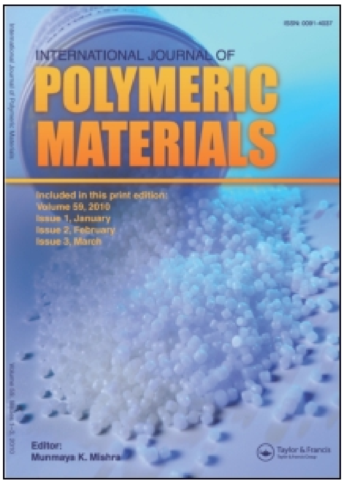

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STUDY OF THERMAL STABILITY AND ABLATION BEHAVIOR OF CARBON FABRIC/EPOXY-NOVOLAC ABLATIVE COMPOSITES

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STUDY OF THERMAL STABILITY AND ABLATION BEHAVIOR OF CARBON FABRIC/EPOXY-NOVOLAC ABLATIVE COMPOSITES

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Use of epoxy-novolac resin systems in carbon fabric ablative composites as advanced insulation materials is studied. Three types of carbon fabrics are used and their composites are prepared by impregnation and hand lay-up methods. In order to study thermal stability and ablation behavior, the composites are tested by thermal tests such as, thermogravimetry and standard oxyacetylene flame tests. It is found that the composite, which is made up of C-9750, high strength carbon fabric, in comparison with steel and the other types of carbon fabric composites, has the highest thermal stability and the best ablation behavior.

Keywords: Ablation, thermal stability, ablative composites, high temperature polymers, epoxy-novolac matrixes

INTRODUCTION

Polymer matrix composites are being used increasingly in a variety of important applications because of their excellent mechanical properties and low weight, combined with advancements in manufacturing technology. In particular, carbon reinforced epoxy composites [1] are playing an important role in the production of high performance

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vehicles as well as critical aerospace structures [2], such as primary structures of commercial and military aircrafts [3].

According to the concept of "effective thermal decomposition," the epoxy-novolac systems are new and excellent, belonging to advanced epoxy systems, which are similar or even better in ablative behavior [4] than conventional phenolic systems [5]. The ability of such systems as ablators first was mentioned by J. Fleming [6] in an ablative symposium. Use of epoxy resin systems in ablative composite structures [7] has been mentioned for many years, but the use of epoxy-novolac as matrix in ablative composites is mentioned as an advanced system and literature surveys confirm this reality [8]. These ablative materials belong to the charring ablators and are commonly used in many applications, especially in cooling systems of the rocket motors, the exit cone of the solid propellant rockets [9, 10], and space shuttles [11].

Generally, with increased cross-linking density of ablative matrix, the percentage of residual char will be higher and the efficiency of such systems as ablative insulators is increased. In this group of ablative materials, the residual char in high temperatures works as a binder and causes a better protection from the substrate degradation [12, 13]. It should be mentioned that the general characteristics of a polymer that protects a substrate material from heat damage [14] are: Relatively high modulus, low elongation at failure, and high hardness.

According to the recommendations made in literature surveys, in order to obtain a high degree of insulation properties in an ablative composite, the weight percentage of reinforcement should be in the range of 60–70%. Such systems, which consist of carbon fabric/epoxy-novolac with the weight percentage mentioned above, belong to the low density ablators. According to the literature surveys, the lower the density of ablative composite insulation, the higher the ability of thermal insulation of the composite [15].

Because the composite systems used belong to the low density ablators, we expect that their abilities as ablative insulations will be very high, which is confirmed in literature studies. It should be mentioned that all ablative composite systems are made up of two different phases: continuous phase (matrix) and discontinuous phase (reinforcement) [16–18]:

Matrix

The most important ablative resins that are used in these systems are phenolics, polybenzithiazoles, epoxy-novolacs, polybenzimidazoles, polyimides [17], and epoxies that belong to the thermosetting resins group.

Reinforcement

The most important reinforcements used in these systems as reinforcing agents are carbon, silica, graphite, asbestos, and glass [18, 19]. These reinforcements may have different physical shapes, such as fabric, fiber, filler (powder), and chopped strand [20].

EXPERIMENTAL

Materials

Resin System

The resin system used is a triple system consisting of resin, hardener, and accelerator [21].

Resin

Epoxy-novolac resin (DEN 431), purchased from Dow Chemicals co., has excellent properties such as processability as an ablator [21]. This epoxy resin is a multi-functional epoxy that could produce higher strength network than the conventional epoxy resins (Bisphenol A) [22–24]. Ease of processability and high thermal resistivity will cause such resin to be used as binder in erosion operations [25, 26].

