

SUPPORTING INFORMATION

Piperazine-Modified Ammonium Polyphosphate as Monocomponent Flame-Retardant Hardener for Epoxy Resin: Flame Retardance, Curing Behavior and Mechanical Property

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Figure S1. XPS spectra (N_{1s}) of PAz-APP.

Figure S2. FTIR spectra of APP and PAz-APP.

Figure S3. 1H and ^{13}C -NMR spectra of APP, PAz and PAz-APP, for comparison, physical mixture of PAz and APP (PAz+APP) was also recorded.

Table S1. Elemental contents of APP and PAz-APP.

Table S2. The corresponding structures of each binding energy in XPS testing.

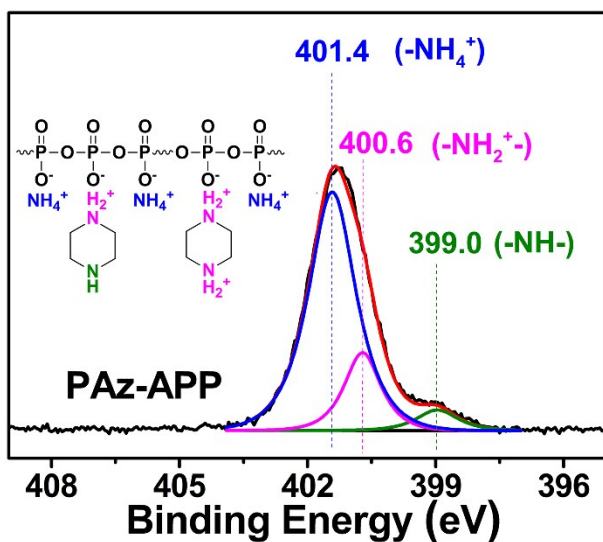


Figure S1. XPS spectra (N_{1s}) of PAz-APP.

There were three binding energy peaks appeared in this spectrum, meaning the existence of three different nitrogen chemical structures in PAz-APP. The binding energy at 401.5 eV corresponded to NH₄⁺. The characteristic binding energy of new formed -NH₂⁺⁻ group was located at 400.6 eV. The peak at 399.0 eV was ascribed to the -NH- group, unambiguously indicated the existing of secondary amino structure in modified APP.

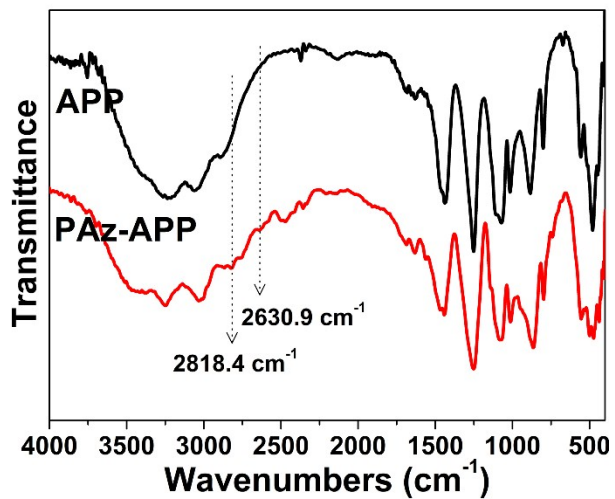


Figure S2. FTIR spectra of APP and PAz-APP.

In the FTIR spectra, compared with APP, the new weak peaks at 2630.9 and 2818.4 cm⁻¹ of PAz-APP were ascribed to the vibration of $-\text{NH}_2^+$ and $-\text{CH}_2-$, respectively. This means that the piperazine salt (R-NH_2^+), instead of ammonium salt (NH_4^+), was formed after modification reaction between PAz and APP.

