Effect of 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide on Liquid Oxygen Compatibility of Bisphenol A Epoxy Resin

Zhanjun Wu, Jialiang Li, Yingpu Chen, Zhi Wang, Shichao Li

School of Aeronautics and Astronautics, Faculty of Vehicle Engineering and Mechanics, State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian 116024, People's Republic of China
Correspondence to: Z. Wang (E-mail: wzdlut@dlut.edu.cn)

ABSTRACT: In this study, bisphenol A epoxy resin (DGEBA) was chemically modified by 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), and the molecular structure of the modified epoxy resin was characterized by Fourier transform infrared spectra. The effects of DOPO on liquid oxygen compatibility of DGEBA were calculated using mechanical impact method. The results indicated that epoxy resin (EP-P1)/4,4-diaminobisphenol sulfone (DDS) was compatible with liquid oxygen. When compared with EP/DDS, differential scanning calorimetry and thermogravimetry analyses showed that EP-P1/DDS and EP-P2/DDS had much higher glass transition temperatures and char yield. X-ray photoelectron spectroscopic analysis suggested that phosphorus atoms on the surface of EP-P1/DDS and EP-P2/DDS could act in the solid phase to restrain the incompatible reaction, which was in accordance with the flame-retardant mechanism of phosphorus-containing compounds. The compatibility mechanism of EP-P1/DDS was further proposed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40848.

INTRODUCTION

Epoxy resins display excellent properties such as high thermal and mechanical stability and good chemical resistance.[1–3] Reinforced with carbon fibers, their composites are used increasingly in aerospace industry where conventional materials, such as metals, are too costly because of their high weight.[4–6] Fully reusable single-stage launch vehicles require extremely high propellant mass fractions to work. It drives the designers to incorporate lightweight materials in as many structures as possible, including the cryogenic propellant tanks, namely, liquid oxygen tanks. As a consequence, there has been an increased awareness of carbon fiber-reinforced epoxy resin matrix composites for manufacturing liquid oxygen tanks, because it could reduce 27–35% of weight when compared with the metal alloy materials.[7,8] However, most epoxy resins and their composites may ignite or initiate reactions when in contact with liquid oxygen if they are subjected to the outside energy, such as mechanical impact, crash, friction, or static electricity, and are considered not suitable in the liquid oxygen application, which means incompatible with liquid oxygen. Only few polymers are known compatible with liquid oxygen but not fit for the liquid oxygen composite tank.[9] It is acknowledged that carbon is compatible with liquid oxygen. To satisfy applied requirements, liquid oxygen compatibility of epoxy resins have to be enhanced, which is important to the development of the aerospace industry.

It has been reported that the chemical mechanism of liquid oxygen incompatibility is in good agreement with that of the oxidative combustion for epoxy resins. In the abstract, better liquid oxygen compatibility could be realized by improving flame retardancy of epoxy resins.[10] There has been extensive researches on enhancing fire resistance of epoxy resins by incorporating phosphorus units, which are more effective and environmental than halogen compounds. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a cyclic phosphate with a diphenyl structure, which has high thermal stability and good oxidation resistance. Using DOPO or its derivatives as flame retardant, significant improvement in the fire behavior of epoxy resins has been reported.[11–15] However, no reference about the effect of DOPO on the liquid oxygen compatibility of epoxy resins is mentioned.

In this work, bisphenol A epoxy resin (DGEBA), as the most widely used epoxy resin nowadays,[16] was modified by DOPO to improve liquid oxygen compatibility. Liquid oxygen compatibility, thermal stability, and compatibility mechanism of the DOPO-modified epoxy resin were analyzed and discussed in detail.

EXPERIMENTAL

DGEBA with an epoxide equivalent of 188–196 g/mol was obtained from Tianjin Ningping Chemical, China. DOPO,

Table I. Information of the DOPO-Modified Epoxy Resins

Epoxy resin	DGEBA : DOPO (mass ratio)	Phosphorous content (wt %)	Epoxy equivalent weight (g/mol)
EP-P1	13 : 1	1%	222
EP-P2	6 : 1	2%	263

industrial grade (purity: 99.0%), was purchased from Huizhou Sunstar Technology, China. 4,4-Diaminobisphenol sulfone (DDS), analytically pure, used as curing agent, was supplied by Sinopharm Chemical Reagent, China.

DGEBA and DOPO were placed in a three-necked round-bottomed flask, equipped with a heating mantle, stirrer, thermocouple, and temperature controller. The mass ratios of DGEBA and DOPO are listed in Table I. The mixture was kept under stirring, gradually heated to 160°C, and maintained at that temperature for 300 min. Then, the DOPO-modified epoxy resin was obtained. The epoxy equivalent weight, phosphorous contents, and designated abbreviations of the final products are listed in Table I. The reaction equation is shown in Scheme 1.

