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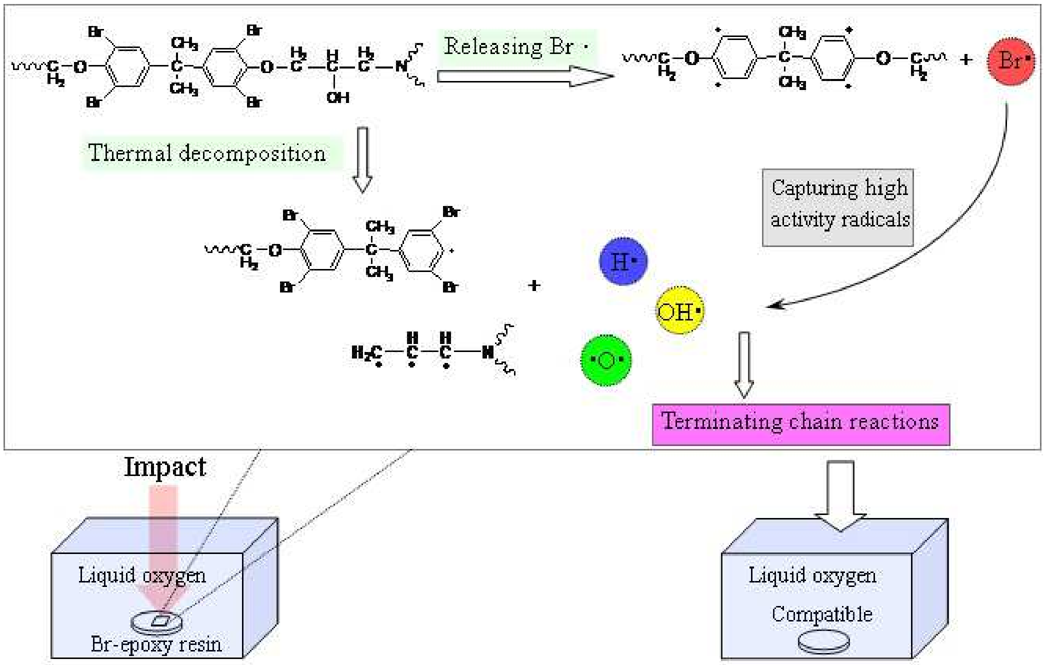
Liquid oxygen compatibility mechanism of bromine-modified epoxy resin



Liquid oxygen compatible epoxy resin: Modification and characterization

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Abstract:

The bisphenol A epoxy resin was modified by the polycondensation between tetrabromobisphenol A and bisphenol A epoxy resin. After curing using 4,4′-diaminodiphenyl methane (DDM) and 4,4′-diaminodiphenyl sulfone (DDS), the liquid oxygen compatibility of bisphenol A epoxy resin and modified bisphenol A epoxy resin was measured by the mechanical impact test (ASTM D2512-95). The results suggested that the modified bisphenol A epoxy resin curing using 4,4′-diamino diphenylmethane (DDM) was compatible with liquid oxygen. The thermogravimetric analysis (TGA) revealed that the modified bisphenol A epoxy resin has lower temperatures of the initial degradation and the maximum mass loss rate compared with unmodified. The X-ray photoelectron spectroscopy (XPS) measurement results indicated that the C-C/H groups were oxidized to C-O-C/H and/or C=O groups during the impact process. The mechanical properties of all samples were measured at room temperature (RT) and nitrogen temperature (77K). The flame-retardant modification of epoxy resin may be an effective way to obtain the compatible epoxy resin material with liquid oxygen.

1.Introduction

Polymer matrix composite materials continue to be primary candidates for many aerospace applications and especially true for space applications where the payoff from weight savings is typically the highest [1, 2]. A number of research efforts have shown that there would be enormous advantage to using polymer matrix composites as a lighter weight and possibly lower cost option for the structure in cryogenic tanks for launch vehicles compared with existing liquid oxygen tank materials which are aluminum (most applications) and stainless steel [3]. Studies show that the total tank weight could be reduced by as much as 27-35% if polymer matrix composites were used to replace metals as the tank material. However, polymer materials may ignite or initiate reactions when in contact with liquid oxygen if subjected to mechanical impact, frictional heating, static electricity, etc [4].

Epoxy resins with a unique combination of properties have occupied a dominant place in the development of high performance light weight composites [1, 2, 5]. The carbon fiber-reinforced epoxy resin composites are being considered as the light weight materials for use in the liquid oxygen tanks. These composites are chosen as the liquid oxygen tank materials because it has been widely studied as high-potential materials for use in cryogenic tanks due to its excellent resistance to micro-cracking under load at cryogenic temperatures [6]. However, epoxy resin materials are known to ignite and burn easily in an oxygen-rich environment. During the mechanical impact process, the impact energy absorbed by epoxy resin is converted into heat energy, resulting in the the generation of ignition point on the local surface of epoxy resin and the detection of an burning, explosion, visible flash or charring [7]. Studies have shown that the epoxy resins incompatible with liquid oxygen may be due to its flammability. Therefore, enhancing the flame retardancy of epoxy resins may be an effective way to realize the epoxy resins compatible with liquid oxygen. Traditionally, the flame retardant epoxy resins are obtained by physically blending the flame retardant additives into the epoxy resins [8, 9]. However, the major shortcomings of all flame retardant additives are that the additives may be lost in processing and using of the epoxy resins and the mechanical properties may be reduced [10, 11]. Fortunately, using reactive flame retardant additives which chemically bonds to the epoxy resins backbone can also enhance the flame retardancy of epoxy resins and does not affect the mechanical properties [11].

