

DEGRADATION OF ROCKET INSULATOR AT HIGH TEMPERATURE

A. S. Deuri and K. Bhowmick

RUBBER TECHNOLOGY CENTRE, INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR 721302, INDIA

(Received March 11, 1986; in revised form August 18, 1986)

The degradation of a rocket insulator compound based on ethylene propylene diene rubber (EPDM) containing asbestos, cork and iron oxide (Fe_2O_3) as fillers has been studied at high temperature (up to 600°) by using differential thermal analysis (DTA) and thermogravimetry (TG). The changes in physical properties on high-temperature aging are also reported. EPDM gum vulcanizates involving different types of diene, namely ethylidene norbornene (ENB), dicyclopentadiene (DCPD) and 1,4-hexadiene (HD), were used. In each case, the kinetic parameters for degradation have been evaluated. From these data, the lifetime of the rocket insulator compound has been found.

The solid propellant rocket insulator compound based on rubber is used between the metal/kevlar case and the propellant. Ethylene propylene diene rubber (EPDM), which has excellent thermal resistance, can be used as a base polymer. Several fillers, such as asbestos, cork and iron oxide (Fe_2O_3), are used as compounding ingredients to impart different properties to the insulator. Aging studies are essential for an understanding of the mechanism of thermal and thermoxidative degradation of this compound.

It was found in earlier studies [1, 2] of the aging of EPDM gum and filled vulcanizates that chain scission occurs with no substantial weight loss during aging in the temperature range $100\text{--}180^\circ$. The strength of the insulator compound continuously increases with the duration and temperature of aging under normal aging conditions, due to the enhanced rubber to filler interaction.

However, for the insulator compound, high-temperature aging (above 180°) is important, as the rocket insulator compound is subjected to burning at very high temperature ($2500\text{--}4000^\circ$) at the time of rocket flight. In the present investigation, the high-temperature degradation of the insulator has been followed by DTA and TG studies, and by measurement of the physical properties of samples after aging at very high temperatures for various times. A method is suggested for estimation of the lifetime of the insulator compound in actual use.

A few studies on the aging of EPDM compounds have been reported [1–4]. Aging characteristics (up to 180°) of EPDM gum vulcanizates having different types of diene, namely ethylidene norbornene (ENB), dicyclopentadiene (DCPD) and 1,4-hexadiene (HD), have been reported [1]. Similar studies have been made on filled EPDM vulcanizates and insulator compound [2].

Results have been published on the thermal analysis of EPDM rubber [5–8]. Sircar and Lamond [6] reported the DTA curves for EPDM raw rubber and gum vulcanizates and found that there is no effect of the termonomer on the DTA curve. Baranwal and Lindsay [7] studied the TG curves for both gum and carbon black-filled EPDM compounds in air and nitrogen atmospheres. They reported that the decomposition of EPDM vulcanizates starts at 175–180°. The main degradation occurs in the range 425–505° in nitrogen atmosphere and 400–505° in air. The degradation patterns of different grades of EPDM vulcanizates having different types of diene are very similar. Sircar and Lamond [8] studied blends of EPDM by thermal analysis.

Experimental

2.1 Materials

Three varieties of EPDM with the same diene content (~4%) but different types of diene, namely ethylidene norbornene (ENB), dicyclopentadiene (DCPD) and 1,4-hexadiene (HD), were used. The Mooney viscosity values (ML 1 + 4 100°) of the above three grades of EPDM are 33, 43 and 44, respectively. The elastomers were of technical grade. Chrysotile [9] asbestos, laboratory grade iron oxide (Fe₂O₃) and cork powder with 30 mesh particle size were used as fillers. Mix formulations for the gum and filled vulcanizates and the insulator compound R are given in Table 1, and the curing characteristics in Table 2 (via an R-100 Rheometer).

2.2 Apparatus and procedure

Thermal analyses, e.g. DTA and TG analysis, were carried out in a Shimadzu DT-30 Thermal Analyser and a DuPont 1090 with a weighed quantity of samples in all cases. Thermal curves in air and in nitrogen atmospheres were recorded between 30° and 600°. A heating rate of 10 deg/min was used. The flow of gas (N₂/air) (60 ml/min) was kept constant in all cases. Kinetic parameters were calculated from the first derivative of the TG curve by using the Freeman and Carrol [10] method.

