Study of Thermal Stability and Ablation Behavior of Carbon/Epoxy-Novolac Composites

M. R. Firouzmanesh, A. Aref Azar

Polymer Engineering Department, Amir Kabir University, Tehran, Iran

Received 17 May 2002; accepted 10 September 2003

ABSTRACT: The use of carbon/epoxy-novolac composites as advanced ablative materials for insulation of exit cone of solid-propellant rocket nozzles are studied. In this article, three types of carbon fabrics are used and their composites are prepared by use of impregnation and hand lay-up methods. To study the thermal stability and ablation behavior, these composites are tested by thermal tests such as thermogravimetric analysis (TGA) and oxyacetylene standard flame tests; the latter test is one of the most important standard tests of ablative materials. The test apparatus is made according to American standard, ASTM-E-285-80, and over 33 polymeric composites and 3 steel specimens were carried out according to its standards. It is found that the composites that are made up of C-9750 fabric (high-strength carbon fabric) in comparison with steel and the other types of carbon fabric specimens have the highest thermal stability and the best ablation behavior. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2455–2461, 2003

Key words: composites; curing of polymers; high-temperature polymers; high-performance polymers

INTRODUCTION

Ablative polymers and polymeric composites serve an important function in aerospace technology. They protect aerodynamic surfaces, propulsion structures, or incident heating rates. This protective function is accomplished by a self-regulating heat and mass transfer process known as ablation. In fact, ablation is a geological term at least 120 years old. It is derived from the suppletive past participle of the Latin "au ferre," which means to remove or carry away.[1–2]

In particular, carbon-reinforced epoxy composites play an important role in the production of high-performance vehicles as well as critical aerospace structures, primary structures of commercial and military aircrafts.[3–5]

According to the concept of effective thermal decomposition, the epoxy-novolac systems belong to the advanced epoxy systems, which are similar or even better in ablative behavior[6] than the conventional phenolic systems.[7] The performance of such systems as ablators was first mentioned by G. J. Fleming[8] in an ablative symposium. Use of the epoxy-novolac as matrix in ablative composites is mentioned as an advanced system and the literature surveys confirm this reality.[9–10] These ablative materials belong to the charring ablators.[11–13] (If elimination of groups along the polymer chain predominates over chain cleavage, then much of the original chain structure will remain as carbon and a char will develop.)

Generally, by increasing the crosslinking density of ablative matrix, the percentage of residual char will be higher and the efficiency of such systems as ablative insulators will increase. In this group of ablative materials, the residual char in high temperatures works as a binder and causes better protection from the substrate degradation.[14–16]

According to the recommendations made in literature surveys, 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 (e.g., carbon/epoxy-novolac composites) 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 composite.[17] Polymeric ablative composite systems are made up of two different phases: continuous phase (matrix) and discontinuous phase (reinforcement).[18–20]

The most important resins as ablators belong to the thermosetting resins (e.g., phenolics, polybenzithiazoles, epoxy-novolacs, polybenzimidazoles, and polyimides),[19] and in the case of reinforcements, carbon, silica, graphite, asbestos, and glass have similar importance in such systems.[20–22]

Correspondence to: M. R. Fizouzmanesh (firouzmanesh@yahoo.com).

Contract grant sponsor: Defense Institute of Science and Technology.

EXPERIMENTAL

Materials

Resin system

The resin system used is a triple system consisting of resin, hardener, and accelerator. Epoxy-novolac resin (DEN 431), which has excellent properties such as processibility as an ablator, was acquired from Dow Chemicals Co (USA).[23] This epoxy resin is a multi-epoxy functional that could produce a higher strength network in comparison with the conventional epoxy resins (bisphenol-A).[24–26] Ease of processibility and high-thermal resistivity will cause such resins to be used as binders in erosion operations.[27–28]

Curing agent

Nadic methyl anhydride (NMA), high-temperature resistant-grade, was supplied by Dow Chemicals Co. and was used as curing agent in hot-cure epoxy-novolac systems, which has the best thermal performance among the other epoxy-curing agents.[29] The high-temperature performance of such cured system depends on the curing agent's abilities. It affects on not only the pot life, but also the required viscosity range of the system. The use of liquid anhydride curing agents (e.g., NMA) is very convenient in such systems because of the decreasing viscosity and also because of the increasing high-temperature performance of the system.[30–31]

Accelerator

Because of the higher thermal stability and performance of a triple component system, a general purpose grade of benzyl dimethyl amine (BDMA; Dow Chemicals Co.) was used as accelerator in this system.

