Preparations of Nonwoven and Green Composites from Collagen Fibrous Networks

by

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Abstract

The disposal of solid wastes, such as trimmings and splits generated in various manufacturing processes in a tannery is a serious challenge to the hides and leather industries. Most of these wastes are transported out of processing plants for landfills, not only incurring the expense of transportation, but also creating environmental issues. Our effort to address these new challenges is to develop new uses and novel biobased products from solid wastes to improve prospective markets for the hides and leather industries. We hypothesize collagen fiber networks derived from solid fibrous wastes 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 the hair removal, liming, and bating steps. Earlier studies were devoted to understand the effects of dehydration on the resultant fiber networks and the effects of processing steps such as bating, pickling and crosslinking treatments on the morphology and physical properties of the fiber networks derived from un-tanned hides, which will be the starting material for constructing air filters and green composites. This study focuses on preparations of nonwoven and green composites derived from fiber networks. Non-woven sheets were prepared using paper-making technology. They were then used as reinforced components to make composites that use gelatin as the matrix. Mechanical properties were evaluated for the resultant composites; results showed that the fiber sizes and gelatin content have significant effects on the properties of the resultant nonwon and composites.

Introduction

The U.S. hides and leather industries are facing many new challenges in the wake of globalization of production and markets for raw animal hides and finished leather products. These challenges include meeting environmental imperatives and improving utilization of waste. We have addressed these new challenges by developing new uses and novel biobased products from the solid fibrous waste generated from tanneries. We hypothesize collagen fiber networks derived from solid fibrous wastes can be utilized in making high performance green composites and air filters, of which both have a great market potential. Green composites are the composites made from bio-based polymers and fibers or fillers that are renewable and degradable.[1] Earlier studies were devoted to understand the effects of dehydration on the morphology and physical properties of the fiber networks derived from un-tanned hides, which will be the starting material for constructing air filters and green composites.[1] 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. 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 from comparisons showed that samples frozen and then followed by vacuum drying offer many advantages over those from the other dehydration methods in terms of economic and open fibrous structure information.

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Manuscript received September 22, 2013, accepted for publication October 10, 2013.

Further study investigated the use of crosslinking and other treatments to improve the integrity of fibrous structures that offer better stability and mechanical properties.[2] Crosslinking is a process to apply a chemical agent - crosslinker to bridge molecular chains, thereby providing stability and improved physical properties to collagen matrices.[3] There are various crosslinking treatments currently being used today for collagen materials. These include ultraviolet light[4], dehydrothermal treatment[5], chemical agents such as glutaraldehyde[6], and enzymatic crosslinking by transglutaminase[7]. Two of the most common methods, i.e. transglutaminase and glutaraldehyde, were used to treat the collagen fiber networks with the purpose of stabilizing the structure and improving the physical properties. Results showed that glutaraldehyde treatment yielded a highly open structure, in which the fibers are well separated from each other. This could be attributed to the action of acids during the pickling step. This study focuses on preparations of nonwoven and green composites derived from fiber networks. To develop the technologies for new products, pieces of limed hides were neutralized, completely dried and then ground in a Wiley Mill using a 1 mm, 2 mm or 4 mm screen size. Nonwoven sheets were prepared using paper-making technology. They were then used as reinforced components to make composites that use gelatin as the matrix.

EXPERIMENTAL

Materials and Procedures

Two types of samples were used in this research. One was un-tanned bovine hides that had been dehaired and limed as described in an earlier report.[2] The other sample was a dried split, as shown in Figure 1a, obtained from a vegetable tannery, which has been tanned with vegetable tannins (vegtan). Pieces of limed hides (LH) were neutralized to approximately pH 7 using 0.5M acetic acid. The LH were cut into approximately 2.5 to 5.5 cm^2 pieces and air dried in a fume hood. Once all of the LH pieces were completely dried they were ground in a Wiley Mill using a 1mm, 2 mm or 4 mm screen. The vegtan pieces were cut up into approximately 2.5 to 5.5 cm^2 pieces, or the materials could be fibrous strips obtained after the shaving process (Figure 1b). They were then also ground into various fiber sizes using a Wiley Mill as described before. After the pieces were ground up they were stored in plastic bags (Figure 1c).