Determination of technical properties: Tensile strength and elongation at break were measured in an Instron machine (1195 model) according to ASTM D412-80,

Table 1 Formulation of mixes

Mix No.	A ₁	A ₂	A ₃	B	C	D	R
Nordel 1040 ^a	—	—	100	100	100	100	100
Keltan 520 ^b	—	100	—	—	—	—	—
EPDM 346 ^c	100	—	—	—	—	—	—
Crystex sulfur ^d	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
Iron oxide (Fe ₂ O ₃)	—	—	—	—	10	—	10
MBT ^e	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD ^f	1	1	1	1	1	1	1
Asbestos fibre ^g	—	—	—	10	—	—	10
Oil ^h	—	—	—	—	—	—	10
Cork ⁱ	—	—	—	—	—	50	50

(a) HD-EPDM samples supplied by V.S.S.C., Trivandrum, (b) DCPD-EPDM samples supplied by V.S.S.C., Trivandrum, (c) ENB-EPDM samples supplied by Polysar Ltd., Canada, (d) & (h) supplied by Dunlop (India) Ltd., (e) & (f) supplied by IEL Ltd., Rishra, (g) & (i) supplied by V.S.S.C., Trivandrum

Table 2 Curing characteristics of the mixes at 150 °C

Mix No.	Initial viscosity, dN/m	Minimum viscosity, dN/m	Scorch time, min	Optimum cure time, min	Cure rate, dN/m, min
A ₁	21.0	11.0	2.5	18.0	12.0
A ₂	25.0	17.5	4.0	22.0	6.4
A ₃	25.0	16.0	4.5	24.0	3.8
B	26.5	17.5	2.5	10.5	4.5
C	25.0	17.0	3.5	11.0	3.0
D	46.0	29.0	3.0	10.5	2.0
R	46.0	29.0	2.5	10.0	4.0

using dumbbell specimens at 22°. Oxidative aging of rubber samples was carried out in an electrically heated furnace at different temperatures (from 180° to 340°).

Determination of volume fraction of rubber: The volume fraction of the rubber (V_r) was determined using a standard procedure described elsewhere [1, 2]. The density of the EPDM was 0.86 g/cm³ and the density of the *n*-heptane used as swelling solvent was 0.68 g/cm³.

Results and discussion

3.1 Thermogravimetric analysis

Thermogravimetric curves of insulator compound *R* in nitrogen atmosphere and in air are shown in Figs 1 and 2, respectively. The decomposition in air and in nitrogen starts at 150–175°. About 20% decomposition occurs at 400°. The derivative curve for degradation in nitrogen shows one major T_{\max} , i.e. the temperature at which the degradation rate is maximum, whereas three major T_{\max} s are observed in air. The main degradation occurs between 450° and 500° with $T_{\max} = 495^\circ$ in nitrogen atmosphere, and in air at 460°, 490° and 520° (Table 3).