Carbon reinforcements

There are a number of 100% carbon fabric categories. Carbon fiber is manufactured in various sizes, specified by the k size of the fiber. The designation k stands for 1000 filaments, so a 1 k carbon fiber has 1000 filaments; a 3k carbon fiber has 3000 filaments in it, and so on.

Because each filament adds more strength and also weight to a fiber, to acquire more weight or strength, fiber size should just be increased (i.e., a 3k carbon fiber has three times the filament count of a 1k, three times the actual tensile strength, and three times the actual weight per given linear length of fibers).

To get more tensile strength in composite specimens, we used a 3k carbon fiber, supplied by the Multi Products Interprise Co., Switzerland. These carbon fibers are superior strength and the other specifications are as follows.

TETEX HP: C_2, 9750; C_2, 9751; C_2, 9756; Carbon plain weave.
TETEX HP: C_2, 9750; Carbon plain weave: 100 cm wide.
Weight: 240 g/m^2; Thickness: 0.31 mm.
Density: 774.2 kg/m.
TETEX HP: C_2, 9751; Carbon plain weave: 100 cm wide.
Weight: 125 g/m^2; Thickness: 0.16 mm.
TETEX HP: C_2, 9756; Carbon plain weave: 100 cm wide.
Weight: 275 g/m^2; Thickness: 0.32 mm.
Density: 859.4 kg/m^3.

Apparatus

Oxyacetylene standard flame test

To evaluate the thermal behavior and ablation performance[32–33] of the ablative composite insulators, the oxyacetylene standard flame test is carried out according to ASTM-E-285-80. The results of the standard test is useful to show the thermal behavior of ablative materials in solid-propellant rocket motors and nozzles.[34] This test method covers the screening of ablative materials to determine the relative thermal insulation effectiveness when tested as a flat panel in an environment of a steady flow of hot gas provided by an oxyacetylene burner. The apparatus includes oxyacetylene burner, specimen holder, burn-through time detector, and back-face temperature recorders. This test is used for the determination of burn-through time, erosion rate, insulating effectiveness, and insulation index numbers of the ablators.

Figure 1 illustrates the oxyacetylene standard flame test apparatus. Hot combustion gases are directed along the normal to the specimen until burn-through is achieved. The erosion rate of the material is determined by dividing the original thickness by the time to burn-through. The insulation effectiveness is determined from back-face temperature measurements. Insulation index numbers are computed by dividing the times for temperature changes of 80, 180, and 380°C, from the initial ambient temperature, by the original thickness. This test method is more applicable to screening materials for nozzles and motor liners than for aerodynamic heating. The conditions generated by the oxyacetylene heat source in this test method represent only one set of conditions; they do not simulate any specific application. Thus, the test results cannot be used to predict directly the behavior of materials for specific environments nor can they be used for design purposes. However, over a number of years, the test has