In the present work, the bisphenol A epoxy resin was modified via the polycondensation between tetrabromobisphenol A and bisphenol A epoxy resin. The liquid oxygen compatibility of modified and unmodified bisphenol A epoxy resin was evaluated through the mechanical impact test (ASTM D2512-95). The relationship between the thermal properties and the liquid oxygen compatibility of epoxy resins, the influences of different curing agents for liquid oxygen compatibility of epoxy resins, and the chemical reactions on the local surface of cured epoxy resins during the mechanical impact process were studied in detail. And the mechanism of Br· promoting the epoxy resin compatible with liquid oxygen was studied.

2. Experimental

2.1 Materials

Tetrabromobisphenol A (TBBPA), industrial grade (purity of 99.0%, bromine content of 58.5%, melting point of 181.7°C), was supplied by Shandong Tianyi Chemicals Co., Ltd., China. Bisphenol A epoxy resin (epoxy value of 0.51~0.53 mol/100 g) was purchased from Tianjin Ningping Chemical Co., Ltd., China. Cetyl trimethyl ammonium bromide, 4,4′-diaminodiphenyl methane (DDM) and 4,4′-diamino- diphenyl sulfone (DDS), analytically pure, were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

2.2 Synthesis of modified epoxy resin

The bisphenol A epoxy resin was reacted with the TBBPA at 180°C for 120 min. The synthesis process of modified bisphenol A epoxy resin is shown as below:

100 g of bisphenol A epoxy resin and 20.49 g of TBBPA were added to a 500-mL three-neck round-bottom flask equipped with a heating device, stirrer, thermocouple, and temperature controller. The entire reaction was carried out under nitrogen atmosphere. The reaction mixture was gradually heated to 120°C and then the 0.041 g of cetyl trimethyl ammonium bromide was added to the flask. Next, the reaction temperature was gradually heated to 180°C and maintained for 120 min. The epoxy value of the modified bisphenol A epoxy resin was 0.396 mol/100 g and the bromine content was 10% (w/w), theoretically.

2.3 Curing Procedure for Modified Epoxy Resin

The epoxy resins were cured by 4,4′-diaminodiphenyl methane (DDM) and 4,4′-diaminodiphenyl sulfone (DDS), respectively. A typical curing process of epoxy resin cured by DDS is shown as below:

The reactant compositions were mixed in a 1:1 equivalent ratio, and then the mixture was heated in a 250-mL three-neck round-bottom flask and the continuous stirring was carried out at about 150°C until a homogeneous solution was obtained. After stirring well, the mixture was held under vacuum at 150°C for 5min to remove residual bubbles, and then the mixture was cast into a mold and cured at 160°C for 1 h and then 180°C for 4 h. Next, the mixture was allowed to cool slowly to room temperature to prevent cracking. The same curing process of epoxy resins cured by DDM is at 100°C for 2h and then 160°C for 4 h. The epoxy resin was cured to wafers of 20 mm in diameter and 4 mm in thickness. The wafers were polished with sandpaper to 2000 grit, cleaned using an ultrasonic cleaner, and then dried at 70°C.

2.4 Liquid oxygen impact test

A test for the compatibility of a material with liquid oxygen basically involves placing the material in liquid oxygen in the presence of a possible ignition source and observing the reaction of the material. The ignition categories mainly consist of mechanical impact, electrical, thermal, acoustic, abrasive, and fracture. One of the most probable ignition sources is mechanical impact in the presence of oxygen [12]. The equipment and parameters adopted as the standard was based on the ASTM D 2512. In this mechanical impact test, a sample of the epoxy resin is placed in a specimen cup, precooled and covered with liquid oxygen, and placed in the cup holder in the anvil region assembly of the impact tester. A precooled striker pin is then centered in the cup. The plummet is dropped from selected heights onto the pin, which transmits the 98J energy to the test specimen. Any explosion, burning, noticeable flash, or evidence of charring is considered a reaction. The compatibility by this ASTM test is defined as no reactions occur in 20 tests or only one reaction occurs in 60 tests with the plummet impact energy adjusted to 72 ft-lb (98J). This standard is commonly assumed that this is a strict “go/no go” test that materials must meet if they are to be used in liquid oxygen systems. Nevertheless, the impact test will be stopped if reaction (explosion, noticeable flash, burning or charring) was observed twice in the first several tests, even if the impact test was done for less than 20 times.

