Degradation of Polymers Subjected to Radio-Frequency Discharges in SF$_6$

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Synopsis

Studies were conducted on the degradation reaction of polyethylene, poly(tetrafluoroethylene), and an expoxy resin resulting from the action of a 13.56-MHz radio-frequency (rf) discharge in SF$_6$. The curves showing the temperature variations of the samples during the experiment suggest that this degradation process occurs in two distinct stages: in the first, the heat released by the electric discharge causes the thermal degradation of the polymers, whereas in the second, the volatile degradation products react in the gas phase with the excited SF$_6$. Analysis of the reaction products shows consistency with this two-step degradation model. The main degradation products have been identified as C$_2$H$_2$, C$_2$H$_4$, SOF$_2$, and CS$_2$ in the case of polyethylene; as CF$_4$, C$_2$F$_4$, and SOF$_2$ in the case of poly(tetrafluorethylene); and finally as CO$_2$ and SOF$_2$ in the case of the epoxy resin. Furthermore, it is interesting to note the formation of polymers of the di(trifluoromethyl) polysulfane type, CF$_3$-S$_n$-CF$_3$, among the reaction products. The more volatile members, $n = 2, 3$, and 4, were identified by mass spectrometry, whereas the heavier members, identified by infrared spectrophotometry, often took the form of a whitish powder deposited on the walls of the reactor.

INTRODUCTION

Polymers are now widely used as insulating materials in electrical apparatus, and it is therefore surprising to find that research in this field has so seldom focused on the degradation reactions of polymers subjected to the action of electric discharges.[1] On the other hand, several studies published have discussed the modification experienced by the surface of polymers when exposed to the action of high-frequency electric discharges in an oxygen or hydrogen atmosphere.[2] Furthermore, sulfur hexafluoride, SF$_6$, is finding increasing applications in gas-insulated high-voltage switchgear because of its high dielectric strength, chemical inertia, and excellent arc-quenching properties. As a result of this new technologic trend, polymers are being used more and more in conjunction with SF$_6$ to form an electrical insulating system. An example that springs to mind is the SF$_6$-insulated underground cable presently under development for which the spacers are made of polymer-based materials. Thus, polymers are liable to find themselves exposed to electric discharges in the presence of SF$_6$, yet there is little information on the practical consequences of this type of stress. Under conditions such as these, the degradation of the polymers is produced by the combined action of heat released by the electric discharge, electron bombardment, and attack by the highly reactive species produced by dissociation of the SF$_6$ molecule.

This paper presents the results of research conducted on the decomposition of polyethylene (PE), poly(tetrafluoroethylene) (PTFE), and an epoxy resin (ER) subjected to an rf discharge of 13.56 MHz sustained in a flow of SF$_6$ under reduced pressure.

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EXPERIMENTAL

The experimental setup illustrated schematically in Figure 1 was used to generate the rf discharges through the SF_6 in the presence of the various polymers. The basic component was a 5-liter Pyrex flask provided with a plane quartz window for observing the discharges as well as a number of openings for the electrodes, connections to the SF_6 cylinder, a vacuum system, and the pressure gauge. The electrodes were 2 cm apart and consisted of a grounded hollow rod containing an iron–Constantan thermocouple and a solid rod supporting a metal disk coupled to the rf generator. Both the rods and the disk were of aluminum, which is well known as the metal most inert to SF_6 decomposition products.[3] The polymers under study were shaped into sleeves, accurately weighed, and placed over the tip of the grounding electrodes to cover 1 cm of its length. This setup was pumped down for several hours before each experiment in order to eliminate as much of the moisture absorbed on the internal walls as possible. The gases were collected as they emerged from the discharge in a trap cooled to −196°C, and kept for analytical purposes.

The pressure and flow rate of the SF_6 in the reactor were maintained constant throughout the tests, namely, at 2 Torr and 11 cm^3/min (normal pressure and temperature), respectively. Under these conditions, the calculated residence time for one molecule of SF_6 is 1.2 min. The power supply from the Tracerlab Model RFG 300 at 13.56 MHz varied despite all attempts to keep it constant.

The SF_6 selected for the tests was an Allied Chemical product in compliance with ASTM standard D 2472-72. The PTFE and PE were commercially available products, but the ER was a mixture, 50/50 by weight, of XB-2900 resin and XB-2888 hardener from Ciba–Geigy.

