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Seung-Hwan Jeong, Joong-Kwon Kim, Young-Woo Lim, Hyun-Bin Hwang, Hee-Young Kwon, Byeong-Soo Bae, and Jungho Jin

Citation: APL Materials 6, 016102 (2018); doi: 10.1063/1.4985754
View online: https://doi.org/10.1063/1.4985754
View Table of Contents: http://aip.scitation.org/toc/apm/6/1
Published by the American Institute of Physics

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Squid pen-inspired chitinous functional materials: Hierarchical chitin fibers by centrifugal jet-spinning and transparent chitin fiber-reinforced composite

Seung-Hwan Jeong,1,a Joong-Kwon Kim,1,a Young-Woo Lim,2
Hyun-Bin Hwang,1 Hee-Young Kwon,1 Byeong-Soo Bae,2 and Jungho Jin1,b
1School of Materials Science and Engineering, University of Ulsan,
Ulsan Metropolitan City 44610, South Korea
2Department of Materials Science and Engineering, Korea Advanced Institute of Science
and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, South Korea

(Received 30 May 2017; accepted 7 November 2017; published online 3 January 2018)

Here, inspired by the fibrous composite structure of a squid pen, we introduce hierarchical chitin fibers (herein, termed "Chiber") and their transparent composites and demonstrate the potential of these chitinous functional materials as a sustainable separation-membrane and reinforcing filler for composites. We employ a centrifugal jet-spinning process to fabricate Chiber with aligned chitin nanofibrillar architectures, for which we discuss the processing-morphology relationship. A nonwoven fiber-mat made of Chiber exhibits excellent adsorbing performance for a toxic ionic dye (Congo Red), and has a low coefficient of thermal expansion comparable to that of glass fibers. Finally, we demonstrate a squid pen-mimetic transparent composite using Chiber and investigate its optical property. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.4985754

Biological composites and adnexa found in some living creatures are compelling inspiration for advanced green composites and functional devices.1,2 Squids, the members of the order Teuthida of Cephalopods, are one of such examples [Fig. 1(a)].3,4 The sucker ring teeth in the arm/tentacles of a squid is a hierarchical proteinous material, which exhibits superior mechanical properties to most synthetic polymers.5–7 The beak of squid represents one of the stiffest wholly organic materials known, which is a nanofibrous composite embedded in a sclerotized protein matrix.8–10 Squid’s eyes are spherical aberration-free optical lenses with graded refractive index,11 while their camouflage strategy is also an exciting inspiration for future display technologies.12,13

Squids have another compelling intracorporeal appendage that may attract material scientists’ interest: the squid pen (or Gladius).14 It is an elongated sword-shaped vestigial shell attached dorsally inside the squids’ mantle, which appears optically transparent [Fig. 1(b)]. The major structural ingredient of the squid pen is chitin [poly(β-(1,4)-N-acetyl-D-glucosamine)],15 the second most abundant polysaccharide only after cellulose,16 which is biodegradable, non-toxic, physiologically relevant, and yet mechanically robust.17–19 As shown in Fig. 1(c), the squid pen is a fibrous composite consisting of multiscale fiber bundles, in which the protein-wrapped chitin nanofibrils (3-5 nm) are aligned collectively to form the fibers of larger scales.14 Such a hierarchical fibrous composite structure of the squid pen contributes to its mechanical stiffness and toughness, allowing this mineral-free chitinous endoskeleton to support and stabilize squids’ body.20

Here, inspired by the squid pen, we report on the fabrication of hierarchical chitin fibers (Chiber) and their fiber-reinforced transparent composites emulating the chitinous fiber composite structure of the squid pen. For the fabrication of Chiber, we adopt a centrifugal jet-spinning (CJS) process.21–23
for which we discuss in detail the relationship between the Chiber morphology and CJS process parameters (e.g., the concentration of spin dope, rotation speed, and nozzle diameter). Following the investigation on the basic mechanical and functional properties of Chiber and its nonwoven mat-type membrane, we finally demonstrate a Chiber-reinforced transparent composite reminiscent of the squid pen.

