Journal of Thermal Analysis, Vol. 46 (1996) 163-176

A THERMAL ANALYSIS INVESTIGATION OF NEW INSULATOR COMPOSITIONS BASED ON EPDM AND PHENOLIC RESIN

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(Received December 10, 1994; in revised form May 20, 1995)

Abstract

New rocket insulator compositions have been studied by adding various types and amounts of fillers, such as graphite and asbestos fibres, Al_2O_3, $MgZrO_2$, Cr_2O_3, SiC, carbon powders and phenolic resin to the base EPDM gum and graphite, kevlar, *E* type glass fibres to the base phenolic resin in order to improve thermal and ablative efficiency. The degradation of the insulators has been investigated by thermogravimetry (TG) analysis to 900°C and DSC analysis to 500°C. Conversion curves of the insulators at different heating rates were performed and maximum degradation temperatures were found as 646 and 661°C for EPDM P and phenolic resin, respectively. The kinetic parameters for degradation have been evaluated and the lifetime of the rocket insulators has been estimated. Thermal analysis has been conducted on the insulators and the in-depth temperature distribution was evaluated in order to find optimum insulation thickness.

Keywords: ethylene propylenediene rubber, phenolic resins, rocket motor insulators

Introduction

Lighter weight structural materials and more efficient propellants are the major factors which are expected to improve the performance of solid propellant rocket motors. The combined use of these materials in rocket systems requires more efficient motor insulation. The light weight metallic and plastic rocket motor materials are generally associated with a high heat flux. The super energetic propellants burn for short times at very high temperatures and produce high internal pressure and erosive combustion products. All these factors indicate the need for improved insulation materials and application techniques. Motor insulators must have heat and erosion resistance in order to withstand the severe rocket operating environments.

Ethylene propylenediene rubber (EPDM) and fibre reinforced phenolic resins, which have excellent thermal resistance and ablation properties, can be used as a rocket insulation material. A variety of fillers and reinforcing materials, such as carbon, silica, asbestos fibres and high heat stable inorganic pow-

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ders, can be added to give a variety of properties to the insulator. The selection of these fillers is based on such properties as heat stability, ability to form char, heat capacity and ablation resistance. The curing characteristics, physical properties and aging behaviour of EPDM gum, filled vulcanizates and phenol-formaldehyde polycondensates have been investigated previously [1–4]. Degradation kinetics [4–7] and ablative properties of the insulators have also been studied [8–10].

In the present investigation, 5, 10, 20, 30 and 40% graphite, asbestos fibres, Al_2O_3, $MgZrO_2$, Cr_2O_3, SiC, carbon powders and phenolic resin were added to base EPDM gum, and graphite, kevlar, *E*-glass fibres were reinforced to the base phenolic resin by 70/30 fibre-resin weight ratio in all cases. The high temperature degradation of the new insulators has been followed by TG and DSC. The lifetime prediction and conversion % of the insulators for rocket operating temperatures have been determined. In addition, thermal analysis has been conducted using 'Finite Element' method and the in-depth temperature distribution was evaluated.

Experimental

Materials

Montedison, Dutrel-Ter 045/E type of EPDM and MIL (Grade A) phenolic resin were used as base materials. Hercules graphite, DuPont kevlar fibres, laboratory grade Al_2O_3, $MgZrO_2$, Cr_2O_3, SiC and commercial grade asbestos fibres were added as fillers and reinforcings to the base material.

Preparation of samples

The composition of EPDM A was used as base for all EPDM mixes (Table 1) and formulation of the mixes is given in Table 2. EPDM mixes were pre-

Table 1 Composition of EPDM A compound

EPDM	100
ZnO	5
Stearic acid	2
ISAF carbon black	40
Wax	4
Aromatic oil	5
4010 Na	2
Kaoline	10
MBT	1
CZ	2
Sulfur (S)	1

