High-Temperature Degradation of Reinforced Phenolic Insulator

İLHAMİ PEKTAŞ

Tübitak, Atatürk Bulvari No:221, Kavaklidere, Ankara, Turkey

ABSTRACT: The thermal degradation of graphite and glass-reinforced phenolic insulators have been studied at high temperature by using thermogravimetric (TGA) and differential scanning calorimetric analyses. TGA analysis was carried out in a stream of pure nitrogen over temperature range ambient to 900°C and DSC analysis to 500°C. A heating rate of 10°C/min was used for the determination of degradation temperature and heating rates of 5, 10, 20, 30, and 50°C/min were used for the estimation of degradation temperature (T_{max}) of the insulator at high-temperature service and calculation of activation. Activation energy of phenolic resin was calculated as 356 kJ mol^{-1} using the Ozawa method. T_{max} was determined as 661°C for 20% conversion. The specific heat capacity of graphite phenolic was found as 970 J kg^{-1} K^{-1} at 100°C. The half-life of the phenolic resin was determined to be approximately 116.2 s at 3500°C. The thermal analysis has been conducted using transient heat conduction and the in-depth temperature distribution was evaluated along the rocket nozzle. The better insulator thickness, including a safety factor for graphite and E-glass-reinforced phenolics were calculated as 3 and 2 mm, respectively. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1337–1342, 1998

Key words: degradation; graphite-reinforced phenolic; glass-reinforced phenolic

INTRODUCTION

The technologies used in the design and development of solid rocket nozzles have been substantially improved over the last decade. The advances in these technologies have made it possible to develop nozzles capable of surviving more severe operating environments generated by current high-performance motors. The evolving technologies are based primarily on the advances in fiber-reinforced phenolics. Carbon, graphite, silica cloth phenolics, and carbon–carbon are generally used in the nozzle design. With the advent of space flight and ballistic missiles, phenolic resins have been used successfully in the ablative heat shields that protect the vehicle. Since thermal degradation of the polymeric material is part of the process ablation, a knowledge of the degradation behavior of the resin over a wide range of the temperatures will be a valuable aid in the overall understanding of the complex processes that occur during ablation. In a number of previous reports,[1–4] the oxidation chemistry and thermal degradation of phenol–formaldehyde polycondensates have been described in some detail. In the present investigation, graphite, E-glass, and Kevlar fibers were reinforced to the base phenolic resin with 70/30 fiber-to-resin weight ratio in all cases. The degradation temperature for the new insulators has been obtained by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The lifetime prediction and conversion percentage of phenolic for rocket operating temperatures have been determined. Thermal analysis has been conducted using transient heat conduction, and the in-depth temperature distribution was evaluated along the nozzle.

Table I   Thermogravimetric Analysis of Reinforced Phenolic Resin from Ambient to 900°C

Material	Temp Range I (25–250°C)		Temp Range II (450–900°C)		Residue (%)	Residue Element
	T_d (°C)	Wt Loss (%)	T_{max} (°C)	Wt Loss (%)		
Phenolic-resin	167	30.46	544	21.16	45.65	Carbon
Cured	249	2.85	544	21.78	69.45	
Graphite-reinforced	169	8.55	552	17.22	71.22	Carbon
Cured	237	1.03	553	21.98	72.29	
E-glass-reinforced	168	4.59	567	11.26	81.89	Carbon
Cured	236	0.25	556	10.43	87.93	Silicon
Kevlar-reinforced	174	15.46	609	30.10	51.32	
Cured	228	3.81	602	19.57	74.15	Carbon

T_d (°C): decomposition temperature. T_{max} (°C): maximum decomposition temperature.

EXPERIMENTAL

Materials

MIL (Grade A) phenolic resin was used as a base material. Hercules graphite, E-type glass, and DuPont Kevlar fibers were added as reinforcings to the base material.

Preparation of Samples

Fiber-reinforced phenolic resin were prepared by winding of graphite, E-glass, and Kevlar fibers as a felt, onto a 300 × 300 mm frame. Fiber and resin ratio was adjusted to 70/30 wt %, respectively. After molding and pressing, the samples were B-staged at 73°C for 3 h, then cured at 171 ± 3°C.

