# Mechanical and Biological Properties of Silk Fibroin/Carbon Nanotube Nanocomposite Films

## Caixia Pan, Qifan Xie, Zeyun Hu, Mingying Yang, and Liangjun Zhu\*

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Abstract: Multi-walled carbon nanotubes (MWCNTs) were homogeneously dispersed in silk fibroin (SF) solutions at different compositions, and a simple solvent-casting method was used to fabricate SF/MWCNT films. Structure, viscosity, and mechanical properties of the SF/MWCNT nanocomposites were characterized by FTIR (Fourier Transform Infrared Spectroscopy), viscometry, and tensile testing. Fibroblast cells were used to examine cell viability and attachment to nanocomposite films. Compared to a pure SF film, adding just 0.5 % (w/w) of MWCNT to the SF matrix could enhance the Young's modulus and ultimate tensile strength by approximately 24 % and 39 %, respectively. In addition, with increasing

## Silk Fibroin Purification

# SF/MWCNT Nanocomposite Film Fabrication

, r.h.r, r,h

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**Figure 1.** (A) SF/MWCNT nanocomposite solutions of different MWCNT compositions (M1, M2, M3 represent 0.1 % (w/w) MWCNT, 0.5 % (w/w) MWCNT, 1 % (w/w) MWCNT respectively.) after 3 days, and MWCNTs in water (Water/M) after only 1 h. (B) Absorbance of SF/MWCNT solutions as a function of relative MWCNT concentration of after 1 h and 3 days in a stationary position.

r'hhr r, · • 1 h r . . . q r r ŗ h h r r. , h h r , h r, 'n h r r. q , r r • r. h ŗ , r r rr ŗ h r ( ), h r r r, hh 27,2.rhrr, r. r h hr. r , r rr hrh r h ŗ

r

h

r.

r

. .

₽.h

, r



Figure 2. The relationship between viscosity and MWCNT concentration.

#### Viscosity

r, 0. h\_ r r, r , h r, r r r r, L hr, r. r r r **?** r h h . h 0. % ŗ h. h . . . r r, h r , % h r , .hh r ĥ h h / r hrr.r r r r, h hrr ŗr r r .

#### Secondary Structure of SF/MWCNT Films

rr, h r, r r r, h r h r r · · · h , r, r r r, h r r r r r h r - 70 r r ( r )-( )). r r r , r r rr , *α*-h  $, \beta h$  $\beta$ -r.h q. h r r r r, r, h , , , ), h r, h r • 1 r ( 0. % 0 h h r r, β-h r β-r ( / ), h r h ( <0.0 ). h h r r r r 0. % ( / ), h r , β- $\beta$ -r h  $\alpha$ -h r h , h h r . r , ( <sup><</sup>0.0 ). h h h r ₽.77 % 0. % (/), h $\beta$ -h r r r r,



**Figure 3.** FT-IR spectra and secondary structure contents of silk films fabricated at various MWCNT concentration; (A) FT-IR spectra of SF (pure silk film), (B) FT-IR spectra of SF/M1 (SF/0.1 % (w/w) MWCNT film), (C) FT-IR spectra of SF/M2 (SF/0.5 % (w/w) MWCNT film), (D) FT-IR spectra of SF/M3 (SF/1 % (w/w) MWCNT film), (E)  $\alpha$ -helices structure content, (F)  $\beta$ -sheets structure content, (G) random coils structure content, and (H) turns structure content. \*Significant difference between groups (\* <0.01). The data represent mean±SD (=4).

