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The Catalytic Curing Reaction and Mechanical Properties of a New Composite Resin Matrix Material for Rocket Fuel Storage Tanks

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Abstract: In this paper, an equimolar blend of bisphenol A dipropargyl ether and cyanate ester was selected to study the effect of different catalysts on the curing reaction of a bisphenol A dipropargyl ether and cyanate ester blended resin system, and the thermal stability and mechanical properties of the catalytically cured blended resin system were investigated. Acetylacetone salts of transition metals and dibutyl ditin laurate reduced the curing temperature of bisphenol AF-type di cyanate ester, and copper acetylacetonate at a mass fraction of 0.3% significantly reduced the curing temperature of bisphenol AF-type di cyanate ester to less than 473 K. Bisphenol A dipropargyl ether pr-polymerized and equimolarly blended with bisphenol A di cyanate ester and bisphenol E-type di cyanate ester also cured below 473 K under the same conditions. Among the cured compounds of the blended resins of bisphenol A dipropargyl ether with bisphenol AF-type di cyanate ester, bisphenol A-type di cyanate ester and bisphenol E-type di cyanate ester, the blended resins of bisphenol A-type di cyanate ester and bisphenol E-type di cyanate ester have better overall performance. The residual rate of 873 K in air was 38%, and the flexural strength, flexural modulus, and impact strength were 129.4 MPa, 4.3 GPa, and 27.3 kJ·m^{-2}, respectively. This kind of blended resin is expected to be used in the liquid oxygen storage tanks of rockets.

Keywords: bisphenol A dipropargyl ether; cyanate ester; catalytic curing; thermal stability; mechanical properties

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1. Introduction

Classic combinations, such as liquid hydrogen/liquid oxygen, liquid oxygen/kerosene, and liquid oxygen/methane, play a crucial role in aerospace launch vehicle fuels [1,2]. The weight of a rocket and its payload capacity are inversely related, with the rocket's tank structure accounting for more than 50% of the total rocket body weight. Therefore, reducing the weight of the fuel tank structure is pivotal in enhancing a rocket's payload capacity [3,4]. Currently, liquid oxygen storage tank composites primarily employ epoxy resin and cyanate ester-based matrix resins. These two resin systems exhibit excellent compatibility with liquid oxygen [5,6]. Epoxy resins boast exceptional processing and mechanical properties, but they are susceptible to high water absorption, and inaccuracies in formulation measurement can adversely affect material processing, molding, and property stability [7–9]. In contrast, cyanate ester resins offer outstanding thermal and mechanical properties, due to the highly cross-linked and symmetrical triazine ring structure resulting from the cyclotrimerization of three cyanate groups [10,11]. Compared to other thermosetting resins, cyanate esters combine the processability of epoxy resins with the thermal stability of bismaleimide and the heat resistance and flame retardancy of phenolic resins.

Consequently, they find widespread use in aerospace, electronic packaging, ablative, and radiation-resistant materials [10,12,13].

However, the high spatial specificity required for cross-linking via cyclotrimerization means the thermally initiated curing reaction of cyanate ester resins typically require high temperatures above 523 K [14,15]. The high curing temperature is one of the disadvantages of cyanate ester resins, as it generates residual thermal stresses in the product and affects its mechanical properties. Therefore, lowering the curing temperature has become one of the main research directions for the development of cyanate ester and its blended resins [16,17]. In addition, the ether-bonded structure of cyanate ester resins provides a certain degree of flexibility in their cured products, showing a toughness comparable to that of epoxy resins, but because of the high cross-linking density of the cyanate ester resins themselves, the cured products are more brittle when they are used alone, and they need to be modified and toughened. Thermosetting resins usually need to be fully cured at high temperatures to have excellent mechanical properties and high temperature resistance. To reduce energy consumption and ensure the mechanical properties of the resin casting body, catalysts can be added to reduce the curing reaction temperature of thermosetting resins, reduce the time, save on costs, and improve the mechanical properties of the resin [18,19]. Water, phenol, transition metal complexes, and active hydrogen compounds have been used in the catalytic curing of cyanate esters to reduce their cure temperature [20–23]. However, there have been some problems during the curing reaction of cyanate ester blend resins, such as incomplete curing at low temperatures and possible residual free isocyanates in the cured products [24]. These problems need to be solved by optimizing the reaction conditions and adding the appropriate additives, etc., to achieve the controlled preparation and application of cyanate ester blend resins. Bisphenol A dipropargyl ether has excellent thermal stability and physical/mechanical properties and its low water absorption makes it suitable for industrial mass production for the preparation of polymeric materials. Alkynyl ethers are very attractive alkyne groups which are easy to prepare, and thermosetting resins with terminal alkyne groups have good processability, low water absorption, excellent thermal stability, and excellent physical/mechanical properties [16,25,26]. Dirlikov et al. [27] synthesized bisphenol A dipropargyl ether pre-polymerized resins with good adhesion and encapsulation, lower moisture absorption than bisphenol A-based epoxy resins, and the tensile properties were better than those of bismaleimide resins. A potential resin substitute is bisphenol A dipropargyl ether monomer pre-polymerization, which enables rearrangement to form benzopyran, obtaining B-phase resins with good solubility, good storage at 373 K, a wide processing window, good adhesive base force, and encapsulation.