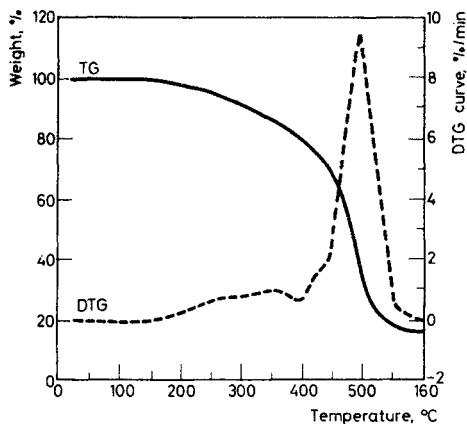


Fig. 1 TG and DTG curves for compound *R* in nitrogen atmosphere

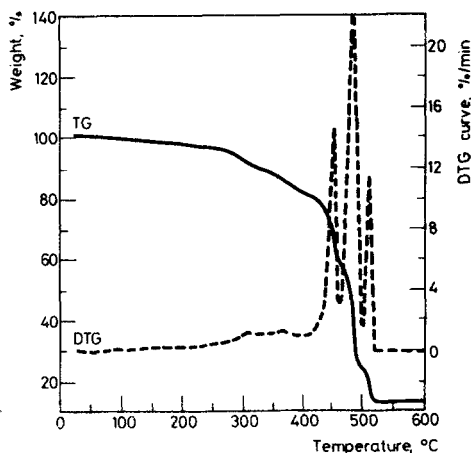


Fig. 2 TG and DTG curves for compound *R* in air

Table 3 Major T_{\max} values of EPDM compounds obtained from TGA

Samples	T_{\max} , °C	
	in N ₂ -atmosphere	in air
Raw HD-EPDM (Nordel 1040)	455	450
ENB-EPDM gum vulcanizate (A_1)	450	—
DCPD-EPDM gum vulcanizate (A_2)	445	—
HD-EPDM gum vulcanizate (A_3)	446	430 (first stage) 500 (second stage)
Asbestos filled HD-EPDM vulcanizate (B)	478	—
Fe ₂ O ₃ filled HD-EPDM vulcanizate (C)	450	—
Cork filled HD-EPDM vulcanizate (D)	460	—
Insulator compound R	495	460 (first stage) 490 (second stage) 520 (third stage)

To understand the degradation mechanism of compound R , TG analyses of the raw polymer, gum vulcanizates and vulcanizates filled with individual fillers were carried out. The curves are shown in Figs 3, 4 and 5. The degradation of the raw polymer starts at 325° in nitrogen atmosphere and at 300° in air. Major decomposition (80%) with some carbonaceous residue (~1%) in nitrogen atmosphere occurs between 410° and 475° ($T_{\max} = 455^\circ$), as shown in Fig. 3, while in air 88% decomposition occurs between 410° and 450° ($T_{\max} = 450^\circ$). However, decomposition of the gum vulcanizates in nitrogen atmosphere starts at 180–200°, with major degradation (80%) between 400° and 475°. The degradation patterns of the three EPDM gum vulcanizates, having different types of termonomers, namely

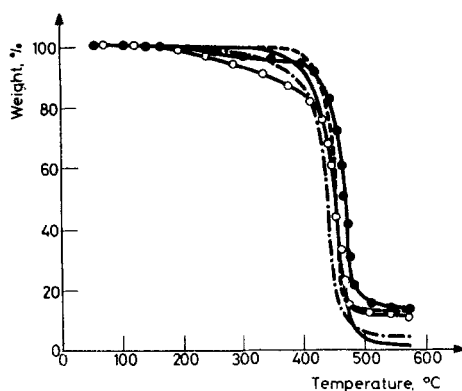


Fig. 3 Thermogravimetric curves in nitrogen atmosphere of: — Raw HD-EPDM; --- HD-EPDM gum vulcanizate; ··· Fe₂O₃ filled HD-EPDM vulcanizate; —●— Asbestos filled HD-EPDM vulcanizate; —○— Cork filled HD-EPDM vulcanizate

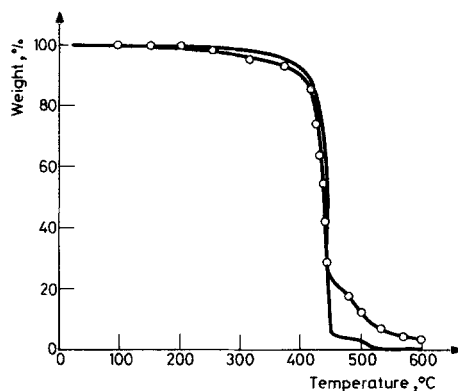


Fig. 4 Thermogravimetric curves in air for: — Raw HD-EPDM; -○- HD-EPDM gum vulcanizate

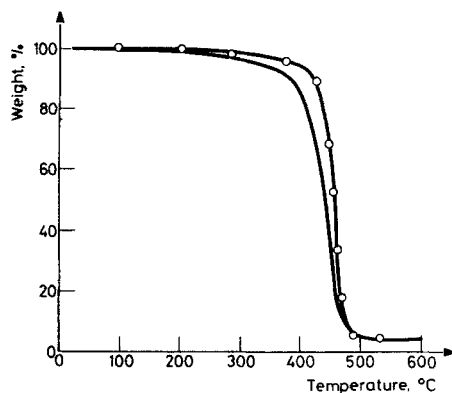


Fig. 5 Thermogravimetric curves in nitrogen atmosphere of: — DCPD-EPDM gum vulcanizate; -○- ENB-EPDM gum vulcanizate

ENB, DCPD and HD, are more or less the same. ENB-EPDM decomposes at higher temperature. However, for HD-EPDM gum vulcanizate decomposed in air, the values of T_{\max} are 430° and 500° (Table 3).