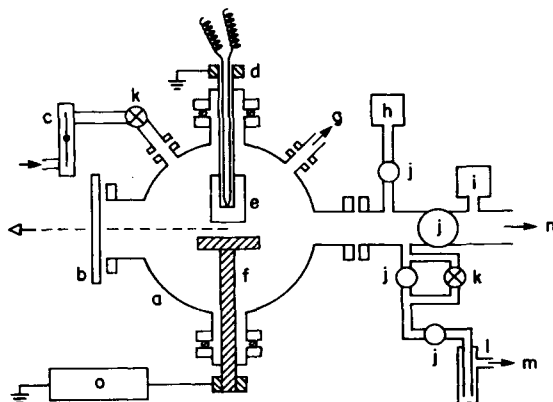The semiquantitative analysis of the gases exposed to the rf discharge was

Fig. 1. Experimental setup: a, 5-liter reactor; b, quartz window; c, flowmeter; d, hollow electrode; e, polymer sleeve; f, disk and electrode; g, McLeod gauge; h, Pirani gauge; i, Penning gauge; j, valves; k, needle valve; l, trap; m, rough pump; n, diffusion pump; o, 13.56 MHz generator.

performed with a Hewlett–Packard Model 700 gas-phase chromatograph equipped with a Porapak Q (3 m × 0.3 cm, 100–120 mesh) in a Hewlett–Packard GC/MS, Model 5980 A, equipped with a flame ionization detector.

The compounds were identified from recordings of their mass spectra as they were eluted from the chromatograph. A Perkin–Elmer Model 180 spectrometer was used to record the infrared spectra in a Teflon cell provided with BaF_2 or KBr windows.

RESULTS AND DISCUSSION

Table I summarizes the experimental conditions to which each of the polymers studied was subjected. One of the main points to be noted is the high proportion of SF_6 decomposed during the discharge. The temperatures given correspond to the values of the plateaus observed when plotting the curves of the temperature variations of the polymer samples during the experiment (Fig. 2). A word of explanation must be given with regard to these curves. As soon as the electric discharge was applied, the temperature increased, reached a plateau, and then, after a certain time, rose again. Not only did each polymer reveal a characteristic temperature plateau but the plateau temperature varied considerably according to the power applied to the discharge (Fig. 3). A similar observation was made by Wilkins and Billings[4] in a study of the effects of discharge on the surface of organic insulation. Furthermore, the same authors showed that an empirical relationship existed between the plateau temperature level and the temperature at which the thermal degradation begins. The second rise in temperature very probably corresponds to a change in the thermal conductivity of the polymers
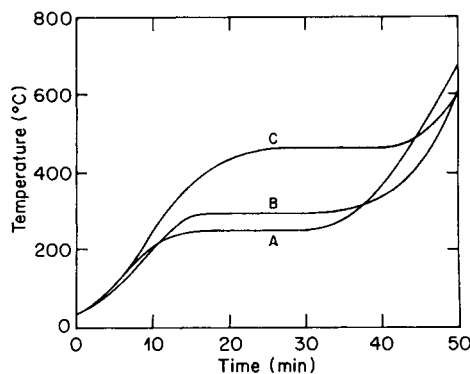

Fig. 2. Temperature of polymer vs time: (a) polyethylene; (b) epoxy resin; (c) poly(tetrafluoroethylene).

TABLE I
Summary of the Experimental Conditions for the Degradation of Polymers Exposed to an RF Discharge in SF_6

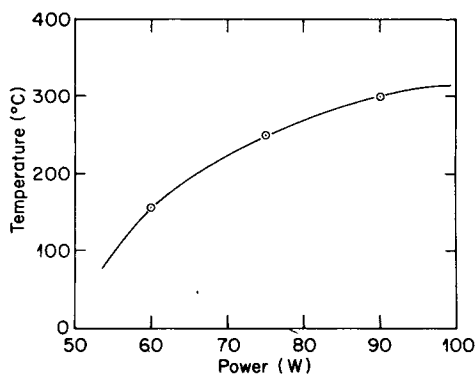| Conditions	SF_6–PTFE	SF_6–PE	SF_6–RE
Power, watts	100	90–95	90
Duration, min	46	45	33.5
Weight loss, g	1.342	~1.300	1.230
Plateau temperature, °C	465	250	300
% SF_6 decomposed	72.2	74.2	81.1

Fig. 3. Equilibrium temperature of epoxy resin plateau vs. power applied to the discharge.

as a result of their carbonization. This interpretation of the temperature variations shown by the sample studied suggests that, under the present experimental conditions, degradation takes place in two separate stages: in the first stage, the heat liberated by the electric discharge causes thermal degradation, whereas in the second, the volatile degradation products react in the gas phase with the SF_6.