The DOPO-modified epoxy resins (EP-P1 and EP-P2) and the control DGEBA (EP) were cured with DDS. To obtain a highly crosslinked polymer with good thermal stability, one epoxy equivalent weight of the epoxy resins was polymerized with 0.25 mol of the curing agent. The mixture was heated in a 150-mL beaker at about 130°C with continuous stirring until a homogeneous solution was obtained. After removing the bubbles in vacuum, the mixture was poured into a hot Teflon mold, cured in oven at 160°C for 1 h, and postcured at 180°C for 4 h. After that the specimens were allowed to cool down slowly to room temperature in order to prevent cracking.

The liquid oxygen compatibility of the cured epoxy was determined under impact energy using the Army Ballistic Missile Agency-type impact tester, as described in ASTM D2512-95 (2008).[17]

A specimen (20 mm diameter and 3–5 mm thickness) of a test material was placed in a specimen cup, precooled and covered with liquid oxygen for 5 min, and placed in the cup holder located in the anvil region assembly of the impact tester. A precooled striker pin was then centered in the cup. The plummet (10 kg) was dropped from 1 m height onto the pin (12.7 mm diameter), which transmitted the energy (98 J) to the test specimen. Twenty separate specimens of the cured epoxy resin submerged in liquid oxygen were tested. Observation for any reaction was made, and the liquid oxygen impact sensitivity (burning, explosion, flash, or charring) of the test material was noted. Drop tests were repeated using new specimen, specimen cup, and striker pin for each drop, until the threshold valve was achieved. More than one indication of sensitivity would be a cause for immediate rejection. A single phenomenon of sensitivity during the initial series of 20 tests requires that an additional 40 specimens must be tested with no incident to ensure acceptability of the material. A material subjected to 20 impact tests revealing no reaction would be regarded compatible with liquid oxygen. This measurement has been acknowledged as a strict pass/fail test, which could also be used for acceptance of testing materials in liquid oxygen systems.

Fourier transform infrared (FTIR) spectra were performed to characterize the DOPO-modified epoxy resin and the cured specimens on a Perkin Elmer Spectrum One FTIR from 4000 to 650 cm^{-1}. Differential scanning calorimetry (DSC) was used to obtain the glass transition temperature (T_g) of the cured resins. It was performed with a Thermal Analysis (TA) DSC-Q10 by heating the sample in a sealed aluminum pan under inert pure nitrogen atmosphere. The instrument was ramped up at 10°C/
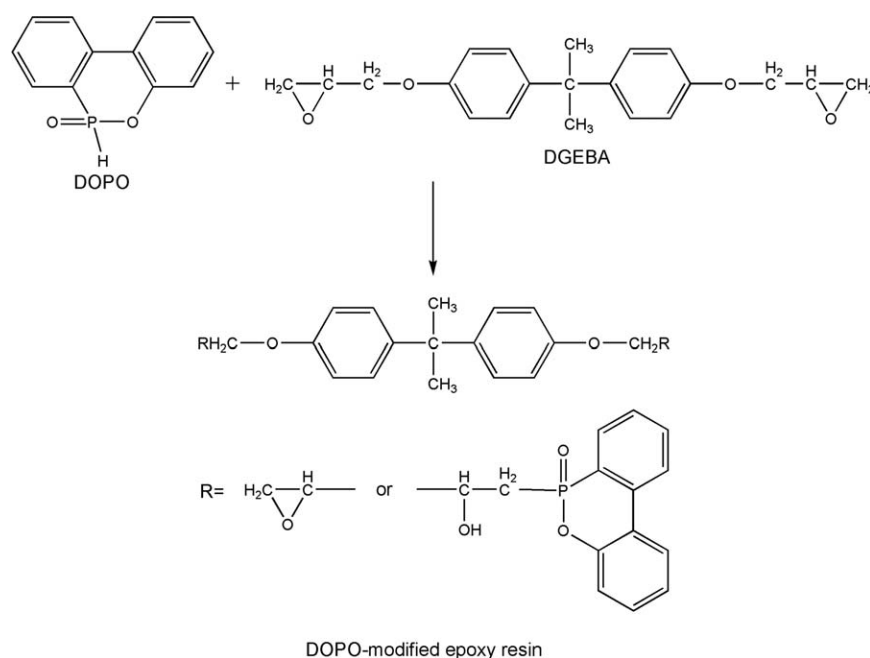
Scheme 1. Reaction process of the DOPO-modified epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
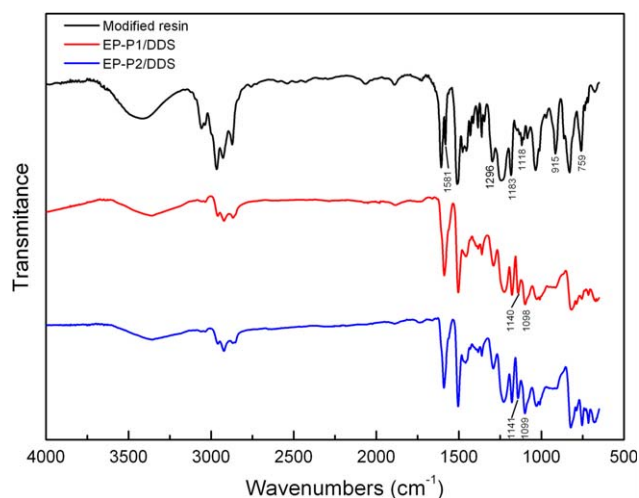
Figure 1. FTIR spectra of the DOPO-modified epoxy resins, EP-P1/DDS and EP-P2/DDS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