Figure 2 displays the materials and CJS setup used to produce Chiber, along with the photographic, scanning electron microscope (SEM), atomic force microscope (AFM), and polarized optical microscope (POM) image of the produced Chiber. We use a squid pen extract \( \beta \)-chitin [Fig. 2(a)] and hexafluoroisopropanol (HFIP) solvent to make the chitin/HFIP spin dope solutions with varying concentrations,\(^{24,25} \) which appear as a clear viscous liquid [Fig. 2(b)]. As for the manufacture of Chiber, we employ a CJS technique because it allows the production of micro- and/or nanofibers in a simple and high-throughput fashion.\(^ {23} \) Figure 2(c) shows our custom-built CJS apparatus consisting of (i) a metallic reservoir connected with an internal duct that enables a continuous supply of spin dope solutions, (ii) two spinneret nozzles heading oppositely, and (iii) collector-bars surrounding the reservoir. Figures 2(d) and 2(e) show the micron-diameter Chiber produced using our CJS setup; a colored Chiber can be also produced from a chitin/HFIP solution incorporating organic dyes (Methyl Violet) as seen in the inset of Fig. 2(d).

In a typical CJS using a polymeric solution, rotating the reservoir at a high speed initiates and discharges liquid jets, which in turn rapidly solidify into fibers by the solvent evaporation. The formation of continuous fibers is achieved when the viscous force acting on the jet stream is greater than the surface tension force, while the opposite condition results in the rupture of liquid jets (i.e., droplets) due to the Rayleigh-Plateau instability.\(^ {26} \) This can be estimated by the ratio of the Weber number \(( \text{We} = \rho U^2 D / \gamma )\) to Reynolds number \(( \text{Re} = \rho UD / \eta )\), which is defined as the capillary number \(( Ca = U \eta / \gamma )\); here, \( \rho \), \( \gamma \), and \( \eta \) are the density, viscosity, and surface tension of spin dope solution, respectively, \( D \) is the nozzle inner diameter, and \( U \) is the liquid jet exit speed which can be experimentally determined from the consumption rate of a given volume of spin dope solution at a given rotation speed (\( \eta \) is dependent on the concentration of spin dope solution).\(^ {22} \) Therefore, it is necessary to control the main CJS process variables—the concentration of spin dope solution, nozzle inner diameter, and rotation speed—to satisfy the regime \( Ca \gg 1 \) for the production of continuous fibers with few defects.\(^ {27} \)

Table I summarizes the CJS process parameters applied to produce Chiber in this study, along with the capillary numbers calculated from each set of conditions, and the SEM images of the produced Chiber are shown in Fig. S1 of the supplementary material. As presented in Table I, all sets of conditions satisfy the regime \( Ca \gg 1 \), suggesting the formation of continuous Chiber. However, despite the high capillary number, we identify a tendency that in most cases the highest-rotation-speed conditions fail to produce continuous Chiber and end up with scattered droplets. This unexpected jet
FIG. 2. (a) Squid pen extract β-chitin and its structural formula. (b) Digital photograph of HFIP solvent and β-chitin/HFIP spin dope solution (0.6% w/v). (c) Digital photograph of the CJS equipment spinning Chiber. (d) Digital photograph of as-spun Chiber (the inset image is a dyed Chiber) and its (e) SEM image. (f) Schematic illustration of the chitin/HFIP solution ejection from a CJS nozzle. (g) AFM topographic image of a single strand of Chiber (the inset shows the phase image, scale bar = 500 nm). (h) POM image of as-spun Chiber.

breakup is thought to be due to the Rayleigh-Taylor instability that can be provoked as the centrifugal force dominates the viscous force at the very high rotation speeds,\textsuperscript{28} which may be susceptibly affected by the low concentration of chitin/HFIP (<1%).