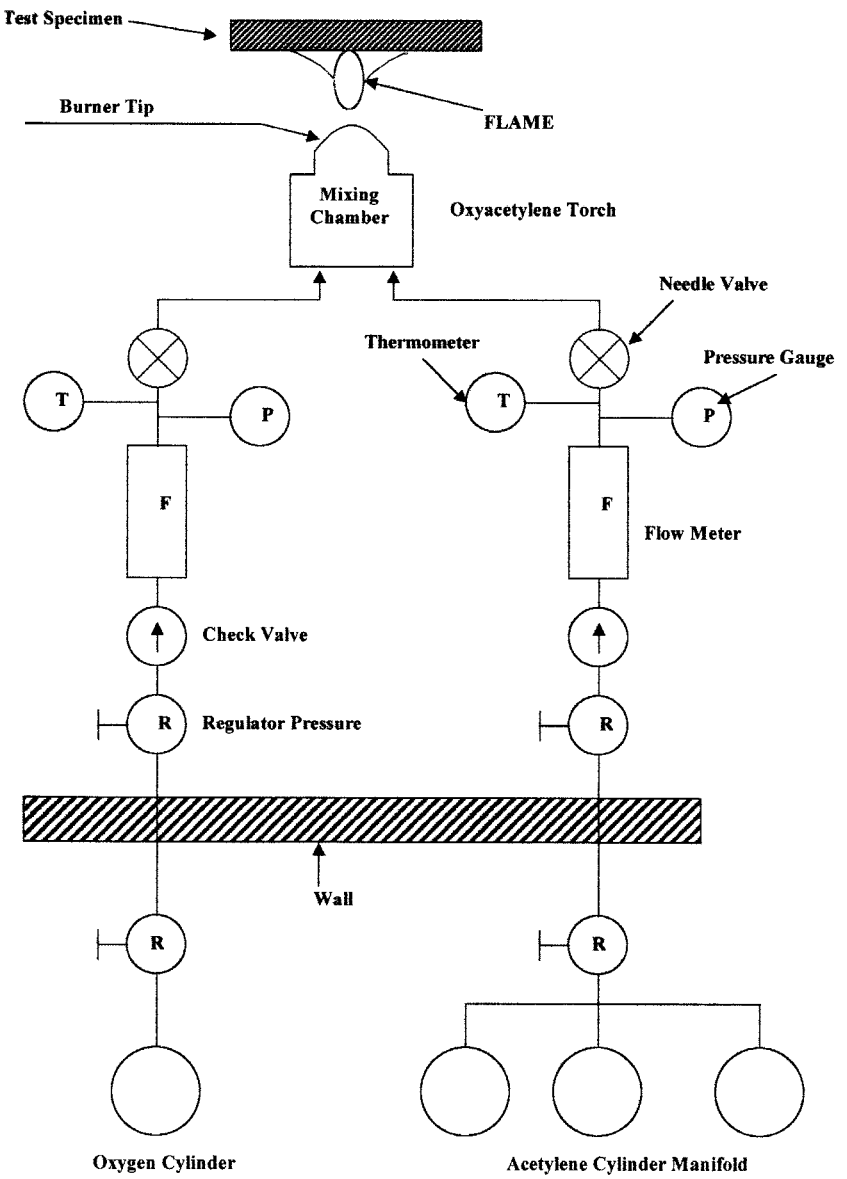

Figure 1 Standard oxyacetylene flame text apparatus.

been useful in determining the relative merit of materials, particularly in weeding out obviously poor materials from more advanced data-generation programs. It has been considered for use as a production quality control test for rocket insulation materials. More information about the measurement techniques is supplied in the following paragraphs.

Pressure regulators. The regulators for the oxygen and the acetylene shall be capable of supplying the flow of gases (pressure gauges graduated 0 to 50 psig for oxygen and 0 to 30 psig for acetylene, both in 1-psig increments).

Flow meters. The flow meters for the acetylene and the oxygen shall be capable of supplying an accurate flow of gases. A variation of ±5% in gas flow rate due to instrumentation inaccuracies shall be permissible.

Flow pressure gauges. Suitable pressure gauges shall be located at the exit (downstream) side of the flow meters to monitor metered gas pressure.

Temperature-measuring devices. Gas temperatures shall be measured with thermocouples, thermistors, or other suitable devices located at the exit side of the flow meters.

Back-face temperature measurement The back-face temperature history shall be measured with a No. 28 AWG-gauge chromel-alumel thermocouple.

Temperature recorder. The thermocouple electromotive force (EMF) shall be recorded as back-face temperature in degrees Celsius, as a function of time during the test.

Calorimeter. The cold wall flux of the hot gas source shall be measured by using a calorimetric device.

Burn-through detector. A device such as a mirror, photocell, or direct visual means shall be used to detect

TABLE I
Composition of samples with different amount of hardener

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

burn-through of the specimen for termination of the test.