Apparatus and Procedure

TGA and DSC were carried out using DuPont 1090 and 910 instruments, respectively. Thermal curves relating to nitrogen atmospheres were recorded over the temperature range ambient to 900°C for TGA and ambient to 500°C for DSC analysis. Heating rates were 5, 10, 20, 30, and
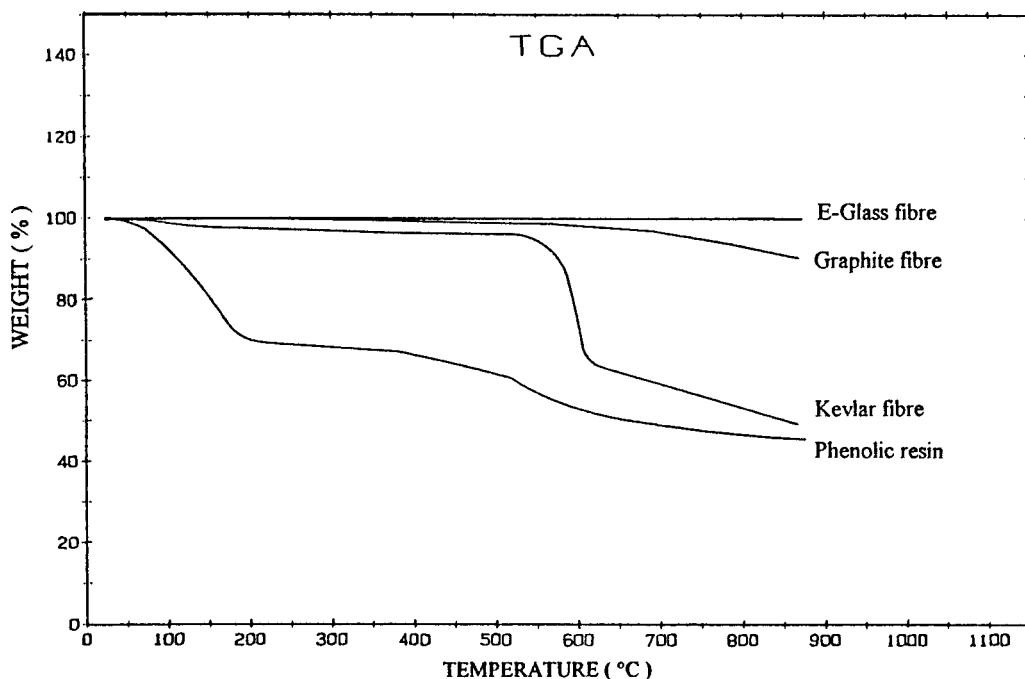

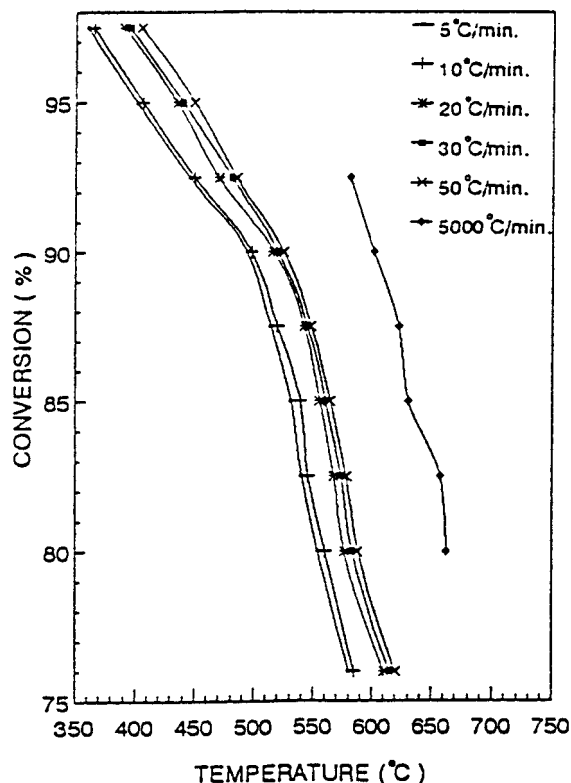**Figure 1**   Thermal behavior of each component in reinforced phenolics.