In general, it is evident from the TG curves that the stability of the vulcanizates at the beginning of the degradation decreases on vulcanization. The presence of volatile matter, e.g. stearic acid, the by-product of sulphur vulcanization, etc., causes an initial weight loss at $180\text{--}200^{\circ}$ for the vulcanizates, as compared to $300\text{--}325^{\circ}$ for the raw rubber. Furthermore, the presence of weak polysulphidic linkages in the network structure, unreacted compounding ingredients in EPDM vulcanizates, and weak links [12] in the skeleton of the macromolecule may cause early degradation. The stability of the vulcanizates at the end of degradation is higher, however, because of the formation of stable products during vulcanization.

TG curves for filled vulcanizates (*B*, *C* and *D*) in nitrogen atmosphere are shown in Fig. 3. T_{\max} values are listed in Table 3. It is evident from the T_{\max} values that asbestos increases the heat stability of the mix ($T_{\max} = 478^\circ$).

3.2 Residue left after thermogravimetric analysis

The residues left after the thermogravimetric analysis of EPDM compounds, including compound *R*, are reported in Table 4.

Table 4 Residue left at 600 °C

Samples	Residue left, % ($w/w \times 100$)		Calculated amount of residue, % ^a ($w/w \times 100$)	Nature of residue
	in N ₂ ^c atmosphere	in air		
Raw HD-EPDM (Nordel 1040)	1.0	0	0	Carbonaceous in nitrogen atmosphere
ENB-EPDM gum vulcanizate (<i>A</i> ₁)	5.0	4.9	4.5	Mainly zinc- oxide
DCPD-EPDM gum vulcanizate (<i>A</i> ₂)	5.0	4.8	4.5	Mainly zinc- oxide
HD-EPDM gum vulcanizate (<i>A</i> ₃)	5.0	4.5	4.5	Mainly zinc- oxide
Asbestos filled HD-EPDM vulcanizate (<i>B</i>)	13.5	13.0	12.5	Zinc oxide & asbestos
Fe ₂ O ₃ filled HD-EPDM vulcanizate (<i>C</i>)	13.0	12.8	12.5	Zinc oxide & ferric oxide (Fe ₂ O ₃)
Cork filled HD-EPDM vulcanizate (<i>D</i>)	12.0	4.0	10.5 ^b 3.6 ^c	Zinc oxide & decomposed product of cork
Insulator compound <i>R</i>	17.0	13.5	16.0 ^b 11.2 ^c	Zinc oxide, ferric oxide, asbestos and decomposed product of cork

^a Calculated on the basis of residue left on heating individual fillers at 600 °C; ^b in nitrogen atmosphere; ^c in air

Iron oxide (Fe_2O_3) and asbestos show no weight loss in air or in nitrogen up to 600° . Only a slight change in weight is observed ($\sim 1\%$) due to the loss of adsorbed moisture. However, cork is very susceptible to thermal and thermoxidative degradation in this temperature range ($250\text{--}600^\circ$). It shows two stages of degradation in air (Fig. 6). The residue left for cork is $\sim 10\%$ in nitrogen and $\sim 1.3\%$ in air.