2.5 Measurements

Fourier transform infrared (FTIR, Nicolet NEXUS) spectroscopy was used to characterize the bromine-modified epoxy resin. The infrared spectrum was recorded in the wave number range of 650 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed by heating samples from 35°C to 600 °C at 20°C /min under nitrogen flow on Al_2O_3 sample pan using a thermobalance TA Instrument TGA Q500. The surface element compositions of the epoxy resin before and after liquid oxygen impact were determined by X-ray photoelectron spectroscopy (XPS) using an X-ray photoelectron spectrometer (Perkin-Elmer, PHI 5300) equipped with a magnesium X-ray source. The tensile samples were prepared according to the recommendation of GBT 2567-2008. The tensile properties of the cured specimens at 77K were measured by a 50KN capacity servo-hydraulic testing machine with a displacement rate of 2.0 mm/min. The cryogenic temperature condition was achieved by spraying the liquid nitrogen into a closed cryostat. The entire testing was conducted when the temperature in the closed cryostat was dropped to 77K. The fracture toughness (K_{IC}) test was carried out using three-point bending specimens with dimensions 60mm × 10mm × 5mm. A notch was introduced at the central of the specimen bar and the notched depth was about 4mm. Fracture toughness (K_{IC}) was calculated using the following equations [13, 14].

$$K_{IC} = \frac{P_m S}{D W^{3/2}} f\left(\frac{a}{W}\right) \qquad (1)$$

where $f\,(a/w)$ is the polynomial geometrical correction factor give as

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}[1.99-(a/W)(1-a/W)\times(2.15-3.93a/W+2.7a^2/W^2)]}{2(1+2a/W)(1-a/W)^{3/2}} \qquad (2)$$

where P_m is the maximum load at crack extension, S is the span of the specimen (40mm), D is the specimen thickness (5mm), W is the specimen width (10mm) and a is the crack length.

For the three-point-bend testing, the cryogenic temperature condition was achieved by immersing the loading fixture and specimen in liquid nitrogen. And the specimens were loaded under displacement control with a rate of 1mm/min.

3. Results and discussions

3.1 FTIR analysis

The FTIR spectrum used to characterize a series of function groups in the synthesized bromine-modified epoxy resin is shown in Fig.1.

The absorption at 661.43 cm^{-1} belongs to the C-Br stretching, which implies that the bromine was successfully introduced into the molecular structure of bisphenol A epoxy resin. The characteristic absorption peak in the range of 3500~3200 cm^{-1} attributes to the characteristic O−H stretching [8, 15]. The absorption at 1105.13 cm^{-1} verifies that the hydroxyl in the molecular backbone of the modified epoxy resin connects with the secondary carbon atom. The bands at 2962.96 cm^{-1} and 2869.73 cm^{-1} are due to methyl group C−H stretching vibration and at 2926.22 cm^{-1} for methylene C−H stretching [16]. The C−H in-plane bending symmetrical vibration δ_s and asymmetrical vibration δ_{as} of methyl is observed respectively at 1383.56 cm^{-1} and 1447.83 cm^{-1}. The characteristic C=C stretching of benzene ring is observed at 1605.60 cm^{-1}, 1581.14 cm^{-1} and 1506.03 cm^{-1}. The appearance of the peaks at 1228.23 cm^{-1} and 1032.62 cm^{-1} corresponds to the C-O stretching, which represents the molecular backbone of the modified epoxy resin containing the anisole function group. The characteristic absorption of C−O−C for epoxy group is observed at 912.95 cm^{-1} [17].

3.2 The phenomena during the impact test

The phenomena of the four types of epoxy resin samples during the liquid oxygen impact process are listed in Tab.1. As shown in Tab.1, the obvious charring, flash or explosion were observed for BADDS, BrBADDS and BADDM during the impact process, which showed that they are incompatible with liquid oxygen. The detection of sensitivity phenomena (burning, explosion, visible flash or charring) was attributed to the generation of ignition points on the local surface of sample. During the impact process, the impact energy was converted into heat energy and finally resulted in the sensitivity phenomena. Nevertheless, there is no any phenomenon was detected for BrBADDM, which indicated that it is compatible with liquid oxygen.

3.3 TGA analysis

The TG and DTG curves of the four types of epoxy resins under nitrogen atmosphere are shown in Fig.2a and b. The temperatures of the 5wt% weight loss ($T_{5\%}$), the 50wt% weight loss ($T_{50\%}$) and the maximum mass loss rate (T_{max}), and the fraction of the char residue at 600°C are shown in Tab.2, and the initial degradation temperature is evaluated by the temperature of 5wt% weight loss ($T_{5\%}$).

As shown in Fig.2a and b, the thermal degradation process of all samples has two stages: the first step is attributed to the elimination of water as a result of formation of unsaturated C-C bonds; and the second process is the main decomposition process, namely the degradation of chemical bonds of the epoxy networks [18, 19]. As shown in Tab.2, the initial degradation temperature (approximately 378°C) of BrBADDS is lower than that of BADDS (approximately 400°C), which may be attributed to the poorer stability of C-Br bond (276KJ/mol) than C-C bond (345 KJ/mol). Meanwhile, the temperature of the $T_{50\%}$ and the T_{max} of BrBADDS are also lower than that of BADDS, which similarly attributed to the poorer stability of C-Br. When the temperature close to 378°C, the heat energy is enough to break the C-Br chemical bond of BrBADDS and finally results in the rapid weight loss [20-22]. Although the initial degradation temperature of the BrBADDS is lower than that of the BADDS, the residue of the BrBADDS at 600°C (approximately 19.3%) is higher than that of the BADDS (approximately 18.1%) at 600°C. The chain scission of bromine-containing groups can generate hydrogen bromide to inhibit the chain reactions of degradation and may cause the relatively high char yields. Compared the thermal degradation process of the BrBADDM and the BADDM, which is similar to the BrBADDS and the BADDS. It is mainly because of the poorer stability of C-Br bond; the heat energy converted from impact energy can cause rapid bond cleavage of C-Br and generates a large amount of hydrogen bromide which inhibits the sensitive reactions of the BrBADDM with liquid oxygen. For the unmodified epoxy resins BADDS and BADDM, the heat energy results in the sustained degradation of the epoxy resins and then induces the detection of incompatible reactions. However, the modified epoxy resin BrBADDS is incompatible according to the results of impact test, which may attribute to the S=O band in the curing agent DDS increasing the sensitivity of the BrBADDS with liquid oxygen. That is to say, the different curing agents may cause considerable difference in the compatibility of the epoxy resins with liquid oxygen. According to the Tab.1, the curing agent DDM is better than DDS in enhancing the compatibility of the epoxy resin with liquid oxygen. Conclusively, there is an effective way for introducing bromine into the molecular structure of an epoxy resin to enhance the liquid oxygen compatibility of epoxy resin. The BrBADDM has the potential to be the material used in liquid oxygen environment.