Timer. An electric time clock, 0 to 1000 s graduated in 0.1-s increments, shall be used to measure the time to burn-through of the specimen.

As previously mentioned, to evaluate the thermal behavior and high temperature performance of such carbon composites, the oxyacetylene standard flame test is carried out.

By installation of proper thermocouples in specified points in composite specimens and by use of a digital temperature recorder and the other necessary instruments (according to ASTM E-285-80), the changes of thickness versus temperature can be easily shown and plotted.

Thermogravimetric analysis (TGA)

TGA is one of the most favored techniques for rapid evaluation in comparing the thermal stability of various materials. TGA was performed by using a Polymer Laboratories Corp. thermogravimetric analyzer with a temperature increase rate of 20°C/min over the range of room temperature to 800°C in air atmosphere.

Resin system preparation

To study the hardener variation effects on the properties of epoxy-novolac resins and their optimization, samples with different hardener values with compositions mentioned in Table I were prepared. The prepared specimens were first cured for 2 h at 90°C, and then postcuring was carried out continuously for 4 h at 165°C and 16 h at 200°C. Then, thermogravimetric analysis was carried out.

Sample preparation

After resin system preparation, carbon fabrics were cut into, and after weighing, the impregnation process was carried out by hand lay-up method, as previously mentioned. Then, the fabrics were immersed into the matrix system. Different numbers of impregnated fabric layers (based on the carbon fabric) were placed on the metal plate (as substrate) to obtain the necessary thickness (according to the ASTM-E285-80 standard) and the impregnation process was carried out until the necessary resin pick-up took place (30–40 wt %).

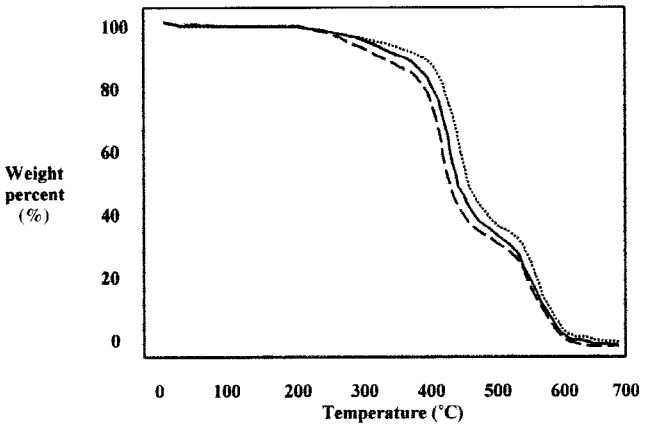

Figure 2 TGA curves of resin systems with different hardener values: - - -, 50 phr; —, 100 phr; · · ·, 87.5 phr.

Then, the curing process was carried out according to the program mentioned before. If no voids or cracks occurred in the cured specimens, they would be reweighed to calculate the resin pick-up and reinforcement percentage (the latter should be in the range of 60–70 wt % carbon fabrics).[9,23] Finally, the sample specimens were cut into the necessary dimensions with a titanium carbide drill to carry out the standard oxyacetylene flame test.

RESULTS AND DISCUSSION

TGA is used to determine the thermal stability of samples. The results are shown in Table I. Figure 2 illustrates the TGA curves of resin systems with different hardener values. Table II shows the changes in weight of the resin systems for different amounts of hardener in different temperatures.

It is observed that all these resin systems are nearly stable up to 275°C. The weight loss of samples started at this temperature, and at 475°C, the weight losses of the samples with the 75-, 87.5-, and 100-phr hardener were 61, 51, and 58%, respectively.