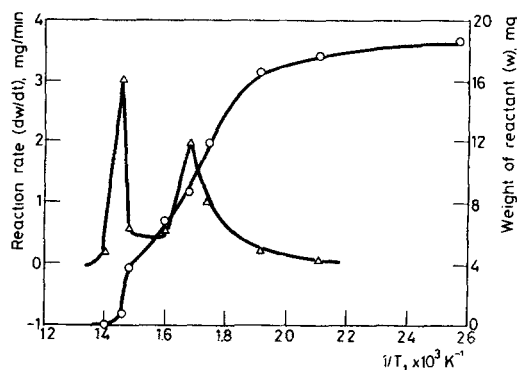


Fig. 6 TG curve and DTG curve for cork in air

For compound *R*, the residue in nitrogen atmosphere is 17% and that in air is 13.5%. The results are very close to the calculated values (Table 4). A good correlation between theoretical and experimental residue values has also been found for the degradation of HD-EPDM, DCPD-EPDM, ENB-EPDM vulcanizates, and iron oxide-, asbestos- and cork-filled EPDM vulcanizates. As explained in Table 4, the residues are due to zinc oxide, iron oxide, asbestos, the product of decomposition of cork or carbonaceous matter.

3.3 Differential thermal analysis

All EPDM compounds are characterized by an endothermic peak in nitrogen atmosphere. The positions of the endothermic peaks for the EPDM compounds are reported in Table 5. For compounds *R*, a very broad endothermic peak appears at 480° .

For the raw polymer it appears at 470° . No substantial difference between the three grades of EPDM is observed in the DTA curves, indicating that the effects of the different monomers are undetectable. A similar observation has been reported by Sircar and Lamond [6]. On vulcanization, the endothermic peak for EPDM is shifted slightly to higher temperature, i.e. 485° . This can be explained by the fact that the number of bonds to be broken per unit mass of polymer is increased by cross-linking [6]. However, the slight variation of the endothermic peak position

Table 5 Results of differential thermal analysis in nitrogen atmosphere

Samples	Endothermic peak, °C
Raw HD-EPDM (Nordel 1040)	470
ENB-EPDM gum vulcanizate (A_1)	490
DCPD-EPDM gum vulcanizate (A_2)	475
HD-EPDM gum vulcanizate (A_3)	485
Asbestos filled HD-EPDM vulcanizate (B)	500
Fe ₂ O ₃ filled HD-EPDM vulcanizate (C)	470
Cork filled HD-EPDM vulcanizate (D)	485
Insulator compound R	480

(Table 5) for the three grades of EPDM gum vulcanizates arises due to the different extents of cross-linking, which depends on the reactivity of the monomers.

It is evident from Table 5 that asbestos increases the thermal stability of the rubber vulcanizates. The very broad endothermic peaks for cork-filled EPDM vulcanizate and compound R as compared to those for the other EPDM vulcanizates (gum and filled) indicate that both rubber and cork decompose in this temperature range.

3.4 Changes in properties due to degradation

The aging of both HD-EPDM vulcanizate and compound R was carried out over a range of aging times and temperatures (from 180° to 340°). The tensile strengths of

Table 6 Retention of tensile strength of HD-EPDM gum vulcanizate aged in air

Temperature, °C	Time, min	Percentage retention of tensile strength, %	V_r
R.T.	0	100	0.256
180	120	92	0.248
	240	72	0.267
	360	74	0.283
	5	75	0.222
230	10	85	0.187
	15	105	0.176
	3	76	0.185
270	7	115	0.168
	10	145	0.145
	1	91	0.198
330	2	175	0.167
	3	110	0.134

Table 7 Retention of tensile strength for compound *R* aged in air

Temperature, °C	Time, min	Percentage retention of tensile strength, %	V_r
R.T.	0	100	0.136
180	120	152	0.265
	240	180	0.271
	360	192	0.285
225	5	108	0.251
	11	130	0.258
	20	135	0.260
270	5	110	0.250
	10	109	0.243
	15	95	0.221
340	1	81	0.195
	2	75	0.165
	4	45	0.115

these aged samples and the values of the volume fraction of rubber (V_r) are reported in Table 6 and 7.

For compound *R*, the tensile strength in general increases with aging time and temperature up to 270°. This is explained by an increase of the rubber to filler interaction on aging, as measured by the V_r values. However, at around 270°, the decomposition of cork starts, which causes a decrease in the values of V_r and the tensile strength.

For the gum compounds, no definite trend is observed. At higher temperature, beyond 200°, the tensile strength increases with aging time and with temperature. The V_r values, however, decrease with increase in the aging time or temperature above 200°, because of the degradation of the network.