Figure 2 Conversion curves of phenolic resin at different heating rates.

50°C/min. Nitrogen gas flow was maintained constant at 50 mL min^{-1}, and sample masses were about 15 mg. Activation energy was calculated from TG and DTG curves by using the Ozawa method.[5] Since the insulator is exposed to high heat flux, thermal conductivity, thermal diffusivity, max degradation temperature, and ablative resistance are important parameters for predicting the insulator performance. Thermal conductivity of composites was measured in a Kem-therm QTM-D3 model apparatus. Specific heat capacity (C_p) and degradation enthalpy (ΔH) of the

samples were calculated from the derived DSC data.

Thermal diffusivity (α) was calculated from

$$\alpha = k/\rho \cdot C_p \qquad (1)$$

where k is the thermal conductivity, ρ is the density, and C_p is the specific heat of the samples.[6] The half-life of the insulator was predicted from the kinetic parameters from

$$dw/dt = k(w_0 - w)^n \qquad (2)$$

where dw/dt is rate of degradation, k is the rate constant, w_0 is the initial weight, w is the decomposed amount at time t, and n is the order of reaction.[7]

Thermal analysis and the in-depth temperature distribution data were interpreted using the results of transient heat conduction analysis. Heat transfer analysis of nozzle was done using a computer program.

RESULT AND DISCUSSION

Thermogravimetric Analysis of Phenolic Base Insulator

The thermogravimetric method of polymer analysis provides an accurate record of the chance in sample weight as a function of linearly increasing temperature. TG data were analyzed for two temperature regions given in Table I.

Thermal behavior of each component and composites have been analyzed from ambient to 900°C in this study. The degradation of the raw phenolic resin commences at 544°C with a 21.8% mass loss. Graphite and E-glass fibers show no mass loss up to 900°C. However, Kevlar fiber gives a 47% mass loss at 596.5°C (Fig. 1).

Table II   Specific Heat Capacity and Thermal Diffusivity of Reinforced Phenolics

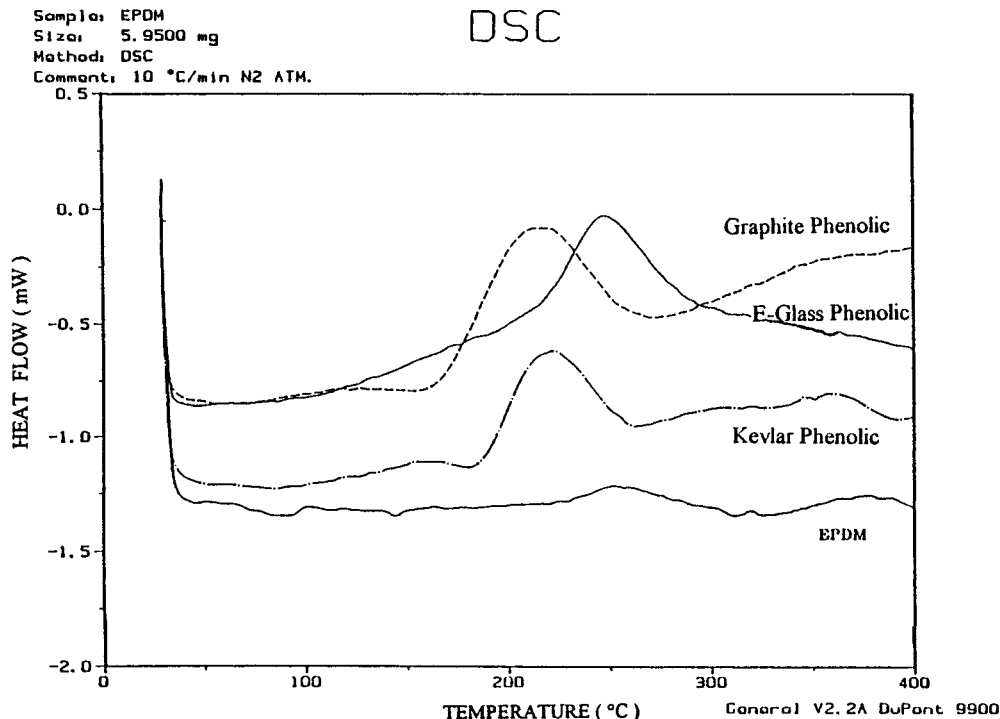| Material	Specific Heat Capacity of Reinforced Phenolic Materials/Cp (J kg^{-1} K^{-1})			Thermal Diffusivity α (*E-4; cm^2 s^{-1}; 100°C)
	25°C	200°C	300°C	
Phenolic resin	1712	2390	2495	7.6
Kevlar phenolic	1115	1142	1120	18.6
E-glass phenolic	986	970	1110	8.1
Graphite phenolic	970	990	600	27.0

