A Novel Process to Isolate Fibrils from Cellulose Fibers by High-Intensity Ultrasonication, Part 1: Process Optimization

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Received 24 September 2008; accepted 17 January 2009
DOI 10.1002/app.30072
Published online 2 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cellulose fibrils of microscale and nanoscale sizes have great strength and hence furnish the possibility of reinforcing polymers. Fibrils can be isolated from natural cellulose fibers by chemical or mechanical methods. However, the existing procedures either produce low yields or severely degrade the cellulose and, moreover, are not environment friendly or energy efficient. The purpose of this study was to develop a novel process that uses high-intensity ultrasonication (HIUS) to isolate fibrils from several cellulose resources. Six factors that may affect the efficiency of fibrillation, including power, temperature, time, concentration, size, and distance, have been considered and discussed. HIUS treatment can produce very strong mechanical oscillating power; therefore, the separation of cellulose fibrils from its biomass is possible by the action of hydrodynamic forces of the ultrasound. Water-retention value and volume change were used to evaluate and optimize the process parameters. The degree of fibrillation of the cellulose fibers treated by HIUS was significantly increased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1270–1275, 2009

Key words: cellulose fibers; microstructure; separation technology; high-intensity ultrasonication; water-retention value

INTRODUCTION

Cellulose fibrils of microscale and nanoscale dimensions are suitable for the reinforcement of some polymers, and hence can be used to fabricate renewable and biodegradable nanocomposites. This usefulness of cellulose fibrils is because small fibrils have better mechanical properties than the individual fibers. Within their structure, small fibrils include more cellulose crystals, having a higher elastic modulus than fibers, which contribute to their increased strengths.[1] The isolation of fibrils from cellulose fibers without severe degradation, at low costs, and using an environment-friendly method is a great challenge. It is one of the most important steps related to the fabrication of nanocomposites reinforced with cellulose fibrils. Although many chemical and mechanical procedures have been developed to isolate fibrils, none of them are high yielding, environment friendly, or energy efficient.

The chemical method, mainly carried out by strong acid hydrolysis, gets rid of the amorphous regions of the cellulose fiber and produces nanosized fibrils called cellulose whiskers or cellulose nanocrystals. Many sources, including wood fibers,[2,3] cotton,[4] tunicate mantles,[5] and sugar-beet pulp,[6] have been used for fibril isolation by chemical methods. The mechanical method of separating fibrils involves a large shearing force. It includes several processes using a high-pressure refiner,[7] a grinder,[8] a microfluidizer,[9] and a high-pressure homogenizer.[10,11] These mechanical methods generate a bundle of single microfibrils, also called microfibrillated cellulose, as the main end product.

Ultrasound is a part of the sound spectrum in the range of 20 kHz–10 MHz generated by a transducer that converts mechanical or electrical energy into high-frequency acoustical energy. High-intensity ultrasonication (HIUS) waves can produce a very strong mechanical oscillating power due to cavitation, which is a physical phenomenon that includes the formation, expansion, and implosion of microscopic gas bubbles when the molecules in a liquid absorb ultrasonic energy. Within the cavitation bubble and the immediate surrounding area, violent shock waves are produced, resulting in a high temperature of up to 5000°C and a high pressure of more than 500 atm at the implosion sites.[12] Ultrasonic radiation is hence used in many processes, including emulsification, catalysis, homogenization, disaggregation, scission, and dispersion.[13]

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Contract grant sponsor: USDA Wood-Utilization Research Program, Tennessee Agricultural Experiment Station project 96.

Ultrasonic waves are helpful in the commercial pulp-fiber refining process, yielding a reduction in the shortening and a lowering of the fiber.[14] Turai and Teng[15] have used ultrasonic waves for de-inking waste paper. As a pretreatment, ultrasonic irradiation has been used to aid a practical high-performance enzymatic hydrolysis of cellulose.[16] The mixture of cellulose fibers and fibrils, together with the fibrils separated by treatment with ultrasonic waves, has been used to reinforce polyvinyl alcohol, polylactic acid, and polypropylene.[17–20]