3.4 XPS analysis

The XPS spectra of all samples before and after the mechanical impact are shown in Fig.3. The peaks at approximately 285.0 eV, 400.0 eV and 532.0 eV are characteristic of C_{1s}, N_{1s} and O_{1s}, respectively [23], as shown in Fig.3. The C_{1s} peaks of the four types of epoxy resins before the mechanical impact are attributed to C–H, C–C, C–N and C–O in the molecular backbone of epoxy resins [24, 25]. For the four types of epoxy resins after the mechanical impact, the C_{1s} peaks are attributed to C–H, C–C, C–N, C–O and extra for C=O and/or O–C=O which resulted from the oxidation of C–H and/or C–O during the impact process. As shown in Fig.3b and 3d, the Br_{3d} peak at approximately 70.48eV is attributed to C–Br [26]. In addition, the F_{1s} characteristic peak is observed at approximately 688.48 eV [27] in Fig.3a and 3b, which is due to the use of polytetrafluoroethylene release paper during the curing process of samples resulting in the element F adhesion on the surface of samples.

The chemical components of all samples before and after the mechanical impacts were summarized in Tab.3. For the sample BADDS, the content of carbon, oxygen and the O/C ratio are 78.89%, 17.94% and 0.23 before the mechanical impacts, respectively. After the mechanical impact, the carbon content of the BADDS without reaction is higher than before, whereas the oxygen content is lower than before, which can be interpreted as the high activity radicals OH· and ·O· being released from C–O function group during the impact process and eventually resulting in the increase of carbon content and the decrease of the oxygen content on the local surface of BADDS. And for the samples BrBADDS and BADDM, the oxygen content after the mechanical impact is also lower than before, which also can be interpreted as the high activity radicals OH· and ·O· being released. The high activity radicals OH· and ·O· can cause the incessant chain reaction [28] and finally induce the detection of liquid oxygen sensitivity reactions (charring, flash, explosion or burning). However, the carbon content of the BADDS after the mechanical impact (with flash) is lower than before and the oxygen content is higher than before, which may be due to the C-C/H were oxidized to C–OH and/or C=O during the mechanical impact and finally resulted in the decrease of carbon content and the increase of oxygen content on the surface of the BADDS. As summarized in Tab.3, the carbon and oxygen content of the four types of epoxy resins after the mechanical impact may be higher or lower than that of the respective sample before the mechanical impact, which can be interpreted as a variety of chemical reactions occurring between the epoxy resins and liquid oxygen rather than single oxidation reaction. In addition, for the samples BrBADDS and BrBADDM, the bromine content after the mechanical impact is always higher than before, which implied that the bromine element was released during the impact process and gathered on the surface of the modified epoxy resins to play an important role in inhibiting the reactions between liquid oxygen and the epoxy resins.

In order to further investigate the oxidation reactions on the surface of the 4 samples during the impact process, the assignment of component peaks corresponding to surface functional groups for the XPS C1_s region scans are listed in Tab.4. For the four types of samples, the content of C-C/H component after the mechanical impact exhibits a significant reduction compared with the respective sample before impact. Tab.4 also shows an increase in the C-O-C/H functional group for the four types of samples after the mechanical impact. Especially for the samples BADDS, BrBADDS and BrBADDM, no carbonyl (C=O) species was observed on the surface of the respective sample before the mechanical impacts. However, a significant increase in C=O functional group was obtained for the BADDS (22.39%, 26.91%), the BrBADDS (13.39%, 20.82%) and the BrBADDM (18.30%) after the mechanical impacts. But for the BADDM, a small number of C=O functional group (5.98%) was detected before the mechanical impact, which may be due to the high temperature oxidation reactions occurring on the surface of the sample during the high temperature (160°C) curing process of the sample. Similarly, the BADDM also shows a significant increase in the C=O functional group (19.46%, 16.39%) after the mechanical impact. The above results reveal that the C-C/H functional groups were oxidized to the C-O-C/H and C=O groups during the impact process. The strong oxidation reactions may cause the generation of a large number of C-O-C/H and C=O functional groups, and further lead to the generation of a large number of high activity OH· and ·O· radicals. Therefore, the strong oxidation reactions on the surface of the samples may be the key factor for the epoxy resins incompatible with liquid oxygen.