Analysis of the gaseous products resulting from the degradation of the polymers in an SF_6 plasma furnishes results that are consistent with the proposed two-stage degradation model (Table II). The main thermal-degradation products of these polymers are ethylene (C_2H_4) in the case of polyethylene,[5] tetrafluorethylene (C_2F_4) in the case of PTFE,[6] and finally carbon monoxide (CO) and carbon dioxide (CO_2) in the case of the epoxy resin.[7] Hence, the composition of the gas mixtures for each of the polymers studied may be interpreted in light of these primary degradation products. According to the data in Table II, for instance, carbon tetrafluoride (CF_4) is the main degradation product of PTFE, whereas acetylene (C_2H_2) is formed predominantly by the degradation of polyethylene. Moreover, it is a well-known fact[8] that hydrocarbons subjected to electric discharges react by cracking to form mainly C_2H_2, whereas fluorocarbons are mainly converted into CF_4.

It has been noted furthermore that some of the compounds listed in Table II form outside the active areas of discharge following various secondary reactions. This is particularly true of SiF_4, which is a result of the reaction of SF_4 with the glass walls of the reactor:

$$2SF_4 + SiO_2 \xrightarrow{H_2O} SiF_4 + 2SOF_2 \tag{1}$$

Reaction (1), which was originally put forward by Manion et al.[9] to account for the presence of SiF_4 among the products of SF_6 decomposition in electric discharges, is extremely rapid when catalyzed by the water absorbed on the glass walls. The same remark holds for the SOF_2 obtained from the hydrolysis of SF_4 in the gas phase:

$$SF_4 + H_2O \rightarrow SOF_2 + 2HF \tag{2}$$

If the moisture content is sufficiently high, thionyl fluoride may also undergo further hydrolysis to generate SO_2 and HF. This reaction is enhanced in the

TABLE II
Composition of the Degradation Products of PTFE, PE, and ER Exposed to a 13.56 MHz RF
Discharge in SF_6

| Products	% Volume		
	PTFE	PE	ER
SF_6	17.2	26.6	19.2
SF_4	b	—	—
SOF_2	13.2	7.3	11.0
SiF_4	a, b	a, b	a
CF_4	43.2	1.0	1.6
C_2F_6	13.5	0.9	2.2
C_3F_8	0.6	—	—
C_2H_2	—	24.7	0.1
C_2H_4	—	10.4	2.0
C_3H_6	—	3.3	3.5
CO_2	—	—	23.5
COS	—	—	b
CS_2	b	5.7	1.4
SO_2	—	—	b
F_2CO	—	—	c
F_2CS	c	c	c
FS_2F	b	—	b
FS_3F	b	—	b
$CF_3—S_2—CF_3$	c	—	, c
$CF_3—S_3—CF_3$	c	—	c
$CF_3—S_4—CF_3$	c	—	c
TOTAL	87.7	79.9	64.5

[a] Could not be quantified since it decomposed in GC column.
[b] Quantity too small to be quantified.
[c] Impossible to measure quantitatively because of lack of sensitivity calibration.

case of systems containing epoxy resin, where traces of SO_2 have actually been found, since the thermal degradation of this type of polymer releases significant quantities of water. Several other methods of producing SOF_2 from reactions between SF_4 and certain polymer degradation products such as ketones, aldehydes, etc. have been mentioned in the literature.[10]

On the other hand, it may be seen that reaction (2) also leads to the formation of hydrofluoric acid (HF) of which large quantities should be present among the SF_6–ER reaction products. This highly corrosive gas is known to attack glass according to the following reaction:

$$4HF + SiO_2 \text{ (glass)} \rightarrow SiF_4 + 2H_2O \tag{3}$$
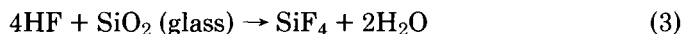
Thus, the formation of SOF_2 and SiF_4 from extremely reactive SF_4 and HF provides an explanation for the difficulty in measuring these gases quantitatively. But even if other experimental procedures and materials were used to handle these corrosive gas mixtures, it would still not be possible to eliminate all the secondary reactions; at the most, only the formation of SiF_4 could be prevented.