This paper aims to investigate the catalytic curing and properties of the bisphenol A dipropargyl ether/cyanate blend resin system to develop a catalytic system that reduces the curing temperature of the blend resin. We will assess the impact of catalytic curing on the properties of the hybrid resin system and analyze the thermal stability and mechanical properties of the bisphenol A dipropargyl ether/cyanate hybrid resin system. This study of the bisphenol A dipropargyl ether/cyanate blend resin has the potential to introduce a novel resin system for low-temperature storage tank composites.

2. Experiment

2.1. Materials

Bisphenol AF-type di cyanate ester (BAFDCy), Bisphenol A-type di cyanate ester (BADCy), and Bisphenol E-type di cyanate ester (BEDCy), industrial grade, supplied by Tianqi New Materials Co., Ltd., Yangzhou, China. Bisphenol A, Tetrabutylammonium Bromide (TABA), Sodium Hydroxide (NaOH), Ethynyl Bromide, Isopropyl Alcohol, Tetrahydrofuran (THF), Toluene Dichloride and Triphenyl Phosphine, analytically pure, supplied by Titan Technology Co., Ltd., Shanghai, China. Cuprous chloride (CuCl), analytically pure, supplied by Zonghe Chemical Technology Co., Ltd., Shanghai, China. Chromium acetylacetonate ($Cr(acac)_3$) and dibutyl ditin laurate (DBDTL), analytically pure, supplied by Sahn Chemical Technology Ltd., Shanghai, China. Copper acetylacetonate ($Cu(acac)_2$), 97% pure, Manganese acetylacetonate ($Mn(acac)_2$), analytically pure, supplied by Aladdin Biochemistry & Technology Co., Shanghai, China.

2.2. Equipment

High performance liquid chromatography (HPLC): Aglient high performance liquid chromatograph Aligent 1260SL, pump flow rate range of 0.001–5.0 mL/min, UV-visible detection wavelength range of 190–640 nm, with a detection limit of 8×10^{-8} g naphthalene/mL. Nuclear magnetic resonance hydrogen spectrometry (^1H NMR): Bruker superconductivity, Berlin, Germany. Fourier Transform Nuclear Magnetic Resonance (FTNMR) spectrometer Avance III400 from Bruker, Germany, operating frequency of 400 MHz, using deuterated chloroform ($CDCl_3$) as the solvent and the tetramethyl silane (TMS) as the internal standard. Infrared spectroscopy: Fourier transform infrared (FTIR) spectrometer Nicolet 6700 from Thermo Fisher, Waltham, MA, USA, scanning range of 400–4000 cm^{-1}, resolution of 0.1 cm^{-1}, with 32 scans. Differential Scanning Calorimetry (DSC): DSC-Q2000, TA, New Castle, DE, USA, in an air atmosphere, flow rate of 50 mL/min, heating rate of 10 K/min, scanning temperature range of 300–650 K. Thermal Weight Loss Analysis (TGA): Thermogravimetric Synchronized Thermal Analyzer TGA/DSC, Mettler Toledo, Greifensee, Switzerland, in an air atmosphere, flow rate of 50 mL/min. Mechanical properties testing: Changchun Institute of Machinery Science and Research Co., Ltd. (Changchun, China) electronic universal testing machine CCSS-44100; for casting body bending properties, following GB/T 2567–2008 using the three-point bending mode testing, with the bending specimen size 80 mm × 15 mm × 4 mm, and an external loading rate of 2.5 mm. Additionally, for bending specimens sized 4 mm × 4 mm, the external loading rate is 2.0 mm. The impact strength tester CEAST 9050, CEAS Company, Italy, with an impact specimen size of the casting body 80 mm × 10 mm × 4 mm.

2.3. Preparation and Pre-Polymerization of BADPE

Experiments were carried out to synthesis bisphenol A dipropargyl ether (BADPE) via the phase transfer pathway using bisphenol A with alkynyl bromide in a nucleophilic reaction via Williams' reaction condensation, as shown in Figure 1. Bisphenol A (0.6 mol), tetrabutylammonium bromide (0.1 mol), and NaOH (3.0 mol) were added to a three-necked flask containing 600 mL of deionized water with strong stirring and increasing temperature. Then, propargyl bromide (1.4 mol) was added dropwise after 1 h, when the solution returned to room temperature, after which the solution was heated to 343 K for 8 h at constant temperature. At the end of the reaction, the solid was filtered, washed with deionized water three times, and then washed with isopropyl ether. At the end of the reaction, the solid was first filtered, washed with deionized water 3 times, washed with isopropanol 2–3 times, and then placed in a vacuum drying oven and dried under vacuum at 333 K for 2 h. Finally, a white solid product was obtained. BADPE yield: 97%; melting point: 354 K (DSC method); purity: 99% (HPLC method); 1H NMR (CDCl3, 400 MHz) δ: 7.15 and 6.86 (m, 8H, aromatic), 4.65 (s, 4H, —CH_2—), 2.49 (s, 2H, —C≡C—H); FTIR: 3283 cm^{-1} (≡C—H), 3036 cm^{-1} (Ph—H), 2118 cm^{-1} (—C≡C—), 1500–1610 cm^{-1} (aromatic), 1219 cm^{-1} (Ph—O), and 1018cm^{-1} (CH_2—O).