The nonwoven sheets were made with a papermaking kit as shown in Figure 1d (Wooden Deckle Paper Making Kits and Supplies, Twin Lakes, WI). Two 100-ml beakers were filled full of the powder or added between 30 and 50 g of the fibers in a 2-L beaker and filled the 2-L beaker with 1-L deionized (DI) water. The vegtan fibers were then neutralized to approximately pH 7 using 4% sodium hydroxide (NaOH). The fibers were soaked overnight on a stirring plate at room

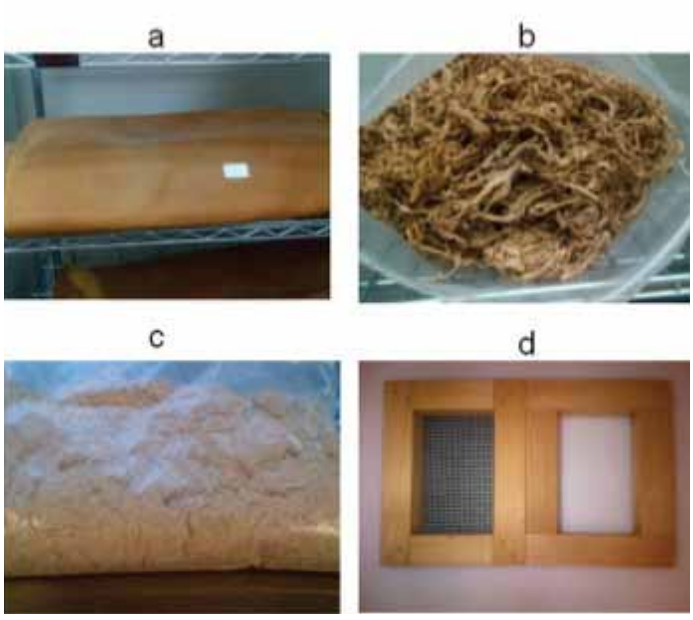

Figure 1. Vegtan split (a), strips of vegtan split (b), fibers after Wiley Mill grinding (c), and paper making kit (d).

temperature. The next day the fibers and DI water were poured in to a 8 ¾ x 9 ¼ x 4 ½ inch deep pan. Two more Liters of DI water were added into the pan, then wearing gloves, we swirled the water and the fibers to bring the fibers up to the surface. Then taking the mold and deckle, as shown in Figure 1d, the deckle was placed over the mold, holding firmly, and both were submerged under the water and fibers. Then the deckle and mold were gently brought up evenly out of the water. It was held level till the fibers were all in place and then tilted back and forth to get as much water out. The mold was removed and the 2- x 3-inch deckle was then placed over the couching sheet (reusable kitchen cloth sheet), pressed down and rocked back and forth and then lifted up and the non-woven or the fibrous network should stick to the couching sheet. The process was repeated till the couching sheet was full, at which time another couching sheet was placed over the nonwoven sheets and the process was repeated until the fibers remaining in the water did not make a uniform sheet.

Gelatin films were prepared to test the mechanical properties. Based on 50 ml DI water, 2, 5, 10, 15 and 20% porcine gelatin samples (Sigma ~300 bloom, Type A) were added into different beakers and heated to 60°C on a hot plate, stirred and then degassed in a vacuum oven at approximately 60°C until the gelatin showed relatively no bubbles. Films were then immediately cast from the gelatin solution, using approximately 10 g, into Petri dishes that were placed in a fume hood to dry.

Composites

To make the composites, the nonwoven sheets were put in a Petri dish. For the limed samples, in separate beakers, the appropriate amount of gelatin and water was added, heated to

60°C on a hot plate, placed into a vacuum oven at ~60°C and degassed and then ~ 10 g of the gelatin mixture was poured into a petri dish over the nonwoven sheet, making sure it was wet from the gelatin. The same procedures were followed for preparing the vegtan composites.

Mechanical Property Evaluations

Mechanical property measurements included tensile strength, elongation, Young's modulus and toughness. Tensile strength is the stress in tension that is required to fracture the samples. Toughness is calculated from the energy needed to fracture the samples. The vegtan nonwoven sheets were cut to 1 cm wide and tested using a 4-cm gage length because the strips were tearing when they were cut 5 mm wide. The limed nonwovens and all of the composites were cut approximately 5 mm wide and used a 2.5 cm gage length. All samples were tested using a 50 mm/min crosshead speed. The tests were done at approximately 20°C and 50% RH. An Insight-5 test frame and Testworks-4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on a minimum of five samples to obtain an average value.