The goals of this study were to investigate the fundamentals of cellulose-fibril isolation and characterization of the fibrils from cellulose biomass by HIUS without any additional chemical treatment. Six factors, including power, temperature, time, concentration, size, and distance, were considered and discussed to check the HIUS efficiency of cellulose fibrillation. A preceding homogenization step and a pretreatment of the fiber with sodium hydroxide have also been tried to compare the fibrillation efficiencies of cellulose that is treated exclusively by HIUS against those treated using the above-mentioned methods. Water-retention value (WRV) and volume change are used to optimize the process parameters. The characterization of the resulting fibers and fibrils will be described in a separate article in this series.[21]

EXPERIMENTAL

Materials

Four cellulose sources were used as raw materials: regenerated cellulose fiber (Lyocell fiber; Lenzing, Austria), pure cellulose fiber (TC40: average width (W) = 18 μm, average length (L) = 30 μm, TC180: W = 20 μm, L = 200 μm, and TC2500: W = 20 μm, L = 900 μm; CreaFill Fibers Corp., Chestertown, MD), microcrystalline cellulose (MCC, Avicel PH-101, FMC BioPolymer, Philadelphia, PA), and pulp fiber (Kimberly-Clark Worldwide Inc., Draper, UT). Sodium hydroxide (NaOH, 97.9%; Fisher Scientific, Hanover Park, IL) and acetate buffer (pH 4.0; Ricca Chemical Company, Arlington, TX) were used to pretreat the experimental fibers. The Lyocell fiber was about 11 μm in diameter and 12.7 mm in length. The pulp fiber was ~30 μm in width and 2–5 mm in length. Both Lyocell fiber and pulp fiber were trimmed by a Willey mill before treatment, facilitating their passage through a screen with holes of 1-mm diameter.

Setup for cellulose HIUS treatment

The cellulose materials were soaked in distilled water for >24 h before ultrasonic treatment. A HIUS processor (1500-W Model; SONICS, Newtown, CT) was directly applied to the cellulose fibers suspended in distilled water. The scheme for the treatment is shown in Figure 1. The fibers were immersed in 60-mL distilled water in a 100-mL beaker in batches. The fiber concentrations ranged from 1 to 4% (w/w), according to the varying dimensions of the fiber. To compare the efficiencies of cellulose fibrillation using the ultrasonic and homogenizer treatments, a high-pressure homogenizer (HPH, Stansted, Fluid Power Ltd., Essex, UK; Model nG12500) was used to treat pure cellulose (TC40). To combine the ultrasonic and homogenizer treatments, TC40 was treated for 30 min by HIUS and subsequently passed through a HPH instrument for 8 passes under conditions of 110 MPa pressure and T = 50–70°C.

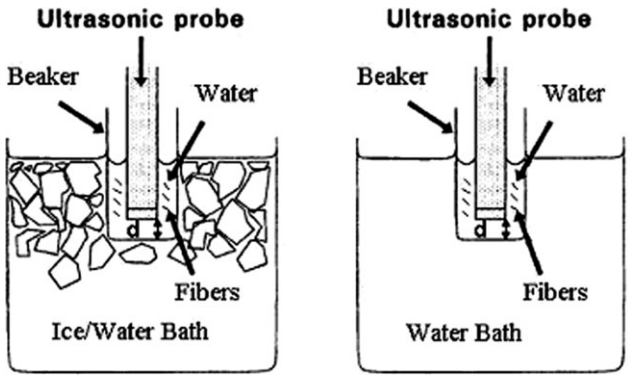

Figure 1 A scheme for HIUS treatment of fibers using ice/water bath or water-only bath.

Factors affecting cellulose fibrillation

Six factors were considered, and three or four levels for each factor were used to check the effects of fibrillation on pure cellulose based on some primary results and observation (Table I). WRV was used to evaluate and compare the effects of different factors. HIUS power was controlled by the output control button of the HIUS system. A time controller was used in the system to adjust treatment time. HOBO Type J thermocouple was used to record temperatures during the treatments. The concentration was estimated as solid weight percent of cellulose in distilled water.