Curing Agent

Nadic methyl anhydride (NMA) is used as curing agent in hot cure epoxy-novolac systems, which has the best thermal performance among the other epoxy curing agents [27]. It is necessary to mention that the high temperature performance of any cured system depends on the curing agent ability and capability. This not only affects the pot life, but also the required viscosity range of the system. Use of liquid anhydride curing agents, (e.g., NMA), is very convenient in such systems, because of decreased viscosity and increased high temperature performance of the system [28, 29].

Accelerator

Because of the higher ability and performance of triple component systems, benzyldimethylamine (BDMA) has been used in such systems, as accelerator.

Reinforcements

High strength carbon fabrics (C-9750, C-9751, C-9756) obtained from the Swiss Multi Products Enterprise Company were used as reinforcements.

APPARATUS

Standard Oxyacetylene Flame Test

To evaluate the thermal behavior and ablation performance [30, 31] of the ablative composite insulators, a standard oxyacetylene flame test is carried out. The results of this standard test are useful in showing the thermal behavior of ablative materials in solid propellant rocket motors, nozzles, etc. According to this standard flame test [32], the apparatus includes oxyacetylene burner, specimen holder, burn-through time detector, and back-face temperature recorders. Figure 1 illustrates the standard oxyacetylene flame test apparatus. This test is used for determination of burn-through time, erosion rate, insulating effectiveness, and insulation index numbers of the ablators.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is one of the most favored techniques for rapid evaluation in comparing the thermal stability of various materials. TGA was performed using a Polymer Laboratories Corporation instrument, with a temperature increase rate of 20°C/min over the range of room temperature to 800°C in air atmosphere.

Resin System Preparation

In order to study the hardener variation effects on the properties of epoxy-novolac resins and their optimization, samples with different hardener values with compositions indicated in Table 1 were prepared. Initially, the prepared specimens were cured in the oven at 90°C for 2 hr, Post-curing was then carried out continuously for 4 hr at 165°C and 16 hr at 200°C. Then, thermogravimetric analysis was carried out.

Sample Preparation

After preparation of the resin system, carbon fabrics were cut in dimension of $25 \times 25\,cm^2$. Impregnation of the fabrics was carried out by hand lay-up method, as previously mentioned. After weighing the carbon fabrics, the reinforcements were immersed in the matrix system. The impregnated fabrics were placed in different number of

