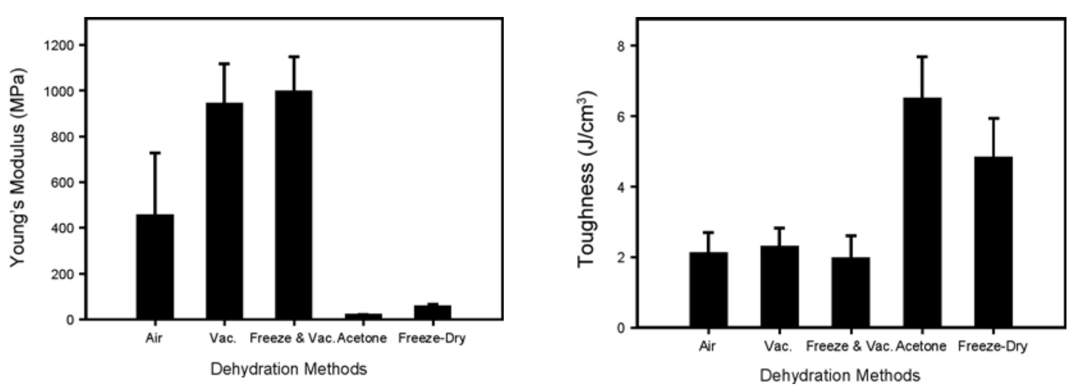


Figure 7. (a)Young's modulus; (b) toughness

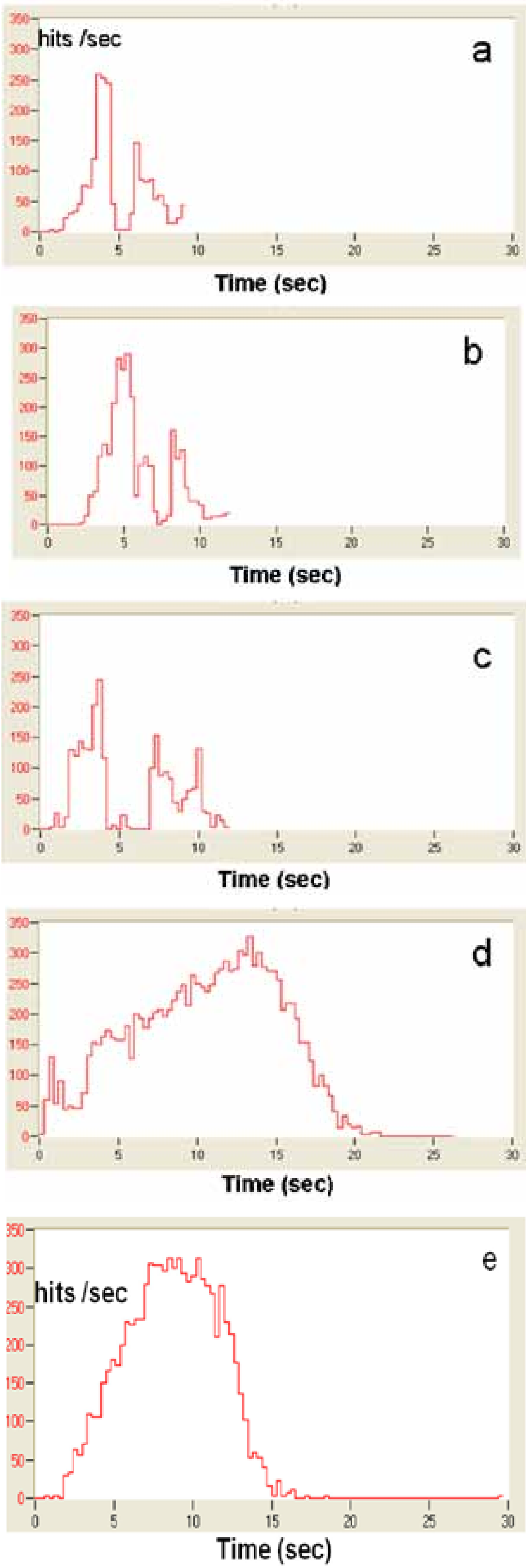


Figure 8. Hit rate vs. time

such as a plastic film (for example, polyester) will not be capable of emitting sound when it is stretched until it is totally fractured. As demonstrated in Figure 9, the solvent- and freeze-dried samples generate more AE hits compared to the other three dehydrated methods. This is ascribed to the more pronounced fibrous structure produced by either the solvent- or freeze dried methods, which can be demonstrated again in Figure 3 d-e. Furthermore, the close relationship between AE hits and toughness is clearly demonstrated in Figure 10. A higher AE hits value indicates better fiber separation, which leads to a more even stress sharing and results in an increase in toughness of the samples.

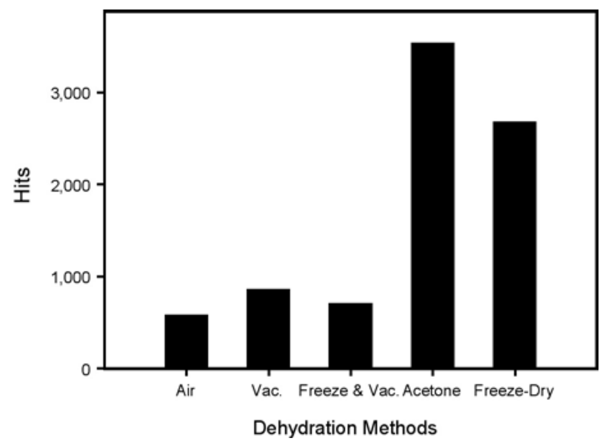


Figure 9. AE hits

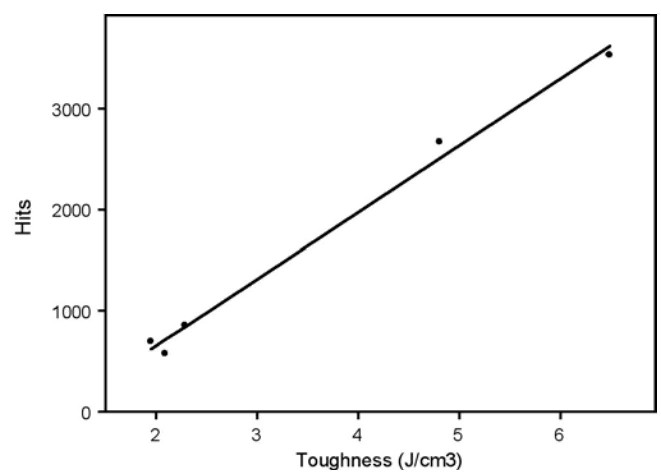


Figure 10. Hits vs. toughness

Conclusions

This study was devoted to understand the effects of dehydration on the morphology and physical properties of the fiber networks derived from un-tanned hide, which will be the starting material for constructing air filters and green composites. Both solvent and freeze-dry methods yield a highly open structure, in which the fibers are well separated from each other. Such fibrous structures are favorable for constructing fibrous products such as air filters and fiber reinforced green composites. Tensile tests showed a correlation between apparent density and tensile strength. We plan to adjust liming and bating conditions to achieve an optimal fibrous structure (nanofibrous network). The results of this research could lead to the production of high quality fibrous products such as high efficiency air filters or fiber-reinforced green composites.

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