Effects of abrasive powder and NaOH pretreatment on cellulose fibrillation

Abrasive powders may be helpful for cellulose fibrillation because the microbubbles generated by the ultrasonic tip could accelerate the powders, which may further collide with the cellulose particles. TC40 was treated by HIUS with alumina particles (d = 0.3, 1.0, and 7.0 μm). Other experimental factors were P

TABLE I
Factors and Levels Influencing the Efficiency of Cellulose Fibrillation

	Factor	Level	Note (other factors)
1	Power (P, %)	40, 60, 80	$t = 10$, $T =$ W, $C = 2$, FS = 30, $d = 7$
2	Time (t, min)	10, 20, 30, 60	$P = 80$, $T =$ W, $C = 2$, FS = 30, $d = 7$
3	Temperature (T)	I/W, W, N[a]	$P = 80$, $t = 10$, $C = 2$, FS = 30, $d = 7$
4	Concentration (C, %)	1, 2, 3, 4	$P = 80$, $t = 10$, $T =$ W, FS = 30, $d = 7$
5	Fiber Size (FS, μm)	30, 200, 900[b]	$P = 80$, $t = 30$, $T =$ W, $C = 2$, $d = 7$
6	Distance (d, mm)	4, 7, 10, 15	$P = 80$, $t = 10$, $T =$ W, $C = 2$, FS = 30

[a] I/W = ice/water bath, W = water-only bath, N = no bath cooling.
[b] 30 = TC40, 200 = TC180, 900 = TC2500.

= 80%, $t = 10$ min, $T =$ water cooling (W), $C = 2$%, and $d = 7$ mm. To check the effect of abrasive powders on cellulose fibrillation, three abrasive levels were tried: 5, 10, and 20% wt of cellulose. Lyocell and TC180 were pretreated with 2.5*M* NaOH for 6 h at room temperature (21°C). This NaOH concentration was reported to be the best for Lyocell fiber splitting.[22] After washing with distilled water and neutralization with acetate buffer, the fibers were treated using HIUS for 20 min with $P = 80$%, $T =$ W, $C = 2$%, and $d = 7$ mm. WRV was used to evaluate the effects of alkali pretreatment. A polarized light microscopy (PLM) was used to observe the treated cellulose fibers.

Yield measurement

The effect of HIUS on the yield of both treated cellulose and cellulose fibrils was gravimetrically determined in two steps. First, the cellulose treated by HIUS was filtered using a membrane of 0.2-μm pore size (Whatman Nuclepore) and dried. Subsequently, after separation of the untreated cellulose fibrils using a centrifuge at 900 g for 5 min (for Lyocell) or 10 min (for other samples), because it was easier to separate small Lyocell fibrils from big ones, the fibril portion was dried and weighed. The treated cellulose and cellulose fibril yields were determined as a percentage of dry weight of the "starting" material.

Volume change and WRV

The degree of homogenization or microfibrillation was related to both fibril-microfibril surface characteristics and volumetric phenomena.[10] Several methods have been used to evaluate cellulose fibrillation. One method is the investigation of volume change between untreated and treated samples. Volume change was defined as the change in suspension volume of cellulose of a certain weight from untreated to treated status in a defined amount of water after being allowed to settle for equal durations. Moreover, the deposits were observed optically by procuring the optical images after the cellulose was treated for a certain time and deposited in beakers or bottles. The evaluation of WRV is another method to measure the degree of homogenization or microfibrillation. The higher the WRV, the more the fibrils isolated or the more the voids obtained among small microfibrils. WRV is the percent ratio of water contained in a sample to the dry weight of sample after centrifugation under a certain force and time.[18]

RESULTS AND DISCUSSION

Temperature change

The temperature of water suspension during HIUS treatment changed greatly depending on the power and cooling methods used (Fig. 2). The higher the power used, the higher the temperature reached, and the higher the rate of temperature increase obtained. When ice/water bath was used for cooling with 80% power, the maximum temperature reached was only 55°C, whereas it was about 75 and 91°C when water-only bath and no cooling were used, respectively.