<table>
<thead>
<tr>
<th>Concentration (w/v %)</th>
<th>Viscosity (mPa s)</th>
<th>Surface tension (mN/m)</th>
<th>Nozzle diameter (µm)</th>
<th>Rotation speed (rpm)</th>
<th>Jet exit speed, U (cm/s)</th>
<th>Capillary number, Ca\textsuperscript{a}</th>
<th>Fiber feature</th>
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<tr>
<td>0.6</td>
<td>17.37</td>
<td>32</td>
<td>100 [32 G]</td>
<td>6 000</td>
<td>18.82</td>
<td>8.2</td>
<td>Fiber</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8 000</td>
<td></td>
<td>25.13</td>
<td>11.25</td>
<td>Fiber</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 000</td>
<td></td>
<td>31.42</td>
<td>14.06</td>
<td>Fiber</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80 [34 G]</td>
<td>6 000</td>
<td>18.85</td>
<td>8.4</td>
<td>Fiber</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8 000</td>
<td>25.11</td>
<td>11.24</td>
<td>Droplet</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 000</td>
<td>31.41</td>
<td>14</td>
<td>Droplet</td>
</tr>
<tr>
<td>0.8</td>
<td>29</td>
<td>51</td>
<td>100 [32 G]</td>
<td>6 000</td>
<td>18.85</td>
<td>10.72</td>
<td>Fiber</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8 000</td>
<td></td>
<td>25.16</td>
<td>14.29</td>
<td>Droplet</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 000</td>
<td></td>
<td>31.42</td>
<td>17.86</td>
<td>Droplet</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80 [34 G]</td>
<td>6 000</td>
<td>18.85</td>
<td>10.73</td>
<td>Fiber</td>
</tr>
<tr>
<td></td>
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<td>8 000</td>
<td>25.43</td>
<td>14.46</td>
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<td>10 000</td>
<td>31.42</td>
<td>17.86</td>
<td>Droplet</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ca: capillary number.
As for the conditions that afford Chiber, the SEM analysis reveals that Chiber with the diameter range 2–5 µm accounts for the majority while submicron Chiber is rarely found (Fig. S1 of the supplementary material). In terms of the morphology, Chiber with irregular ribbon-shape and partial crumpling is often observed, although only a trace of such defects is identified in Chiber obtained from the following optimal condition: 0.6%/34 G/6000 rpm [this optimal Chiber is shown in Figs. 2(d) and 2(e) and is subsequently used for the nonwoven-mat and composite]. The defective morphologies of Chiber are thought to stem from the nature of chitin/HFIP solution in which the crystalline chitin tends to form crystallosolvates with HFIP. These crystallosolvates are likely to cause uneven evaporation of the solvent within the same solution jet, which may lead to the morphologic unevenness.

On the other hand, another important yet promising morphological feature of Chiber is that it has a structural hierarchy consisting of ultrafine (3-5 nm) chitin nanofibrils that collectively align along the Chiber-axis as in the natural squid pen. Figure 2(f) schematically illustrates the formation process of Chiber from a chitin/HFIP solution jet ejecting through a CIS nozzle. During this process, the high-speed rotation generates a strong shear on the ejecting jet, which can guide the chitin molecules to align and self-assemble into nanofibrils that ultimately make up the Chiber. This is well validated in the AFM analysis of a single Chiber strand [Fig. 2(g)], which clearly shows that the chitin nanofibrils are aligned collectively along the direction of the jet-ejection (i.e., Chiber-axis). In addition, the POM image of Chiber shown in Fig. 2(h) also confirms the hierarchically aligned nanofibrillar architecture of Chiber, which clearly shows a birefringence with interference colors; note that an optically isotropic film consisting of randomly entangled chitin nanofibrils does not exhibit such birefringence (Fig. S2 of the supplementary material). We also investigate the crystal structure of Chiber using x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), which is shown in Fig. S3 of the supplementary material. The data indicate that Chiber has a biphasic crystalline characteristic of both α- and β-polymorph of chitin, which also verifies the hierarchical structure of Chiber consisting of supramolecular chitin nanofibrils.