Acoustic Emission (AE)

AE measurements were simultaneously performed with the tensile stress-strain tests for the samples previously described to achieve a better understanding of the stress-strain behavior for fibrous materials in this study. When a fibrous material is 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 catches 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 processed into an 18 bit 40 x 10^6 samples/sec analog to digital PCI board and analyzed using the software AE WIN. This AE system has been used for studying the deformation and fracture mechanisms of fabrics, leather and green composites, in which the typical test samples were dumbbell or rectangular in shape with a thickness less than 3 mm.

Microscopic Observations

A scanning electron microscope (SEM) was used to compare the structural difference between the different fibrous materials prepared. The samples were freeze fractured and glued to specimen holders using Duco cement. They were sputter-coated twice for 90 seconds with a thin layer of gold using a Scancoat Six Sputter coater. Images were collected using a Model JSM 840A scanning electron microscope (JEOL USA, Peabody, MA), integrated with a model Imix 1 digital image workstation (Princeton Gamma-Tech, Princeton, NJ), and operated in the secondary electron imaging mode.

Results and Discussion

The resultant nonwoven sheets are shown in Figure 2: (a) nonwoven made from limed split fibers, (b) composite of limed split fibers/gelatin, (c) nonwoven made from vegtan fibers, and (d) composite of vegtan fibers/gelatin. Observations showed that both nonwoven and composites from limed split fibers are much stiffer than vegtan fibers. It is also interesting to note that composites of vegtan fibers show a dark brown color. It appears that for some reasons that when vegtan fibers were mixed with gelatin, the tone of brown color of vegtan was greatly enhanced.

Figure 3 shows the morphology of the fibrous structure as shown in the SEM cross-sectional micrographs for the air dried samples: (a) nonwoven from limed fibers, (b) nonwoven from vegtan fibers, (c) composites of limed fibers/gelatin, and (d) composites of vegtan fibers/gelatin. One observation stands out here is that vegtan nonwoven has much higher open structure that those of the limed nonwoven. This is ascribable to the relative stable structure of vegtan fibers, which have been tanned and have better resistance to shrinkage caused by drying. On the other hand, because gelatin infused into the nonwoven, the fibrous structure of the resultant composites shows a more compact structure than the nonwoven alone.

Mechanical Properties of Nonwovens

Figure 4 displays the resultant mechanical properties of the nonwovens made from limed split fibers as a function of fiber sizes. As demonstrated in this figure, (a) tensile strength, (b) Young's modulus, and (c) toughness of the nonwovens all decrease with increasing fiber size. The test results for vegtan nonwoven show the same behavior in Figure 5. This general trend is probably ascribable to the better binding between fibrous networks when the fiber size is smaller, thereby improving the tensile strength of nonwovens.

Gelatin Properties

Gelatin can be economically extracted from tannery wastes such as chrome shavings, trimmings, splits, etc. However, in order to reduce the number of variables and for better control of the composite samples, in this research, commercial porcine gelatin was used to mix with the nonwovens to form a composite as shown in Figure 2b and 2d. The relationship of viscosity (at 60°C) and gelatin concentration is demonstrated in Figure 6. It is clearly shown that viscosity increases significantly with gelatin concentration. Compared to other polymer solutions, the viscosity of the gelatin solution is relatively low at the same concentration level. In fact, this is a favorable factor in the preparation of a composite because the

higher the viscosity of a gelatin solution, the more difficult it is to be mixed uniformly with fibers.

Figure 7 shows the test results of tensile strength and Young's modulus of the gelatin films as a function of gelatin concentration used in casting the films. It appears the gelatin concentration does not have a significant effect on the mechanical properties of the casted films.

Mechanical Properties of Composites

A close relationship is clearly demonstrated in Figure 8, in which the greater gelatin concentration and smaller the fiber size in the composite will result in a greater (a) tensile strength and (b) elongation of a composite of limed fibers/gelatin up to gelatin concentration of around 10%. Increasing the gelatin concentration from 10% to 20%, in Figure 8, shows that the tensile strength and elongation only increased slightly for the 1 mm fiber size, decreased for the 2 mm fiber size and increased significantly for the 4mm fiber size. Figure 9a demonstrates a similar behavior in tensile strength for the composites of vegtan fiber nonwoven/gelatin. It shows that the smaller size of fibers, 1 and 2 mm, have a better tensile strength than the 4 mm fiber composites. The significant increase in tensile strength as fiber size decreases could be due to the better bonding between the fibers and gelatin. However, the effects of fiber size on elongation were not as significant as shown in Figure 8b.