min from 25 to 250°C. Thermogravimetric analysis (TGA) was performed at a heating rate of 20°C/min under oxygen atmosphere (40 mL/min) from 25 to 600°C by using a thermal analyzer TA Instrument TGA Q500. The surface element compositions of the cured epoxy resins before and after the liquid oxygen impact were measured using the X-ray photoelectron spectroscopy (XPS) along with an X-ray photoelectron spectrometer (Perkin-Elmer, PHI 5300) equipped with magnesium X-ray source.

RESULTS AND DISCUSSION

FTIR Analysis

FTIR spectra were widely used to characterize chemical structures. Figure 1 shows the FTIR spectra of the DOPO-modified epoxy resin and the specimens of EP-P1/DDS and EP-P2/DDS. For the DOPO-modified epoxy resin, the distinctive absorption around 2400 cm^{-1} for P—H stretching in DOPO disappeared, and the absorption at 759 cm^{-1} for P—C was observed, which demonstrated the reaction between DGEBA and DOPO was completed. The absorption at 1581 cm^{-1} implied the existence of P—Ph. The absorption at 1118 cm^{-1} for P—O—Ph was observed. The peaks of P=O stretching were observed at 1296 and 1183 cm^{-1}. The characteristic absorption of epoxy group was observed at 915 cm^{-1}.[18,19] The above results verified that DOPO was successfully introduced into the molecular chain of

the epoxy resin. After curing, the peak of epoxy group disappeared, which indicated that the curing reaction was completed, as shown in the FTIR spectra of EP-P1/DDS and EP-P1/DDS. The peaks of 1140, 1098, 1041, and 1099 cm^{-1} verified the existence of sulfone.

Results of the Liquid Oxygen Mechanical Impact Test

The phenomena of the liquid oxygen mechanical impact test for the cured epoxy resins are listed in Table II. According to ASTM D2512-95 (2008), more than one indication of sensitivity is cause for immediate rejection. A single explosion, flash, or other indication of sensitivity during the initial series of 20 tests requires that an additional 40 samples be tested without incident to ensure acceptability of the material. A vidicon device has been used to record the reaction phenomena generated during impact process. The obvious three times flash and two times charring were detected for EP/DDS during 20 tests, indicating that EP/DDS was incompatible with liquid oxygen. Nevertheless, no reactions (explosion, visible flash, burning, or charring) were observed in 20 times of mechanical impact process for EP-P1/DDS, which indicated that EP-P1/DDS was compatible with liquid oxygen. Unfortunately, one acute burning was found for EP-P2/DDS during the 20 times impact test.

