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THE THERMAL DEGRADATION OF SOME FLUORINE-CONTAINING ELASTOMERS *

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ABSTRACT

Polymers containing both hydrogen and fluorine atoms can give rise to the evolution of hydrogen fluoride (HF) on thermal and thermo-oxidative degradation. This evolution has been studied with the aid of a fluoride ion specific electrode. The effect of formulation has been examined in some detail for a hydrofluoro-elastomer and it has been shown that the yield of HF is greatly affected by changes in formulation. The effect of variation in chemical structure has also been studied by comparing the degradation of hydrofluoro-, perfluoro-, phosphazene- and fluorine-containing siloxane elastomers. The perfluoro elastomer is the most stable, and the phosphazene elastomer the least stable of the polymers examined, although they both give low yields of HF.

INTRODUCTION

The most thermally stable elastomers currently available are of two main types, fluorine-containing carbon-based polymers and polysiloxanes. With the latter type, fluorine is also sometimes incorporated into the structure to give improved solvent and fluid resistance. As the majority of the polymers synthesised contain both hydrogen and fluorine atoms in proximity to one another, the possibility arises of the evolution of hydrogen fluoride (HF) as a degradation product. This can cause stress-corrosion-cracking of metals such as titanium and stainless steel and instances of this occurring at temperatures as low as 160°C have been recorded when fluorine-containing polymers have been used as seals and sealants in contact with these metals. It is with the specific problem of HF evolution that this paper is largely concerned.

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EXPERIMENTAL

Samples (approximately 5 mg for dynamic experiments and 1 g for isothermal measurements) in thin sheet form were heated at a rate of temperature rise of 2°C min^{-1}, or isothermally in a stream of dry air or nitrogen (50 ml min^{-1}). The sample was contained in a platinum crucible in a calcium fluoride tube and the gas stream only contacted calcium fluoride or polytetrafluoroethylene before passing into a buffer solution containing initially 10^{-5} mole l^{-1} of F^- ion. The change in F^- ion concentration was monitored with a fluoride ion specific electrode and the output of this was fed to a suitable recorder, thus yielding a record of pF versus temperature, or pF versus time at constant temperature. In the case of hydrofluoro polymers, it has been confirmed by mass spectrometry that the F^- ions arose from HF only and not from oxygenated species such as COF_2 [1,2].

Separate weight loss determinations were made using the DuPont 951 thermogravimetric analyser to ascertain what proportion of the total volatile products the HF formed.

RESULTS AND DISCUSSION

Two different aspects of the problem must be considered: (1) the effect of formulation of the elastomer upon HF elimination, and (2) the effect of

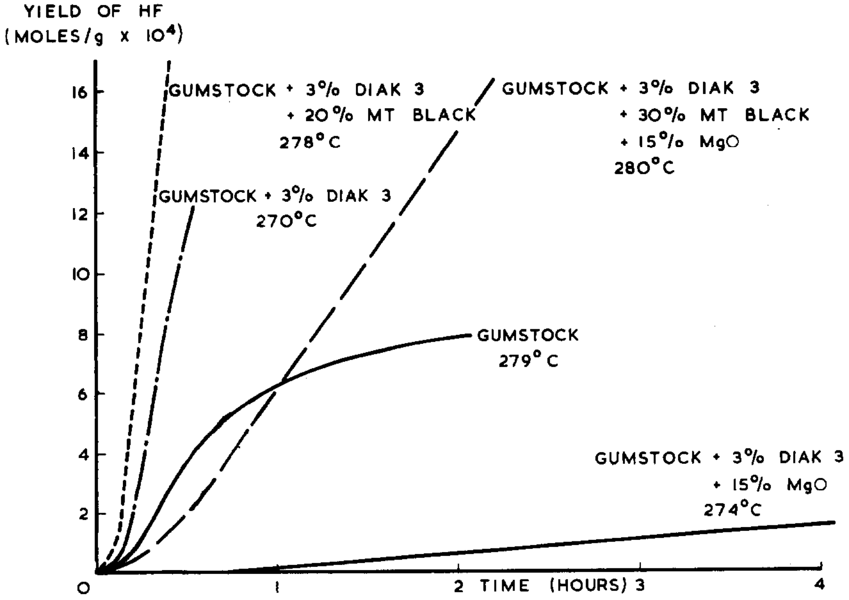
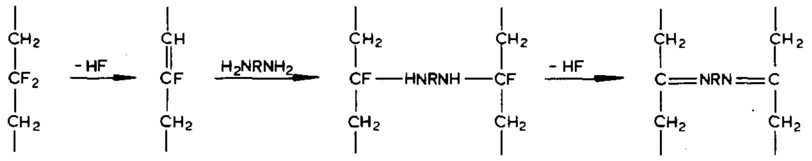


