Supplementary Information (SI) for Journal of Materials Chemistry A.

Construction of Phosphonitrile Derivatives-Hybridized EPDM Dense Crosslinked Network for Enhanced Mechanics and Ablation Resistance

Supporting Information

The thermal decomposition of phosphonitrile derivatives is shown in Fig. S1. HAPPCP begins to decompose at lower temperatures, with an $T_{5\%}$ (the temperature of the 5% weight loss) of 203°C. As the temperature increased, HAPPCP decomposed rapidly in a shorter time with a mass residual rate of 21.5% at 800°C (Fig. S1 (a)). The thermal decomposition process of HEACP is relatively slow (Fig. S1 (b)), and can remain stable below 400 °C, with an $T_{5\%}$ of 457°C. As the temperature increased, HEACP decomposed slowly, and the mass residual rate at 800°C is as high as 74.4 %, showing significantly higher thermal stability than HAPPCP. This may be due to the intramolecular conjugation effect of HEACP and more N atoms, which exist to inhibit thermal decomposition.

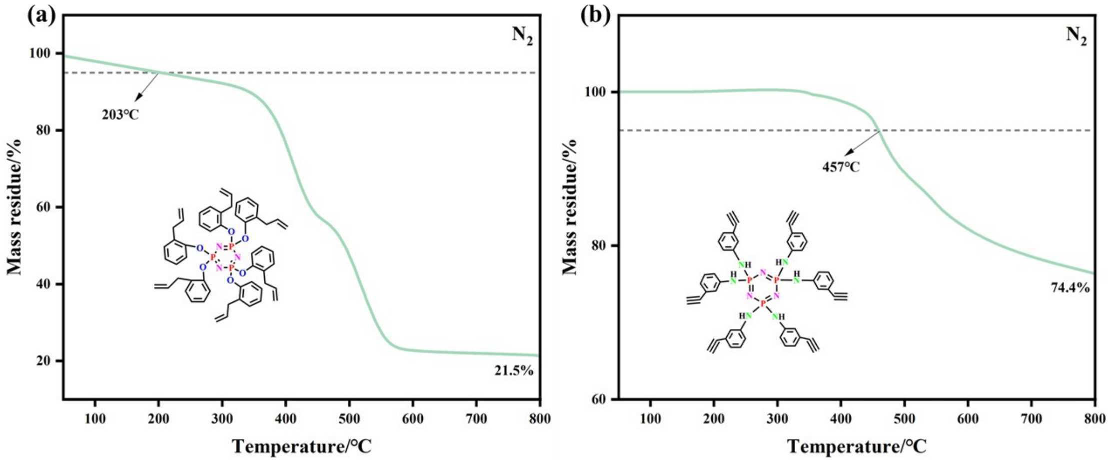

Fig. S1 The TG curves of HAPPCP (a) and HEACP (b)

Fig.S2 (a, b) shows the mechanical properties of phosphonitrile modified EPDM/SiO_2 composites. It can be seen that the tensile strength and elongation at break of unmodified EPDM/SiO_2 were low, with values of 9.79 MPa and 363%, respectively. With the addition of HAPPCP, the mechanical properties of HAPPCP modified EPDM/SiO_2 composites firstly improved and then declined, and the tensile strength and elongation at break of 3phr HAPPCP modified EPDM/SiO_2 composites reached the maximum value of 20.17 MPa and 575%, which were enhanced by 106.03% and 58.4% compared with unmodified EPDM/SiO_2, respectively. Similarly, the mechanical properties of HEACP modified EPDM/SiO_2 composites firstly improved and then declined with the addition of HAPPCP, and the tensile strength and elongation at break of only 1phr HEACP modified EPDM/SiO_2 composites reached the maximum value of 25.41 MPa and 599%, which were enhanced by 154.86% and 65.01% compared with unmodified EPDM/SiO_2, respectively. The tensile cross sections of unmodified EPDM/SiO_2, 3phr HAPPCP and 1phr HEACP modified EPDM/ SiO_2 composites were observed in Fig. S2 (c-e). The 3phr HAPPCP and 1phr HEACP modified EPDM/SiO_2 composites had rougher tensile sections with denser, larger and deeper pores than EPDM/SiO_2, which can be understood as stronger interfacial interactions within the modified rubbers that require more energy for fracturing to form these cavities, resulting in macroscopically boosted mechanical properties.

