Silk/natural rubber (NR) and 3,4-dihydroxyphenylalanine (DOPA)-modified silk/NR composites: synthesis, mechanical properties and secondary structures

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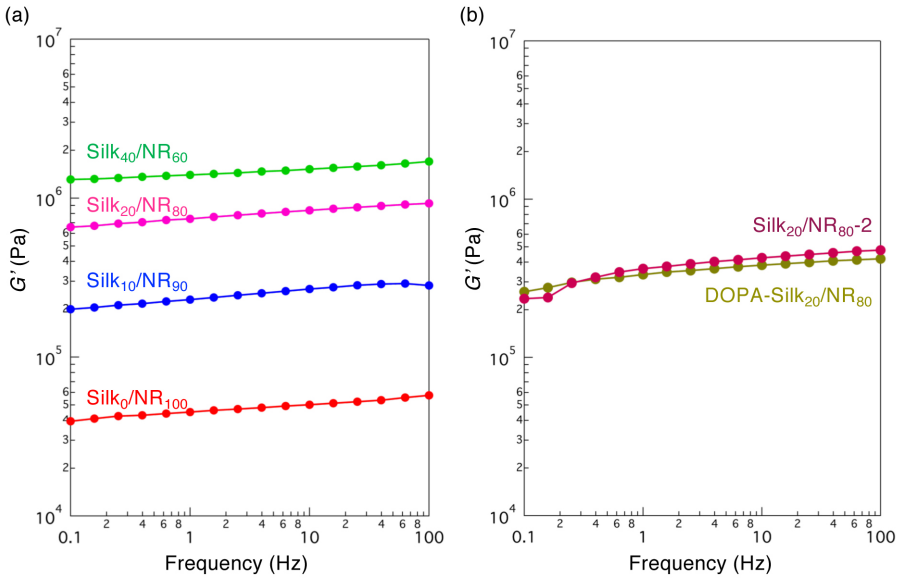

Figure S1. The frequency dependency of (a) silk/NR with different silk contents and (b) DOPA-silk$_{20}$/NR$_{80}$ and its control (silk$_{20}$/NR$_{80}$-2). The strain was fixed at 0.1%.

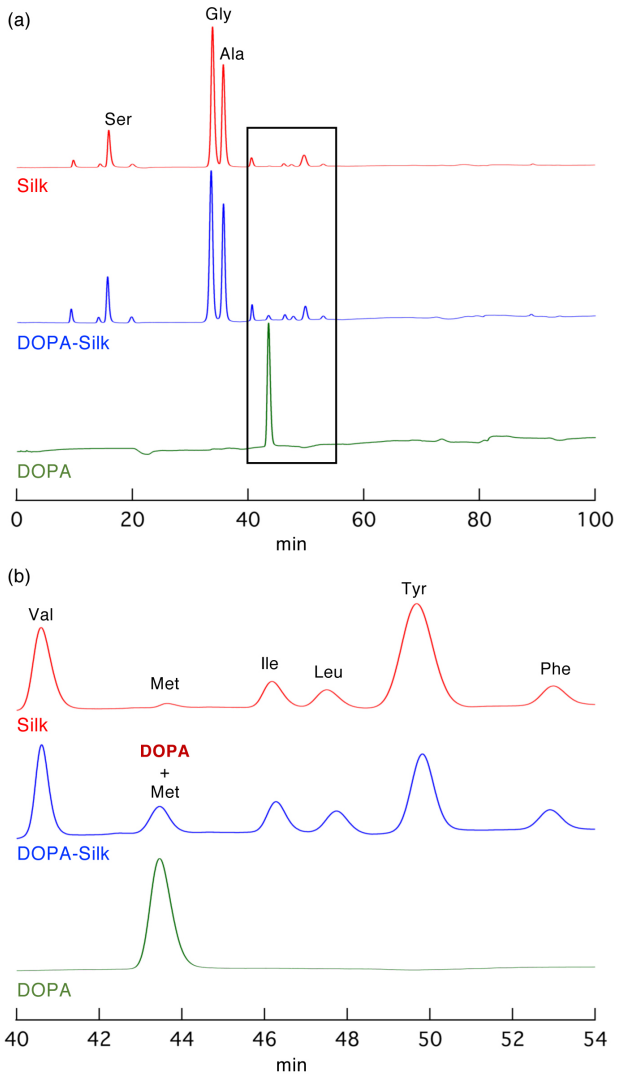

Figure S2. Amino acid analysis data by HPLC. Peaks for pure (unmodified) silk solution, DOPA-modified silk solution, and DOPA (control) in the range of (a) 0–100 min and (b) 40–54 min. Although the methionine peak, which was originally included in silk from *B. mori* cocoons, overlapped with the DOPA peak, the peak ratio of methionine was subtracted appropriately from DOPA-silk to properly determine the DOPA content.