Table 2 Formulations of EPDM mixes

Material No.	Graphite fibre	Asbestos fibre	Al_2O_3	Magnez. zirkonat	Cr_2O_3	SiC	Phenolic resin
A (base)	–	–	–	–	–	–	–
B_1	–	–	5	–	–	–	–
B_2	–	–	10	–	–	–	–
B_3	–	–	20	–	–	–	–
B_4	–	–	30	–	–	–	–
C_1	–	–	–	5	–	–	–
C_2	–	–	–	10	–	–	–
C_3	–	–	–	20	–	–	–
C_4	–	–	–	30	–	–	–
D_1	–	–	–	–	5	–	–
D_2	–	–	–	–	10	–	–
D_3	–	–	–	–	20	–	–
D_4	–	–	–	–	30	–	–
E_1	–	–	–	–	–	5	–
E_2	–	–	–	–	–	10	–
E_3	–	–	–	–	–	20	–
E_4	–	–	–	–	–	30	–
F_1	–	–	–	–	–	–	5
F_2	–	–	–	–	–	–	10
G_1	5	–	–	–	–	–	–
G_2	10	–	–	–	–	–	–
H_1	–	5	–	–	–	–	–
H_2	–	10	–	–	–	–	–
H_3	–	20	–	–	–	–	–
I	5	–	15	–	10	–	–
J	5	10	5	5	5	–	–
K	5	5	–	–	–	–	–
L	5	–	–	–	5	–	5
M	5	–	–	–	–	–	5
N	5	5	–	–	–	–	5
P	5	5	10	–	–	–	5

pared on a laboratory mill and vulcanization was carried out at 150°C in an electrically heated press. Curing characteristics were examined with Rheometer 100-S. Fibre reinforced phenolic resins were prepared by winding of graphite, kevlar and *E*-glass fibres as a felt, on to 300×300 mm frame. Fibre and resin ratio was adjusted to 70/30 by weight percent, respectively. After molding and pressing of the composite, the curing procedure was carried out 171±3°C in a laboratory oven.

Apparatus and procedure

Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) analysis 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 TG analysis and ambient to 500°C for DSC analysis. 10 $\text{deg}\cdot\text{min}^{-1}$ heating rate was used for the determination of degradation temperature, and 5, 10, 20, 30 and 50 $\text{deg}\cdot\text{min}^{-1}$ heating rates were used for estimation of insulator degradation temperature in rocket motor operating environments and calculation of activation energies. Nitrogen gas flow was maintained constant at 50 $\text{ml}\cdot\text{min}^{-1}$ and sample masses were ≈15 mg. Activation energies were calculated from TG and DTG curves by using the Ozawa and Freeman-Carrol methods [11, 12]. Determination of tensile strength and elongation at break point were measured in a Testometric Micro 350 test machine according to ASTM D412-75. Since the insulator is exposed to high heat flux, thermal conductivity, thermal diffusivity, maximum degradation temperature and ablative resistance are important parameters for predicting the insulator performance. Thermal conductivity of the composites was measured in a Kemtherm QTM-D3 model test machine. Specific heat capacity (C_p) and degradation enthalpy (ΔH) of the selected samples were calculated from the derived DSC data. Thermal diffusivity (α) was calculated from:

$$\alpha = \frac{k}{\rho \cdot C_p} \tag{1}$$

where k is the thermal conductivity, ρ is the density and C_p is the specific heat capacity of the samples [8]. The half-life of the insulator was predicted from the kinetic parameters from:

$$\frac{\mathrm{d}w}{\mathrm{d}t} = k(w_o - w)^n \tag{2}$$

where $\mathrm{d}w/\mathrm{d}t$ is rate of degradation, k is the rate constant, w_o is the initial weight, w is the decomposed amount at time t and n is the order of reaction [5]. Thermal analysis data were interpreted using the Marc ‘Finite element’ method.