The formation of fairly large quantities of fluoroformaldehyde (F_2CO) is probably due to the fluor atoms generated in the discharge which attack the carbon monoxide[11]:

$$2F + CO \rightarrow F_2CO \tag{4}$$

Finally, it is interesting to note in Table II the presence of new products of the di(trifluoromethyl)polysulfane type corresponding to the general formula $CF_3-S_n-CF_3$:

Members of $n = 2, 3,$ and 4 have a sufficiently high vapor pressure for them to be identified in the gas phase by GC/MS. Typical mass spectra are reproduced in Figure 4; in each case the molecular ion is present, and the isotopic ratio $^{34}S/^{32}S$ allows immediate identification of the compound. To the author's knowledge, only di(trifluoromethyl)disulfane has ever been mentioned in the literature, and this was synthesized from CF_3SF and potassium fluoride (KF) in the presence of water.[12] The higher members of these compounds are doubtless to be found in the condensed phase of the decomposition products.

A propos, during the experiments with SF_6–PTFE, a white solid was deposited on the wall of the reactor which was insoluble in tetrahydrofuran (THF) and during the experiments with SF_6–PE and SF_6–RE, a brownish solid was formed which was soluble in THF. However, these deposits did not consist only of the volatilization products of the polymers, as could be seen, for example, from the IR spectrum shown in Figure 5. Moreover, it is quite interesting to note that the IR spectrum recorded for the SF_6–PE system presents almost identical band patterns to those of the SF_6–ER system (Fig. 5). As a matter of fact, these spectra are characterized by bands appearing in the 800–1200 cm^{-1} region which
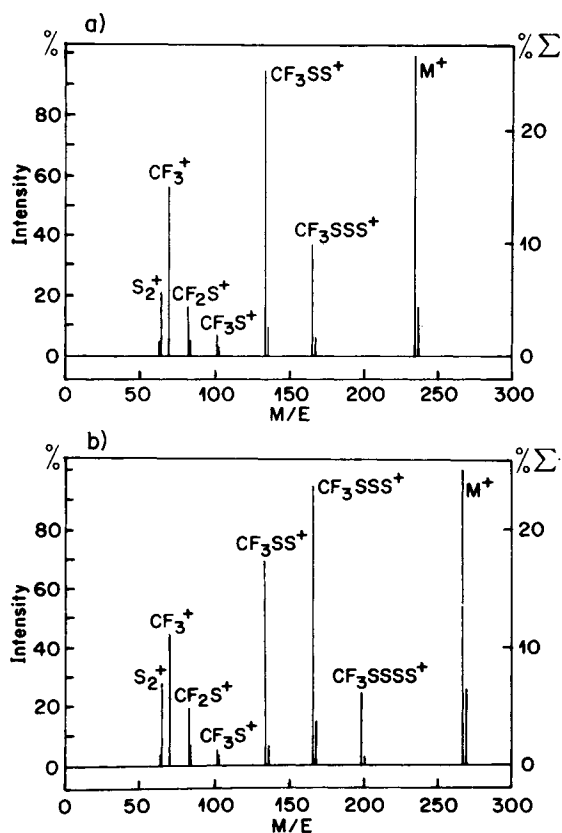

Fig. 4. Mass spectrum of the di(trifluoromethyl) polysulfane-type products.
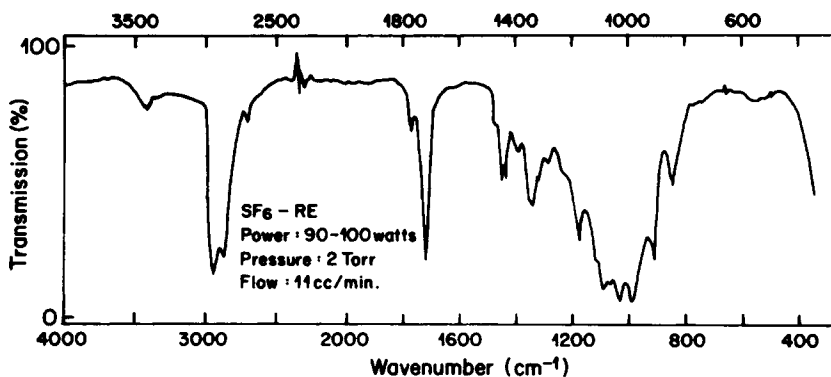
Fig. 5. Infrared spectrum of the solid products resulting from the decomposition of the SF_6—epoxy resin system.

are typical of the valence vibration of C—F and SF bands.[13] The fact that the solid products formed from chemically very different polymers (PE and ER) are also physically similar seems to indicate that the plasma deposition processes depend to a large extent on the quantity of fluorine and sulfur atoms provided by the SF_6 as to whether they generate polysulfane-type products.