With Stretching photos Fig. S2 (f-i).

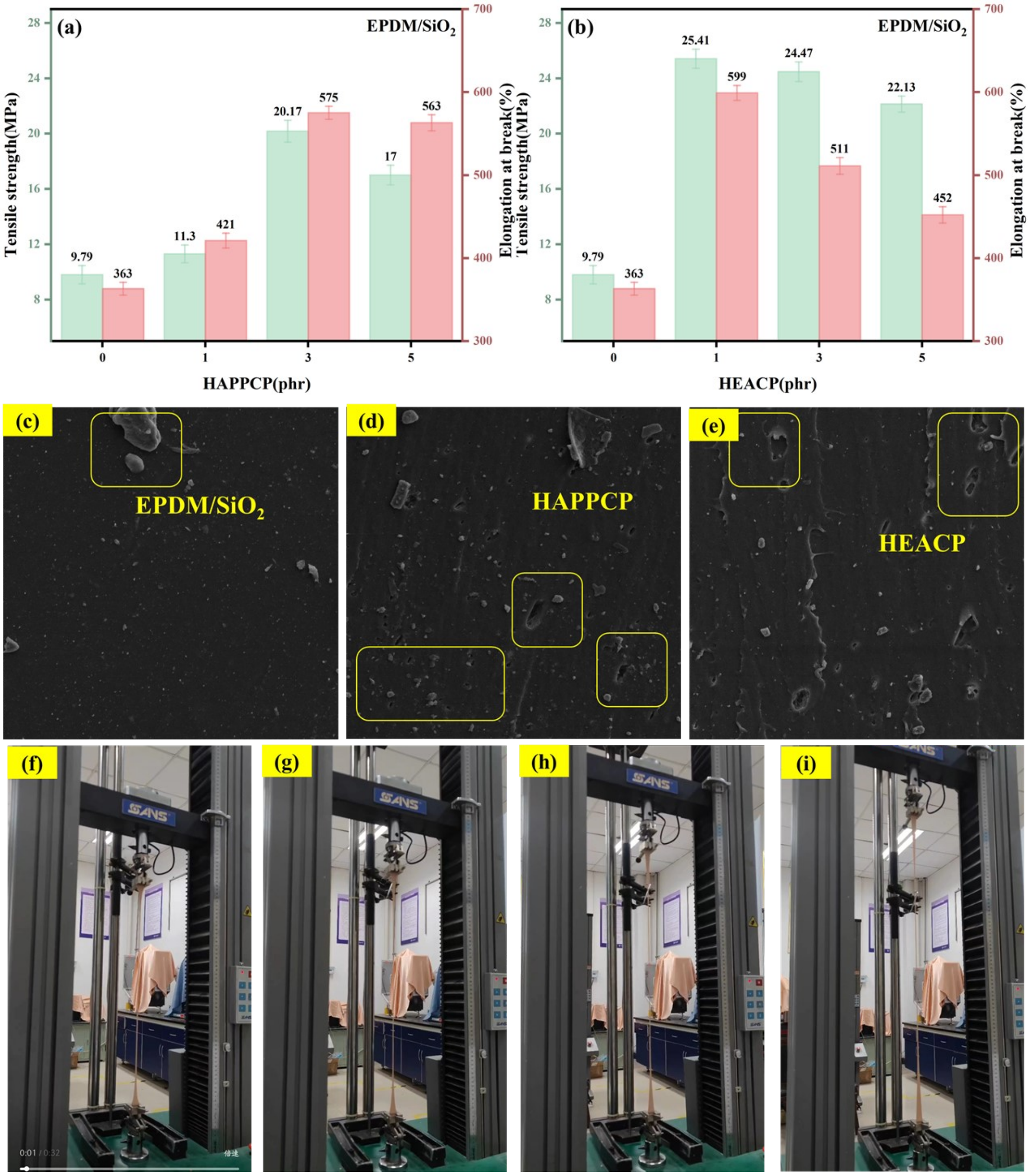

Fig. S2 Variation of mechanical property with phosphonitrile derivatives content for HAPPCP (a) and HEACP (b) modified EPDM/SiO$_2$ composites and correspondingly the SEM image of tensile section (c-e); Stretching photos (f-i)