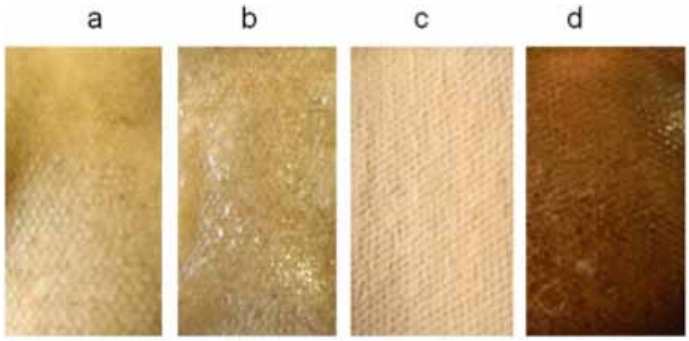

Figure 2. Stereo-micrographs of (a) nonwoven made from limed split fibers, (b) composite of limed split fibers/gelatin, (c) nonwoven made from vegtan fibers, and (d) composite of vegtan fibers/gelatin.

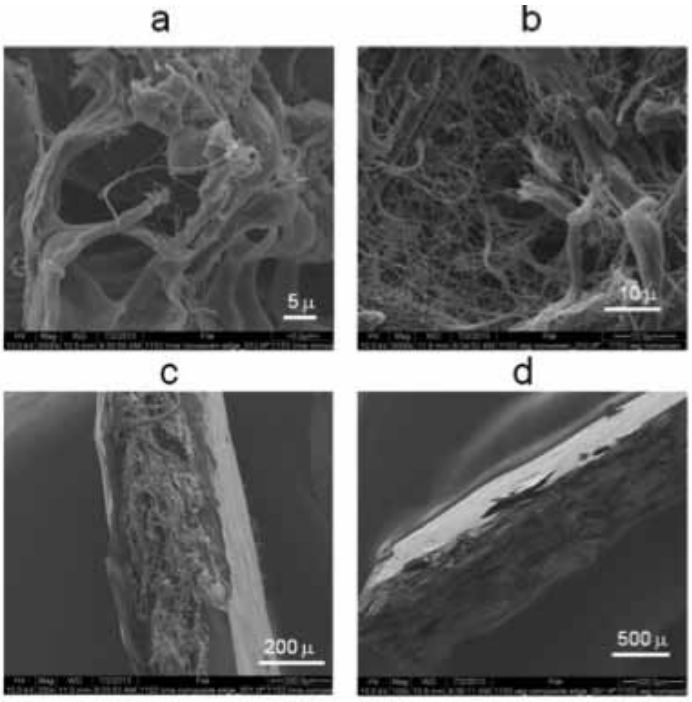

Figure 3. Micrographs of cross-sectional view of (a) nonwoven from limed fibers, (b) nonwoven from vegtan fibers, (c) composites of limed fibers/gelatin, and (d) composites of vegtan fibers/gelatin.

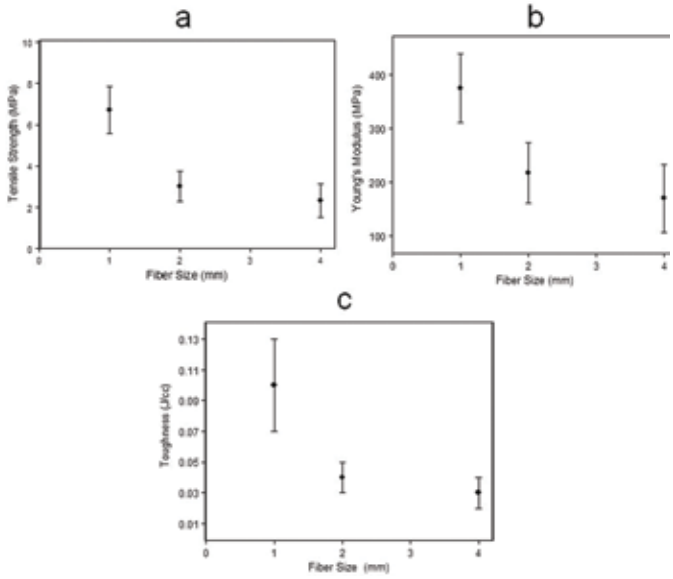

Figure 4. Mechanical properties of nonwovens from limed hides (a) Tensile strength, (b) Young's modulus, and (c) toughness.

