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Supporting information for:

Fluorescence quantification of inorganic particle dispersity for anti-aging evaluation of polymer composites

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EXPERIMENTAL SECTION

Chemicals and materials. Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, urea, K₂CO₃, KHCO₃, acetone, methanol, xylene, and absolute ethanol were purchased from Beijing Chemical Reagent Company . Low-density polyethylene (LDPE) was purchased from Alfa Aesar Chemicals Co., Ltd. Tetramethylrhodamine isothiocyanate (TMRITC) was purchased from HWRK Chem Co. Ltd. (3-aminopropyl) triethoxysilane (APTES) was brought from J&K Chemical Co. Ltd. SiO₂ particles with an average diameter of 3.0 µm were acquired from Macklin Biochemical Co. Ltd. Polypropylene (PP) was purchased from Aladdin Chemical. All the chemicals were used without further treatment.

Preparation and modification of MgAl-CO₃ LDHs. MgAl-CO₃ layered double hydroxide (LDHs) was synthesized through a hydrothermal method. Briefly, 2 mmol $Mg(NO_3)_2 \cdot 6H_2O$, 1 mmol Al(NO₃)₃·9H₂O and 12 mmol urea were dissolved in 80 mL deionized water and thermally treated in a reaction kettle at 100 °C for 24 h. The products were washed repeatedly with deionized water until the pH of the LDHs gel approached 7. The as-prepared LDHs were dispersed in acetone and stirred for different time (0 min, 6 min, 20 min and 240 min), and the LDHs were then filtered to obtain the acetone-LDHs gel.

Preparation of acetone-LDH/LDPE composites. Acetone-LDH/LDPE composites were prepared by solvent mixing method. Typically, 5 g LDPE, 100 mL xylene and LDHs (with the weight content of 0.5 % in LDPE) were added into a 250 mL flask. The mixture was refluxed at 140 °C for 2 h, and the mixture was then dispersed in the methanol. Afterwards, the mixture was filtered and washed with anhydrous ethanol. The as-prepared filter cake was then placed into a vacuum oven and dried at 65 °C for 24 h. The dried product was molded at 120 °C to obtain acetone-LDH/LDPE

composites with a thickness of 0.5 mm.

Thermal treatment of acetone-LDH/LDPE composites. The thermal treatment of acetone-LDH/LDPE composites was carried out by accelerated thermal aging experiments. The composite films were heated in an oven at 100 °C for 150 h and sampled for the measurements.

Quantification method for the dispersity of LDHs in the composites. We have proposed a calculation model to quantify both the uniformity and the dispersity of acetone-LDHs in the composites. Firstly, the volumes of the acetone-LDH particles were acquired by the Leica Application Suite X software and utilized as the critical parameters. Secondly, the dispersion uniformity for the acetone-LDH particles was acquired by calculating the volume deviations for the acetone-LDH particles in the polymer composites. Thirdly, the dispersion/aggregation degree of acetone-LDH particles was calculated according to the following steps. (I) Measuring the particle sizes of acetone-LDHs by SEM images and calculating the mean particle diameters as d_{LDH} . (II) Taking the acetone-LDH particles in the LDPE matrix as spherical model, volume of the acetone-LDH particles and the can be calculated as $V_{\rm LDH} = (4/3) \times \pi \times (d_{\rm LDH}/2)^3$. The aggregates of the acetone-LDH particles were regarded as the enlarged spheres with the diameter and volume as nd_{LDH} and n^3V_{LDH} , where n stands for the folds of the enlargement. (III) Dividing the acetone-LDH particles into three categories with the varied diameters and volumes of acetone-LDHs:

large aggregates (L):
$$d_L > 6d_{LDH}, V_L > 6^3 V_{LDH} = 216 V_{LDH},$$
medium aggregates (M): $6d_{LDH} > d_M > 3d_{LDH}, 6^3 V_{LDH} > V_M > 3^3 V_{LDH},$ small aggregates (S): $d_S < 3d_{LDH}, V_S < 3^3 V_{LDH} = 27 V_{LDH}.$

(IV) Calculating the volume distribution percentage of large (L), medium (M), and small (S) acetone-LDH aggregates. (V) Defining the degree of dispersity (A) as the

ratio of the percentages for the large aggregates to that for the small aggregates (A = L/S).

Fabrication of the SiO₂/LDPE composite films. SiO₂ of 5.0 g was dispersed in 50 mL NaOH aqueous solution (0.01 mol/L) for activation, followed by the washing with deionized water and anhydrous ethanol and drying at 60 °C. The activated SiO₂ (4.0 g) was dispersed in a mixture containing 150 mL anhydrous ethanol and 7.5 mL deionized water. Afterwards, 4.8 mL of APTES was added to the mixture at 80 °C, and the mixture was thoroughly washed after cooling. To realize the fluorescent labelling process, TMRITC was dissolved in DMSO and diluted in Na₂CO₃-NaHCO₃ buffer at pH 9 (0.056 mmol/L) for use. The as-prepared APTES-SiO₂ was added into the TMRITC fluorescent solution and stirred for 2h to acquire TMRITC-labelled SiO₂. The TMRITC-labelled SiO₂ particles were dried and ground with PE with a content of 0.5wt%, followed by the moulding at 120 °C to obtain SiO₂/LDPE composite films.

Preparation of melt-blended LDHs/PP composite films. PP and LDHs were mixed in a two-high mill at 170°C for 10 min with the contents of LDHs of 0.5 wt%. The mixture was moulded at 170°C to acquire a LDHs/PP composite with a thickness of ~ 0.5mm.