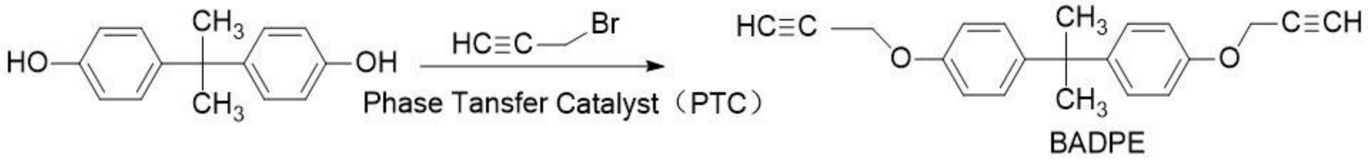

Figure 1. Synthesis of bisphenol A dipropargyl ether.

The resins were pre-polymerized with BADPE prior to blending. The experiments were carried out in a four-necked round-bottomed flask with mechanical stirring and a condenser tube and thermometer. A certain volume of dichlorobenzene was first added to the flask, followed by the incorporation of BADPE. CuCl was used as a catalyst and nitrogen was passed to make the reaction more complete. The reaction mixture was then heated to 458 K for 6 h. After the reaction was completed, the mixture was slowly cooled to room temperature, followed by the addition of a large amount of frozen petroleum ether, after which it was precipitated and isolated. Finally, vacuum drying was carried out for 4 h at 323 K. The pre-polymer BADPE-B was successfully obtained. BADPE was subjected to heat to undergo a Claisen rearrangement (Claisen) to form a B-stage resin with a bichromene structure, i.e., a cyclisation reaction to produce benzopyran, which is further crosslinked via free radical polymerization of the double bond in the presence of heat [16], as shown in Figure 2.

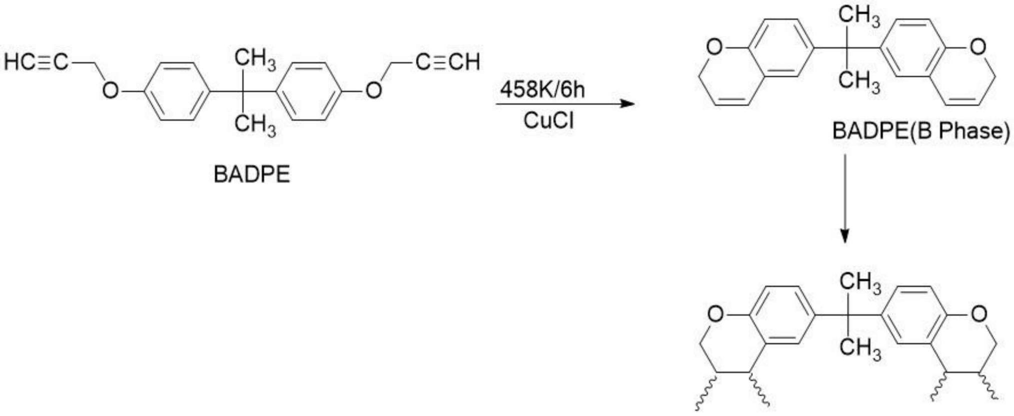

Figure 2. Pre-polymerization of bisphenol A dipropargyl ether resins.

Using HPLC analysis, 84% of the bichromene structure of the B-stage resin was detected in the BADPE prepolymer. The infrared and hydrogen NMR spectra of bisphenol A dipropargyl ether after 6 h of pre-polymerization at 458 K in a nitrogen atmosphere are shown in Figure 3. By tracking the infrared spectra of the pre-polymerized reactants, it can be seen that after 6 h of pre-polymerization, most of the characteristic carbon–carbon triple-bond peaks of alkynyl propoxyls in the structure of BADPE (at 2128 cm^{-1}) disappeared, indicating that a Claisen rearrangement had occurred. In the hydrogen NMR spectrum of the pre-polymerized BADPE, δ4.79 is the methylene hydrogen in the pre-polymerized benzopyran structure, and δ5.72 and δ6.35 are the hydrogens on the double bond in the benzopyran structure, respectively, which indicates that the benzopyran structure was indeed formed by the pre-polymerization reaction of BADPE. DSC analysis of this prepolymer revealed that the temperatures of the further polymerization reaction of the BADPE prepolymer: the initial temperature (T_i), peak temperature (T_p), and final temperature (T_f) of the curing reaction were 354, 380, and 433 K, respectively, and the exothermic enthalpy of the reaction ((ΔH)) was 280 $J \cdot g^{-1}$. The T_f of the curing reaction of the BADPE pre-polymerization was higher than that of the unpolymerized BADPE. The T_f of the curing reaction of BADPE after pre-polymerization was nearly half of that of BADPE without pre-polymerization, and the curing temperature was lower than 473 K.