The results indicated that thermal stability of the sample with 87.5-phr hardener is more than the others. The sample with 87.5-phr hardener has the lowest emission and weight loss among the others. It is shown that the weight loss of this resin system com-

TABLE II
Weight Loss of Resin Systems with Different Amounts of Hardener at Three Different Temperatures

	Sample		
Temperature (°C)	1	2	3
275	2.3	2	3.3
380	11	8	14
475	58	51	61

TABLE III
The Results of Standard Oxyacetylene Flame Tests (specimen dimension: 10 × 10 cm^2 and oxygen pressure: 6 bar)

No.	A[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	6.60	1.139	1.7	1.6	13	32	15	33	45	66	11	11	2515
2	9750	15	242.71	373.4	65	6.55	1.138	1.7	17	13.5	30	16	31	40	58	11	11	2470
3	9750	15	222.40	347.5	64	6.55	1.130	1.75	14	13	32	15	33	43	58	6	10	2400
4	9750	15	234.57	350.1	67	6.60	1.129	1.7	15	14.5	31	14	32	46	60	7	7	2450
5	9750	15	248.75	360.5	69	6.55	1.137	1.75	16	12.5	30	14	31	44	58	7	7	2463
6	9750	15	244.82	365.4	67	6.60	1.136	1.7	17	13	30	16	29	47	60	7	8	2465
7	9750	15	216.54	360.9	66	6.60	1.140	1.8	14	13.5	31	15	30	50	65	8	8	2239
8	9750	15	240.18	369.5	65	6.55	1.145	1.8	16	13	32	15	32	42	58	8	8	2260
9	9750	15	238.46	361.3	66	6.60	1.140	1.7	17	14	32	17	25	39	62	8.5	8.5	2500
10	9750	15	230.02	359.4	64	6.60	1.139	1.7	14	14.5	32	14	29	38	59	8.5	9	2500
11	9751	35	164.15	237.9	69	5.40	1.200	1.75	14	14	31	13	20	28	54	10	8.5	2550
12	9751	35	158.30	232.8	68	5.45	1.210	1.7	13	13	32	13	21	30	55	10	10	2450
13	9751	35	157.92	235.7	67	5.50	1.230	1.7	13	13	31	13	21	31	61	10	11	2240
14	9751	35	154.84	234.6	66	5.45	1.240	1.75	16	16	31	12	20	29	62	10.5	11	2450
15	9751	35	165.4	239.7	69	5.50	1.23	1.8	16	16	32	16	28	38	60	10.5	11	2250
16	9751	35	158.30	232.8	68	5.55	1.235	1.7	14	17	32	14	27	40	62	11	11	2480
17	9751	35	156.58	233.7	67	5.50	1.30	1.8	15	17	32	13	21	32	56	11	12	2520
18	9751	35	158.14	239.6	66	5.55	1.25	1.7	17	16	31	13	19	27	53	10	12.5	2500
19	9751	35	156.46	240.7	65	5.40	1.24	1.8	15	14	31	14	26	39	60	10.5	10	2510
20	9751	35	151.67	229.8	66	5.50	1.235	1.7	17	13	32	14	27	41	60	11	10	2500
21	9756	15	219.13	405.8	64	6.70	1.2	1.7	14	14	30	13	17	24	40	10	11	2500
22	9756	15	227.37	429	63	6.60	1.21	1.8	17	11	30	13	17	26	41	10	12	2450
23	9756	15	208.71	386.5	64	6.75	1.28	1.7	15	13	30	15	18	23	43	11	10	2490
24	9756	15	206.69	375.8	65	6.77	1.26	1.75	14	14	31	14	18	24	41	11	11	2380
25	9756	15	201.88	380.9	62	6.60	1.25	1.8	17	12	32	13	18	25	42	10	11	2350
26	9756	15	209.74	388.4	61	6.40	1.24	1.7	16	11	32	14	17	26	39	10.5	10	2400
27	9756	15	209.72	381.3	66	6.50	1.29	1.8	17	13	32	15	19	25	41	10.5	10.5	2515
28	9756	15	214.15	382.4	67	6.60	1.28	1.7	14	12	31	15	18	24	38	10	11	2470
29	9756	15	222.59	390.5	65	6.70	1.27	1.8	15	13	32	16	20	28	42	11	10	2510
30	9756	15	219.35	391.7	66	6.60	1.21	1.75	17	14	31	15	18	23	42	10	11	2500
31	Steel[b]	—	—	—	—	9.0	—	1.7	18	15	31	7	12	17	23	11	11	2550
32	Steel[b]	—	—	—	—	9.0	—	1.75	17	15.5	31	7	11	16	22	10	11	2050
33	Steel[b]	—	—	—	—	9.0	—	1.7	17	15	32	7	11	17	22	10.5	11	2100