Figure 3   DSC analysis of reinforced phenolics.

For the composite insulators, graphite, E-glass, and Kevlar phenolics, the major degradation temperatures and the percentance of mass loss are at 553.2, 555.6, and 602.3°C and 21.98, 10.43, and 19.57%, respectively (Table I). A range of heating rates were applied in TGA, and it is apparent that the max degradation temperature (T_{max}) is dependent on the heating rate. High heating rates increase the degradation temperature. The dependence of T_{max} on the heating rate can be represented for phenolic resin at 20% conversion as

$$\text{Log } H = -22.14 + 2.77 * 10^{-2} T_{max}$$

where H is the heating rate, and T_{max} is the maximum decomposition temperature, assuming the heating rate for the insulator used in a rocket

operating environment is between 5000 and 6000°/min^{-1} and the T_{max} calculated using this equation for phenolic resin is found as 661°C. Conversion curves of phenolic resin with 5, 10, 20, 30, 50, and 5000°/min^{-1} heating rates are shown in Figure 2.

The activation energy of phenolic resin was calculated from TG data using the Ozawa method[5] as 356 kJ mol^{-1}.

DSC Analysis

Endothermic and exothermic degradation reaction peaks relating to degradation in nitrogen, specific heat capacity (C_p), and major degradation enthalpy (ΔH) values were determined. Endothermic peaks are noted at 164, 230, and 370°C and exothermic peaks are noted at 180°C. The degradation enthalpy (ΔH) is 15 J g^{-1} at 207°C and 301 J g^{-1} at 540°C for the phenolic resin. Specific heat capacity (C_p) and thermal diffusivity (α) values of the phenolic composites at different temperatures were calculated using ASTM E 968-87 and are listed in Table II.

The DSC thermographs of graphite, E-glass, and Kevlar phenolics are given in Figure 3.

Lifetime Prediction

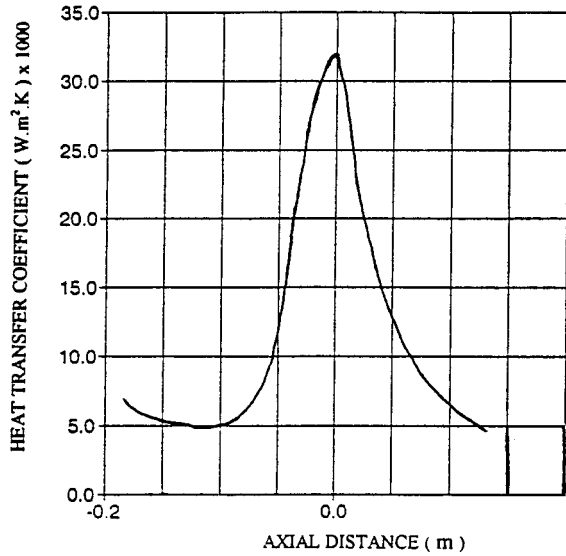On combustion of propellant at the time of rocket flight, large amounts of low molecular gas prod-

Table III   Half-Life of the Phenolics as a Function of Temperature

Temperature (°C)	Phenolic Resin $t_{1/2}$ (s)
1000	118.8
1500	117.7
2000	117.1
2500	116.7
3000	116.5
3500	116.2

Figure 4 H_D values along the nozzle.