All of the above results show that a variety of chemical reactions may occur between the four types of epoxy resins and liquid oxygen rather than single oxidation reactions during the impact process. The difference between the four types of samples is that the reactions or oxidative degree of the compatible epoxy resin material are lower than that of the incompatible one. The sample BrBADDM is compatible with liquid oxygen, which is attributed to the Br element inhibiting the further reactions of the epoxy resin with liquid oxygen.

3.5 Mechanical properties

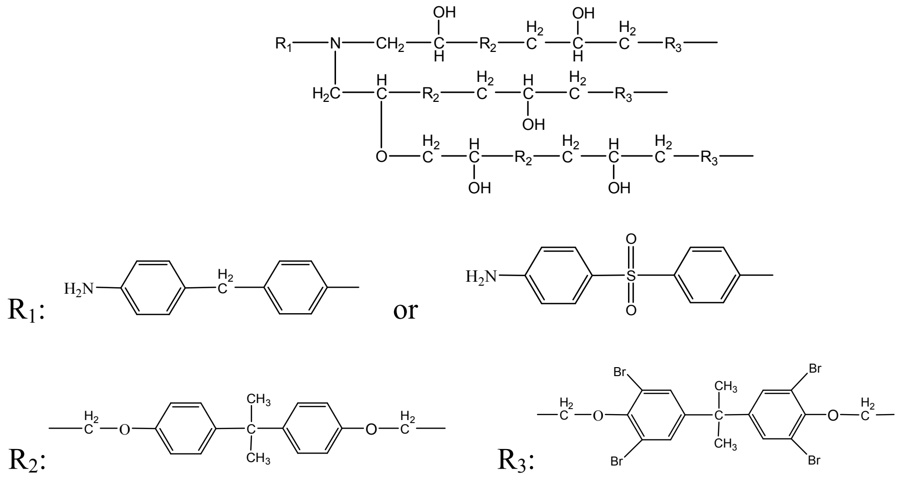
In order to investigate the influence of TBBPA to the mechanical properties of neat epoxy resins and modified epoxy resins, the tensile strength and fracture toughness of all samples was measured at RT and 77K. The results are shown in Tab.5.

The tensile strength of samples BADDS, BrBADDS, BADDM and BrBADDM at RT was 74.50MPa, 53.09MPa, 70.37MPa and 75.10MPa, respectively. The results showed that the introduction of bromine element had no significant influence on the tensile strength of brominated epoxy resin. The tensile strength of all samples at 77K was generally higher than that at RT. This might be mainly attributed to that the epoxy resins become brittle at 77K and thus the reduction in internal stress will be more important to enhance the tensile strength at cryogenic temperature than at RT. The fracture toughness K_{IC} was evaluated in terms of Eq. (1) based on the maximum load. The fracture toughness of neat epoxy resins and modified epoxy resins at RT had no obvious difference, which indicated that the introduction of bromine element had no significant influence on the fracture toughness. Nevertheless, the K_{IC} of all samples at 77K was generally lower than that at RT due to the epoxy resins becoming brittle.

In a word, the mechanical properties of neat epoxy resin and bromine modified epoxy resin have no obvious difference, which reveals that the additive of TBBPA has no significant decreasing the mechanical properties of epoxy resin at RT and 77K.

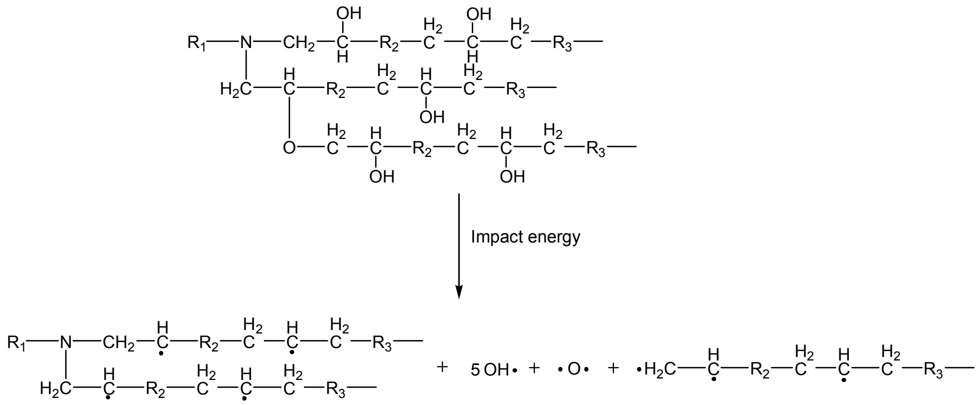
3.6 Compatibility mechanism

The general reaction mechanism for epoxy resin cured by amines is that almost all reactions involve opening the unstable epoxy group to form a CH–OH group and ether bridge, and then the functional group CH–OH can react again with epoxy group to form a new CH–OH group and ether bridge [29]. Finally, the cured epoxy resin shows excellent mechanical properties due to the generation of cross-linked structure. The major cross-linked structures of the epoxy resins curing using DDM and DDS are shown in Eq. 3.



