

SUPPORTING INFORMATION

for

A phosphorus-containing imidazole derivative towards liquid oxygen compatibility and toughness of epoxy resin

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CONTENT

1 DMA analysis

2 Post-impact topography

1 Dynamic Thermomechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was carried out by Pyris Diamond dynamic thermal mechanical analyzer (PE, USA) in the three-point bending mode (30-200 °C, heating rate = 5 °C/min, constant frequency = 1.0 Hz). The sample's size was 40 × 6 × 3 mm³.

The influence of VAD on the thermomechanical properties of EP was researched by DMA. Fig.S3 manifested the DMA curves of (a) tan δ and (b) storage modulus in relation to temperature for EP thermosets. Detailed data were shown in Table S1, including crosslinking density ρ and glass transition temperature (T_g). ρ was computed in the light of the following formula:¹

$$\rho = E' / 3RT \quad (1)$$

Where E' is the storage modulus when the temperature is 40 °C higher than T_g , and the ideal gas constant is represented by R (8.314 KJ/mol).

As shown in Fig. S3 (a), all the peaks were single peaks, indicating good compatibility between VAD and EP, and there was no phase separation. The shape of the secondary transition β peak of the modified epoxy resin was basically the same, and with the increase of VAD content, T_{β} decreased at first and then increased, but it was still lower

than that of pure EP. The shift of β peak to low temperature indicated that the flexible methylene chain introduced into EP/VAD thermoset increased the intermolecular free volume, enhanced the plastic deformation ability, and made the modified resin systems can withstand lower temperature and improved its toughness although the polymer volume shrunk and the molecular chains accumulated more closely at low temperature.

Furthermore, with the increase of VAD content, the storage modulus at 50 °C increased incrementally from 1815 MPa of pure EP to 2506 MPa of EP/VAD-7.5, which was attributed to the introduction of rigid aromatic rings in the network and the physical interaction (such as hydrogen bonding) between VAD and EP matrix. However, the glass transition temperature T_g (the peak temperature in the $\tan \delta$ curve is related to T_g) of the EP/VAD system slightly declined as the VAD content increased. On the one hand, the large groups in VAD hindered EP from forming the cross-linking network structure, which resulted in a decrease in crosslinking density, and a strong limiting effect which limited the cooperative movement of EP networks;^{2, 3} on the other hand, the flexible methylene of VAD increased the mobility of its neighboring networks.⁴

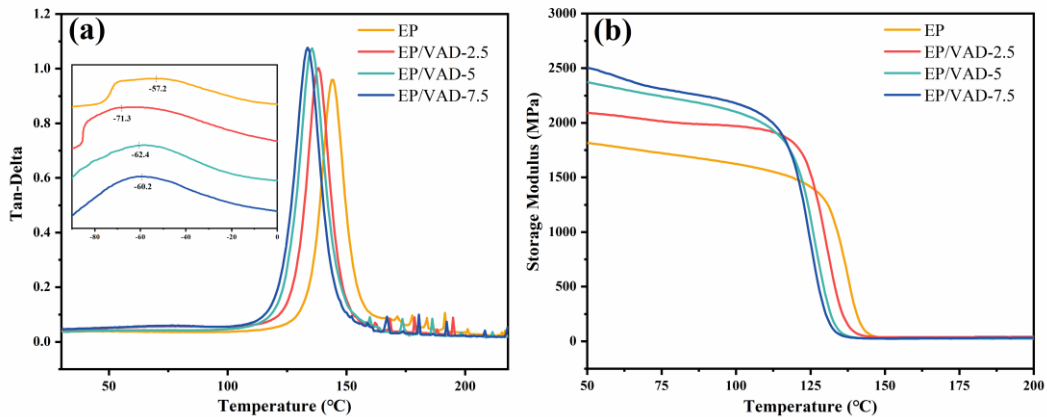


Fig. S1 DMA curve of modified epoxy resin.

Table S1

Thermomechanical properties of EP/VAD-x.

Samples	T_g (°C)	T_{β} (°C)	$E'_{50^{\circ}\text{C}}$ (MPa)	$E'_{(T_g+40)^{\circ}\text{C}}$ (MPa)	ρ (mol/m ³)
EP	144.5	-57.2	1815	39.8	3820
EP/VAD-2.5%	138.4	-71.3	2090	37.6	3663
EP/VAD-5%	135.5	-62.4	2371	32.5	3188
EP/VAD-7.5%	133.7	-60.2	2506	27.5	2709

2 Morphology by the impact with LOX

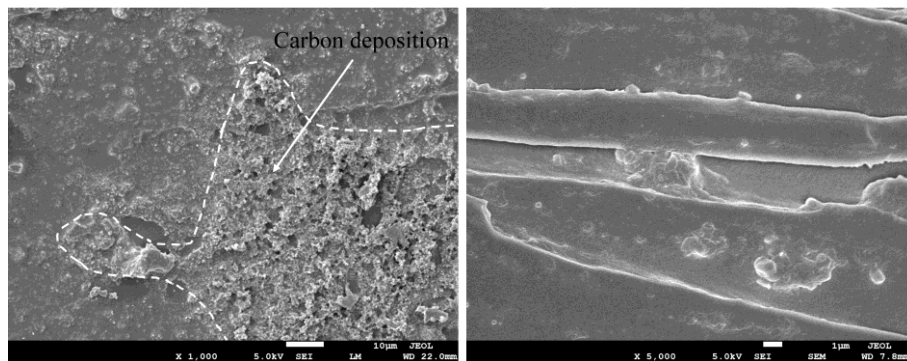


Fig. S2 Failed surface micro-morphology of EP/VAD-5 by the impact with LOX.

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