Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Tough and strong nacre-like composites from hyperbranched poly(amido amine) and clay nanosheets cross-linked by genipin

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1. **UV-Vis absorption of genipin crosslinked composite film, HPAMAM/nanoclay composite film and genipin aqueous solution**

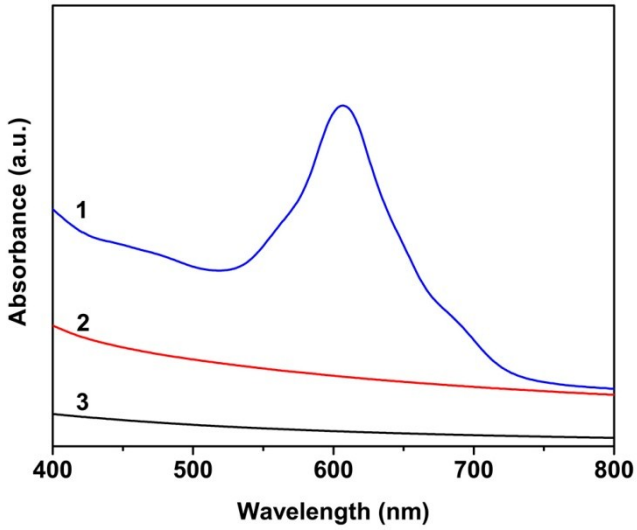

Fig. S1 UV-vis spectra of genipin crosslinked composite film (blue), HPAMAM/nanoclay composite film (red), and genipin aqueous solution (black). 1 - Concentration of genipin solution was 0.025 wt%; Reaction time was 3 hours

2. **Comparison of stress-strain curves of slightly crosslinked HPAMAM/nanoclay composite films and densely crosslinked samples**

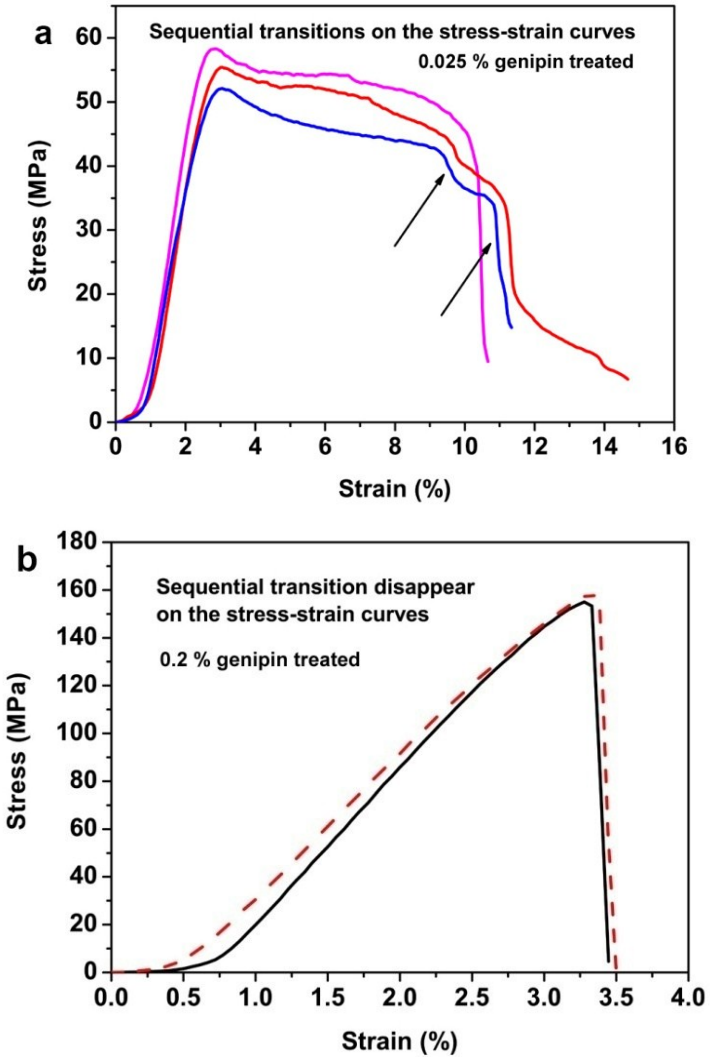

Fig. S2 Stress-strain curves of slightly and densely crosslinked HPAMAM/nanoclay composites. Concentration of genipin aqueous solution was 0.025% and 0.2 % respectively. Sequential transitions can be found on the stress-strain curves of slightly crosslinked samples. They suggest the rupture of sacrificial bonds inside the composites. However, for the densely crosslinked samples, sequential transitions disappeared due to the restriction on molecular motion.