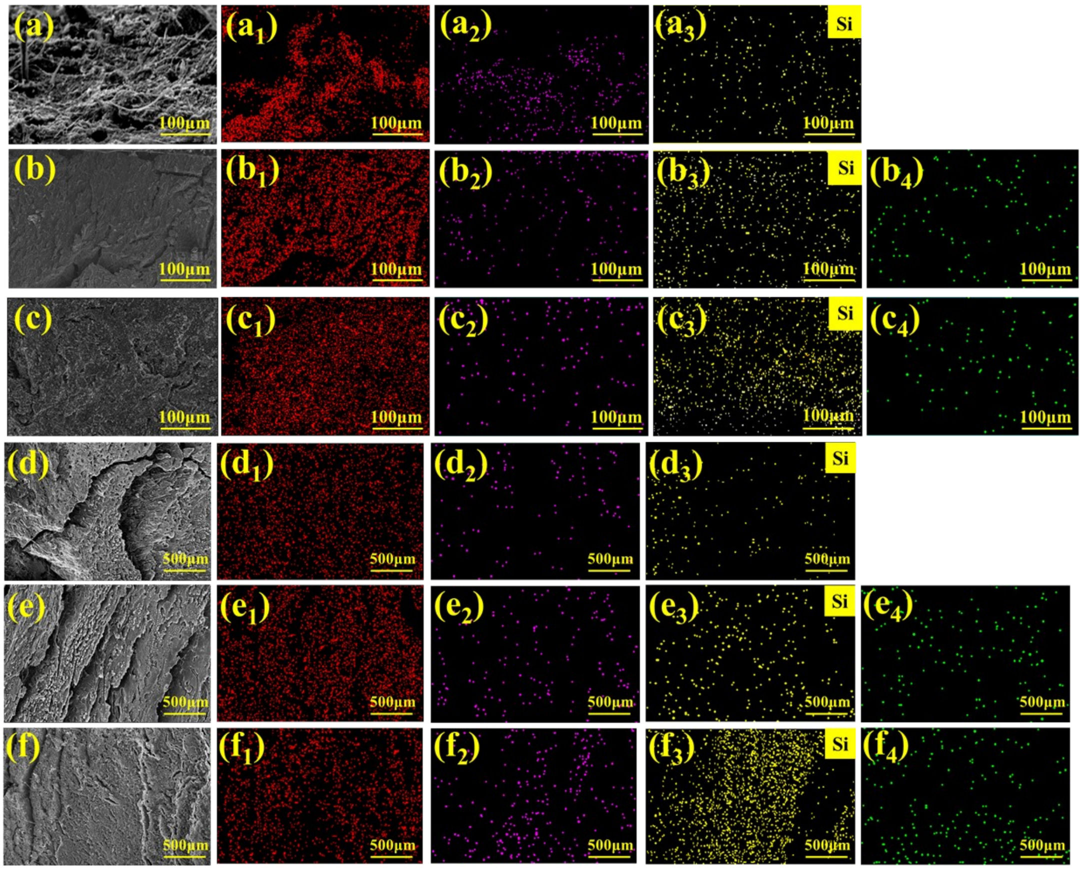

Fig. S3 The cross-section micro-morphology and EDS scans of ablated carbon layer of EPDM/AF/SiO_2 (a-a$_3$), 3phrHAPPCP/EPDM/AF/SiO_2 (b-b$_4$) and 1phrHEACP/EPDM/AF/SiO_2 (c-c$_4$); The surface micro-morphology and EDS scans of ablated carbon layer of EPDM/AF/SiO_2 (d-d$_3$), 3phrHAPPCP/EPDM/AF/SiO_2 (e-e$_4$) and 1phrHEACP/EPDM/AF/SiO_2 (f-f$_4$)

Table S1 Crystal size of ablated carbon layers from phosphonitrile derivatives modulated EPDM/AF/SiO_2 composites

sample	EPDM/AF/SiO_2	EPDM/AF/SiO_2/HAPPCP-3	EPDM/AF/SiO_2/HEACP-1
I_D/I_G	1.24	0.90	0.75
La(nm)	3.55	4.89	5.87