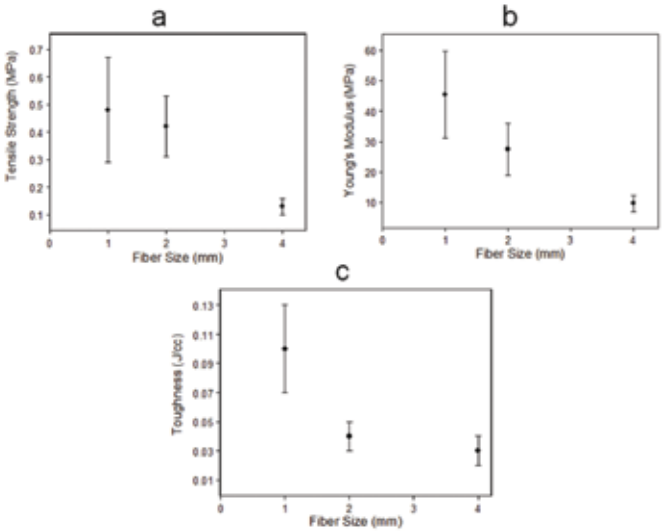

Figure 5. Mechanical properties of nonwovens from vegtan splits (a) tensile strength, (b) Young's modulus, and (c) toughness.

Acoustic Emission Studies

Many of our previous studies demonstrated that the acoustic emission (AE) technique is very instrumental in characterizing the structure of fibrous materials. The AE test results very often reveal some structural information that other methods cannot offer.[8-9] A basic way to graph AE activities is to plot the rate of hits as a function of time when the sample is under a constant rate of deformation. As demonstrated in Figure 10a and 10b, it appears that the nonwoven from the limed fibers has a more pronounced AE activity compared to the vegtan fibers. It also shows the vegtan nonwoven breaks earlier than the limed fiber nonwoven. Moreover, the comparison of AE results indicates that in the nonwoven structure, the bonding of fibers is much weaker in the vegtan fibers than the limed fibers. This agrees with the observation in SEM as shown in Figure 3. On the other hand, the composite of vegtan fibers/gelatin (Figure 10d) show greater AE activity than that of the vegtan nonwovens (Figure 10b). This is due to the gelatin binding with the fibers in the composite, resulting in a stronger force required to break the embedded fibers, consequently producing more AE hits. This behavior is not shown for composites from limed fibers because the fibers are already fused very tightly in the nonwoven structure, therefore the composite does not produce more AE hits than the nonwoven.

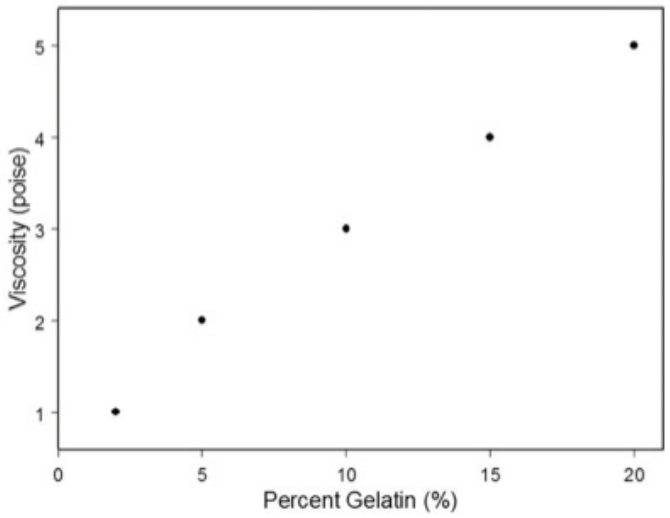

Figure 6. Viscosity vs. percent gelatin.