Fig. 1. Comparison of the effect of normal formulation components on the HF yield at ~ 275°C.

variation in chemical structure of the elastomer itself upon HF elimination.

Figure 1 shows the effect on HF yield at 275°C of omitting one or more of the components normally included in the elastomeric formulation of a particular terpolymer of vinylidene fluoride, hexafluoropropene and tetrafluoroethylene. Experiments have been carried out at a number of temperatures between 200 and 275°C and the same relative behaviour was observed at each temperature.

Crosslinking the terpolymer with a diamine (Diak 3) destabilised it with respect to HF elimination. The initial rate of HF production from the crosslinked material was greater than from the gumstock and the rate remained essentially unchanged throughout the timescale of the experiments. In contrast, the rate for the gumstock decreased steadily with time. The cure of the elastomer with a diamine is thought to take place as follows [3]. (a) Elimination of HF from the vinylidene fluoride segments of the main chain to leave double bonds; (b) reaction of the diamine with the double bond to form crosslinks; and (c) elimination of HF from the crosslink to form further double bonds. The increase in yield of HF in the presence of a diamine is therefore understandable, especially as the double bonds in the crosslinks tend to lower the activation energy for elimination of HF from the next units in the main chain.



If, however, a peroxide curing system was used, then the HF yield from a compounded sample was much lower than that from the basic polymer (Fig. 2).

If 20% of a medium thermal (MT) black (the normal reinforcing filler)

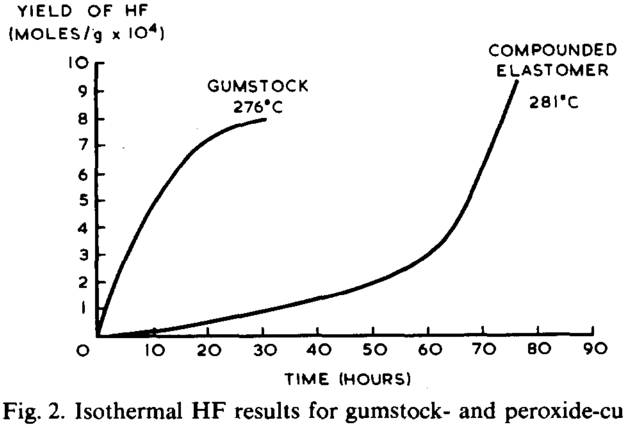


Fig. 2. Isothermal HF results for gumstock- and peroxide-cured elastomer.

was added to the formulation, the stability was slightly less than in the presence of diamine alone. The black obviously does not act as a chemically inert diluent (Fig. 1).