DSC Analysis

T_g is a very important parameter for epoxy resins and epoxy matrix composites, and in most applications, the working temperatures of epoxy-based materials are below their T_gs.[20] DSC was performed to measure T_gs of the cured epoxy resins. T_g was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquids and glass lines. Figure 2 shows the DSC curves and T_gs of the cured epoxy resins. As shown in Figure 2, EP-P1/DDS had a much higher T_g than EP/DDS, from which it could be inferred that EP-P1/DDS was more rigid than EP-P1/DDS. It has been reported that incorporating the bulky rigid DOPO structure into the epoxy resin would increase the rigidity and motion barrier of the molecule, and therefore, increasing T_g of the cured epoxy resin.[21] However, T_g of EP-P2/DDS was lower than that of EP-P1/DDS. Actually, introducing a DOPO group into the molecular chain of the epoxy resin would consume an epoxy group, which means that excessive DOPO significantly increased the epoxide equivalent and stereo-hindrance effect, resulting in lower crosslinking density, leading to a lower T_g. It was noteworthy that EP-P2/DDS still obtained a higher T_g than that of EP/DDS, which implied that the effect of the rigidity and motion barrier to T_g is greater than that of crosslinking density. EP-P1/DDS, with the greatest liquid oxygen compatibility, also had a highest T_g. When subjected to the mechanical impact in liquid oxygen, the epoxy resins would thermally decompose due to the heat energy that the impact energy was transformed into, finally causing the incompatible reaction. When compared with the epoxy resins with lower T_gs, the higher the T_g of the epoxy resin, the harder the occurrence of the incompatible reaction, considering that high T_g indicated better thermal resistance. Consequently, T_g might also be considered as a parameter for evaluating liquid oxygen compatibility of epoxy resins.

Table II. Phenomenon During the Impact Test

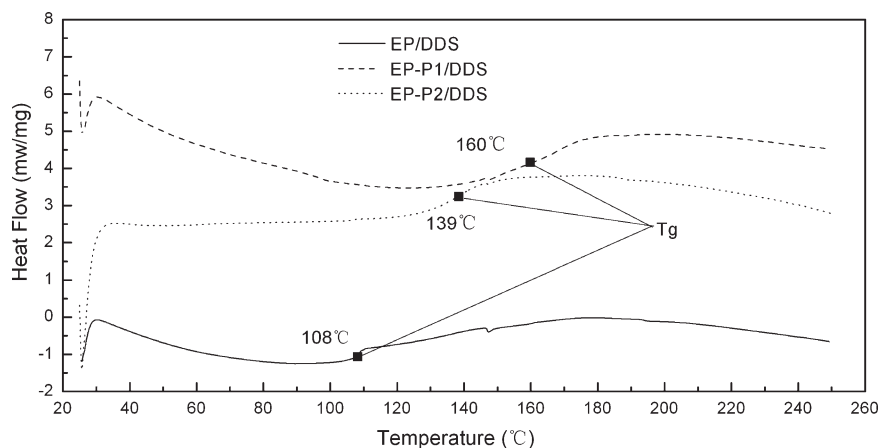| Specimen	Experimental phenomena (frequency)				Test times
	Charring	Flash	Explosion	Burning	
EP/DDS	2	3			13
EP-P1/DDS					20
EP-P2/DDS				1	20

Figure 2. DSC curves of the cured epoxy resins.

Thermogravimetric Analysis

TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers.[22] TGA measurements of the cured epoxy resins were carried out under oxygen atmosphere at a heating rate of 20°C/min from 25 to 600°C. Figure 3(a,b) shows TGA and DTG curves of the cured epoxy resins, and the TGA data as the degradation temperatures at different weight losses together with the final char yields at 600°C are listed in Table III. The pyrolysis processes of EP/DDS, EP-P1/DDS, and EP-P2/DDS had two stages, as shown in Figure 3(a). From the DTG curves, it could be seen that the weight loss rate of EP-P1/DDS and EP-P2/DDS was significantly lower than that of EP/DDS. From Table III, it could be noted that the temperatures of 10 and 30% weight loss for EP-P1/DDS and EP-P2/DDS were obviously lower than that of EP/DDS. This phenomenon could be attributed to the poorer stability of C—P and O=P—O than —C—C— bond and the decrease of crosslink density of EP-P1/DDS and EP-P2/DDS.[23] However, the temperature of 50% weight loss for EP-P2/DDS was higher than that of EP/DDS. At 70% weight loss, EP-P1/DDS and EP-P2/DDS exhibited much higher temperatures than EP/DDS. The degradation of phosphorus-containing groups at relatively low temperature range played an important role in enhancing flame retardancy, because the degraded products of phosphoric unit had great contributions to the formation of phosphorus-rich crosslinking carbonization char at high temperature. The char formed acted as a protective layer on the polymer surface against heat and prevented the further decomposition of epoxy resins. As a result, the cured epoxy resin modified by DOPO was more stable at high temperature and yielded more char after degradation. This could be verified by the data in Table III, which shows that the final char yields significantly increased from 1.8% of EP/DDS to 7.9% of EP-P1/DDS and 15.7% of EP-P2/DDS. This behavior was in accordance with the mechanism of improved flame retardancy via phosphorus modification in previous studies.[24] High char yields always led to high flame retardancy of epoxy resins. Furthermore, liquid oxygen compatibility of the cured epoxy resins also obviously improved with introducing DOPO into epoxy resin network. This could be interpreted that when EP-P1/DDS and EP-P2/DDS were impacted in liquid oxygen, the heat energy