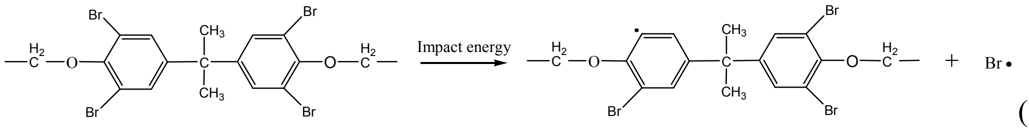
(3)

The impact sensitivity reactions (charring, flash, explosion, burning) of cured epoxy resin during the impact process are similar to the combustion chain reactions of polymer. The schematic of the liquid oxygen compatibility mechanism of the bromine-modified epoxy resin is shown in Fig.4. During the impact process, a lot of relatively high activity hydroxyl radicals and oxygen radicals were released on the local surface of the cured epoxy resin because the higher impact energy resulted in the local temperature rapid increase and the local thermal decomposition, as shown in Eq. 4.

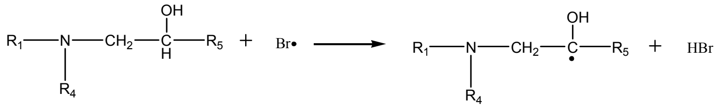


(4)

It is similar to the combustion chain reactions; the relatively high activity radicals can react with the cured epoxy resin and further promote the decomposition of cured epoxy resin [30]. The rapid and incessant chain reactions result in the releasing of a large amount of heat in a very short time, which may lead to the rapid expansion of liquid oxygen, eventually causing the liquid oxygen impact sensitivity reactions. The bromine element, as an effective flame retardant element, is introduced into the molecular backbone of the epoxy resin to terminate the incessant occurrence of chain reactions through capturing the activity radicals [28, 30 and 31], and eventually promote the epoxy resin compatible with liquid oxygen. The bromine element on the molecule backbone is transformed into the bromine radical when the cured epoxy resin sample subjected to the higher energy impact during the impact process, as shown in Eq. 5. The HBr is generated through the bromine radical seizing the hydrogen atom on the molecular backbone of the cured epoxy resin. The relatively high activity radicals OH· and ·O· can be captured by HBr to generate H_2O and Br·. The new generated Br· can continue to seize the high activity radicals until the termination of chain reactions [31], as shown in Eqs. 6-8.



(5)



$$R_1{-}N(R_4){-}CH_2{-}\overset{OH}{\underset{H}{C}}{-}R_5 + Br\bullet \longrightarrow R_1{-}N(R_4){-}CH_2{-}\overset{OH}{\underset{\bullet}{C}}{-}R_5 + HBr \quad (6)$$

$$HBr + \cdot O \cdot \longrightarrow HO\cdot + Br\cdot \quad (7)$$

$$HBr + HO\cdot \longrightarrow H_2O + Br\cdot \quad (8)$$

According to the impact test results, as shown in Tab.1, the impact sensitive phenomena of the same modified bisphenol A epoxy resin cured by different curing agents were different. The BrBADDM was compatible with liquid oxygen whereas the BrBADDS was incompatible, which may attribute to the functional group S=O causing the generation of a number of extra radicals ·O· during the impact process. Therefore, the BrBADDS showed incompatible with liquid oxygen. The BrBADDM showed a good compatibility with liquid oxygen according to the liquid oxygen impact test results, which implied that the flame-retardant modification of epoxy resin may be an effective way to obtain the compatible epoxy resin material with liquid oxygen.

4. Conclusions

The liquid oxygen mechanical impact test results confirmed that the bromine-modified bisphenol A epoxy resin curing using 4,4′-diamino diphenyl-methane (DDM) has the potential to be the material used in liquid oxygen environment. The curing agent DDM was better than DDS in improving the liquid oxygen compatibility of epoxy resin. The thermogravimetric analysis (TGA) results demonstrated that the rapid chain scission of C-Br at the second stage decomposition can inhibit the sensitive reactions between epoxy resin and liquid oxygen and finally promote the epoxy resin compatible with liquid oxygen. During the impact process, the C-C/H can be oxidized to C-OH or C=O and the oxidation reactions may be the key factors for the epoxy resin incompatible with liquid oxygen. The mechanical properties tests showed that the additive of TBBPA has no significant decreasing the mechanical properties of all samples at RT and 77K. The flame-retardant modification of epoxy resin may be an effective way to obtain the compatible epoxy resin material with liquid oxygen.

Acknowledgements

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Fig. 4 The schematic of the liquid oxygen compatibility mechanism of the bromine -modified epoxy resin.