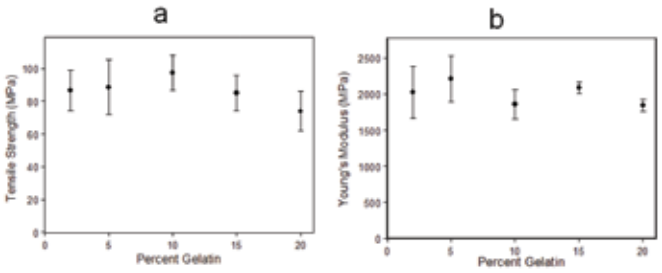

Figure 7. Mechanical properties of gelatin films (a) tensile strength and (b) Young's modulus as a function of percent gelatin.

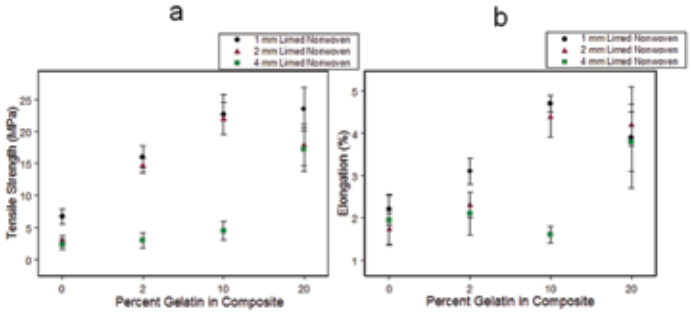

Figure 8. Mechanical properties of composites of nonwoven of limed fiber/gelatin (a) tensile strength, (b) elongation as a function of percent gelatin.

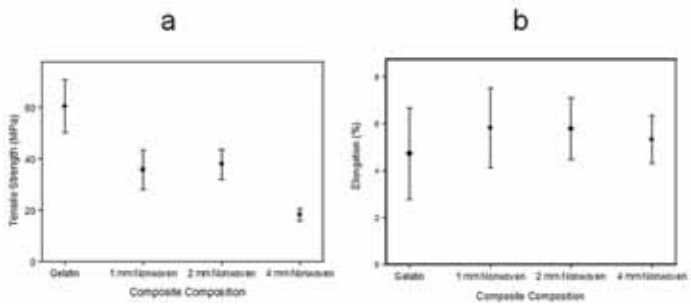

Figure 9. Mechanical properties of composites of (40/60) vegtan nonwoven/gelatin (a) tensile strength, (b) elongation as a function of different fiber sizes.

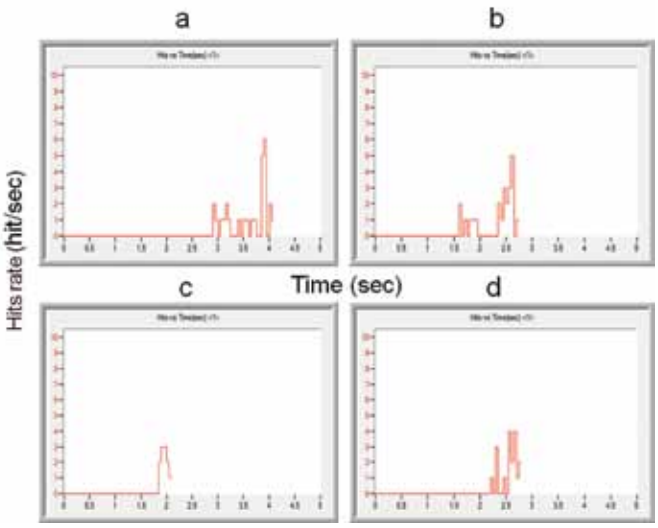

Figure 10. The rate of AE hits as a function of time (a) nonwoven from limed fibers, (b) nonwoven from vegtan fibers, (c) composite of limed fibers/gelatin, and (d) composite of vegtan fibers/gelatin.

CONCLUSIONS

This study focuses on preparations of nonwoven and green composites derived from fiber networks. Results showed that the fiber sizes and gelatin content have significant effects on the properties of resultant nonwoven mats and composites. Finer size fibers and higher portions of gelatin yielded better tensile strength and higher stiffness. The results of this research are useful to the production of high quality fibrous products such as high efficiency air filters or green composites.

ACKNOWLEDGMENTS

We thank ARS, ERRC scientists: Joseph Uknalis for SEM photos, Lorelie Bumanlag and Joe Lee for samples preparations.

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