that the impact energy was converted into caused the phosphorus-containing groups decomposed at first and then formed a phosphorous-rich protective layer on the surface of the test specimen to inhibit the reaction between the epoxy
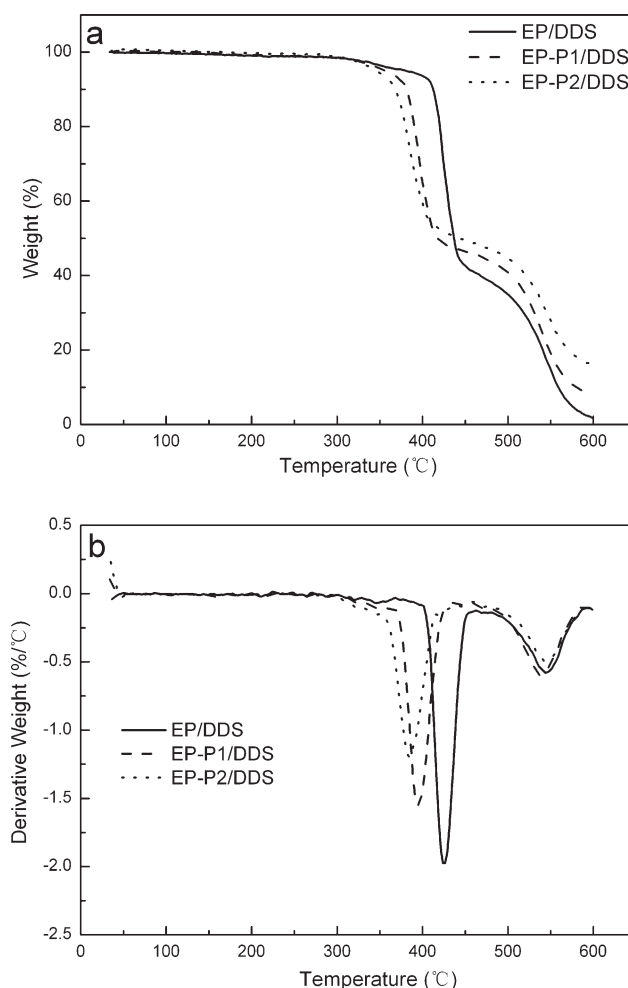

Figure 3. TG (a) and DTG (b) curves of the cured epoxy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. TGA Data of the Cured Epoxy Resins

Specimen	$T_{10\%}$ (°C)	$T_{30\%}$ (°C)	$T_{50\%}$ (°C)	$T_{70\%}$ (°C)	Char yield at 600°C (%)
EP/DDS	412	424	436	516	1.8
EP-P1/DDS	381	396	416	531	7.9
EP-P2/DDS	367	387	440	545	15.7

resin and liquid oxygen. In consequence, the char yield might also characterize liquid oxygen compatibility of epoxy resins.

XPS Analysis

XPS investigations were performed to determine the changes of the elements on the surface of the specimens before and after the mechanical impact, and their particular elemental compositions were measured at three different locations on the sample surface and the average values are recorded. The concentrations of C, O, P, O/C, and P/C of the cured epoxy resins before and after the mechanical impact are summarized in Table IV.

For EP/DDS, when compared with the specimen before the mechanical impact, carbon and oxygen concentrations of the specimen with no reaction after the mechanical impact did not show any obvious changes, resulting in O/C ratio almost the same, which revealed that the mechanical impact caused little reaction of liquid oxygen and the surface of the specimen. However, the O/C ratio of the specimen with flash after the mechanical impact increased to 0.261. It could be concluded that the surface of the specimen was oxidized because of the mechanical impact.

In case of EP-P1/DDS, a decrease of the O/C ratio was detected after the mechanical impact, which could be explained by that oxygen atoms were consumed in the form of free radicals. Meanwhile, when compared with the specimen before the mechanical impact, the P/C ratio of the specimen after the mechanical impact unchanged. This phenomenon indicated that phosphorus atoms stayed in the surface of the specimen to inhibit the reaction of the specimen and liquid oxygen; therefore, indicating that EP-P1/DDS was compatible with liquid oxygen according to the liquid oxygen mechanical impact test.

With regard to EP-P2/DDS, before the mechanical impact, the ratios of O/C and P/C were 0.254 and 0.010, respectively. After the mechanical impact, the ratios of O/C and P/C for the specimen with no reaction did not indicate any significant changes. It was evident that a huge enrichment about 300% in the P/C ratio of the specimen with burning after the mechanical impact was observed. Because the burning resulted from the mechanical impact, the phosphorus atoms on the surface of the specimen acted in the solid phase to restrain combustion, which was in accordance with the flame-retardant mechanism of phosphorus-containing compounds.