Results and discussion

Thermogravimetric analysis

TG data were analyzed for three temperature regions from the overall data given in Table 3. The individual fillers were also evaluated from the corre-

Table 3 TG data for EPDM compounds

Material No.	T_{max} /	Max. degrad./ %	Residue/ %	Nature of residue
Raw EPDM	450	92.2	0.84	Carbonaceous product
A (base)	477	58.4	30.0	C, ZnO, Al_2O_3, SiO_2
B_1	486	58.3	34.7	Same
B_2	490	53.4	39.1	Same
B_3	480	50.6	39.2	Same
B_4	487	47.4	44.2	Same
C_1	477	55.0	33.2	C, ZnO, Al_2O_3, SiO_2, ZrO_2
C_2	480	54.0	37.8	Same
C_3	479	49.8	39.2	Same
C_4	485	47.6	45.0	Same
D_1	491	58.5	34.7	C, ZnO, Al_2O_3, SiO_2, Cr_2O_3
D_2	480	51.6	35.5	Same
D_4	489	47.6	45.3	Same
E_1	486	54.1	34.2	C, ZnO, Al_2O_3, SiO_2, SiC
E_2	479	53.7	36.4	Same
E_3	480	50.5	39.7	Same
G_1	488	57.9	32.9	C, ZnO, Al_2O_3, SiO_2
G_2	485	51.7	40.0	Same
H_1	492	59.1	32.9	C, ZnO, Al_2O_3, SiO_2, MgO
H_2	490	57.2	35.6	Same
H_3	490	51.4	40.1	Same
I	485	44.5	46.6	C, ZnO, Al_2O_3, SiO_2, Cr_2O_3
J	481	45.3	46.9	Same plus ZrO_2, Cr_2O_3
K	485	57.8	32.2	C, ZnO, Al_2O_3, SiO_2, MgO
L	484	55.1	33.2	C, ZnO, Al_2O_3, SiO_2, Cr_2O_3
M	489	57.5	31.8	C, ZnO, Al_2O_3, SiO_2
N	483	56.7	33.8	C, ZnO, Al_2O_3, SiO_2, MgO
P	485	55.1	35.6	C, ZnO, Al_2O_3, SiO_2, MgO
Phenol resin	544	21.8	45.7	Carbonaceous product
Grap. phenolic	553	22.0	72.3	Same
E glass phenolic	556	10.5	87.9	C, SiO2, CaO
Kevlar phenolic	602	19.6	74.1	Carbonaceous product

sponding data. The presence of stearic acid, aromatic oil, wax and sulfur product cause in initial mass loss between 180 and 250°C. Graphite and *E*-glass fibres, Al_2O_3, $MgZrO_2$, Cr_2O_3, SiC show no mass loss up to 900°C. Only about

10% change in mass is observed in asbestos due to loss of moisture and 47% mass loss at 596.5°C is observed for kevlar fibre. The degradation of the raw EPDM commences at 286°C and major decomposition occurs between 407 and 460°C (T_{max}, 450°C) with 0.835% residue. Decomposition of EPDM A and P compounds commences over the range 200–250°C and the main decomposition is noted at 477 and 484.5°C, respectively. The difference in maximum degradation temperature is 27°C for raw EPDM and EPDM A and 8°C for EPDM A and EPDM P compounds. Comparison of the TG data in Table 3 shows that the maximum degradation temperatures apply to EPDM H series (contains 5, 10, 20% asbestos), B_2(10% Al_2O_3), D_1(5% Cr_2O_3), G_1(5% Graphite fibre).

For fibre reinforced phenolic resins – Graphite, *E*-glass and kevlar phenolics, the major degradation temperatures and % mass loss are at 553.2, 555.6, 602.3°C and 21.98%, 10,43%, 19.57%, respectively (Table 3). A range of heating rates were applied in TG analysis for both EPDM and phenolic resin and it is apparent that the maximum degradation temperature (T_{max}) is depend-

