Exponential growth of layer-by-layer assembled coatings with well-dispersed ultrafine nanofillers: a facile route to scratch-resistant and transparent hybrid coatings

Xiaokong Liu, a Lu Zhou, a Feng Liu, a Mingyang Ji, a Wenge Tang, b Meijuan Pang, b and Junqi Sun* a

a State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
E-mail: sun_junqi@jlu.edu.cn.; Fax: 0086-431-85193421; Tel: 0086-431-85168723

b National Center of Quality Supervision and Inspect of Automobile Spare Parts, Changchun 130012, P. R. China.

*To whom correspondence should be addressed. Fax: 0086-431-85193421. E-mail: sun_junqi@jlu.edu.cn.

Figure S1. FT-IR absorbance spectra of the as-prepared (black line) and thermally cross-linked (red line) (PAA-CaCO3/PAH)*30 coatings. The appearance of the amine I peak at ~1640 cm⁻¹ in the FT-IR spectrum of the thermally cross-linked (PAA-CaCO3/PAH)*30 coating confirms the formation of amide bonds between the amine groups of PAH and the acid groups of PAA.
Figure S2. AFM image of the cross-linked (PAA-CaCO$_3$/PAH)$^{*20}$ coating. The coating has a root-mean-square (rms) roughness of 0.8 nm as measured by atomic force microscopy.

Figure S3. The energy dispersive X-ray (EDX) spectra of a thermally cross-linked (PAA-CaCO$_3$/PAH)$^{*30}$ coating which was scratched with a sharp scalpel to different depth. a) Before scratching, b-e) The (PAA-CaCO$_3$/PAH)$^{*30}$ coatings with a residual thickness of $2.83\,\mu m$ (b), $2.42\,\mu m$ (c), $1.12\,\mu m$ (d) and $0.45\,\mu m$ (e).

The energy dispersive X-ray analysis (EDX) has a deep depth detection which allows to identifying element distribution in the whole (PAA-CaCO$_3$/PAH)$^{*30}$ coating, as the Si signal from the underlying silicon substrate is detected for the 3.2-$\mu$m-thick (PAA-CaCO$_3$/PAH)$^{*30}$ coating. With more layers being removed from
(PAA-CaCO3/PAH)*30 coating, the intensity of Si signal in the corresponding EDX spectra increases gradually. The constant ratio of Ca to C, N and O in the coatings confirms the homogeneous dispersing of CaCO3 in the normal direction of the (PAA-CaCO3/PAH)*30 coating.

**Figure S4.** Optical image of a thermally cross-linked (PAA-CaCO3/PAH)*20 coating deposited on a glass substrate after adhesion test. The (PAA-CaCO3/PAH)*20 has a ASTM class 5B adhesion with the underlying glass substrate, which represents the highest level of adhesion.

**Figure S5.** Top-view SEM image of the piece of ramee cloth used in the rubbing test.