To analyze the changes of the phosphorus-containing groups on the surface of the cured DOPO-modified epoxy resins before and after the mechanical impact, the P2p spectra were extensively studied. Figure 4(a,b) illustrates the peaks fitting of the P2p spectra for EP-P1/DDS. It could be seen that two bands were observed from P2p spectra before the mechanical impact: the peak at around 131.9 eV is attributed to C—P between the DOPO group and epoxy resin, and the peak at around 133.0 eV is assigned to O=P—O in the DOPO group. After the mechanical impact, the peaks of C—P and O=P—O could still be detected. Remarkably, a new peak at 134.3 eV was observed. It has been reported that the peak at 134.3 eV could be attributed to the PO_3 in the pyrophosphate and polyphosphate groups.[25] Similarly with EP-P1/DDS, as shown in Figure 5, no matter the mechanical impact resulted in no reaction or burning for the specimen, a new peak of PO_3 could be detected after the mechanical impact. This phenomenon indicated that a lot of instantaneous energy during the mechanical impact resulted in the rapid increase of temperature of the local surface of the specimen, which led to the phosphorus-containing groups on the surface of the specimen

Table IV. Relative Elemental Concentrations on the Surface of the Cured Epoxy Resins Before and After the Mechanical Impact

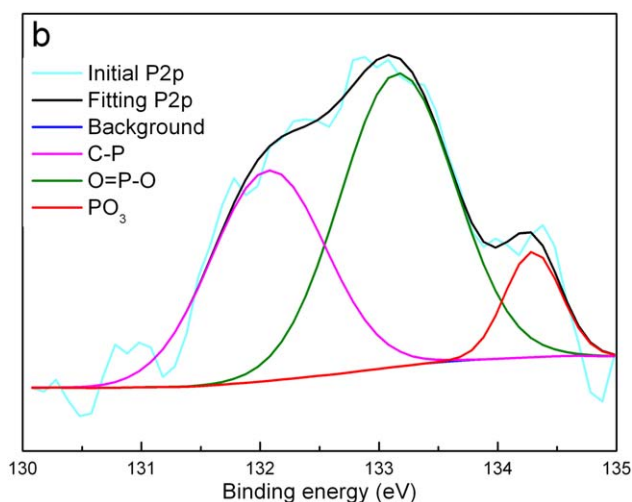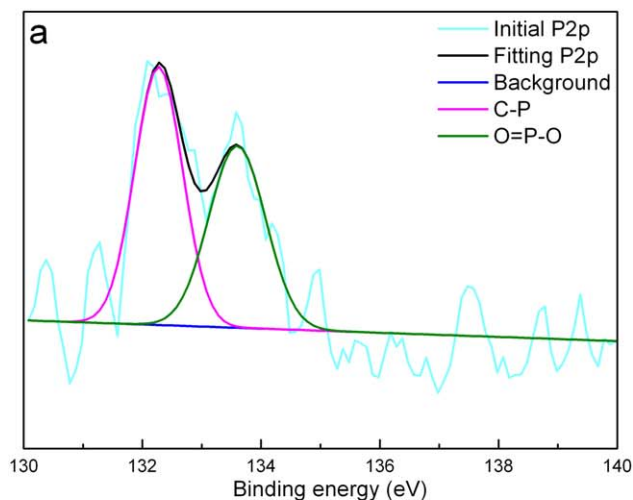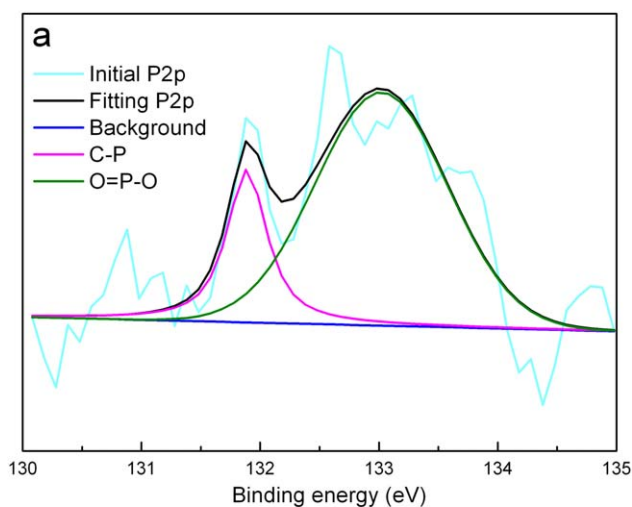| Specimen		Elemental concentration (%)				
		C	O	P	O/C	P/C
EP/DDS	Before	78.89	17.94		0.227	
	After (no reaction)	79.10	17.54		0.222	
	After (flash)	75.78	19.77		0.261	
EP-P1/DDS	Before	73.71	21.41	0.55	0.290	0.007
	After	80.14	15.62	0.60	0.195	0.007
EP-P2/DDS	Before	76.51	19.41	0.78	0.254	0.010
	After (no reaction)	76.94	18.61	0.92	0.242	0.012
	After (burning)	78.63	14.69	3.28	0.187	0.042
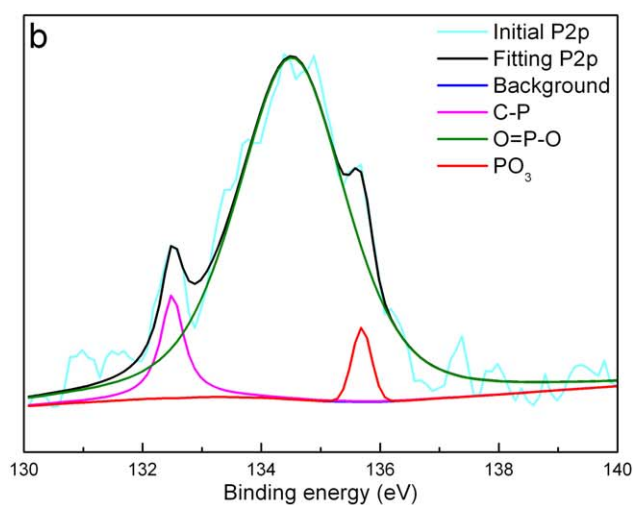
Figure 4. Peaks fitting curves of P2p spectra for EP-P1/DDS: (a) before the mechanical impact and (b) after the mechanical impact. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermally decomposed to form the phosphoric oxyacid. It covered over the surface of the specimen to prevent the reaction of the specimen and liquid oxygen.