3.5 Isothermal kinetics

Isothermal thermogravimetry, in which the weight loss was recorded for vulcanizates (gum and filled) heated to a pre-determined constant temperature, was carried out at three different temperatures, and the results are reported in Figs 7 and 8. The values of the rate constant (k) were found from the initial slopes of the plots, assuming zero-order kinetics. It is observed, as expected, that the rate of degradation increases with temperature. The activation energy for degradation, calculated from the Arrhenius plot, was 50 kJ/mol for both gum and filled samples in this temperature range (230–340°). It must be mentioned here that the activation energy for low-temperature aging was 30–36 kJ/mol for the gum vulcanizate and

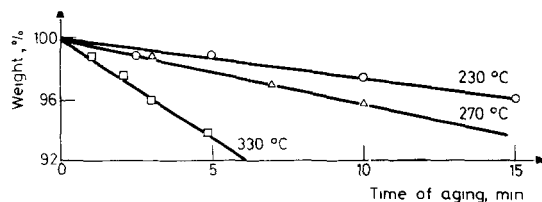


Fig. 7 Isothermal weight loss at different temperatures of HD-EPDM gum vulcanizate

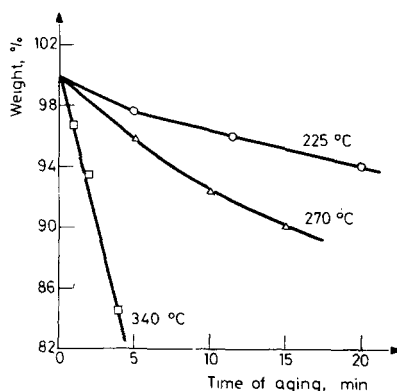


Fig. 8 Isothermal weight loss at different temperature of compound R

56 kJ/mol for the filled one, as found from tensile strength measurements [1, 2]. In the case of low-temperature degradation measured by strength properties, few chains in front of the propagating crack path on the fracture plane are involved. However, in the high-temperature case (up to 340°), the volatilization of low molecular weight species occurs.

3.6 Kinetics from non-isothermal thermogravimetry

The kinetic parameters, e.g. the order of reaction and the energy of activation of the overall degradation of the EPDM-rubber compounds at high temperature, were calculated from the non-isothermal TG curve by using the well-known method of Freeman et al. [10, 11].

The overall order and energy of activation for the degradation of the EPDM compounds are reported in Tables 8 and 9. In general, these parameters are calculated for the weight loss range 10–90%.

Nitrogen atmosphere: The rate parameters for the degradation of the EPDM compounds in nitrogen atmosphere are listed in Table 8.

The results show that the decomposition of compound R follows a first-order rate

Table 8 Kinetic parameters from non-isothermal thermogravimetric study in nitrogen atmosphere

Sample	Order of decomposition	Energy of activation, kJ/mol	Remarks
Raw HD-EPDM (Nordel 1040)	1.0	270	—C—C— single bond breakage
ENB-EPDM gum vulcanizate (A_1)	1.0	270	—S—S—, —C—S— bond scission & —C—C— single bond breakage
DCPD-EPDM gum vulcanizate (A_2)	1.0	260	—S—S—, —C—S— bond scission & —C—C— single bond breakage
HD-EPDM gum vulcanizate (A_3)	1.0	260	—S—S—, —C—S— bond scission & —C—C— single bond breakage
Asbestos filled HD-EPDM vulcanizate (B)	1.0	350	Asbestos retards decomposition
Fe ₂ O ₃ filled HD-EPDM vulcanizate (C)	0.5	200	Fe ₂ O ₃ catalyses the decomposition
Cork filled HD-EPDM vulcanizate (D)	1.0	250	—S—S—, —C—S— bond scission & —C—C— single bond breakage
Insulator compound R	1.0	330	—S—S—, —C—S— bond scission & —C—C— single bond breakage

law; the energy of activation is found to be 330 kJ/mol. The mechanism of degradation and the effect of the filler can be followed by evaluating the rate parameters for the decomposition of raw rubber and vulcanizates (both gum and filled). The first-order decomposition of raw rubber with an energy of activation 270 kJ/mol indicates that the rate-determining step in the mechanism of degradation is depolymerization involving —C—C— single bond breakage. It has been reported [12] for a typical carbochain elastomer that the energy of single —C—C— bond breakage varies between 244 and 324 kJ/mol. On vulcanization, the energy of activation is slightly decreased, i.e. 260 kJ/mol, because the energy of the C—S bond formed during vulcanization is \sim 220 kJ/mol. The degradation of the

vulcanized rubber sample involves —C—C— single bond breakage, as well as —S—S— and —C—S— bond breakage.