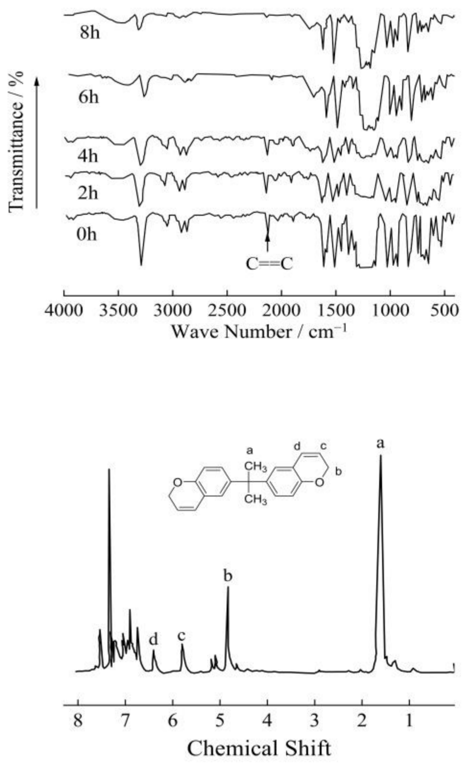

Figure 3. Infrared and hydrogen NMR spectra of bisphenol A dipropargyl ether resin prepolymerization. (a, b, c, d represent the peaks of hydrogen atoms at the corresponding positions in the molecular structure).

2.4. The Blending and Curing of BADPE with BAFDCy/BADCy/BEDCy

In a three-necked round-bottomed flask with mechanical stirring, after adding 175 mL of tetrahydrofuran solution, 0.5 mol each of bisphenol A dipropargyl ether prepolymer and cyanate ester were added in an equimolar ratio for stirring, and then a quantitative amount of catalyst was added, and stirring continued. Finally, the resin was transferred to a round-bottomed flask and the solvent was removed via vacuum evaporation to obtain the bisphenol A dipropargyl ether/cyanate blend resin. The curing method was in accordance with the curing gradient, holding at 433 K for 2 h, warming up to 453 K for 4 h, and warming up to 473 K for 12 h, i.e., the curing process 433 K/2 h + 453 K/4 h + 473 K/12 h, and finally the cured products were naturally cooled to room temperature.

The cyanate group (—OCN) undergoes a trimeric cyclisation under heat treatment (shown in Figure 4a) and the alkynyl ether group (—O—CH_2—C≡CH) undergoes a Claisen rearrangement reaction under heat treatment to form a 1-chromene ring, which in turn undergoes a radical photopolymerization of the chromeno (as shown in Figure 4b) [14]. The chromene ring formed by the rearrangement of the alkynyl ether in the blended resin undergoes a thermal rearrangement in which the lone pair of electrons on the oxygen atom binds to the electrophilic carbon atom in the cyanate root, ionizing —O—CN on the cyanate ester molecule, which then improves the carbon atoms in the cyanate root until trimeric cyclisation and elimination of the alkynyl ether occurs to form a triazine ring (shown in Figure 4c). The difference in the curing reaction mechanism of bisphenol A dipropargyl ether and cyanate ester makes the bisphenol A diynyl ether/cyanate blend resin form an interpenetrating network structure, which is conducive to the improvement of the mechanical properties of the blended resin.