Table 1 The mechanical impact phenomena

Number	Epoxy resin	Curing agent	Experimental phenomena (frequency)				
			Charring	Flash	Explosion	Burning	Test times
BADDS	bisphenol A epoxy resin	DDS	2	3	0	0	13
BrBADDS	modified bisphenol A epoxy resin	DDS	0	3	0	0	20
BADDM	bisphenol A epoxy resin	DDM	1	0	2	0	15
BrBADDM	modified bisphenol A epoxy resin	DDM	0	0	0	0	20

Table 2 Thermal properties of all samples curing using DDS and DDM

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	Tmax (°C)	Residue (%wt)
BADDS	400	438	435	18.1
BrBADDS	378	385	383	19.3
BADDM	385	417	406	21.0
BrBADDM	365	375	370	25.0

Table 3 XPS results of all samples before and after the mechanical impacts

Specimen		Elemental content (%)				
		C	N	O	Br	O/C
BADDS	Before	78.89	2.17	17.94	0	0.23
	No reaction	79.10	3.35	17.54	0	0.22
	Flash	75.78	2.25	19.77	0	0.26
BrBADDS	Before	78.12	1.9	17.58	1.42	0.23
	No reaction	78.30	2.81	16.29	1.71	0.21
	Flash	77.22	2.76	16.89	1.95	0.22
BADDM	Before	80.72	2.68	16.60	0	0.21
	No reaction	82.49	3.41	14.10	0	0.17
	Flash	81.19	2.91	15.90	0	0.20
BrBADDM	Before	82.42	1.88	14.44	1.27	0.18
	No reaction	79.80	3.14	15.45	1.61	0.19

Table 4 Relative atomic concentrations of carbon species determined from curve fitting of high resolution C1_s XPS spectra

Sample		C_{1S}			
		C-C/H	C-N	C-O-C/H	C=O
BADDS	Before	57.18%	20.40%	22.42%	0
	No reaction	6.93%	40.33%	30.35%	22.39%
	Flash	20.51%	31.60%	20.98%	26.91%
BrBADDS	Before	65.59%	11.72%	22.69%	0
	No reaction	35.86%	13.37%	37.76%	13.39%
	Flash	7.44%	29.42%	42.32%	20.82%
BADDM	Before	76.22%	8.45%	9.34%	5.98%
	No reaction	15.31%	16.84%	48.39%	19.46%
	Flash	33.43%	29.32%	20.86%	16.39%
BrBADDM	Before	70.26%	10.32%	19.42%	0
	No reaction	10.80%	24.30%	46.60%	18.30%

Table 5 Tensile strength and fracture toughness at RT and 77K of all samples

Sample	Tensile strength (MPa)		Fracture toughness (MPa·m$^{1/2}$)	
	RT	77K	RT	77K
BADDS	74.50 ± 5.35	91.64 ± 8.95	1.93 ± 0.5	1.68 ± 0.2
BrBADDS	53.09 ± 10.41	66.36 ± 7.96	2.23 ± 0.1	1.83 ± 0.1
BADDM	70.37 ± 2.99	95.14 ± 7.03	1.98 ± 0.1	1.62 ± 0.3
BrBADDM	75.10 ± 8.15	86.37 ± 3.76	2.06 ± 0.2	1.63 ± 0.1

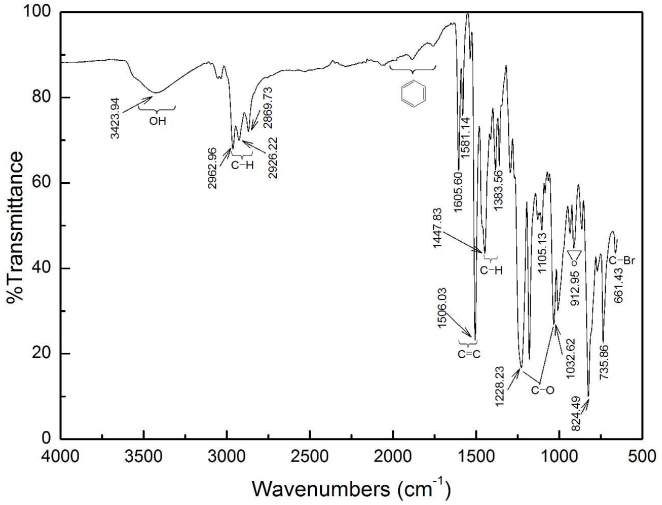

Fig. 1 FTIR spectrum of bromine-modified epoxy resin.