We create a nonwoven mat-type membrane of Chiber using an isotactic cold pressure method as shown in Fig. 3(a) and investigate the basic functional and mechanical properties of the Chiber membrane; for comparison, a glass microfiber filter (GF) (Whatman® GF/C), a woven E-glass fabric, and a porous polypropylene membrane (Celgard® 2400) are also used as the reference. As seen in the photographic and SEM images [Figs. 2(a) and 2(b), respectively], the Chiber membrane has an appearance and morphology typical of nonwoven fiber mat, analogous to those of GF (see also Fig. S4 of the supplementary material); we have recently reported on the application of Chiber membrane as a separator for lithium metal batteries. We assess the porosity and surface area of Chiber using mercury porosimetry [Fig. 3(c)] and the BET (Brunauer–Emmett–Teller) method [Fig. 3(d)], respectively, and also examine its air permeance using a Gurley densometer [Fig. 3(e)]. The average pore size of Chiber measures 4.5 µm and is only slightly smaller than that of GF (6.6 µm), which is in contrast with the nanoporous Celgard (50 nm). Also, the Chiber membrane has a specific surface area (2.9 m²/g) comparable to that of GF (3.4 m²/g), as shown in Fig. 3(d). On the other hand, Chiber shows a greater air permeance than the GF, which is thought to be simply due to the smaller thickness of the Chiber membrane (40 µm) than that of the GF (200 µm) [Figs. 3(b) and S4 of the supplementary material]. We then perform a set of experiments to check the functional property of Chiber as a separation membrane for the removal of Congo Red, a toxic anionic salt-type organic dye, as well as Methyl Violet, a typical cationic organic dye. Figure 3(f) compares serial photographs of the dye-removal experiment using Chiber, cotton, and GF membranes; the weight of all membranes is equivalently set to 270 mg, and the concentration of the aqueous Congo Red effluent is set to 0.005%. It is notable that Chiber membrane adsorbs the dye completely while the others do not. Figure 3(g) verifies this result, which presents the concentrations of the filtrates determined from the linear regression of the calibration line obtained based on Beer-Lambert’s law; note that the concentration of the filtrate from the Chiber membrane is nearly zero. This result is notable, given that both the GF and Chiber membrane have a comparable pore size and specific surface area. The excellent adsorability of Chiber for Congo Red is attributed to the acetylamino groups present in chitin that are active sites for adsorbing the dye via the ionic or hydrogen bond interaction. Unlike the anionic Congo Red, however, the removal of the cationic Methyl Violet (0.0005% aq.) by the Chiber membrane is not effective as much [Fig. 3(h)].
This is presumably due to the electrostatic repulsion by the cationic nature of chitin in the aqueous environment (due to the amine groups being protonated). In the following experiment, we perform a thermomechanical analysis (TMA) and measure the coefficient of thermal expansion (CTE) of the Chiber membrane. Figure 3(g) displays the TMA profile of the Chiber membrane, GF, woven E-glass fabric, and polyimide (PI). Surprisingly, the CTE of the Chiber membrane measures 5.5 ppm/°C and is even lower than that of PI (17.2 ppm/°C), which is of a similar level of that of GF (3.9 ppm/°C) and woven E-glass fabric (3.0 ppm/°C). The low CTE of Chiber membrane may be attributed to the collectively aligned chitin nanofibrils with high elastic modulus. Such mechanical anisotropy due to the hierarchical alignment of chitin nanofibrils is also confirmed in the tensile testing (Fig. S5 of the supplementary material), in which the unidirectional Chiber mat exhibits higher tensile properties over the omnidirectional one.
Finally, we create a squid pen-mimetic transparent composite using a Chiber membrane as the reinforcement [Fig. 4(a)]. Displayed in Fig. 4(b) is a Chiber-reinforced transparent composite film cut into the shape of the squid pen. We fabricate this composite film by impregnating a Chiber membrane with a typical UV-curable organosiloxane matrix resin followed by vacuum-bag molding and UV-curing (Fig. S6 of the supplementary material). This type of fiber composites can be designed to attain a high optical transparency by introducing a matrix that has a refractive index (RI) similar to that of the fiber (i.e., $\Delta RI = |RI_{fiber} - RI_{matrix}| \approx 0$), and the level of optical transmittance and haze can be affected and controlled by $\Delta RI$ as well as the fiber diameter. Figure 4(c) shows the UV-vis spectrum of the Chiber-reinforced composite, from which its total ($T_t$) and parallel ($T_p$) transmittances at 550 nm measure 87% and 54%, respectively. This result indicates that the Chiber-reinforced composite film has a high optical haze ($T_t - T_p$) of 33%. This is well demonstrated in the laser scattering experiment shown in Fig. 4(d), where the light scattering effect is markedly greater for the Chiber-reinforced composite film (left) compared to the reference film having a low haze level ($\sim 1\%$); this reference film is a pure chitin film made up of randomly entangled chitin nanofibrils, which we have reported recently. It is worth noting that the Chiber-reinforced composite has a high optical haze (33%) coupled with a high $T_t$ of 87%, which is a promising attribute of a substrate film for optoelectronic devices such as solar cells.

In conclusion, we report on the fabrication of squid pen-inspired, hierarchical chitin fibers (Chiber), and a Chiber-reinforced transparent composite and investigate their basic properties (e.g., dye-removal and transparent/hazy film) as functional chitinous materials. We produce Chiber using a centrifugal jet-spinning (CJS) technique and discuss the process conditions under which micron-diameter Chiber with aligned nanofibrillar architectures can be produced. The nonwoven mat-type membrane of Chiber shows an excellent adsorptive property for a typical anionic dye (Congo red) and also exhibits a low coefficient of thermal expansion (CTE) of 5.5 ppm/°C. On the other hand, the Chiber-reinforced composite film shows a high optical transmittance (87%) coupled with a high haze (33%). We envisage the usage of Chiber and its transparent composite as a sustainable functional material, given the promising macroscopic properties of these chitinous materials.

See supplementary material for detailed information.

ACKNOWLEDGMENTS

This work was supported by the 2015 Research Fund of University of Ulsan.