For the filled vulcanizates, first-order decomposition was observed for the asbestos-filled and cork-filled EPDM vulcanizates. However, the iron oxide-filled EPDM vulcanizates follow a different mechanism for degradation (the overall order is 0.5). Furthermore, it is evident from the values of the energy of activation for degradation that iron oxide catalyses the degradation ($\Delta E = 200$ kJ/mol), while asbestos retards it ($\Delta E = 350$ kJ/mol). However, all the degradation reactions for the EPDM compounds proceed through —S—S— , —C—S— or —C—C— single bond breakage.

Table 9 Kinetic parameters from non-isothermal thermogravimetry study in air

Sample	Stage of decomposition	Order of decomposition	Energy of activation, kJ/mol	Remarks
Cork	First	0	140	Volatilization of fatty acids etc. from cork
	Second (main degradation)	0.5	250	—C—C— single bond breakage
Raw HD-EPDM (Nordel 1040)	Only one stage decomposition	0.5	270	—C—C— single bond breakage
HD-EPDM gum vulcanizate (A_3)	First (main degradation)	0.5	260	—S—S— bond scission & —C—C— single bond breakage
	Second	0	450	Oxidation of stable intermediate formed during the course of reaction
Compound R	First	0	230	Due to cork decomposition
	Second (main degradation)	0.5	320	Rubber decomposition involving —S—S— , —C—S— , —C—C— single bond breakage
	Third	0	480	Oxidation of stable intermediate formed during the course of reaction

Air: The rate parameters for the decomposition of cork (Fig. 6) and EPDM compounds are reported in Table 9. As discussed in Section 3.1, the EPDM compounds show one-stage degradation in nitrogen atmosphere, while more than one stage of degradation is observed in air. Similar observations were made by Bhowmick et al. [13] for natural rubber. The occurrence of more than one stage of degradation in air indicates the formation of stable intermediates during the reaction.

However, the energy of activation for the degradation of raw EPDM rubber and the major degradation (e.g. first stage degradation) of EPDM gum vulcanizate is the same as in nitrogen. Nevertheless, this degradation follows a 0.5-order rate equation, which implies that the mechanism of degradation in air is quite different from that in nitrogen atmosphere.

For compound *R*, three stages of degradation are observed in air. The first stage decomposition follows a zero-order rate equation and arises due to the decomposition of cork. The second stage degradation (energy of activation 320 kJ/mol) can be assigned to the breakage of —S—S— , —C—S— or —C—C— single bonds. This also follows a 0.5-order rate law. The last decomposition ($\Delta E = 480$ kJ/mol) may arise due to the oxidation of certain stable intermediates formed during the reaction. The difference in the order of the reaction in air as compared to that in nitrogen suggests a difference in the mechanism.

3.7 Prediction of lifetime for compound *R*

The lifetime of the insulator compound is the time required to complete the decomposition of the insulator compound when the propellant burns (at 2500–4000°). Prediction of the lifetime is important, in order to know the stability of the composite during operation.

The time required to complete any reaction is presumably infinite, except for a zero-order reaction. Accordingly, it is better to express the lifetime as the half-life, which is defined as the time required for one-half of a given reactant to be degraded.

