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An Innovative Halogen-Free Flame-Retardant Thermosetting Carbon Fiber Laminate

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In this study, we evaluated a flame-retardant hardener for epoxy resins and a flame-retardant resin consisting of the same components, which can be applied to materials used in the aerospace, automotive, and construction industries. To overcome the predicaments associated with curing agents such as 9,10-dihydro-9-oxa-10-phosphaphenanathrene-10-oxide (DOPO)-dicyandiamide (DICY) that are difficult to synthesize successfully, we provided novel flame-retardant hardeners by attaching the phosphorous-containing group of DOPO to a carbon of DICY. We also provide a method beneficial for mass production of the flame-retardant hardener for epoxy resins. To measure the characteristics of the flame-retardant hardener, carbon fabrics were preimpregnated with these epoxy resins to form a halogen-free flame-retardant thermosetting carbon fiber prepreg. Then, samples of carbon fiber laminate with eight layers of prepregs were pressed at 180 °C under thermosetting conditions. The tensile, compressive, flexural, interlaminar shear, and in-plane shear properties of the carbon fiber laminate were measured in accordance with American Society for Testing and Materials (ASTM) D3039, D3410, D790, D2344, and D4255 standard testing protocols, respectively. The results indicate that the proposed material provides high strength and stiffness. Finally, according to the flammability rating of the UL-94 standard method, all samples were determined to be V-0. The results demonstrate that a flame-retardant hardener for epoxy resins could be mixed with resins to produce a standard qualified flame-retardant resin based on the UL-94 standards.

1. Introduction

When resins are used as a carbon fiber prepreg material, the monomer of the resins is used to make products with flame-retardant characteristics. Although the carbon fiber prepreg material made with brominated resins usually has good flame-retardant characteristics, the brominated resins produce highly corrosive bromine free radicals, hydrogen bromide (HBr), high toxic polybrominedibenzofurans, and polybrominedibenzodioxins when incinerated. These substances cause huge damage to both people and the environment. To overcome these problems, a phosphorus-containing group in 9,10-dihydro-9-oxa-10-phosphaphenanathrene-10-oxide (DOPO) is attached to the epoxy resin to provide a flame-retardant resin, which can replace the toxic

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brominated resin. When a product made of DOPO is heated at a high temperature, the phosphorus-containing group in DOPO produces nonvolatile phosphorous compounds such as phosphoric acid (H_3PO_4) and polyphosphorous acid. Because polyphosphorous acid has the ability to protonate organic molecules and has a strong dehydrating effect, and because H_3PO_4 can be an agglutinant for carbon to form an insulated layer and also a strong dehydrating effect, nonvolatile phosphorous compounds can import a desirable flame-retardant characteristics to resins.

Generally, resins for carbon fiber prepreg materials must be synthesized with a curing agent (hardener) and treated with other processes. Because DOPO can provide flame-retardant characteristics to resins, a halogen-free flame-retardant carbon fiber prepreg material can also be obtained using a DOPO-containing curing agent.

This hypothesis, that a curing agent attached to a phosphorous-containing group in DOPO may give rise to a flame-retardant material, has been well known in related areas. However, a feasible and specific process and technique have still not been developed. Many articles(1,2) have disclosed a compound of the sort represented in Fig. 1.

This compound is obtained by attaching a phosphorous-containing group of DOPO to a curing agent (dicyandiamide, DICY) and is called DOPO-DICY. According to the preparation method disclosed in the publications, DICY must be heated at 120 °C until it is completely melted. However, DICY has a high melting point of about 209.5 °C. It is difficult to use the conventional apparatus as disclosed in the published literature to synthesize DOPO-DICY. Moreover, there is still a need to develop other curing agents to improve technical progress.

To overcome the problem that curing agents such as DOPO-DICY (an agent for curing materials) are difficult to synthesize successfully, a novel flame-retardant hardener made by attaching the phosphorous-containing group of DOPO to a carbon of DICY is proposed in this study. We also provide a method beneficial for mass production of the flame-retardant hardener for epoxy resins.

2. Preparation and Manufacture of Halogen-Free Flame-Retardant Thermosetting Carbon Fiber Laminate

The preparation of a flame-retardant hardener for epoxy resin is as follows.

(1) A reaction flask equipped with an electric stirrer, a thermocouple, and an adjustable thermostat heater was provided. The reaction flask should be filled with nitrogen to isolate the contents from the air and moisture.

(2) An appropriate amount of DOPO was added to the reaction flask and heated to a temperature ranging from 120 to 135 °C until the DOPO was completely melted.