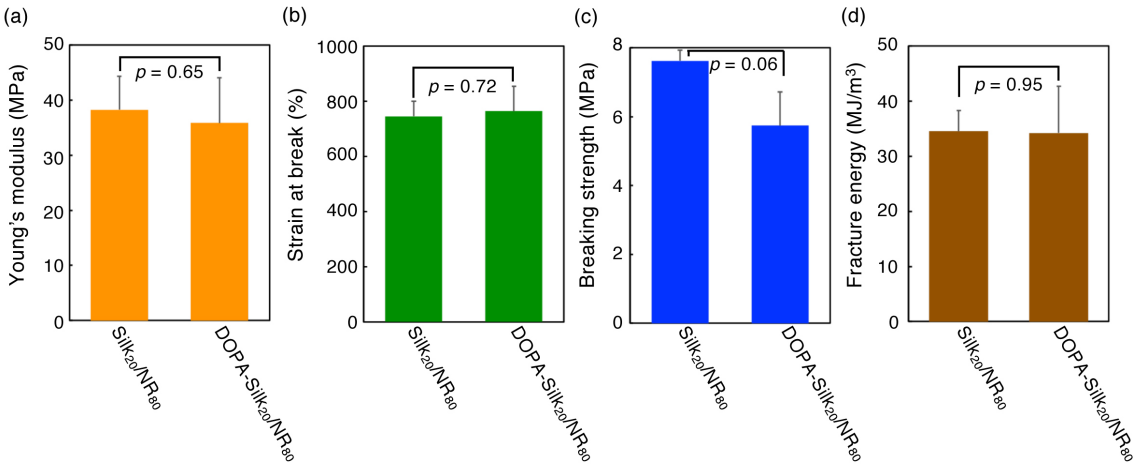

Figure S3. Mechanical properties of silk$_{20}$/NR$_{80}$ and DOPA-silk$_{20}$/NR$_{80}$: (a) Young's modulus, (b) strain at break, (c) breaking strength, and (d) fracture energy. No significant differences were found between these groups. The *p*-values between groups were described for each graph.

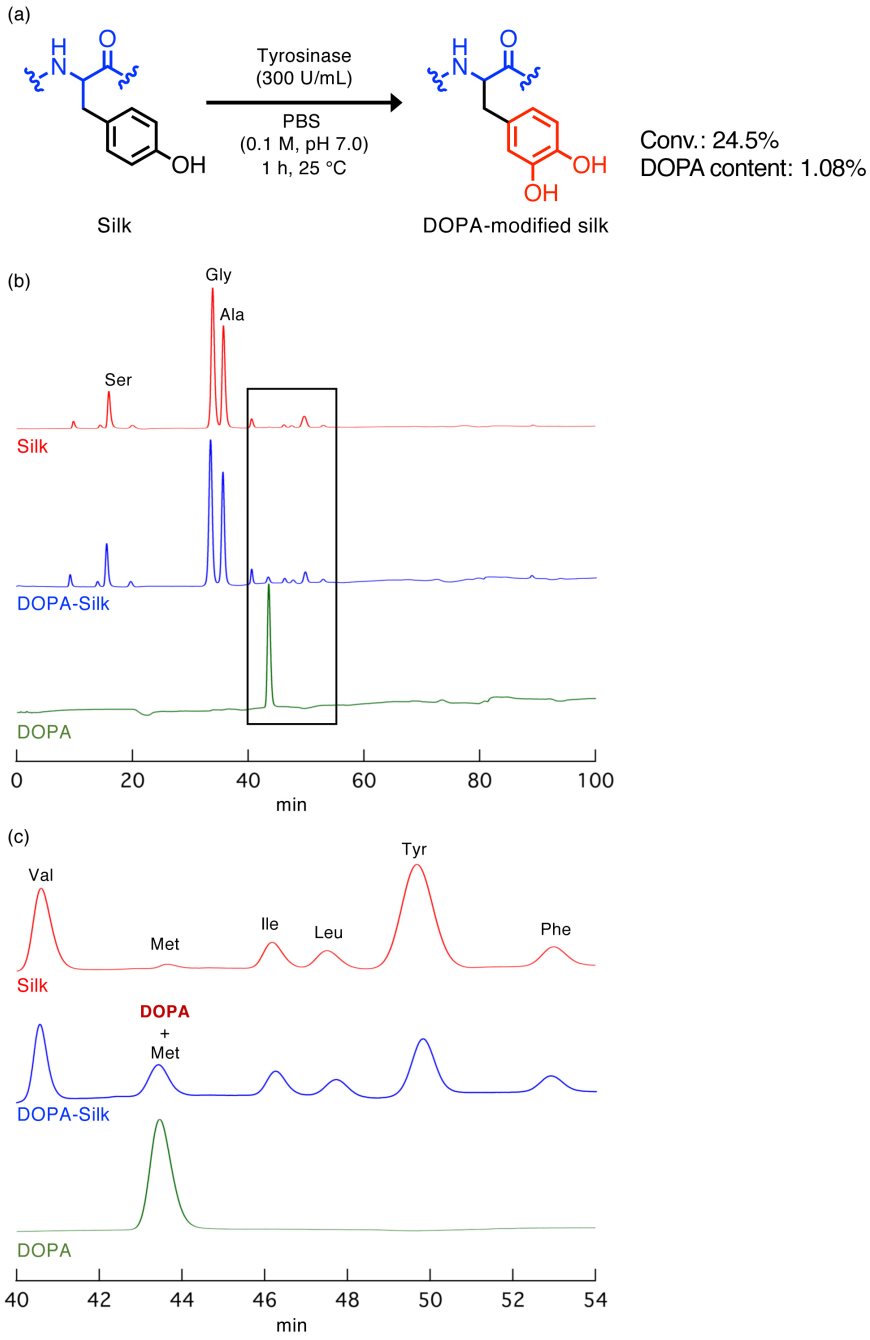

Figure S4. (a) Tyrosinase-catalyzed DOPA modification of silk. Silk solution was mixed with tyrosinase (300 U/mL) and PBS (0.1 M, pH 7.0) and stirred for 1 h at 25 °C. The reaction conversion and DOPA content were determined by below amino acid analysis data by HPLC. Peaks for pure (unmodified) silk solution, DOPA-modified silk solution, and DOPA (control) in the range of (b) 0–100 min and (c) 40–54 min. Although the methionine peak, which was originally included in silk from *B. mori* cocoons, overlapped with the DOPA peak, the peak ratio of methionine was subtracted appropriately from DOPA-silk to properly determine the DOPA content.