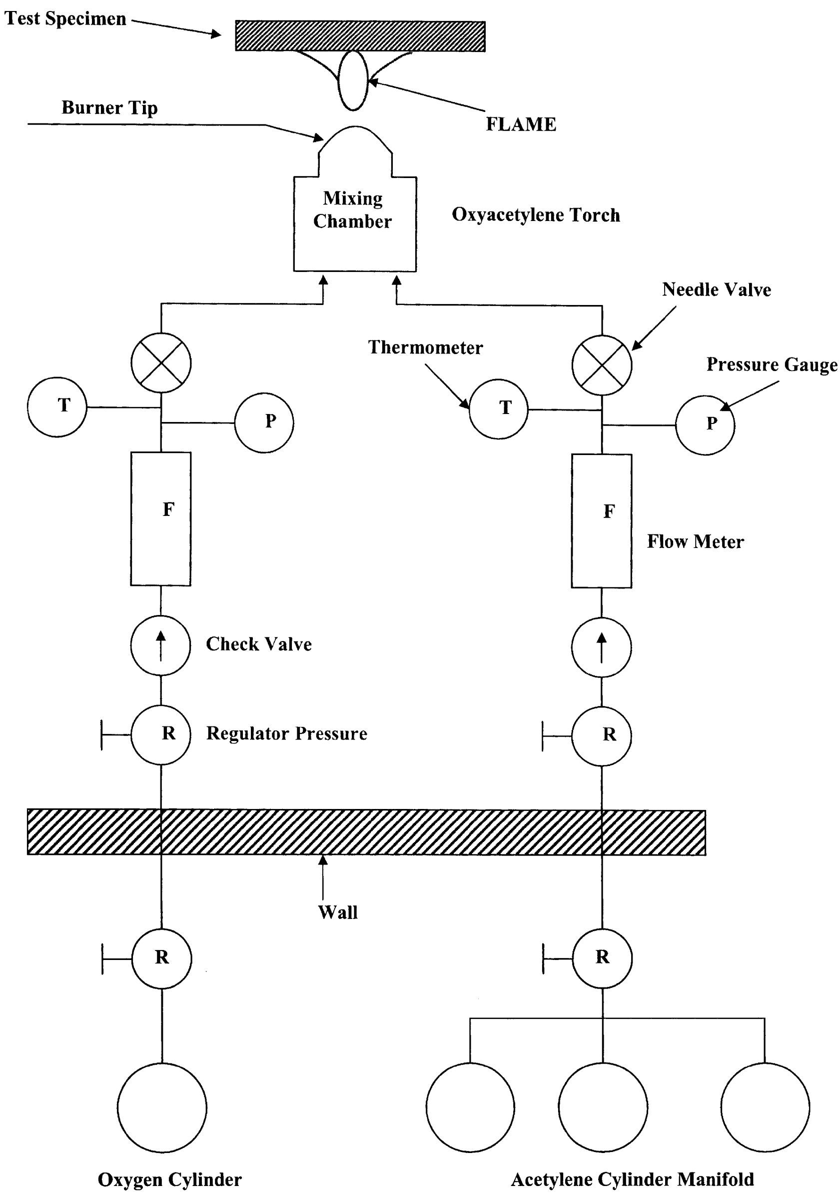

FIGURE 1 Standard oxyacetylene flame test apparatus.

TABLE 1 Composition of Samples with Different Amounts of Hardener

Sample	Resin	Hardener (phr)	Acc. (phr)
1	100	100	1.5
2	100	87.5	1.5
3	100	75	1.5

layers of fabrics on the metal plate to obtain the necessary thickness (according to the ASTM E285-80 standard) and the necessary resin pick up occurred.

The curing process was carried out according to the program mentioned and in cases where there were no voids or cracks in the cured specimens, they were reweight in order to calculate the resin pick up and reinforcement percentage (the latter should be in the range of 60–70% wt carbon fabrics) [7, 21]. Finally, the sample specimens were cut into $10 \times 10\,cm^2$ pieces with a titanium carbide drill, for carrying out a standard oxyacetylene flame test.

RESULTS AND DISCUSSION

Thermogravimetric analysis is used to determine the thermal stability of samples (Table 1). Figure 2 illustrates the TGA curves of resin systems with different hardener values. Changes in weight of the samples for three different temperature thus reported in Table 2.

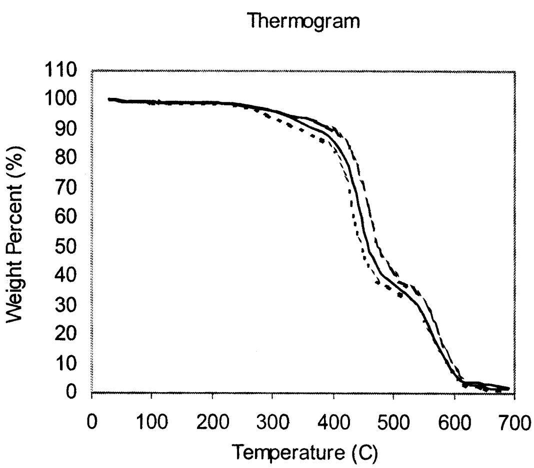

FIGURE 2 TGA curves of resin systems with different hardener values (.......75 phr, _____100 phr, _ _ _ 87.5 phr).

TABLE 2 Weight-Loss of Samples with Different Amounts of Hardener at Three Different Temperatures

Temperature (°C)	1[a]	2[b]	3[c]
275	2.3	2	3.3
380	11	8	14
475	58	51	61

[a]Sample with 75 phr hardener; [b]Sample with 87.5 phr hardener; [c]Sample with 100 phr hardener.

It is observed that all these systems are nearly stable up to 275°C. The weight loss of the samples started at this temperature and at 475°C the weight loss of the samples with the amount of 75, 87.5, and 100 phr hardener, are 39%, 49%, and 42%, respectively.

The results indicated that the thermal stability of the sample with 87.5 phr hardener is better than the others and we used this optimized amount to prepare samples. The ablation behavior of about 30 composite specimens and three steels are shown in Table 3, which also shows the carbon 9750 fabric/epoxy-novolac resin composites have the best ablation behavior among the others. To improve the processability of the resin system, it was preheated to 40°C, the temperature in which the impregnation of reinforcement could be carried out, for an hour. Then the other components were added and mixed well. The curing program was obtained from the literature and depended on the matrix system and selected process. Impregnation of the fabrics was carried out by hand lay-up method. In order to compare the thermal behavior of such materials, the temperature variations for the three types of carbon fabric/epoxy-novolac composites and one kind of steel is shown in Figure 3 which illustrates temperature profile distribution for different samples.