3. **SEM images of the non-crosslinked composite film and crosslinked films**

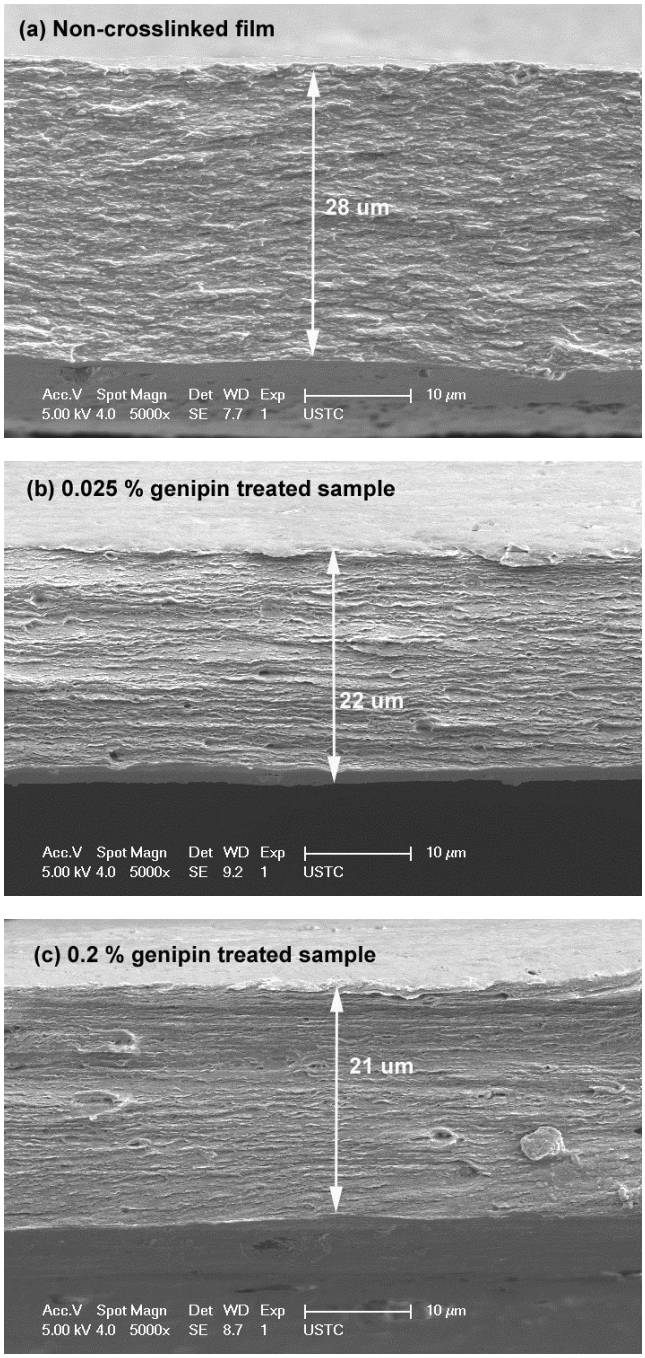

Fig. S3 Reduction of thickness of genipin crosslinked HPAMAM/nanoclay composite films. The genipin crosslinking greatly reduces the thickness of the HPAMAM/nanoclay composite films, suggesting the contraction of HPAMAM molecules. It will inevitably strengthen the interaction among the HPAMAMs and that between the HPAMAMs and clay nanosheets. That is, the mechanical strength of the composite films can be drastically improved.

4. **Demonstration to the FTIR results of genipin crosslinked composite films**

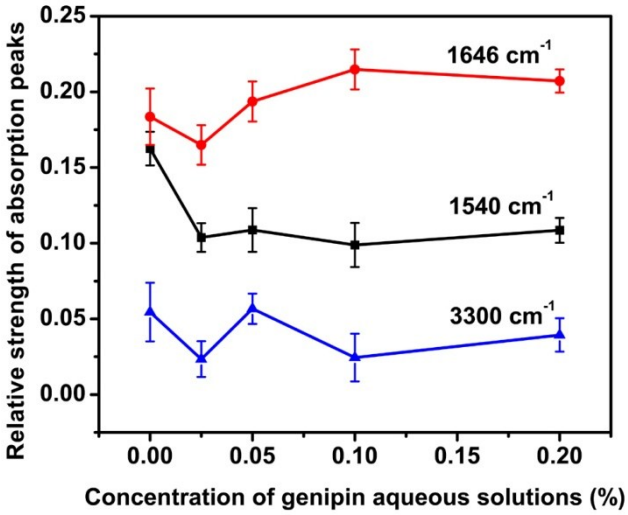

Fig. S4 Relative strength of absorption peaks of genipin crosslinked HPAMAM/nanoclay composite films. Strength of absorption peaks at 1646 cm^{-1} (amide I), 1540 cm^{-1} (amide II), and 3300 cm^{-1} (hydrogen bonded amine groups) were compared with the strength of absorption peak at 969 cm^{-1}, which was assigned as the absorption of clay, to give rise to relative values.

The crosslinking reaction between HPAMAM and genipin was characterized by ATR-FTIR. The results indicated that absorption peak at 1646 cm^{-1} (amide I) increased its strength, but the peak at 1540 cm^{-1} (Amide II) decreased the strength. Consequently, the ratio of Amide I/Amide II becomes higher as more genipin being applied. It indicates that the crosslinking degree increases as more genipin is used. According to the literature, [S1] the increase in absorbance at 1646 cm^{-1} suggests amine groups on the HPAMAM molecule are partly converted into the genipin-cross-linked heterocyclic amines. The decrease in absorbance at 1540 cm^{-1} indicates a nucleophilic attack by the amino groups of HPAMAM on the olefinic carbon atom at C-3 of deoxyloganin aglycone followed by the opening of dihydropyran ring.

However, the relative strength of hydrogen bonded amine groups (3300 cm^{-1}) decreased only a little. It suggests that the hydrogen bonds in the composite films are slightly affected during genipin crosslinking. Those hydrogen bonds can function as sacrificial bonds. As a result, the genipin crosslinked HPAMAM/nanoclay composite films are able to keep their excellent toughness.

References:

S1. F. L. Mi, *Biomacromolecules,* 2005, **6**, 975-987.