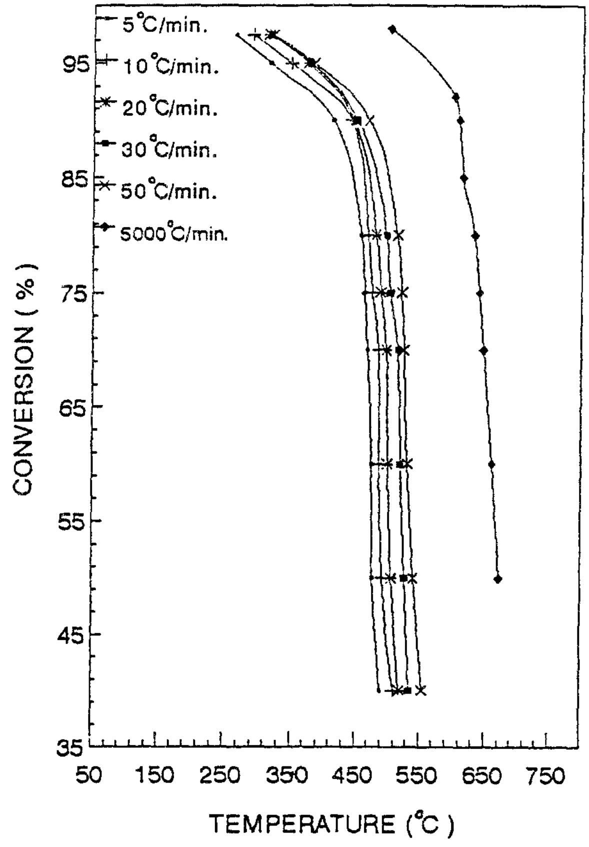


Fig. 1 EPDM P compound at different heating rates

ent on heating rate. High heating rates increase the degradation temperature. The dependence of T_{max} on heating rate can be represented for EPDM P at 30% conversion as:

$$\log H = -11.0 + 1.6\cdot 10^{-2}\cdot T_{max} \tag{3}$$

for phenolic resin at 20% conversion as:

$$\log H = -22.14 + 2.77\cdot 10^{-2}\cdot T_{max} \tag{4}$$

where H is heating rate. By assuming the heating rate for the insulator used in a rocket operating environment is between 5000 and 6000 deg·min^{-1} [8], T_{max} calculated using Eq. (3) for EPDM P compound and Eq. (4) for phenolic resin are found as 646 and 661°C, respectively. Conversion curves of EPDM P and phenolic resin with 5, 10, 20, 30, 50 and 5000 deg·min^{-1} heating rates are shown in Figs 1 and 2. However, addition of fillers and reinforcing materials

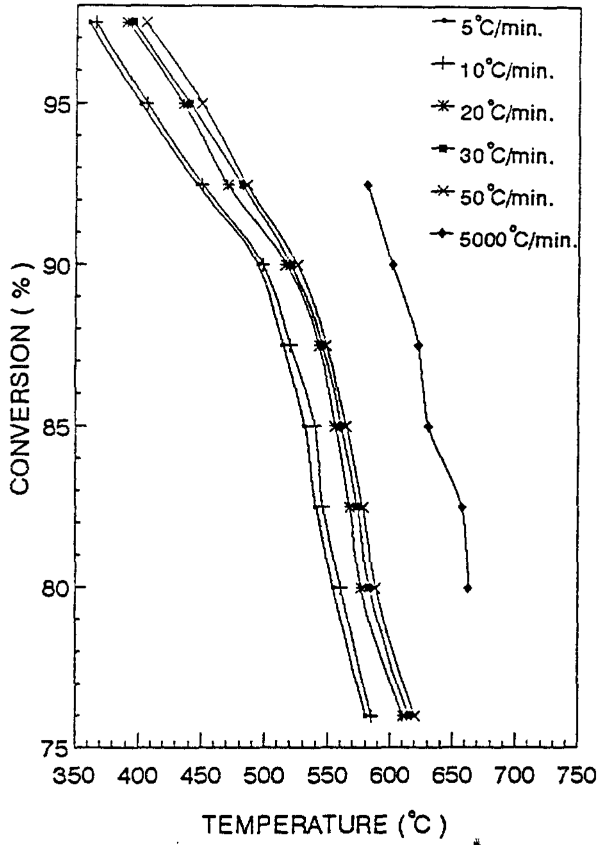


Fig. 2 Phenolic resin at different heating rates

provide extra improvement in thermal and ablative properties of the insulation materials. Activation energies of EPDM P compound and phenolic resin were calculated from the TG data using the Ozawa method [11] as 320 $kJ\cdot mol^{-1}$ and 356 $kJ\cdot mol^{-1}$, respectively.