In order to determine the thermal stability of samples with different carbon fabrics TGA analysis was carried out. Results are given in Figure 4 which illustrates the weight loss of such materials. The weight changes of these composites in three temperatures can be seen in Table 4.

Regarding these results, the thermal degradation of all samples started at about 320°C but the weight loss rate of the sample that is reinforced with carbon fabric 9750 is much slower than the others. At 575°C, the weight loss of the sample is 9%. This rates for samples that are reinforced with carbon fabrics 9751 and 9756 are 15% and 19%, respectively.

TABLE 3 Results of Standard Oxyacetylene Flame Tests (Specimen Dimension: $10 \times 10\,Cm^2$ and Oxygen Pressure: 6 Bar)

No.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1	9750	15	255	375.0	68	8.8	1.139	1.7	1.6	13	32	15	33	45	66	11	11	2515
2	9750	15	242.71	373.4	65	8.75	1.138	1.7	17	13.5	30	16	31	40	55	11	11	2470
3	9750	15	222.40	347.5	64	8.75	1.130	1.75	14	13	32	15	33	43	54	6	10	2400
4	9750	15	234.57	350.1	67	8.8	1.129	1.7	15	14.5	31	14	32	46	60	7	7	2450
5	9750	15	248.75	360.5	69	8.75	1.137	1.75	16	12.5	30	14	31	44	58	7	7	2463
6	9750	15	244.82	365.4	67	8.8	1.136	1.7	17	13	30	16	29	47	60	7	8	2465
7	9750	15	216.54	360.9	66	8.8	1.140	1.8	14	13.5	31	15	30	50	65	8	8	2239
8	9750	15	240.18	369.5	65	8.75	1.145	1.8	16	13	32	15	32	42	52	8	8	2260
9	9750	15	238.46	361.3	66	8.8	1.140	1.7	17	14	32	17	25	39	62	8.5	8.5	2500
10	9750	15	230.02	359.4	64	8.8	1.139	1.7	14	14.5	32	14	29	38	59	8.5	9	2500
11	9751	35	164.15	237.9	69	7.6	1.200	1.75	14	14	31	13	20	28	54	10	8.5	2550
12	9751	35	158.30	232.8	68	7.65	1.210	1.7	13	13	32	13	21	30	55	10	10	2450
13	9751	35	157.92	235.7	67	7.7	1.230	1.7	13	13	31	13	21	31	61	10	11	2240
14	9751	35	154.84	234.6	66	7.65	1.240	1.75	16	16	31	12	20	29	65	10.5	11	2450
15	9751	35	165.4	239.7	69	7.7	1.23	1.8	16	16	32	16	28	38	60	10.5	11	2250
16	9751	35	158.30	232.8	68	7.75	1.235	1.7	14	17	32	14	27	40	62	11	11	2480
17	9751	35	156.58	233.7	67	7.7	1.30	1.8	15	17	32	13	21	32	56	11	12	2520
18	9751	35	158.14	239.6	66	7.75	1.25	1.7	17	16	31	13	19	27	53	10	12.5	2500
19	9751	35	156.46	240.7	65	7.6	1.24	1.8	15	14	31	14	26	39	60	10.5	10	2510
20	9751	35	151.67	229.8	66	7.7	1.235	1.7	17	13	32	14	27	41	64	11	10	2500
21	9756	15	219.13	405.8	54	8.9	1.2	1.7	14	14	30	13	17	24	40	10	11	2500
22	9756	15	227.37	429	53	8.8	1.21	1.8	17	11	30	13	17	26	41	10	12	2450
23	9756	15	208.71	386.5	54	8.95	1.28	1.7	15	13	30	15	18	23	43	11	10	2490
24	9756	15	206.69	375.8	55	8.97	1.26	1.75	14	14	31	14	18	24	41	11	11	2380

25	9756	15	201.88	380.9	53	8.8	1.25	1.8	17	12	32	13	18	25	42	10	11	2350
26	9756	15	209.74	388.4	54	8.6	1.24	1.7	16	11	32	14	17	26	39	10.5	10	2400
27	9756	15	209.72	381.3	55	8.7	1.29	1.8	17	13	32	15	19	25	41	10.5	10.5	2515
28	9756	15	214.15	382.4	56	8.8	1.28	1.7	14	12	31	15	18	24	38	10	11	2470
29	9756	15	222.59	390.5	57	8.9	1.27	1.8	15	13	32	16	20	28	42	11	10	2510
30	9756	15	219.35	391.7	56	8.8	1.21	1.75	17	14	31	15	18	23	42	10	11	2500
31	Steel*	—	—	—	—	9.0	—	1.7	18	15	31	7	12	17	23	11	11	2550
32	Steel*	—	—	—	—	9.0	—	1.75	17	15.5	31	7	11	16	22	10	11	2050
33	Steel*	—	—	—	—	9.0	—	1.7	17	15	32	7	11	17	22	10.5	11	2100