According to simple reaction kinetics, for an x -th order reaction, the rate equation can be expressed as

$$\frac{dw}{dt} = k(w - w_1)^x \quad (1)$$

where

$\frac{dw}{dt}$ = rate of the degradation

k = rate constant

w = initial weight

w_1 = amount decomposed at time t

x = order of reaction

Table 10 Half life time of compound *R*, at various temperatures

Temperature, °C	Half life time, sec. In nitrogen atmosphere
1000	27.1
1500	26.9
2000	26.8
2500	26.7
3000	26.6
4000	26.5

The expressions for the half-life period ($t_{1/2}$) are as follows:

$$\text{for } x = 1, t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

and

$$\text{for } x \neq 1, t_{1/2} = \frac{(2^{x-1} - 1)}{k(x-1)w^{x-1}} \quad (3)$$

It is assumed that the above equations are applicable in the case of the degradation of compound *R*. The rate constant is calculated at T_{\max} using Eq. (1), and the half-life period is calculated by applying Eqs (2) and (3), in the temperature range 1000–4000°. The results are reported in Table 10. The half-life is practically constant in this temperature range, at about 0.5 minute.

* * *

The authors are grateful to the Indian Space Research Organization for funding, and acknowledge the help and suggestions from Mr. T. S. Ram and Mr. Baby John, R.P.P., V.S.S.C., Trivandrum. The authors are also grateful to Prof. S. K. De, Rubber Technology Centre, and Prof. R. Ghosh, Chemistry Department, I.I.T., Kharagpur.

The authors thank Mr. Asutosh Ghosh, Indian Association for the Cultivation of Science, for experimental assistance.

References

- 1 A. Saha Deuri and Anil K. Bhowmick, *J. Appl. Polym. Sci.* (in press).
- 2 A. Saha Deuri and Anil K. Bhowmick, presented at the 128th Rubber Div. A.C.S. meeting, Cleveland, 1985. *Polymer Degradation and Stability* (in press).
- 3 F. P. Baldwin, *Rubber Chem. Technol.*, 43 (1970) 1040.
- 4 F. P. Baldwin and G. Verstrate, *Rubber Chem. Technol.*, 45 (1972) 709.
- 5 E. A. Turi Ed., *Thermal Characterization of Polymeric Materials*, Academic Press, New York, 1981.

- 6 A. K. Sircar and T. G. Lamond, *Rubber Chem. Technol.*, 45 (1972) 329.
- 7 K. C. Baranwal and G. A. Lindsay, *Rubber Chem. Technol.*, 45 (1972) 1334.
- 8 A. K. Sircar and T. G. Lamond, *Rubber Chem. Technol.*, 48 (1975) 631.
- 9 Martin Grayson, *Encyclopedia of Glass, Ceramics and Cement, Encyclopedia Reprint Series, A.*, Wiley-Interscience Publication, John Wiley and Sons, 1985.
- 10 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
- 11 D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, 54 (1961) 253.
- 12 L. Sluraski, *J. Thermal Anal.*, 29 (1984) 905.
- 13 A. K. Bhowmick, S. Rampalli, K. Gallagher and D. McIntyre, *J. Appl. Polym. Sci.* (in press).

Zusammenfassung — Die Zersetzung einer Raketenisolator-Verbindung auf Äthylen-Propylen-Dien-Gummibasis (EPDM) mit Asbest, Kork und Eisenoxid (Fe_2O_3) als Füllstoffe wurden bei hohen Temperaturen (bis 600°) mittels Differentialthermalanalyse (DTA) und Thermogravimetrie (TG) untersucht. Die bei Hochtemperaturen eintretenden Veränderungen der physikalischen Eigenschaften sind ebenfalls angegeben. Verschiedene Typen von Dienen, nämlich Äthyliden-norbornen (ENB), Dicyclopentadien (DCPD) und 1,4-Hexadien (HD) enthaltenden EPDM-Gummivulkanisate waren Gegenstand der Untersuchung. In allen Fällen wurden die kinetischen Parameter der Zersetzung ermittelt. Aus diesen Daten wurde die Lebensdauer der Raketenisolator-Verbindung bestimmt.

Резюме — Методом ТГ и ДТА изучено при температурах до 600° разложение ракетного изоляционного материала на основе этиленпропилендиенового каучука (ЭПДМ), содержащего в качестве наполнителей азбест, пробковое дерево и окись железа. Приводятся также изменения физических свойств, вызванных высокотемпературным старением. Были использованы различные вулканизаты ЭПДМ резины, главными из которых были этилиденнорборнен, дициклопентадиен и 1,4-гексадиен. Для каждого случая были вычислены кинетические параметры реакции разложения. На основе полученных результатов установлено время жизни ракетного изоляционного материала.