Supplementary Information

Simultaneously enhancing the flame retardancy and toughness of epoxy by lamellar dodecyl-ammonium dihydrogen phosphate

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General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Bisphenol A diglycidyl ether epoxy (DGEBA, E-44) was supplied by Jiangsu Sanmu Group Corporation. The epoxy resin was cured by *4,4*-diaminodiphenyl methane (DADPM) which was purchased from Aladdin Reagent Co., Ltd.. The ratio between epoxy resin and curing agent was 100:22 by weight. Dodecylamine ($C_{12}A$), tetradecylamine ($C_{14}A$), hexadecylamine ($C_{16}A$), octadecylamine ($C_{18}A$) (and phosphoric acid (85%) were supplied by Aladdin reagents Co., Ltd. and Sinopharm Chemical Reagent Co., Ltd., respectively.

Preparation of flame retardant $C_{12}ADP$

Lamellar dodecyl-ammonium dihydrogen phosphate was synthesized by one-pot method[1]. To take the monolayer $C_{12}ADP$ as example, Firstly, 6.0 mmol phosphoric acid were dissolved into 6 mL deionized water, then 3.0 mmol dodecylamine were drop wisely added into the above mentioned solution under stirring with subsequent ultrasonication for 15 minutes. After that, the resulting mixture statically reacted at room temperature for 48 hours; a white powder ($C_{12}ADP$) was obtained by vacuum filtration and washed with ethanol to remove the excess reactants. Finally, the powder was dried in a vacuum oven at 40 °C over night.

Preparation of EP/$C_{12}ADP$ composites

The process of preparing EP/$C_{12}ADP$ composites is as follows. First, 30.0 g DGEBA was heated in 90 °C for 10 min before mixing with a certain amount of $C_{12}ADP$ and 6.5 g curing agent (DADPM). Then, the mixture was mixed in an ultrasonication bath for 10 min, with subsequently vacuum to remove air bubbles. After that the mixture was poured into silicon rubber mold which was vacuumed to remove air bubbles. The samples were cured at 90 °C for 2 hours, subsequently at 120 °C for another 2 hours. The EP/$C_{12}ADP$ composites were named in abbreviation as EP, EMP-1.5, EMP-5, and EMP-10 according to the contents of $C_{12}ADP$ (0, 1.5 wt.%, 5 wt.%, and 10 wt.%, respectively).

Measurements

The powder X-ray diffraction (PXRD) patterns were recorded on a PHILIP Panalytical X-pert powder diffractometer (Netherlands) equipped with a Cu *Kα* tube (λ=1.54056 Å) and graphite monochromator at a scan rate of 0.02 °/s. The operating voltage and current was 40 kV and 50 mA, respectively.

Scanning electron microscopy (SEM) images were collected on a LEO-1530. Samples were coated with a gold layer of about 10 nm in thickness in order to improve conductivity.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to analyze the elements composition of samples. Samples were first dissolved in the HCl/HNO_3 mixed solution. The spectrometer applied was Varian Vista RL.

The thermal behavior of samples was investigated by using a SDT Q600 thermogravimetric

analyzer in air atmosphere at a heating rate of 10 °C/min with a sample weight of approximately 10 mg.

The flame retardant properties of samples were studied by HC-2 oxygen index meter with the sample size of 100×6.5×3 mm according to GB/T 2406.1-2008cone calorimeter with the sample size of 100×100×3 mm according to ISO 5660 standard. The heat flux in Cone Calorimeter test was 35 kW/m^2. Measurements of each sample were carried out in duplicate.

Impact toughness values of samples were obtained from the ZBC1400-B un-notched Charpy impact test machine according to GB/T 1403-93 standard with the sample size of 4×10×100 mm, and measurement was carried out for 10 times and the average result was considered as a valid value.