Effect of abrasive powder on cellulose fibrillation

Compared with untreated sample suspension, the volumes of suspended cellulose from all the treated

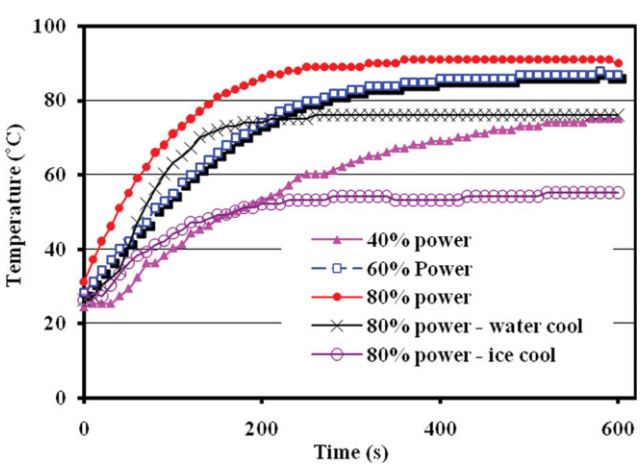

Figure 2 Temperature changes using different powers and cooling methods during HIUS treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

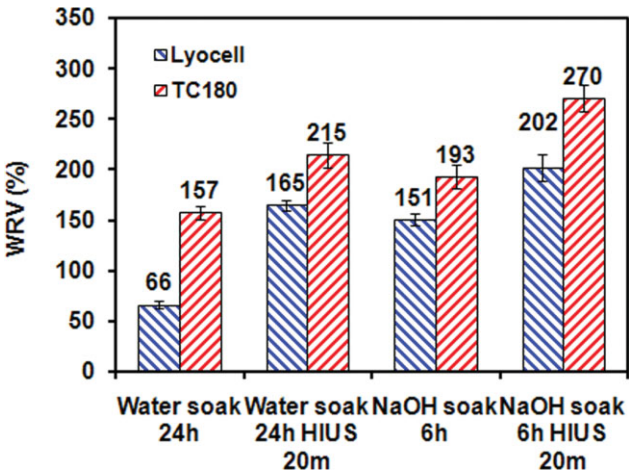

Figure 3 WRV of cellulose fibers soaked in water or NaOH and treated by HIUS for 20 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sample suspensions were significantly increased, and there were no big differences among the loading amounts (5, 10, and 20%) and among the different sizes of abrasive powder (0.3, 1, and 7 μm). The powders may ensure faster fibrillation, especially the 0.3-μm powder, because the smaller powders are quicker to respond to acceleration by the microbubbles generated by cavitations, and the powder may consequently strike the cellulose to accelerate fibrillation; however, it was very difficult to separate the powder from cellulose fiber and fibrils even after centrifugation.

Effect of pretreatment by NaOH

For both Lyocell and TC180 fibers, the WRVs were increased significantly after soaking in NaOH for about 6 h (Fig. 3). This indicates that the pretreatment by NaOH swelled the fibers, and the fibers were thus more amenable to fibrillation[22]; therefore, the WRVs of fibers soaked in NaOH and treated by HIUS for 20 min were higher than those of fibers without NaOH immersion. A PLM image of treated Lyocell fiber shows that the fibers were fibrillated substantially, and many small fibrils were split from big fibers (Fig. 4).

Combination of ultrasonication and homogenizer treatments

After the treatment by HPH at different pressures, thorough suspensions of TC40 could be obtained. The higher the pressure, the better the fibrillations of fiber observed. The dimensions of the fibrils became progressively smaller with higher pressures. The suspension temperature increased at a faster rate for higher pressures, which was also helpful for the fibrillation of cellulose fibers.[10,11] Furthermore, increased fibrillation of cellulose fibers was observed in the combined treatments of HIUS and HPH. The process of HIUS treatment could make the suspension more uniform only when it was followed by several passes of HPH treatment (Fig. 5).