[a] Column heads are defined as follows: A, fabric type; B, the number of layers; C, fabrics weight (g); D, total weight (g); E, weight percentage of fibers; F, thickness (mm); G, specimen density (g/cm^3); H, acetylene pressure (bar); I, oxygen volume rate (L/min); J, acetylene volume rate (L/min); K, specimen initial temperature (°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 temperature (°C); Q, acetylene temperature (°C); R, flame temperature (°C).

[b] Special steel in solid propellant rockets.

position is only 2% at 275°C, 8% at 380°C, and 51% at 475°C.

The ablation behavior of about 30 composite specimens and three steels are shown in Table III. As shown in this table, the Carbon 9750 composites have the best ablation behavior among the others. To improve the processibility of the resin system, it was preheated to 40°C, the temperature in which the impregnation of reinforcement could be carried out, for 1 h. Then, other components were added and mixed well. The curing program was obtained from literature on the matrix system and selected process. Impregnation of the fabrics was carried out by hand lay-up method.

To compare the thermal behavior of such materials, the temperature profile versus time for three types of carbon composites and one kind of steel is shown in Figure 3. Figure 3 illustrates temperature profile distribution for different samples. According to the ASTM-E-285-80 standard, the insulating effectiveness in these samples are determined from back-face temperature measurements. As shown in that figure, the back-face temperature of C-9750, C-9751, C-9756, and steel specimens rise to 2050°C after 61, 59, 41, and 23 s, respectively.

The above results and the results obtained from Table IV show that carbon fabric, C-9750 composites are better than the other two fabric composites.

To determine the thermal stability of samples with different carbon fabrics, TGA analysis was carried out. The results are given in Figure 4, which illustrates the weight loss of such materials of the fabrics at three different temperatures. Regarding these results, the thermal degradation of all samples started at about 320°C but the weight loss rate of the sample which is reinforced with carbon fabric 9750 is much slower