ucts are produced, generating very high temperature and pressure. So, lifetime prediction is important in order to know insulator stability during operation. The lifetime of the insulator is the time required to complete the decomposition of the insulator when the propellant burns between 2500–4000 K. The lifetime is generally expressed as the half-life of material to be degraded.[7] The half-life of the insulator was predicted from the following equation:

$$dw/dt = k(w_0 - w)^n \qquad (3)$$

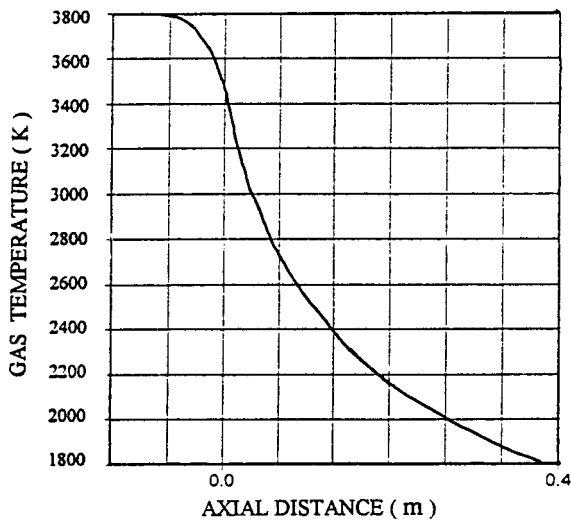where dw/dt is the rate of degradation, k is the

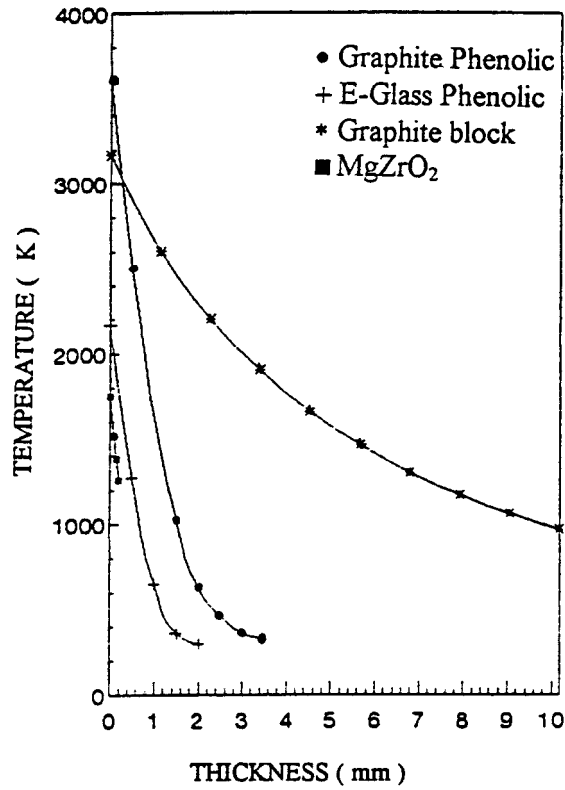**Figure 5** T_D values along the nozzle.

Figure 6   The in-depth temperature distribution of nozzle materials.

rate constant, w_0 is the initial weight, w is the decomposed amount at time t, and n is the order of reaction. The half-life of phenolic resin can be given as follows:

$$t_{1/2} = \ln 2/k, \quad \text{for } n = 1, \qquad (4)$$

and

$$t_{1/2} = (2^{n-1} - 1)/k(n - 1)w^{n-1}, \quad \text{for } n \neq 1 \quad (5)$$

The rate constant is calculated at T_{max} using eq. (3) and the half-life is calculated by applying eq. (4) in the temperature range of 1000–4000°C. The results are given in Table III.