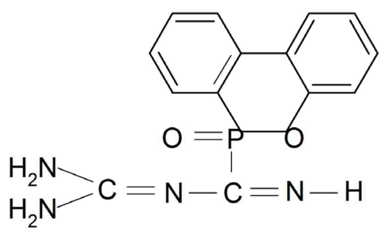


Fig. 1. Typical structure of DOPO-DICY.(1,2)

(3) An appropriate amount of DOPO was added to the reaction flask to form a mixture. In this step, the reaction temperature must be higher than 110 °C to ensure that the DOPO was in a molten state. In the sample prepared, the molar ratio of DOPO to DICY was 1:1, 1.8:1, and 5:1.

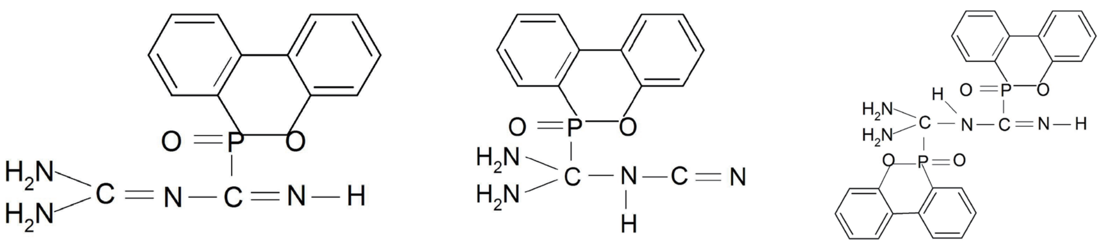
(4) The reaction flask was slowly heated to 175 °C from 4 to 14 h. In the samples prepared, the reactions were carried out for 6 and 14 h when the molar ratio of DOPO to DICY was 1:1. The reactions were carried out for 2 and 8 h when the molar ratio of DOPO to DICY was 1.8:1. The reaction was carried out for 14 h when the molar ratio of DOPO to DICY was 5:1.

(5) The mixtures obtained in the precious step were subsequently cooled. The mixtures comprising three products represented by structures (A), (B), and (C) were produced, as shown in Fig. 2.

After the flame-retardant hardener for epoxy resins were manufactured, high grade carbon fabrics were pre-impregnated with the resins to form a halogen-free flame-retardant thermosetting carbon fiber prepreg. Then, samples of the halogen-free flame-retardant thermosetting carbon fiber laminate (Fig. 3) with eight layers of prepregs were pressed at 180 °C under thermosetting conditions. The thickness of this laminate was 1.38 mm.

3. Performance Testing of Halogen-Free Flame-Retardant Thermosetting Carbon Fiber Laminate

The tensile, compressive, flexural, interlaminar shear, and in-plane shear properties of the halogen-free flame-retardant thermosetting carbon fiber laminate were measured by American Society for Testing and Materials (ASTM) D3039, D3410, D790, D2344, and D4255 standard



(a) (b) (c)

Fig. 2. Structures of DOPO-DICY samples synthesized in this study.

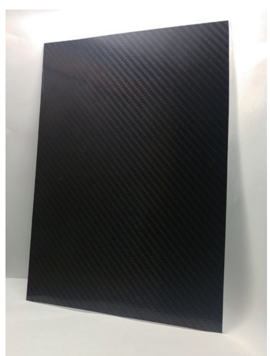


Fig. 3. Picture of halogen-free flame-retardant thermosetting carbon fiber laminate.

testing protocols,[3–7] respectively. All data were generated in the 0 direction and tested at room temperature. The measured mechanical properties of the halogen-free flame-retardant thermosetting carbon fiber laminate are shown in Tables 1–5. The proposed carbon fiber laminates have the following averaged properties: tensile strength, 1109.67 MPa; tensile modulus, 128.97 GPa; compressive strength, 1003.33 MPa; compressive modulus, 134.95 GPa; flexural strength, 2306.33 MPa; flexural modulus, 131.94 GPa; interlaminar shear strength, 12483.99 MPa; interlaminar shear modulus, 36.32 GPa; in-plane shear strength, 43.24 MPa; in-plane shear modulus, 6.048 GPa. These results indicate that our proposed halogen-free flame-retardant thermosetting carbon fiber laminate provided high strength and stiffness. The mechanical properties of the composites can be enhanced by changing the fiber orientation and increasing the number of laminates.[8]

In addition, the flame-retardant properties of the halogen-free flame-retardant thermosetting carbon fiber laminate were determined by official standard flame-retardant UL-94 test.[9] The results for samples 1 to 5 are listed in Table 6. According to the flammability rating of the UL-94 standard method, the qualified ratings are classified as V-0, V-1, and V-2. As shown in Table 6, all samples are self-extinguishing, which meets the UL-94 V-0 classification. The results demonstrate that the flame-retardant hardener for the epoxy resins could be mixed with resins to produce a standard qualified flame-retardant resin based on the UL-94 standards. Hence, the flame-retardant resin material could be used to replace the halogenated resin in conventional processes.