Fiber and fibril yields

The yields of treated pulp and Lyocell fibers were about 100 ± 2%, which implied that there were no water soluble components in the water suspensions of fibers treated by HIUS. It is hard to define the small fibril yield after separation by centrifugation because the fibril fraction on top of the suspension could be affected by the duration of centrifugation, the ensuing deposition, and the concentration of the suspensions. A centrifugation period of 5 min for Lyocell and 10 min for other samples, and a deposition time of 5 min after centrifugation were used in

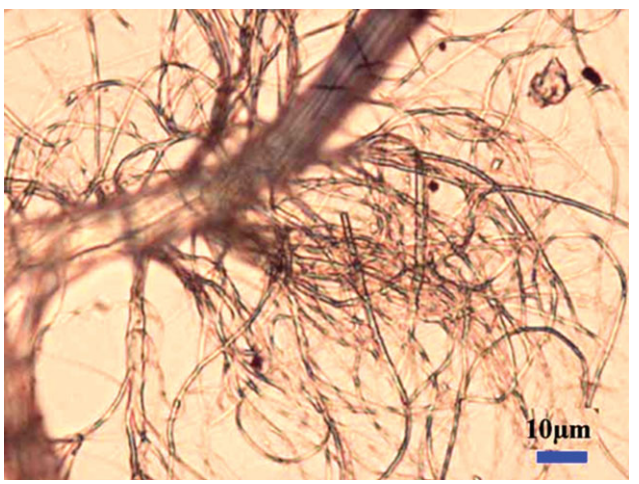

Figure 4 PLM image of Lyocell treated for 30 min by HIUS after pretreatment with NaOH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

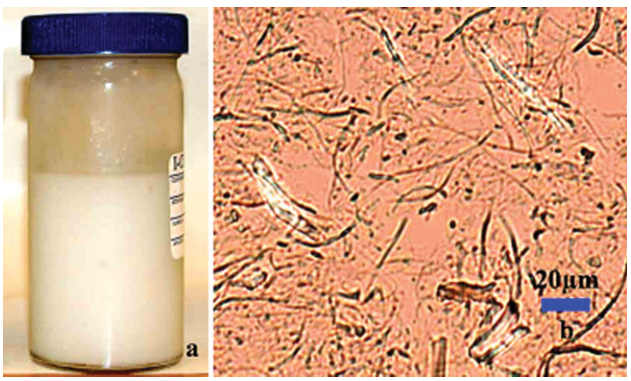

Figure 5 Suspension (a) and PLM image (b) of TC40 treated by HPH after HIUS 30-min treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

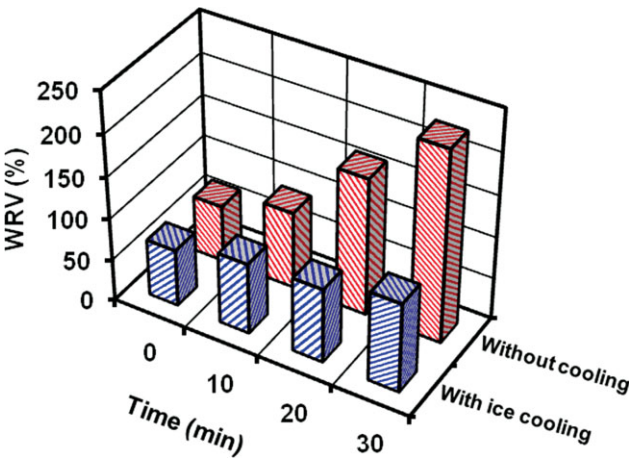

Figure 6 WRVs of Lyocell fibers treated by HIUS for different durations and at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

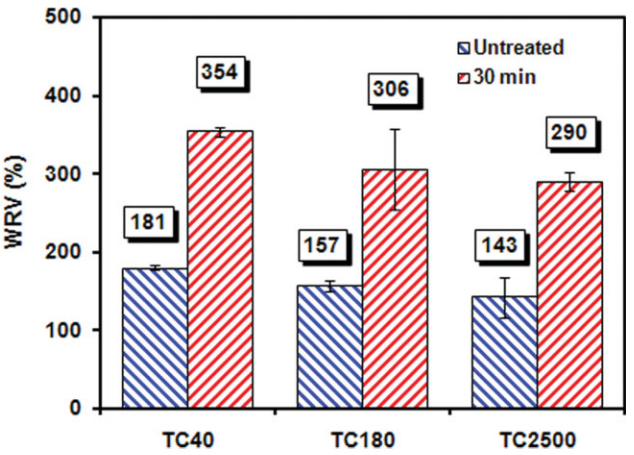

Figure 7 WRVs of different pure cellulose fibers before and after treatment by HIUS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

this study. The yields of fibrils from Lyocell were ~ 3 and 5% for 30- and 60-min HIUS treatment separately, whereas they were ~ 40 and 53% for 30- and 60-min HIUS treatment from Avicel cellulose separately. Longer fibers such as Lyocell (~ 1 mm) were much difficult to be fibrillated than shorter fibers such as Avicel (~ 50 μm) in this case.