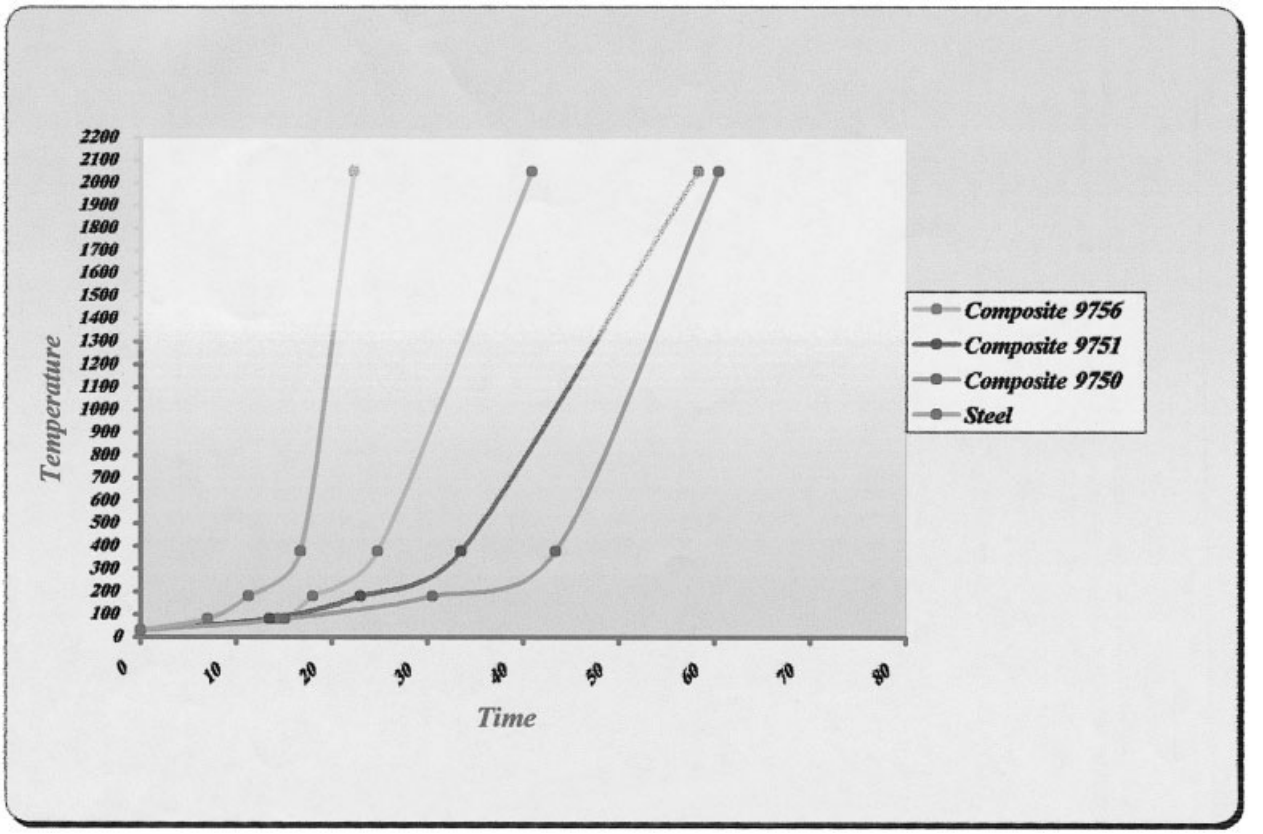

Figure 3 Temperature versus time for different samples.

than the others. At 575°C, the weight loss of this sample is 9%. The rates for samples that are reinforced with carbon fabrics 9751 and 9756 are 15 and 19%, respectively, and at 800°C, the weight loss of C-9750, C-9751, and C-9756 composites are 35, 40, and 43%, respectively.

CONCLUSION

Carbon/epoxy-novolac composites belong to the advanced ablative systems, which have the highest temperature performance among the others. In this article, ablation behavior of three kinds of carbon fabric composites were compared together and with the steel. According to the experimental results, carbon fabric 9750/epoxy-novolac composite systems had the best thermal and ablative behavior among the others, even compared 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. Oxyacetylene standard 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. TGA results indicate that the samples reinforced with carbon fabric 9750 have the highest thermal stability among the others.

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

	Sample[a]		
Temperature (°C)	C-9751	C-9756	C-9750
325	3	4	2
575	15	19	9
800	40	43	35

[a] 87.5 parts nadic methyl anhydride (NMA) as hardener per hundered parts of resin.

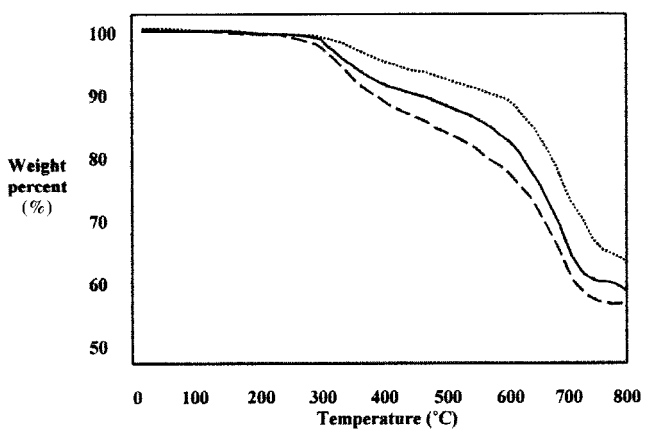

Figure 4 TGA curves of composite samples with different carbon fabric: - - -, 9756; —, 9751; · · ·, 9750.

The authors acknowledge the financial and technical support of Defense Institute of Science and Technology, Department of Composite Materials, Dr. Saberi Moghaddam, and special thanks to the Iran Polymer Institute for cooperation in thermal analysis tests, Dr. H. Mirzadeh, and the thermal analysis laboratory in the Polymer Engineering Department of Amir Kabir University of Tehran.