Compatibility Mechanism of EP-P1/DDS

After curing, DDS and EP-P1 were polymerized to form a cross-linked structure, as shown in the following equation:
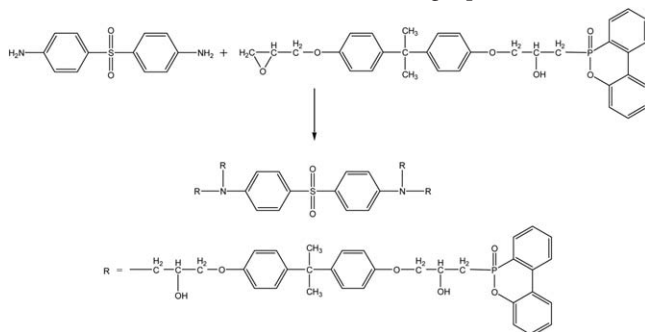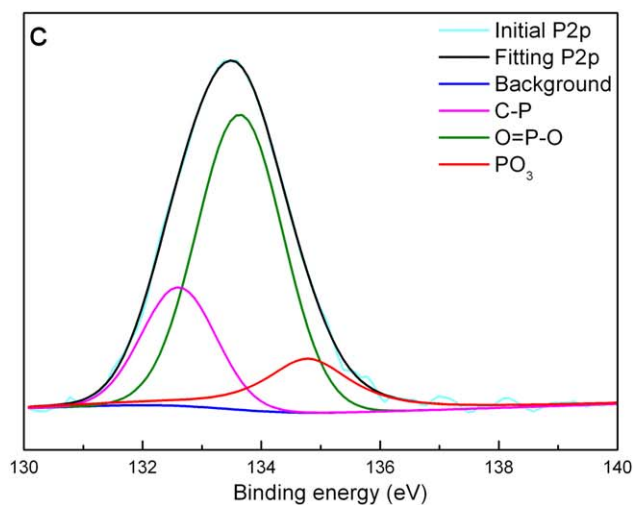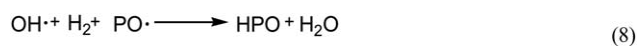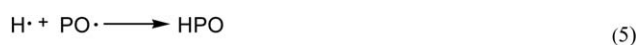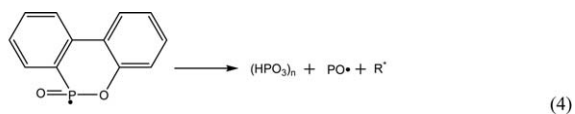

(1)