Evaluation of the efficiency of cellulose fibrillation

The WRV of treated fibers increased as the treatment time increased, and a higher temperature of the suspension was also very helpful for cellulose microfibrillation (Fig. 6). It indicated that the degree of microfibrillation was increased and the fibers became smaller, and more surface area on the fibrils was exposed as the treatment time and temperature increased because WRV was related to the surface area of both fibrils and microfibrils, in addition to being controlled by other volumetric phenomena.[10] The longer the treatment time, the smaller the size of fibrils obtained in the suspension mixture.

The WRVs of TC40 treated by HIUS with different treatment powers, cellulose concentrations, and distances from the tip of the HIUS probe to the beaker bottom are shown in Table II. Higher operating power facilitated cellulose microfibrillation because it transferred more energy to the probe, thus increasing the temperature of the suspension at a quicker rate, which helped cellulose microfibrillation (Figs. 2 and 6). Higher concentrations of cellulose suspensions had lower WRV, because the aquatic force generated by the microbubbles could not agitate and stir the cellulose fiber in the suspensions substantially, so that the fibers had a lower chance of passing the probe tip. If the distance from the tip of the HIUS probe to the beaker bottom was more than 10 mm, the WRV significantly decreased. This might be because the fibers that were accelerated by the aquatic force of the microbubbles merely by a small degree reached the bottom of the beaker, so that the suspension could not be agitated and stirred adequately; consequently, the fibers had a lower chance of passing the probe tip. Figure 7 shows the WRV of different-sized pure cellulose fibers treated by HIUS. The treated smaller fiber (TC40) had a much higher WRV than the treated bigger fiber (TC2500), but the increase in percent WRV for each fiber from the untreated fiber was not much different among the three fibers.

On the basis of the WRV measurements, the optimum process conditions of HIUS for TC40 could be summarized as follows: $P = 80\%$, $T =$ without cooling, $C = 1\%$, $d = 7$ mm, and $t > 30$ min; however, a longer treatment time could result in higher cellulose degradation.

TABLE II
WRVs of TC40 Treated by HIUS with Different Factors Described in Table I

Power (%)			Concentration (%)				Distance (mm)			
40	60	80	1	2	3	4	4	7	10	15
204 (21)[a]	202 (19)	261 (8)	287 (9)	264 (15)	246 (19)	240 (8)	251 (4)	264 (15)	208 (5)	204 (14)

[a] Standard deviation

CONCLUSIONS

HIUS treatment has been developed as a novel method for fibril isolation and used to treat several cellulosic materials to generate small fibrils. HIUS treatment in a batch process can be used to isolate fibrils from several cellulose resources: regenerated cellulose fiber, pure cellulose fiber, MCC, and pulp fiber. A mixture of fibrils in the microscales and nanoscales was obtained. Small fibrils could be separated from HIUS-treated cellulose-water suspension by centrifugation. WRV was significantly increased by HIUS treatment for all cellulose resources. The temperature of the fiber suspension increased at a faster rate when the power was larger, and the higher the power, the better the fibrillation. The temperature of the water suspension could reach up to 91°C without water cooling. The higher the temperature, the better the cellulose fibrillation, whereas the longer the raw fiber, the lower the fibrillation. Cellulose concentration of the suspension depended on the dimensions of the cellulose fiber, resulting in lower concentrations when the fiber was longer. A larger distance from the HIUS probe tip to the beaker bottom was not beneficial to fibrillation. Pressure and passage time are very important parameters for homogenization. Several passes using HPH after HIUS treatment can yield a thorough cellulose suspension as well as cellulose fibrils that are more uniform than those treated by HIUS only.

We thank Dr. Qingyou Han of Purdue University for his help in the ultrasonic experiments; and Dr. David Harper and Dr. Federico Harte of University of Tennessee for their valuable assistance in the PLM experiments and the homogenization treatment.

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