Table 4 Physical properties of EPDM compounds at ambient temperature

Material No.	Tensile streng./ $kg\cdot cm^{-2}$	Elongation/ %	Hardness (Shore A)	Density/ $g\cdot cm^{-3}$
A	169	630	65±2	1.113
B_1	173	590	65	1.152
B_2	155	526	65	1.217
B_3	148	808	65	1.252
B_4	141	772	65	1.315
C_1	186	646	65	1.151
C_2	180	610	65	1.198
C_3	170	813	65	1.246
C_4	154	770	65	1.333
D_1	167	607	63	1.160
D_2	179	593	65	1.195
D_3	148	764	63	1.254
D_4	147	797	65	1.337
E_1	190	580	67	1.147
E_2	176	670	66	1.202
E_3	138	840	67	1.236
E_4	128	746	67	1.297
F_1	142	460	69	1.120
F_2	87	540	70	1.122
G_1	191	570	72	1.146
G_2	149	558	75	1.172
H_1	135	542	73	1.139
H_2	187	576	74	1.180
H_3	130	503	80	1.224
I	150	475	80	1.312
J	132	420	85	1.339
K	137	470	72	1.151
L	162	510	72	1.179
M	150	420	70	1.152
N	140	450	72	1.173
P	151	410	73	1.203

Determination of physical properties

Curing characteristics of selected samples were studied. Addition of fillers to base EPDM had no significant effect on scorching and optimum curing time. Only a slight change (about 1 minute) in curing time was observed. Tensile strength and elongation % at break were measured according to ASTM D412-75 using dumbbell specimens at ambient temperature. Hardness tests were effected in accordance with ASTM D 2240 in Shore A hardness. The physical properties obtained are listed in Table 4. The maximum tensile strength values were obtained with EPDM G_1(5% graphite fibre), E_1(5% SiC), H_2(10% asbestos), C_1,C_2(5% and 10% $MgZrO_2$) and B_1(5% Al_2O_3) compounds. Minimum density was apparent for the EPDM G_1 compound.

Table 5 Specific heat capacity and thermal diffusivity data for selected insulators

Insulation materials	Specific heat capacity C_p / J·kg^{-1}·K^{-1}			Thermal diffusivity $\alpha\cdot10^{-4}$/cm^2·s^{-1}
	100°C	300°C	400°C	100°C
EPDM P	1660	1930	1915	14.9
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

* Fibre/resin ratio is 70/30 by mass

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 350 and 470°C for the EPDM A compound. For fibre reinforced phenolics, endothermic peaks are noted at 164, 230, 370°C and exothermic peaks at 180°C. Degradation enthalpy (ΔH) is 538 J·g^{-1} for EPDM P compound at 471°C and 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 values of some selected samples at different temperatures were calculated and are listed in Table 5.

Determination of thermal conductivity and thermal diffusivity

The derived thermal conductivity coefficients of EPDM vulcanizates and composite phenolic samples are listed in Table 6. Thermal conductivity of E glass, kevlar and graphite fibre reinforced phenolics are 0.139 W·m^{-1}·K^{-1}, 0.281 W·m^{-1}·K^{-1} and 0.38 W·m^{-1}·K^{-1}, respectively. Thermal diffusivity of the

Table 6 Thermal conductivity coefficients measured at ambient temperature

Material No.	Conductivity coefficient/ $W \cdot m^{-1} \cdot K^{-1}$
A	0.310
B_1	0.3136
B_2	0.3205
B_3	0.3220
B_4	0.3355
C_1	0.2977
C_2	0.3259
C_3	0.3287
C_4	0.3316
D_1	0.3177
D_2	0.3262
D_3	0.3270
D_4	0.3290
E_1	0.3131
E_2	0.3211
E_3	0.3446
E_4	0.3610
F_1	0.2880
F_2	0.2700
H_1	0.2850
H_2	0.2670
I	0.3116
J	0.3286
M	0.2860
N	0.2833
P	0.3025
E glass phenolic cured	0.1390
Graphite phenolic cured	0.3762
Kevlar phenolic cured	0.2811
E glass felt	0.240
Asbestos phenolic	0.291

selected samples are calculated using Eq. (1) and given in Table 5. The specific heat capacity (C_p) of the insulators was measured using a DuPont 910 Thermal analyser following ASTM E 968-87. The results show that the loading of asbestos and phenolic resin on EPDM gum decreases thermal conductivity and thermal diffusivity. Loading of ceramic and carbon fillers increases both thermal conductivity and thermal diffusivity.