A. fabric type
B. the number of layers
C. fabrics weight (gr)
D. total weight (gr)
E. percent of fibers
F. width (mm)
G. specimen density (gr/cm^3)
H. acetylene pressure (bar)
I. oxygen volume rate (L/min)
J. acetylene volume rate (L/min)
K. specimen initial temp. (0°C)
L. time to reach 80°C (s)
M. time to reach 180°C (s)
N. time to reach 380°C (s)
O. burn—through time (s)
P. oxygen temp. (°C)
Q. acetylene temp. (°C)
R. flame temp. (°C)
*Special steel used in solid propellant rockets.

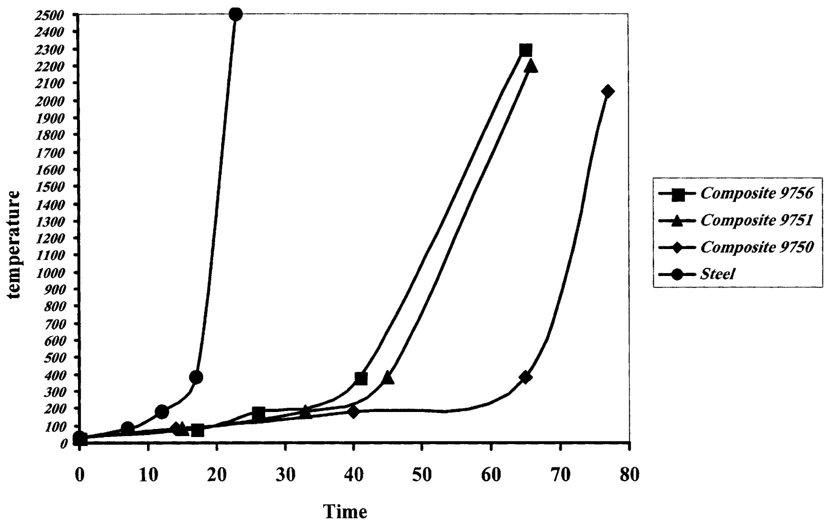

FIGURE 3 Temperature versus time for different samples.

CONCLUSION

Carbon fabric/epoxy-novolac composites belong to the advanced ablative systems, which have the highest temperature performance among all others. In this article ablation behavior of three kinds of carbon fabric composites were compared with each other and with steel.

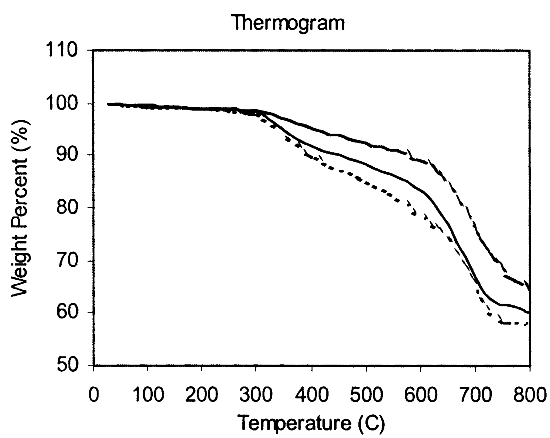

FIGURE 4 TGA curves of composite samples with different carbon fabrics (....... ... C- 9756, _____ C- 9751, _ _ _ C- 9750).

TABLE 4 Weight-Loss of Samples with Different Carbon Fabrics at Three Different Temperatures

Temperature (°C)	1[a]	2[b]	3[c]
325	3	4	2
575	15	19	9
800	40	43	35

Sample: 87.5 parts Nadic Methyl Anhydride (NMA) as hardener per hundred parts of resin.

[a]Composite with carbon fabric 9751; [b]composite with carbon fabric 9756; [c]composite with carbon fabric 9750.

According to the experimental results, carbon fabric 9750/epoxy-novolac composite systems had the best thermal and ablative behavior among the others, even in comparison with the special steel.* According to our results, the compound with 87.5 phr hardener has the highest thermal stability in comparison with the others.

Standard oxyacetylene flame test shows that the samples that are reinforced with carbon fabric 9750 have a longer average burn-through time and better ablation specification in comparison with the others. Thermogravimetric analysis results indicate that the sample reinforced with carbon fabric 9750 is the most thermally stable among the others.

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