Mass Balance

A mass balance was calculated on the basis of the products analyzed in the gas phase compared with the reagents consumed in the discharge in the form of SF_6 and polymer. The results, presented in Table III, emphasize the low recovery rate of the sulfur atoms which, in the SF_6–PTFE experiments, reaches a maxi-

TABLE III
Material Balance of Products Analyzed in the Gas Phase Compared with the Reagents
Consumed in the Form of SF_6 and Polymer

System	Atoms	Quantity of reagents consumed, g	Quantity of products analyzed, g	% Recovered
	S	0.478	0.141	29.5
	F	2.723	1.808	66.4
SF_6–PTFE	C	0.322	0.289	89.6
	H	—	—	—
	O	—	—	—
	F/S	5.69	12.84	
	S	0.481	0.098	20.4
	F	1.713	0.090	5.2
SF_6–PE	C	—	0.213	—
	H	—	0.023	—
	O	—	0.019	—
	F/S	3.56	0.91	
	S	0.391	0.063	16.1
	F	0.393	0.125	9.0
SF_6–ER[a]	C	0.872	0.086	9.9
	H	0.087	0.005	5.6
	O	0.271	0.137	50.5
	F/S	3.56	1.99	

[a] The empirical formula of ER used for the calculation was $C_{30}H_{36}O_7$.

mum of only 30%. The same remark applies equally well to the fluor atom balance, particularly as a large proportion of these atoms must exist in the form of HF in the case of PE and ER, which are polymers rich in hydrogen atoms. However, the high reactivity of HF prevented a quantitative analysis of this compound, and low recovery rates were therefore recorded. On the contrary, the SF_6–PTFE system showed a recovery rate of 66% owing to the absence of hydrogen atoms in the gas phase. Likewise, since it was impossible to determine the SiF_4 quantitatively, the fluor atom balance showed an even greater deficit. Table III also contains an oxygen balance for the SF_6–PE experiments although the amount of oxygen extracted from the walls of the container cannot be determined here using reaction (1).

The low yield of sulfur atoms in the form of fluorinated gaseous products is quite a normal result if the SF_6 decomposition mechanism is based on total elimination of all the fluorine atoms. Moreover, this is corroborated by certain experimental facts.

Firstly, a significant quantity of the liquid- and solid-state products formed were not taken into account when calculating the mass balance. In connection with this, it was noticed that the nature of the solid products resulting from the SF_6–PE and SF_6–ER systems depends to a large degree on the amount of the fluorine and sulfur atoms supplied by the SF_6. In addition, the experiments conducted in the dynamic state did not allow all the gases to be trapped at $-196°C$, namely, H_2 and CO; and even for the trapped ones, analysis was incomplete. Finally, no account was taken of the greyish deposits adhering firmly to the surface of the aluminum electrodes, x-ray fluorescence spectra of these deposits reveal the presence of sulfur and fluorine atoms, and consequently it is believed that they consist of aluminum fluorides and sulfides.

CONCLUSIONS

From the results presented in this paper, it can be seen that the degradation of polymers exposed to radio-frequency electric discharge in SF_6 is caused initially by the heat released by the discharge. Thereupon, the secondary reactions between the volatile decomposition products and the SF_6 produced by the electric discharge account for the formation of the products collected on the traps. The nature of the reaction products seems to indicate that in electric discharges, the SF_6 decomposition process is based on the stripping of all the fluorine atoms of this molecule, an interpretation which is further strengthened by the fact that the emission spectra recorded during the degradation reactions reveal the presence of the S_2 emitter.[14] Furthermore, the presence of moisture on the glass walls of the experimental setup favors the formation of certain products such as SOF_2, SiF_4, and HF, to name just the principal ones. Finally, the low balance of fluorine and sulfur atoms calculated on the basis of the trapped gaseous products provides an indication of the importance of these atoms in the synthesis of the solid products which, as identified by mass spectrometry and infrared spectroscopy, suggest the formation of fluoromethyl polysulfane polymers.

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