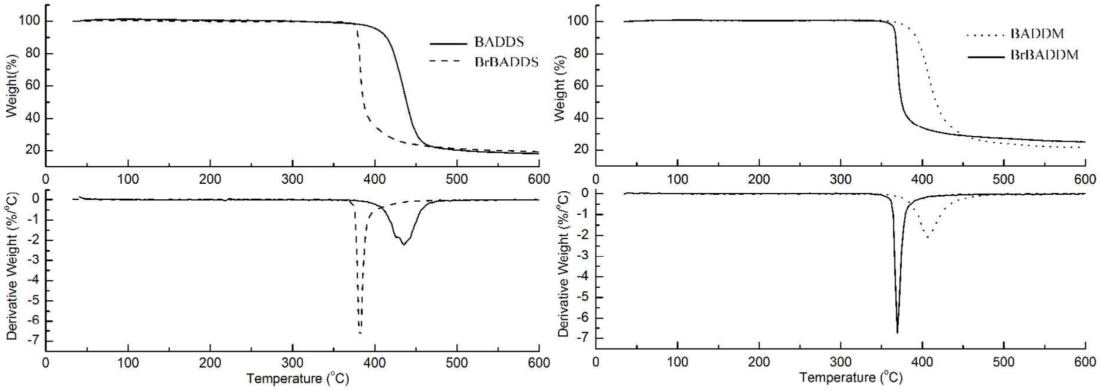

Fig. 2 TG and DTG curves of all cured epoxy resins in N_2 atmosphere

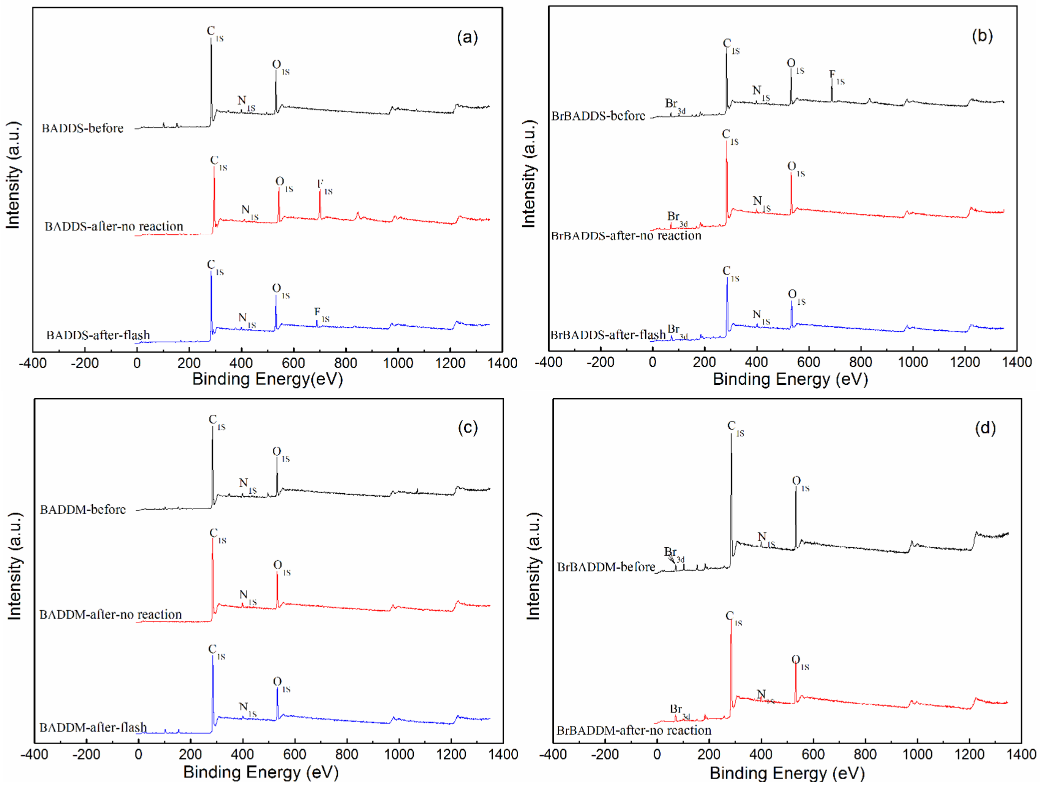

Fig. 3 XPS spectra of all samples before and after the mechanical impact (BADDS-before: XPS spectra of sample BADDS before impact; BADDS-after-no reaction: XPS spectra of sample BADDS without flash after impact; BADDS -after-flash: XPS spectra of sample BADDS with flash after impact)

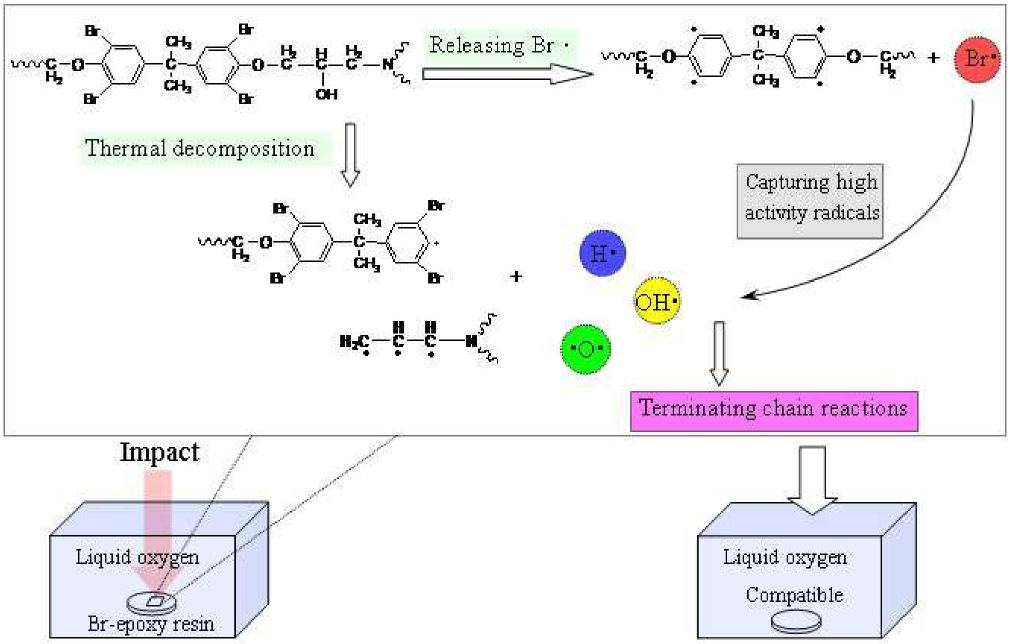

Fig. 4 The schematic of the liquid oxygen compatibility mechanism of the bromine -modified epoxy resin