Apparatus and characterizations. The structures of LDHs and acetone-LDHs were characterized by D8 ADVANCE X-ray diffraction (XRD) at 40 kV, 50 mA with a Cu K α radiation ($\lambda = 0.1541$ nm) in the range of $2\theta = 2 - 70^{\circ}$. Morphologies of LDHs and acetone-LDHs were characterized by the JSM-7800F scanning electron microscope (SEM). Fluorescence spectra of LDHs, acetone-LDHs and TMRITC-labelled SiO₂ were measured on an F-7000 fluorescence spectrometer (Hitachi, Japan) with a scanning rate of 2400 nm/min. Fluorescence images of LDHs, acetone-LDHs, acetone

laser scanning microscope (CLSM) with the excitation wavelength of 405 nm and acquisition range of 415 - 485 nm. The excitation wavelength was set as 488 nm for the SiO₂/LDPE composites, and the emissions were collected in the range of 560 - 600nm. Fourier-transform infrared (FT-IR) spectra of the composite films were measured on a Nicolet 6700 infrared microscopy equipped with attenuated total reflection (ATR), and the scan range was set in the range of 400 - 4000 cm⁻¹.



Fig. S1 Dispersion of acetone-LDHs (left) and LDHs (right) in xylene.



Fig. S2 XRD patterns of LDHs and acetone-modified LDHs.



Fig. S3 SEM images of (A) LDHs and (B) acetone-modified LDHs.



Fig. S4 Fluorescence excitation spectra (dotted line) and emission spectra (solid line) of LDHs and acetone-LDHs after thermal treatment.



Fig. S5 Fluorescence images of (A) LDHs and (B) acetone-LDHs powder after thermal treatment.



Fig. S6 (A) Dark-field, (B) bright-field and (C) merged images captured by CLSM, and (D) showed the statistical process for the particles with different volumes acquired by Leica Application Suite X software.



Fig. S7 Three-dimensional fluorescence images of acetone-LDH/LDPE composite films from the other three parallel experiments (the LDHs were stirred in acetone for 0 min).



Fig. S8 Three-dimensional fluorescence images of acetone-LDH/LDPE composite films from the other three parallel experiments (the LDHs were stirred in acetone for 6 min).



Fig. S9 Three-dimensional fluorescence images of acetone-LDH/LDPE composite films from the other three parallel experiments (the LDHs were stirred in acetone for 20 min).



Fig. S10 Three-dimensional fluorescence images of acetone-LDH/LDPE composite films from the other three parallel experiments (the LDHs were stirred in acetone for 240 min).



Fig. S11 Enlarged three-dimensional fluorescence images of LDHs/LDPE composites.



Fig. S12 (A) The number percentages and (B) volume percentages of LDH particles in different volume intervals in the composite films after different modification time.



Fig. S13 (A) Photos under the UV irradiation and (B) fluorescence spectra of SiO_2 and TMRITClabelled SiO_2 under the excitation wavelength of 488 nm.



Fig. S14 Three-dimensional fluorescence images of $SiO_2/LDPE$ composite films.



Fig. S15 Three-dimensional fluorescence images of LDHs/PP composite films manufactured by melt blending method.



Fig. S16 Carbonyl index variations of acetone-LDH/LDPE composite films after thermal treatment under 100 °C for 150 h.

Table S1. The variations for the largest volumes of acetone-LDH particles in composite films under

 different modification time from four parallel experiments.

| | 0 min | 6 min | 20 min | 240 min |
|--|---------|---------|--------|---------|
| $V_{\rm max}$ -1 (μm^3) | 11846.1 | 6628.9 | 3222.8 | 3260.3 |
| $V_{\rm max}^{}$ -2 ($\mu { m m}^3$) | 10420.5 | 6991.0 | 2483.7 | 2506.9 |
| $V_{\rm max}$ -3 (μm^3) | 10164.8 | 12690.9 | 5158.6 | 1409.8 |
| $V_{\rm max}$ -4 (μm^3) | 6923.9 | 7755.1 | 2391.9 | 2828.7 |
| Average value (µm ³) | 9838.8 | 8516.5 | 3314.3 | 2501.4 |
| Standard deviation (µm ³) | 2079.3 | 2822.3 | 1284.6 | 790.5 |

Table S2. The variations for the average volumes of acetone-LDH particles in composite films under

 different modification time from four parallel experiments.

| | 0 min | 6 min | 20 min | 240 min |
|---------------------------------------|-------|-------|--------|---------|
| $V_{\rm ave}$ -1 (μm^3) | 63.7 | 72.3 | 18.9 | 33.5 |
| $V_{\rm ave}$ -2 (μm^3) | 89.2 | 76.5 | 33.5 | 33.2 |
| $V_{\rm ave}$ -3 (μm^3) | 118.7 | 104.7 | 40.2 | 39.2 |
| $V_{\rm ave}$ -4 (μm^3) | 189.8 | 51.8 | 36.3 | 24.3 |
| Average value (µm ³) | 115.3 | 76.4 | 32.2 | 32.5 |
| Standard deviation (µm ³) | 54.5 | 21.8 | 9.3 | 6.1 |

| | 0 min | 6 min | 20 min | 240 min |
|--------------------|--------|--------|--------|---------|
| С.І1 | 0.2683 | 0.2633 | 0.0665 | 0.0669 |
| С.І2 | 0.3652 | 0.2819 | 0.0786 | 0.0672 |
| С.ІЗ | 0.3175 | 0.2264 | 0.0872 | 0.0638 |
| С.І4 | 0.3335 | 0.2084 | 0.0816 | 0.0522 |
| С.І5 | 0.2687 | 0.2043 | 0.0754 | 0.0423 |
| Average value | 0.3107 | 0.2369 | 0.0779 | 0.0585 |
| Standard deviation | 0.0421 | 0.0343 | 0.0077 | 0.0109 |

Table S3. Carbonyl index variations of composite films after heat treatment under 100 °C for 150 h.