Thermal Analysis

Thermal analysis was conducted along the nozzle, and the in-depth temperature distribution was evaluated over 1 minute. During this time interval, it was assumed that there was no heat loss
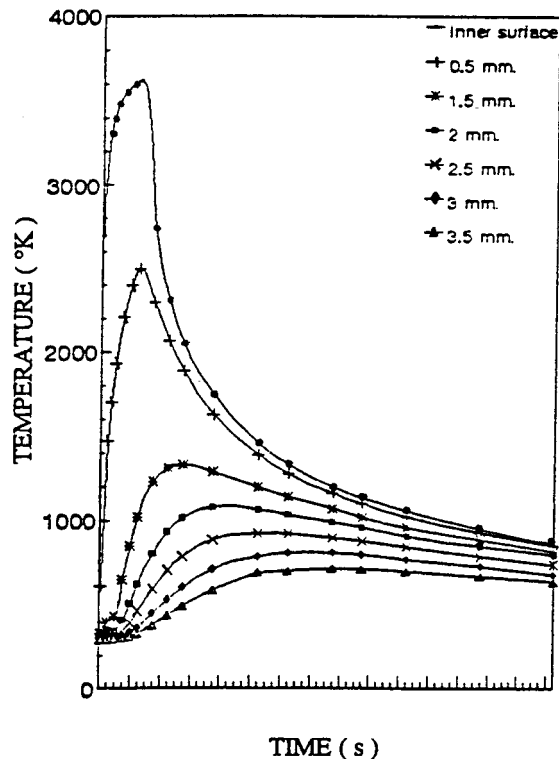
Figure 7 The in-depth temperature distribution of graphite phenolic.

to the surroundings, the transient heat conduction was taking place, and heat radiation was neglected at the nozzle. The thermal analysis consists of a number of steps. The process begins with the free stream calculations. These calculations use the propellant formulation, heats of formation, and the motor chamber conditions and produce the velocity, pressure, and temperature profiles along the nozzle.[8,9] All of the computer calculations develop information that serve as input data to the in-depth temperature predictions. Graphite and E-glass phenolic were applied to the entrance and the exit cone of the nozzle. The temperature of the combustion gases was determined as 3750 K corresponding to the ideal gas formulation. The nozzle was assumed to expose to the combustion gases. The 8-node finite element method was used for thermal analysis along the nozzle model geometry. The convective heat transfer coefficient of the hot gases at throat, h_D, was found as 31.7 kw m^{-2} K^{-1}, including the safety factor, and the nozzle throat temperature, T_D, was determined as 3450 K. The variation of h_D and T_D along the nozzle are given is given in Figures 4 and 5.

Graphite phenolic, graphite insert and E-type glass phenolic were applied to the entrance, throat and the exit cone of the nozzle. The in-depth temperature distribution at the nozzle materials is given in Figures 6 and 7.

CONCLUSION

High-temperature degradation of graphite and E-type glass-reinforced phenolic materials (70/30 wt %) have been investigated, and thermal properties have been estimated. The specific heat capacity of graphite phenolic was found as 970 J kg^{-1} K^{-1} at 100°C. Activation energy of phenolic resin was calculated from the TG data using the Ozawa method as 356 kJ mol^{-1}, and the maximum degradation temperature for 20% conversion was found as 661°C, assuming the heating rate to be between 5000 and 6000°/min^{-1}. The half-life of phenolic resin was determined about 116.2 s at 3500°C. The convective heat transfer coefficient of the hot gases, h_D, was found as 31.7 kW m^{-2} K^{-1} at the nozzle throat, and the in-depth temperature distribution was evaluated along the nozzle. Hence, these data indicate that graphite phenolic with 3 mm thickness and the E-glass phenolic with 2 mm thickness are in the reliable and safe side during the operation of the rocket motor.

REFERENCES

1. M. W. Jackson and T. R. Conley, *J. Appl. Polym. Sci.,* **8,** 2163 (1964).
2. L. H. Friedman, *J. Polym. Sci., Part C,* **6,** 183 (1964).
3. G. P. Shulman and H. W. Lochte, *J. Appl. Polym. Sci.,* **10,** 619 (1966).
4. T. R. Conley and F. J. Bieron, *J. Appl. Polym. Sci.,* **7,** 103 (1963).
5. T. Ozawa, *Bull. Chem. Soc. Jpn.,* **38,** 1881 (1965).
6. S. A. Deuri, A. K. Bhowmick, R. Ghosh, B. John, T. Sriram, and K. S. De, *Polym. Degrad. Stab.,* **21,** 21 (1988).
7. S. A. Deuri and K. Bhowmick, *J. Therm. Anal.,* **32,** 755 (1987).
8. R. J. Howell, K. M. Strite, and H. Renkel, *AIAA J.,* **3,** 669 (1965).
9. S. Gordon and B. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions,* NASA, Washington, DC, 1971.