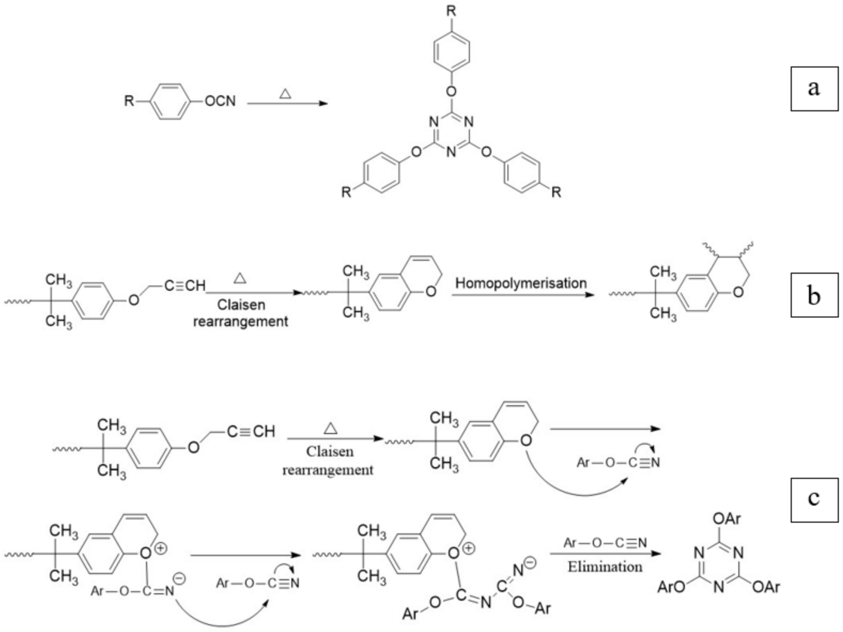

Figure 4. Reaction mechanism of bisphenol A dipropargyl ether/cyanate blend resin. (**a**) trimeric cyclisation of the cyanate group by heat; (**b**) Claisen rearrangement of the propargyl ether group by heat to form the chromene ring and free radical homopolymerisation of the chromene; (**c**) formation of the triazine ring by trimer cyclisation and elimination of the propargyl ether.

3. Results and Discussion

3.1. Thermal Analysis

a. Catalytic curing of BAFDCy via individual catalysts

Bisphenol A dipropargyl ether and cyanate ester are cured at high reaction temperatures and for long periods of time during their respective heat curing. In order to reduce the curing reaction temperature of bisphenol A dipropargyl ether and cyanate ester blended resins, and to reduce the residual thermal stress of the resin system during curing, catalysts are added to reduce the curing reaction temperature. In the BAFDCy resin curing experiments, Cu(acac)$_2$, Mn(acac)$_2$, Cr(acac)$_3$, and DBDTL, with a mass fraction of 0.1%, were added as catalysts. The effect of catalytic curing on the curing reaction was tested using DSC, and the results are shown in Figure 5. The initial temperature, peak temperature, final temperature, and exothermic enthalpy of the curing reaction are shown in Table 1. The addition of several catalysts with a mass fraction of 0.1% resulted in a decrease in the curing temperature of BAFDCy, which was accompanied by a decrease in the exothermic heat of polymerization, producing a higher heat of polymerization [28,29]. The curing temperatures of BAFDCy could be significantly decreased by Mn(acac)$_2$, Cr(acac)$_3$, and DBDTL, whereas the curing temperatures of BAFDCy were significantly decreased by adding Cu(acac)$_2$ to BAFDCy, which reduced the peak curing temperature from 521 K to 444 K.

Table 1. Results of DSC analysis of BAFDCy containing 0.1% of different catalysts.

Mass Fraction/%	T_i/K	T_p/K	T_f/K	$\Delta H/(J \cdot g^{-1})$
None	470.15	521.15	569.15	404
Cu(acac)$_2$	426.15	444.15	493.15	400
Mn(acac)$_2$	429.15	465.15	499.15	382
Cr(acac)$_3$	453.15	492.15	539.15	352
DBDTL	435.15	465.15	481.15	363

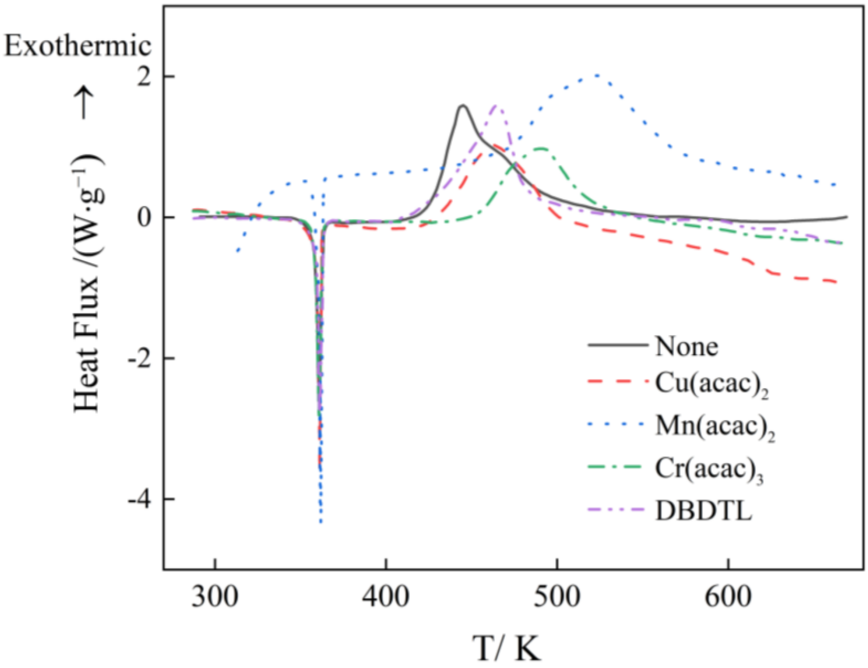

Figure 5. DSC plots of the BAFDCy curing reaction catalyzed by the addition of 0.1% of different catalysts.

b. Catalytic curing of BAFDCy with different amounts of Cu(acac)$_2$

The addition of different mass fractions of Cu(acac)$_2$ catalyzed the curing reaction of BAFDCy. The effect was analyzed via DSC, as shown in Figure 6, and the results are analyzed in Table 2. From the results, it can be seen that the curing temperature of BAFDCy showed a decreasing trend with the increase of the mass fraction of Cu(acac)$_2$ catalyst added, and the end temperature of BAFDCy curing was lower than 463 K with the addition of a mass fraction of 0.3%. From the results, it can be seen that there was no exothermic peak of the cured BAFDCy, which indicated that it had been cured completely [30].