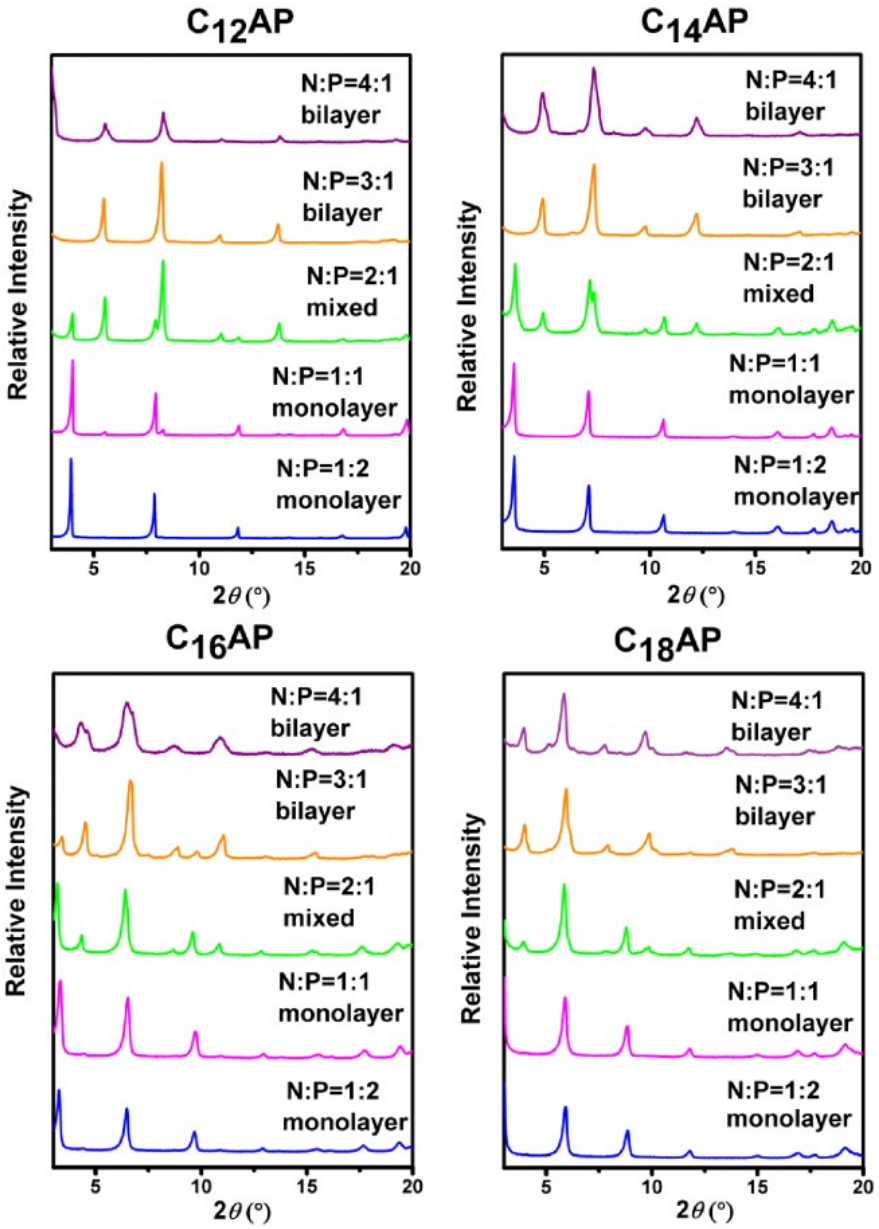

Fig. s1 Effect of molar ratio of amine to phosphoric acid on the layer structure of Alkyl-ammonium (di)hydrogen phosphates. C_{12}AP, C_{14}AP, C_{16}AP and C_{18}AP represent phosphates based on C_{12}A, C_{14}A, C_{16}A and C_{18}A, respectively.

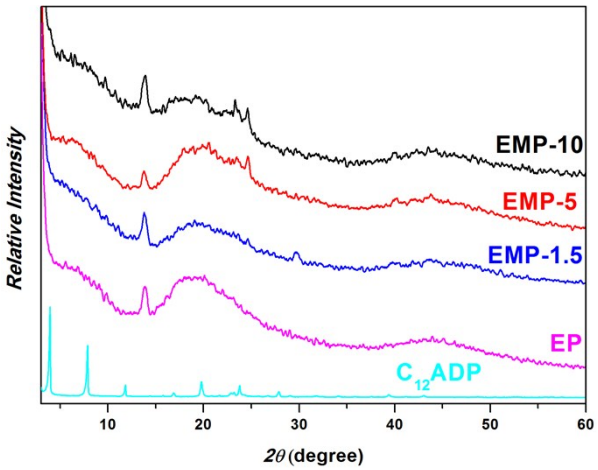

Fig. s2 Powder XRD patterns of EP/C_{12}ADP composites in comparison with that of EP modifier C_{12}ADP

Reference

1 S. Chen, H. Borrmann, Y.X. Huang, Z.J. Zhang, H.H. Chen, J.T. Zhao, Langmuir 2008, 24, 9323.