Table 1
Tensile properties of samples by ASTM D3039.

No.	Width (mm)	Thickness (mm)	Tensile load (kN)	Tensile strength (MPa)	Tensile modulus (GPa)	Failure code
1	10.50	1.36	12.238	857.036	129.19	SGM
2	10.49	1.34	17.241	1226.537	131.87	SGM
3	10.45	1.40	17.800	1216.683	125.09	SGM
4	10.45	1.40	16.899	1155.077	130.18	SGM
5	10.47	1.37	156.781	1093.016	128.51	SGM

Table 2
Compressive properties of samples by ASTM D3410.

No.	Width (mm)	Thickness (mm)	Compressive load (kN)	Compressive strength (MPa)	Compressive modulus (GPa)	Failure code
1	24.01	1.37	26.312	799.91	109.91	TAT
2	24.03	1.40	36.211	1076.37	129.99	TAT
3	24.02	1.32	36.414	1148.47	155.90	TAT
4	24.01	1.34	36.402	1131.43	138.41	TAT
5	24.02	1.37	28.315	860.44	140.55	TAT

Table 3
Flexural properties of samples by ASTM D790.

No.	Length (mm)	Width (mm)	Thickness (mm)	Flexural load (kN)	Flexural strength (MPa)	Modulus (GPa)
1	50.52	12.93	1.38	1.397	2162.03	117.00
2	50.48	12.81	1.32	1.244	2123.45	136.22
3	50.52	12.95	1.35	1.522	2456.95	139.08
4	50.58	12.98	1.36	1.448	2297.92	136.18
5	50.52	12.92	1.36	1.533	2491.32	131.36

Table 4
Interlaminar shear properties of samples by ASTM D2344.

No.	Width (mm)	Thickness (mm)	Interlaminar load (kN)	Interlaminar strength (MPa)	Interlaminar modulus (GPa)
1	9.88	1.35	7.195	12946.73	36.33
2	9.65	1.35	7.029	12949.70	36.62
3	9.84	1.32	6.237	11491.00	35.67
4	9.84	1.32	7.051	12989.32	36.95
5	9.88	1.33	6.985	12043.18	36.01

Table 5
In-plane shear properties of samples by ASTM D4255.

No.	Ultimate load (kN)	Ultimate shear strength (MPa)	Modulus (GPa)
1	9.090	43.35	6.155
2	8.915	43.21	6.015
3	8.755	41.98	5.984
4	9.114	43.65	6.213
5	9.200	44.01	5.871

Table 6
Flame-retardant properties of samples by UL-94.

No.	Afterflame time t_1 (s)	Afterflame time t_2 (s)	Afterglow time t_3 (s)	Whether ignited the cotton (Yes/No)	Whether burn up to the holding clamp (Yes/No)
1	3.5	0	0	No	No
2	2.7	0	0	No	No
3	4.0	0	0	No	No
4	0	0	0	No	No
5	0	0	0	No	No

4. Conclusions

Carbon fibers with ultralight, energy-saving, and harder-than-steel properties have received significant attention from researchers. In particular, their applications in information technology, automobile, aviation, sports, and the military produce profits for manufactures. To overcome the problem that curing agents such as DOPO-DICY are difficult to synthesize successfully, a novel flame-retardant hardener formed by attaching the phosphorous-containing group of DOPD to the carbon of DICY is proposed in this study. This method for manufacturing a flame-retardant hardener for an epoxy resin can be directly applied in a resin curing process after a cooling step without additional purification. To evaluate the applicability of this hardener for manufacturing carbon fiber composite materials, high-grade carbon fabrics were preimpregnated with these epoxy resins to form a halogen-free flame-retardant thermosetting carbon fiber prepreg. Then, samples of the halogen-free flame-retardant thermosetting carbon fiber laminate with eight layers of prepregs were pressed at 180 °C under thermosetting conditions to measure the mechanical properties and flame-retardant characteristics of the proposed carbon fiber laminate. The obtained results indicate that the laminate has greater strength than steel and a V-0 flammability rating in accordance with the UL-94 standard.

We conclude that the flame-retardant hardener for epoxy resins in accordance with this invention can replace conventional toxic halogenated resins and provide an environmental-friendly flame-retardant hardener for epoxy resins for applications in the aerospace, automotive, marine, and construction industries.

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