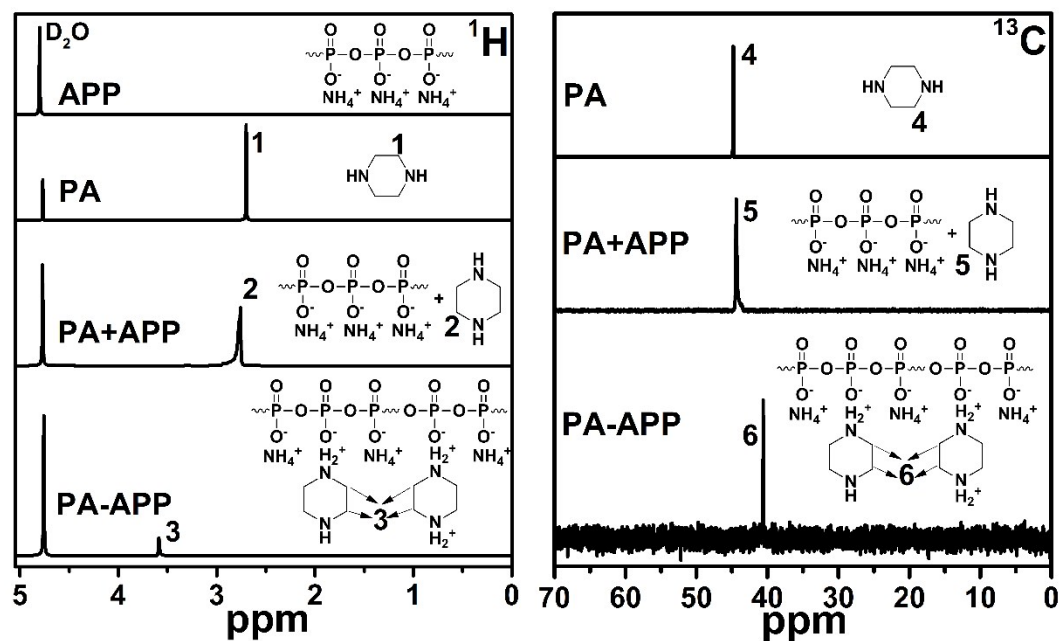


Figure S3. ^1H and ^{13}C -NMR spectra of APP, PAz and PAz-APP, for comparison, physical mixture of PAz and APP (PAz+APP) was also recorded.

To further confirm the chemical structure of functional PAz-APP, ^1H and ^{13}C -NMR were conducted. For comparison, both the APP, PAz, PAz-APP and physical mixture of PAz and APP (PAz+APP) were tested. These shifts extensively indicated the successful cation exchange reaction between PAz-APP and PAz.

Table S1. Elemental contents of APP and PAz-APP.

	C (%)	N (%)	H (%)	P (%)
II-APP	0.1	13.0	4.2	28.9
PAz-APP	11.5	12.5	5.5	23.3

After cation exchange reaction with PAz, the corresponding elemental contents in PAz-APP all changed more or less. Particularly, the content of C greatly increased from 0.1 % to 11.5 %. Conversely, the P content in PAz-APP was obviously decreased from 28.9 % to 23.3 %. Both predicting results remarkably demonstrated the successful reaction between PAz and APP.

Table S2. The corresponding structures of each binding energy in XPS testing.

binding energy (eV)	the corresponding structure
132.9	organic or inorganic phosphates
133.7	P-O-P
133.9	phosphorus oxides
134.3	the further crosslinking of phosphoric acid
135.0	phosphorus oxides
284.5	C-H, C-C in aliphatic and aromatic groups
285.2	C=C
286.2	C-O-C, C-OH, or C-N
286.6	C-O-C, C-OH, or C-N
397.0	nitrogen oxides
398.3	-N= group in a cyclic structure
398.9	-C=NH or N-C groups (pyridinic N in initial resin)
399.0	-NH-
399.6	tertiary amino groups
399.7	P-N-P
400.6	R-NH ₂ ⁺
401.4	NH ₄ ⁺

530.6	oxides in the residue
531.6	O=P, O=C
532.0	-OH
532.5	the ether bonds
532.8	C-O
533.1	P-O-P, C-O-P
534.3	C-O
538.6	C-O