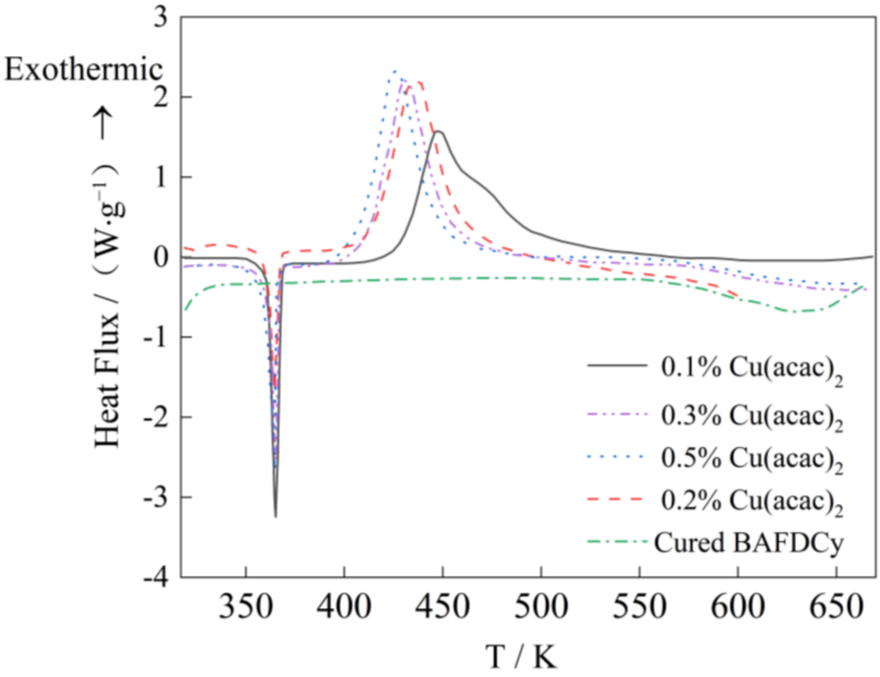

Figure 6. DSC plots of BAFDCy catalyzed by different mass fractions of copper acetylacetonate.

Table 2. Results of BAFDCy curing catalyzed by different mass fractions of copper acetylacetonate.

Mass Fraction/%	T_i/K	T_p/K	T_f/K	$\Delta H/(J\cdot g^{-1})$
0.1	426.15	444.15	493.15	403
0.2	411.15	433.15	458.15	389
0.3	408.15	427.15	448.15	396
0.5	404.15	423.15	444.15	410

c. The 0.3% Cu(acac)$_2$-catalyzed curing of BADCy/BEDCy

Similarly, the curing reactions of the cyanate esters BADCy and BEDCy were catalyzed with 0.3% mass fraction of Cu(acac)$_2$, and the results are shown in Table 3. It can be seen that Cu(acac)$_2$ also catalyzed the curing reactions of the two cyanate esters, BADCy and BEDCy, resulting in a significant decrease in their curing temperatures.

Table 3. Results of DSC analysis of the copper acetylacetonate-catalyzed curing reaction of cyanate esters.

Cyanate	T_i/K	T_p/K	T_f/K	$\Delta H/(J\cdot g^{-1})$
BADCy	520.15	563.15	628.15	871
BADCy + 0.3% Cu(acac)$_2$	398.15	444.15	491.15	526
BEDCy	459.15	502.15	533.15	834
BEDCy + 0.3% Cu(acac)$_2$	409.15	450.15	484.15	734

d. The 0.3% Cu(acac)$_2$-catalyzed curing of BADPE with BAFDCy/BADCy/BEDCy, and its thermal stability study

Using the above method, after equimolar blending of the synthesized bisphenol A dipropargyl ether with the cyanate ester, the curing reaction of the blend resins was catalyzed by the addition of Cu(acac)$_2$ with a mass fraction of 0.3%, and the DSC analysis of this is shown in Figure 7. It can be seen that the final temperature of the curing reaction of the three hybrid resins was lower than 473 K. The curing process of the three hybrid resins was determined to be 363 K/2 h + 433 K/2 h + 473 K/4 h.