Prediction of lifetime for compound EPDM P and phenolic insulators

The lifetime of the insulator materials is the time required for completion of the decomposition procedure during rocket operation at high temperatures. The lifetime is generally expressed as the half-life of material to be degraded [5]. According to simple reaction kinetics, the rate can be expressed as Eq. (2). Since order of the reaction is 1 for our degradation process, the following half-life equation can be used,

$$t_{1/2} = \frac{\ln 2}{k} \qquad (5)$$

where k is the rate constant of the reaction. It is assumed that the above Eq. (5) is applicable in the case of the degradation of compound EPDM P and graphite phenolic. The rate constant is calculated at T_{max} using Eq. (2) and the half-life is calculated by applying Eq. (5) in the temperature range 1000–3500°C. The half-life is practically constant in this temperature range (Table 7). From this data, half-life of the EPDM P compound is 26 secs and graphite phenolic requires 147 secs at 3500°C, respectively.

Table 7 Half-life of the insulators as a function of temperature

Temperature/ °C	EPDM P $t_{1/2}$ /s^{-1}	Graphite phenolic $t_{1/2}$ /s^{-1}
1000	26.6	151.3
1500	26.3	149.7
2000	26.2	149.0
2500	26.1	148.4
3000	26.0	148.1
3500	25.9	147.6

Oxygen-acetylene flame tests

In order to simulate the ablative environment in rocket motors, selected insulation materials have been exposed to oxygen-acetylene flame (ASTM E 285-65) and penetration of the flame through the insulator is calculated. The maximum ablation resistance was found for the graphite phenolic insulator (0.017 mm·s^{-1}), followed by 0.087 mm·s^{-1} for EPDM P, 0.100 mm·s^{-1} for N, 0.112 mm·s^{-1} for M, 0.125 mm·s^{-1} for A compound, 0.175 mm·s^{-1} for E glass fibre phenolic and 0.200 mm·s^{-1} for kevlar phenolic insulator. By comparison the results from the literature [8–10], similar results are obtained from the experimental oxygen-acetylene flame tests.

Thermal analysis using the 'Finite element' method

Thermal analysis of the insulators was studied using 'Finite element' method. This is a method of data analysis. The eight node axisymmetric quadrilateral elements were chosen. Analysis was conducted along the rocket motor model and the in-depth temperature distribution was evaluated over 60 secs. During this time interval it was assumed that there was no heat loss to the surroundings and the transient heat conduction was taking place. The convective heat transfer coefficient of the hot gases, *h*, was found as 31.7 KW/m^2·K at the nozzle throat. Three kind of materials were taken into account for the nozzle design. Graphite phenolic, graphite insert and *E*-type glass phenolic were applied to the entrance, throat and the exit cone of the nozzle, respectively. The in-depth temperature distribution at the nozzle materials is given in Fig. 3 and Fig. 4.