Addition of 15% magnesium oxide (MgO) as well as the curing agent and medium thermal black (the standard commercial formulation) resulted in an HF yield which, in the short term, was very similar to that of the terpolymer alone. In the long term, however, the rate of HF yield did not decrease as rapidly with the compounded material. The addition of MgO in the absence of black had a much greater effect, the HF yield being at least a factor of ten below that obtained with the terpolymer alone. The presence of the medium thermal black therefore causes a reduction in the efficiency of the MgO as an HF acceptor. Interpretation of the results is difficult because the MgO does not act solely as an acid acceptor, but also plays an essential part in the curing (crosslinking) reaction. In its absence, the elastomer does not develop optimum properties by any of the known curing methods. The MgO is thought to catalyse HF elimination and thus aid crosslinking and the attainment of a higher crosslink density. The effect of using different blacks together with 15% MgO is illustrated in Fig. 3. It can be seen that, in contrast to the thermal black, the channel and furnace blacks had relatively little effect upon the efficiency of MgO as an HF acceptor. It is known that the chemical nature of the surface differs in the different blacks (Table 1). Channel black has the greater area of oxidised surface, furnace black

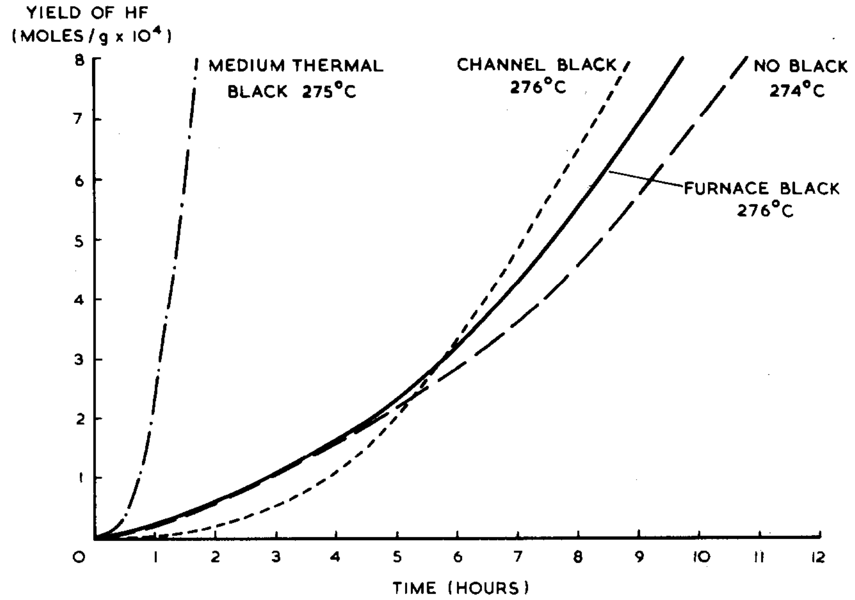


Fig. 3. Comparison of the effect of various blacks on the HF yield at ~ 275°C. (All formulations contain 15% MgO.)

TABLE 1

Comparison of the properties of carbon blacks

Type of black	Particle size (nm)	pH	Oxygen content (%)
Medium thermal	300	7.0	0
Furnace	70	9.5	0.22
Channel	32	4.5	3.6

considerably less and thermal black virtually no chemisorbed oxygen at all. The blacks also differ in acidity, or basicity, and particle size, so it is difficult to envisage precisely what is happening chemically in the systems.

Figure 4 shows the variation in HF yield as a function of MgO content. The presence of MgO does not prevent HF elimination, it merely reduces its rate of evolution, a 15% addition giving a result comparable with that of the gumstock alone. This is true over a range of temperatures.

Other basic oxides, hydroxides and carbonates may be used as acid acceptors instead of MgO (provided that an acceptable crosslink density is attained during the curing process). A comparison of the effectiveness of some of these compounds at ~ 275°C relative to MgO as unity is made in Table 2. It should be noted that the relative efficiencies are *not* the same at different temperatures.