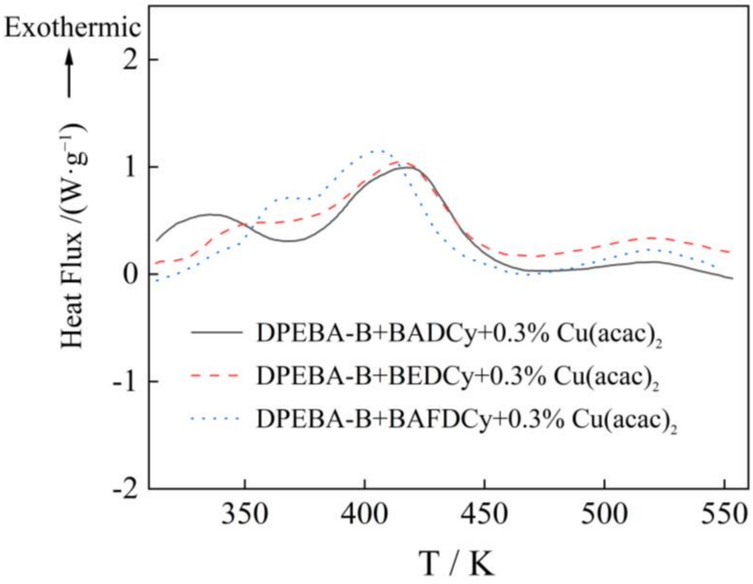

Figure 7. DSC plots of the catalytic curing of three hybrid resins.

The initial temperature, peak temperature, and final temperature of the blended resin were lower than those of the pure resin, T_i was 67 K lower and T_p was 45 K lower than that of BADCy, and the exothermic peak of the blended resin's cure was widened. This indicates that the curing temperature of BADCy can be reduced by blending BADCy with BADPE and then curing. After the addition of the catalyst, the curing reaction temperature T_i decreased significantly, and the curing reaction peak temperature also changed from one to three, indicating that the curing reaction of the blended resin changed with the addition of the catalyst. The highest peak curing temperature of the blended resin, which should be the temperature at which the free radical polymerization and cross-linking of chromene occurs, did not decrease much with the addition of the catalyst, and so did the temperature at which the catalyst catalyzes the cyanate ester trimerization and cyclization reaction. The significantly lower first peak temperature is the temperature at which the catalyst catalyzes the cyclisation of the propargyl ether and the linear polyene oligomerization reaction, the intermediate peak temperature belongs to the rearrangement reaction of the propargyl ether and is the temperature at which the ether oxygen atom catalyzes the cyanate ester triple cyclisation reaction, and the final peak temperature is the temperature at which the free radical polymerization of the alkene bond takes place.

To investigate the thermal stability of three hybrid resin systems cured by $Cu(acac)_2$-catalyzed curing, thermogravimetric analysis (TGA) was used as a research tool, as shown in Figure 8. In contrast, the hybrid resin cures of the bisphenol A dipropargyl ether prepolymer and the three cyanate esters showed different residual rates (Yr873 K) of 35.9%, 37.9%, and 0.7%, respectively, in the air system at 873 K. The cures of the bisphenol A dipropargyl ether prepolymer and the three cyanate esters were found to be more stable in the air system. The residual rates (Y_r) obtained from the TGA of the cured compounds of the blended resins in air can be used for the estimation of the Limited Oxygen Index (LOI) of the resins, according to the Van Krevelen-Hoftyzer equation [31]:

$$\mathrm{LOI} = 17.5 + 0.4\mathrm{Y_r} \quad (1)$$

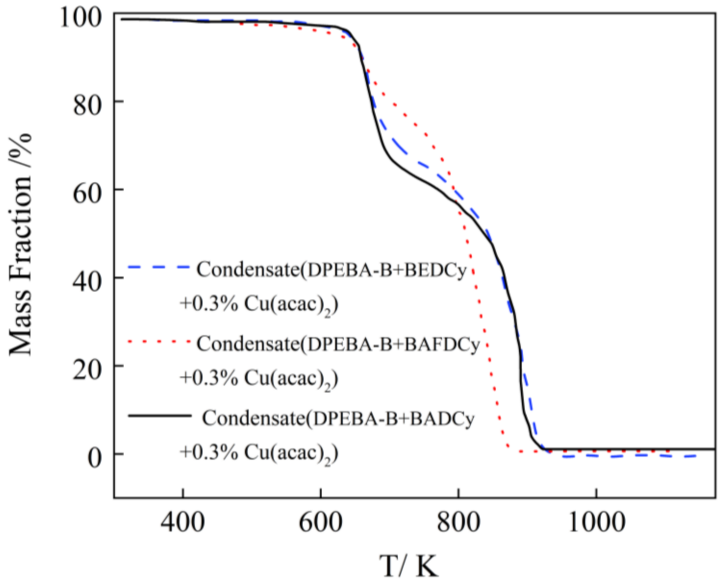

Figure 8. TGA plots of the three hybrid resins cured in air.