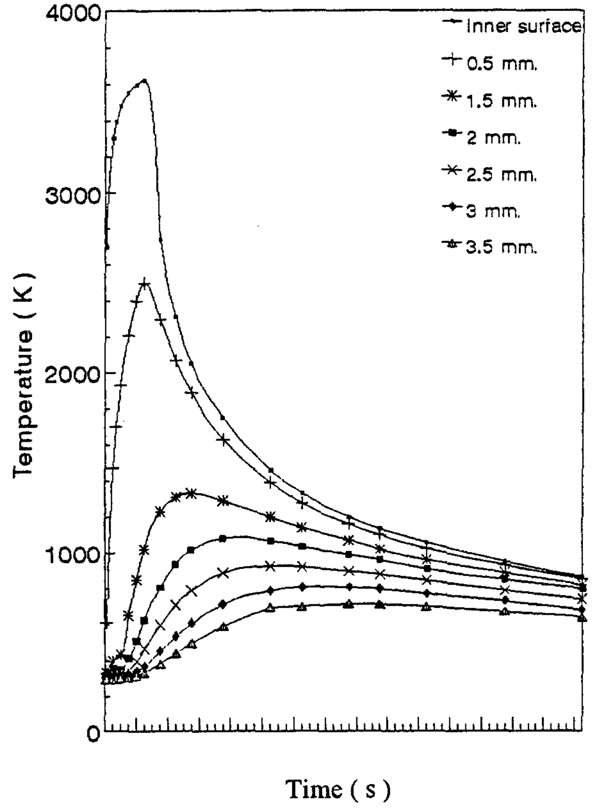
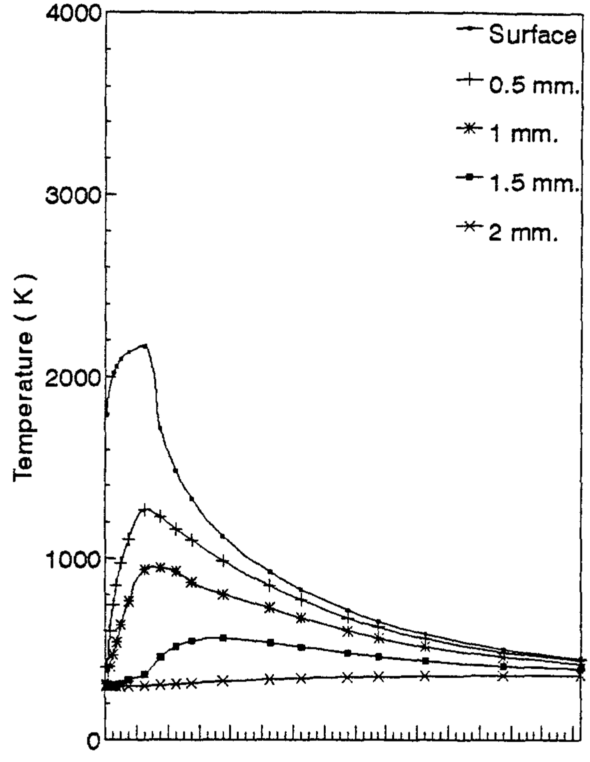


Fig. 3 The in-depth temperature distribution of graphite phenolic



Time (s)

Fig. 4 The in-depth temperature distribution of *E*-glass phenolic

Since the maximum thermal loads occur at the time that burning of the solid propellant is completed, the gas film temperatures on the inner surface of the entrance, throat and the exit cone were determined at this critical time as 3650, 3170 and 2170 K, respectively. The temperature reaches to 360 K on the boundary of graphite phenolic/steel structure, 359 K on the outer surface of the nozzle and 364 K on the boundary of *E*-glass phenolic/steel structure and 363 K on the nozzle outer surface at the end of 60 secs. EPDM P insulator was applied to the rocket motor combustion chamber. The temperature of the combustion gases was determined as 3750 K corresponding to the ideal gas formulation from the computer program. Insulator was assumed to expose to the combustion gases. When the insulator decomposition temperature is reached, the insulator begins to pyrolyse to yield a charring residue. Hot gases cause 2.17 mm char depth at the end of 7th secs and char depth reaches to 2.38 mm at the end of 20th secs. Hence these data indicate that new insulator compositions with 3 mm thickness are in the reliable and safe side during operating of the rocket motors.

Conclusion

New insulator materials have been studied experimentally and thermal data have been estimated. Conversion curves of EPDM P and phenolic resin at different heating rates were performed and the major degradation temperatures for 30 and 20% conversions were found as 646 and 661°C, respectively. Life-time predictions were found as 26 secs. for EPDM P and 148 secs. for graphite phenolics. The half-life is practically constant in the temperature range 1000–3500°C. Comparison of thermal analysis data, erosion and half-life predictions with actual performance tests, good agreement between them was found. Thermal analysis has been conducted along the insulators using finite element model. The better insulator thickness both EPDM P and graphite phenolic were found as 3 mm include safety factor using the in-depth temperature data.

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