Figure 5. Peaks fitting curves of P2p spectra for EP-P2/DDS: (a) before the mechanical impact; (b) no reaction after the mechanical impact; and (c) burning after the mechanical impact. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The substance of impact reaction between the epoxy resin and liquid oxygen is acute oxidation and rapid decomposition of the epoxy resin, which means that improving the flame retardancy of the materials would enhance their liquid oxygen compatibility. During the mechanical impact, a lot of instantaneous heat energy, which the impact energy was transformed into, resulted in the rapid increase of the temperature on the local surface of the specimen, causing EP-P1/DDS thermally decomposed. Meanwhile, a lot of highly active radicals of OH^- and H^- were released, which could further accelerate the decomposition of the cured epoxy resin, finally leading to the incompatible reaction, as shown in the following equations:

(2)

(3)
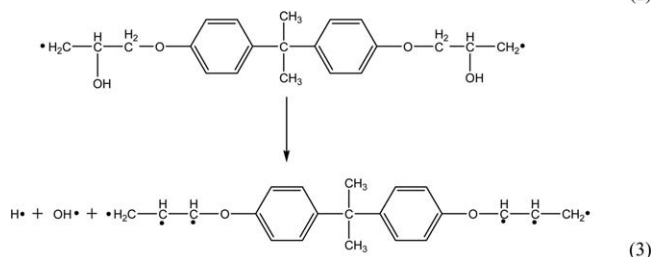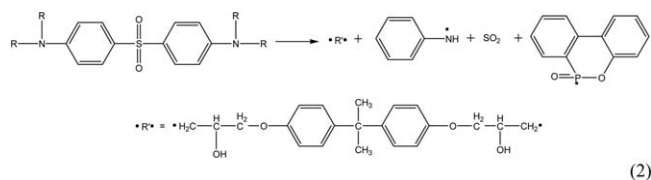
It has been reported that organophosphorus compounds demonstrate good ability in imparting flame retardancy to epoxy resins and that they work either in the condensed or in the gas phase to inhibit degradation and combustion. Consequently, when EP-P1/DDS decomposed, the phosphorus-containing groups in the resin also began to decompose, generating a polymeric form of phosphoric oxyacid $[(HPO_3)_n]$ and a lot of PO^- radicals, as shown in eq. (4). The existence of the phosphoric oxyacid was already confirmed by XPS analysis. This acid caused a phosphorus-rich char layer, which shields the material from liquid oxygen, in that way preventing the oxidation and decomposition of the epoxy resin in the condensed phase. Furthermore, in the gas phase, PO^- captured H^- and OH^- radicals, as shown in eqs. (5)–(8). The removal of H^- and OH^- radicals resulted in a slowdown of the decomposition process of the epoxy resin and restraining the incompatible reaction.

(4)

$$H\cdot + PO\cdot \longrightarrow HPO \qquad (5)$$

$$HPO + H\cdot \longrightarrow H_2 + PO\cdot \qquad (6)$$

$$PO\cdot + OH \longrightarrow HPO + O\cdot \qquad (7)$$

$$OH\cdot + H_2 + PO\cdot \longrightarrow HPO + H_2O \qquad (8)$$

CONCLUSIONS

In this study, DGEBA was chemically modified by DOPO to improve its liquid oxygen compatibility. The structure of the modified epoxy resin was confirmed by FTIR spectra. DDS was used to cure the epoxy resins. The liquid oxygen compatibility of the cured DOPO-modified epoxy resins and DGEBA was examined using the liquid oxygen mechanical impact test according to ASTM D2512-95(2008). The flash and the burning were observed for EP/DDS and EP-P2/DDS, respectively, which indicated that they were incompatible with liquid oxygen. EP-P1/DDS did not show any flash and explosion during the 20 times of mechanical impact, revealing that it was compatible with liquid oxygen. DSC and TG analyses showed that EP-P1/DDS and EP-P2/DDS had much higher glass transition temperatures and char yield than EP/DDS. Glass transition temperature and char yield might be considered as factors for evaluating liquid oxygen compatibility of epoxy resins. The XPS analysis confirmed that phosphorus atoms on the surface of EP-P1/DDS and EP-P2/DDS could act in the solid phase to restrain the incompatible reaction, which was in accordance with the flame-retardant mechanism of phosphorus-containing compounds. The compatible mechanism of EP-P1/DDS was further investigated. The phosphorous-containing groups in the cured resin could work either in the condensed or in the gas phase to inhibit the incompatible reaction of the epoxy resin and liquid oxygen. These results suggest that the DOPO-modified epoxy resin has the potential as the matrix of the liquid oxygen composite tank.

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