The LOI of the cured resin needs to be higher than the threshold value of 26 to show that the resin is self-extinguishing and can be applied as a good flame-retardant material. That is, the residual rate of the resin in air at a certain temperature needs to be higher than 21.25% to be flame retardant. The results of the TGA tests of the three hybrid resin cures in air are shown in Table 4. The hybrid resin system consisting of bisphenol A diynyl propylene ether prepolymer with bisphenol E-type di cyanate ester and bisphenol A-type di cyanate ester has flame retardancy at the alcohol temperature (873 K). All three resin systems were flame retardant at flame temperature (673 K), and the cured blend resin of bisphenol AF-type di cyanate ester had the highest residue in air. The residual rate in air at

873 K was only 0.7% for bisphenol AF-type di cyanate ester, with dimethyl hydrogen fully substituted with fluorine atoms in the structure of the bisphenol AF-type di cyanate ester, which was much lower than that of the bisphenol AF-type di cyanate ester blended resin curing material. This is because the C—F bond length (0.138 nm) is larger than the C—H bond length (0.109 nm), and it reacts easily with oxygen radicals at high temperature in air, causing bond breakage and decomposition.

Table 4. TGA test results of three hybrid resin cures in air.

Catalytic Curing Hybrid Resins	$T_{5\%}$/K	Y_{r673K}/%	Y_{r873K}/%
BADPE/BADCy	652.15	81.6	35.9
BADPE/BEDCy	652.15	85.5	37.9
BADPE/BAFDCy	647.15	88.6	0.7

3.2. Mechanical Analysis

To the bisphenol A dipropargyl ether prepolymer and three kinds of cyanate ester equimolar, respectively, add and mix 0.3% $Cu(acac)_2$ to the catalytic hybrid resin system, and then cast the solvent removal hybrid resin into a mold coated with mold releasing agent. It first goes in the oven to vacuum pump the bubbles, and then into the high temperature oven for curing. At the end of curing, the cured resin is allowed to cool naturally to room temperature to obtain the casting body. To avoid non-essential influencing factors, the molds should be preheated before use. A catalyst is added to reduce the curing reaction temperature of the bisphenol A dipropargyl ether and cyanate ester blend resin system, so that the residual thermal stresses of the cured resin system can also be reduced, and the toughness and strength of the material can be increased. In addition, based on the different curing mechanisms of bisphenol A diynyl propyl ether and cyanate ester, the bisphenol A diynyl propyl ether-modified cyanate ester resin system can form an interpenetrating network structure, and the interaction between the polar groups can improve the strength of the resin network. The mechanical properties of the bisphenol A diynyl propyl ether/cyanate blend resin casting body are shown in Table 5.

Table 5. Mechanical properties of cured resin blends of bisphenol A diethyl propynyl ether and cyanate ester.

Hybrid Resin Casting Body	Bending Strength/Mpa	Bending Modulus/GPa	Impact Strength/kJ·m^{-2}
BADPE/BAFDCy	92 ± 2.11	3.6 ± 0.22	15.9 ± 0.82
BADPE/BADCy	79.7 ± 2.41	4.1 ± 0.11	12.2 ± 1.24
BADPE/BEDCy	129.4 ± 2.33	4.3 ± 0.09	27.3 ± 0.62

4. Conclusions

In this paper, we synthesized bisphenol A dipropargyl ether and prepared blended resins by molar blending it with bisphenol AF-type di cyanate ester, bisphenol A-type di cyanate ester, and bisphenol E-type di cyanate ester, respectively, in a solution. We investigated the curing reactions and properties of the catalytically cured resin systems using copper acetylacetonate, manganese acetylacetonate, chromium acetylacetonate, and dibutyl ditin laurate as catalysts. The results demonstrated that the acetylacetone salts of transition metals and dibutyl ditin laurate effectively lowered the curing temperature of bisphenol AF-type di cyanate esters. Specifically, copper acetylacetonate, with a mass fraction of 0.2%, significantly reduced the curing temperature of bisphenol AF-type di cyanate esters to below 473 K. Furthermore, after the pre-polymerization of bisphenol A dipropargyl ether and equimolar blending with bisphenol AF-type di cyanate ester, bisphenol A-type di cyanate ester, and bisphenol E-type di cyanate ester, all three blended resins could be cured below 473 K under the catalysis of copper acetylacetonate. Among these, the blended resin of bisphenol A dipropargyl ether and bisphenol E-type di cyanate ester exhibited superior overall performance, featuring a residual rate of 38% in air at 873 K, as well as an impressive flexural strength (129.4 MPa), flexural modulus (4.3 GPa), and impact strength (27.3 kJ·m^{-2}).

Our next steps will involve further investigations into a bisphenol A dipropargyl ether/bisphenol E-type di cyanate ester blended resin reinforced by carbon fiber. We will delve into the mechanical properties of the composites, their compatibility with liquid oxygen, and the catalytic curing of the blended resin. Carbon fiber-reinforced resin matrix composites are widely used mainly because of their light weight, high strength, good heat resistance, plasticity, and corrosion resistance. In aerospace and other fields, the use of carbon fiber-reinforced hybrid resin matrix composites can significantly improve the safety of their products, increase the quality of products, and play a good role in promoting the development of the industry.

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