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.7%, β-r . % 7.7%. r. r h h . h **q** , , r r r , β- r h r, , *a*-h , r, , , r h , r , r , h

# Mechanical Properties of SF/MWCNT Films

h h r r , r h h r r , , r r r r r h ' (), r r (E), r h (), r h () r , r h r , r h r r . r h r r,

r r , h0. % (/) h 2% r h , , % r h r r , %



MWCNT ralative concentration (%)

r h r h, 0% r, h r h. h h **r**, . . . h h ŗ r r r r r , r. h r r h r r r . ŗ r r h. r r h β-h r h , hhhh h r rh, h , h • . r, r, . r h rhr, ŗ, rh, r h h h . r r r, . h r h r h h ŗ . h r h h , r r r h . . . . . rr h r , . r, . hrh, r r h r h , r r r , h h r

r h h h r % ( / ) /

## Biocompatibility of SF/MWCNT Films

 $\mathbf{r}$ r, , r, r, ', h, h r, , h h • h , h r h r, n r r r, r 7 h r , rh, h h h r, r. . ŗ ) r ( r. r r

h h r r r, r. r . . r ( ) h h , , h , rh r , q ŗŗŗ r r r r r, nr rr h 7 / ş / h r ₽. h / r r r h r h r r, r , r (, )), h h , , , ( r, h r h, .\_r,r hrr r. r .rhr ŗ r r rh •

#### Conclusion

h hrr, h rr,



**Figure 5.** Attachment and proliferation of fibroblast cells on nanocomposite surfaces; (A) microscopic images of cultured fibroblast cells on SF (pure silk film), SF/M1 (SF/0.1 % (w/w) MWCNT film), SF/M2 (SF/0.5 % (w/w) MWCNT film) and SF/M3 (SF/1 % (w/w) MWCNT film) after 3 days and 7 days, (B) 3 h attachment of fibroblast cells on nanocomposite films, and (C) 3 day and 7 day proliferation of fibroblast cells on nanocomposite films. \*Significant difference between groups (\* <0.05). The data represent mean±SD ( =4).



# Acknowledgements

#### References

- A. K. Mohanty, M. Misra, and G. Hinrichsen, *Macromol. Mater. Eng.*, 276, 1 (2000).
- R. A. MacDonald, B. F. Laurenzi, G. Viswanathan, P. M. Ajayan, and J. P. Stegemann, *Biomed. Mater. Res. A.*, 74, 489 (2005).
- 3. S. Iijima, Nature, 354, 56 (1991).
- M. Shokrieh and R. Rafiee, *Mech. Compo. Mater.*, 46, 155 (2010).
- 5. A. A. Balandin, Nat. Mater., 10, 569 (2011).
- R. A. MacDonald, C. M. Voge, M. Kariolis, and J. P. Stegemann, *Acta Biomater.*, 4, 1583 (2008).
- S. Agarwal, X. Zhou, F. Ye, Q. He, G. C. Chen, J. Soo, F. Boey, H. Zhang, and P. Chen, *Langmuir*, 26, 2244 (2010).
- S. K. Misra, F. Ohashi, S. P. Valappil, J. C. Knowles, I. Roy, S. R. P. Silva, V. Salih, and A. R. Boccaccini, *Acta Biomater.*, 6, 735 (2010).
- J. E. Tercero, S. Namin, D. Lahiri, K. Balani, N. Tsoukias, and A. Agarwal, *Mater. Sci. Eng. C-Mater. Biol. Appl.*, 29, 2195 (2009).
- A. Lobo, E. Antunes, A. Machado, C. Pacheco-Soares, V. Trava-Airoldi, and E. Corat, *Mater. Sci. Eng. C-Mater. Biol. Appl.*, 28, 264 (2008).
- 11. B. S. Harrison and A. Atala, Biomaterials, 28, 344 (2007).

- G. H. Altman, F. Diaz, C. Jakuba, T. Calabro, R. L. Horan, J. Chen, H. Lu, J. Richmond, and D. L. Kaplan, *Biomaterials*, 24, 401 (2003).
- U. J. Kim, J. Park, H. J. Kim, M. Wada, and D. L. Kaplan, *Biomaterials*, 26, 2775 (2005).
- Y. Wang, H. J. Kim, G. Vunjak-Novakovic, and D. L. Kaplan, *Biomaterials*, 27, 6064 (2006).
- 15. J. Qu, Y. Liu, Y. Yu, J. Li, and J. Luo, *Mater. Sci. Eng. C-Mater. Biol. Appl.*,