References

1. Meyers, H.; Harmon, D. S.C.I. Monograph No.13; Macmillan: New York, 1961.
2. Schmidt, D. SAMPE J 1966, 2, 10.
3. Scott, E. P.; Beck, J. V. J Comp Mater 1992, 26, 1.
4. Sohi, J. D. NASA Technical Report; 1971, p. 25.
5. Hsu, M. T. S. NASA Technical Report; 1982.
6. Mathis, J. R.; Laramee, R. C. NASA Technical Report; 1970.
7. Clayton, W. A. Boeing Company Aerospace Systems Division, Technical Report; 1970.
8. Fleming, G. J. The Effect of Epoxy Resin and Caring Agent Structure on Ablative Properties; U.S. Naval Ordnance Laboratory; White Oak, Silver Spring, MD, 1966.
9. D'Alelio, G. F.; Parker, J. A. Ablative Plastics; Marcel Dekker: New York, 1971.
10. Mohanty, D. K.; Kilic, S.; McGrath, J. E. Epoxy Novolac Thermosetting Resins, Formulation, Network Behavior and Thermal Studies; Virginia Polytechnic Institute and State University, Blacksburg, 1978.
11. Cline, P. B.; Schultz, F. E. NASA Technical Report; 1967.
12. Scott, E. P. Ph.D. Dissertation, Michigan State Univ., East Lansing, MI, 1989.
13. Schultz, W. NASA Technical Report; 1971.
14. Matzkanin, G. A.; Hansen, G. P. Heat Damage in Graphite Epoxy Composites: Degradation, Measurement and Detection, Non Destructive Test. Net, 1999, Vol. 3, A State of Art Report; NTIAC.
15. Matzkanin, A. Nondestructive Characterization of Heat Damage in Graphite/Epoxy Composites, Non Destructive Test. Net, 1999, A State of Art Report; TX 78746.
16. Pavli, A. J. NASA Technical Report; 1969.
17. Sigur, W. A. 17th National SAMPE Technical Conference; Martin Marietta, Denver: Aerospace Michoud Division, New Orleans, LA, 1985.
18. Mccomas, T. D. NASA Technical Report; 1968.
19. Laius, L. A., Dergacheva, E. N., Zhukova, T. J. Role of the Physical State of Polyimides in the Process of their Thermal Degradation, In Polyimides: Materials, Chemistry and Characterization; Feger, C. ed.; Elsevier Science: Amsterdam, Netherlands, 1989.
20. Lubin, G. Handbook of Composite Materials; Van Nostrand: New York, 1969.
21. Schwartz, M. Handbook of Composite Materials Processing; Wiley, New York, 1967.
22. Mallick, P. K. Fiber Reinforced Composites; Marcel Dekker: New York, 1988.
23. Dow Chemical Epoxy Novolac Resins, Tech Catalogue.
24. Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1967.
25. Potter, W. G. Uses of Epoxy Resins; Butterworth: London, 1975.
26. Clayton, A. Epoxy Resins Chemistry and Technology; Marcel Dekker: New York, 1988.
27. Bank, L. C.; Gentry, T. R; Barkatt, A. J Reinforced Plast Composites 1995, 14, 559.
28. Turi, E. A.; Prime, R. B. Thermal Characterization of Polymeric Materials, 2nd ed.; Academic Press: New York, 1997.
29. Vyazovkin, S.; Sbirrazuoli, N. J. Macromol Rapid Commun 1999, 20, 387.
30. Woo, E. M.; Seferis, J. C. J Appl Polym Sci 1990, 40, 1237.
31. Vyazovkin, S.; Sbirrazzuoli, N. J Macromol Chem Phys 1999, 200, 2294.
32. ASTM-E-458. Annu Book ASTM Stand 1972, Test Method For Heat of Ablation, 303.
33. ASTM-E-377. Annu Book ASTM Stand 1968, Test For Internal Temperature Measurement in Ablative Materials, 274.
34. ASTM-E-285. Annu Book ASTM Stand 1980, Oxyacetylene Ablation Testing of Thermal Insulation Materials, 212.