The following conclusions may therefore be drawn from the study of formulation variation. To *minimise* HF elimination (it cannot be stopped completely)

(a) cure with a peroxide rather than a diamine;

(b) use a channel, or furnace black rather than a thermal black;

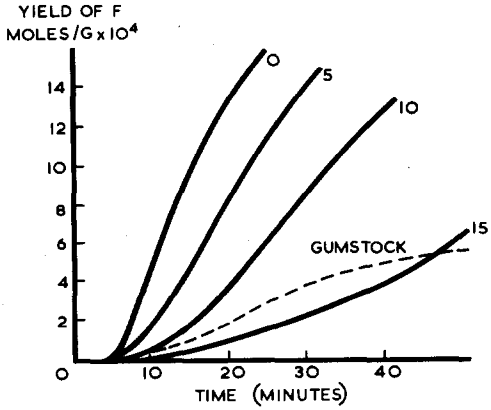


Fig. 4. Effect of the MgO content % at ~ 275°C.

TABLE 2

Comparison of the efficiencies of HF acceptors at ~ 275°C

HF acceptor (15% by weight)	Relative efficiency
MgO	1.0
TiO_2	0.2
Al_2O_3	1.5
BeO	1.5
B_2O_3	2.1
Li_2O	1.5
CaO	25.6
$Al(OH)_3$	2.2
LiOH	6.9
$Mg(OH)_2$	37.0
$Ca(OH)_2$	42.5
K_2CO_3	0
Na_2CO_3	2.6
$MgCO_3$	12.2
Li_2CO_3	21.4
$CaCO_3$	41.3

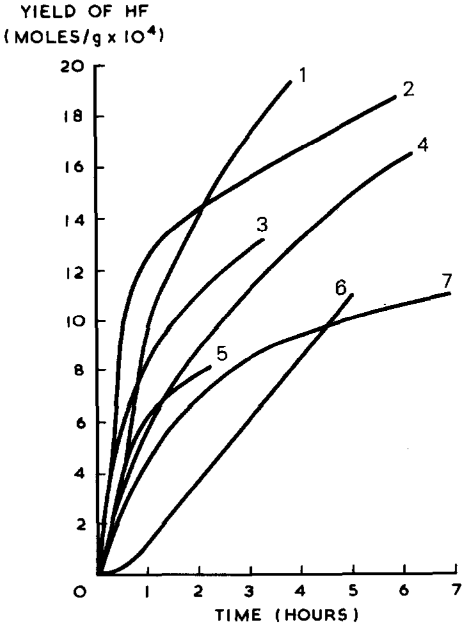


Fig. 5. Comparison of the HF yields at 280°C for various hydrofluoro elastomers. 1, Viton C10; 2, Fluorel 2160; 3, Viton A; 4, Tecnoflon T; 5, Viton B; 6, Viton LM; 7, Viton LD2669.

(c) use as much HF acceptor as possible concomitant with the retention of other desired properties;

(d) instead of MgO as HF acceptor, substitute $MgCO_3$, Li_2CO_3 or $Ca(OH)_2$, the last being preferred for maximum high-temperature use (250–275°C).

What then is the influence of the chemical structure of the polymer upon HF yield? Most of the early elastomer systems were based upon copolymers of vinylidene fluoride (VF) and hexafluoropropene (HFP), or terpolymers of VF/HFP and tetrafluoroethylene, although pentafluoropropene and propene have also been used as comonomers. In all these systems, the fluorine content only varies between 63.8 and 66.1% and the hydrogen content between 1.7 and 2.0%. The HF yield as a function of time at approximately 280°C for seven different copolymers/terpolymers is shown in Fig. 5. Although there are differences, these are relatively minor compared with the effect of formulation within a single system.

A perfluoroelastomer based upon a copolymer of tetrafluoroethylene and perfluoromethyl vinyl ether has recently become available, as has a phosphazene elastomer of basic structure $[PN(OCH_2CF_3)_2\text{–}PN(OCH_2C_4F_8H)_2]_n$. It was of interest to determine the evolution of HF from these materials and to compare their behaviour with that of poly(methyltrifluoropropylsiloxane) another thermally stable elastomer with fluorine present only in the side groups.

The perfluoro elastomer was quite appreciably more thermally stable (on a weight loss basis) than the other two materials (Fig. 6) and the latter were

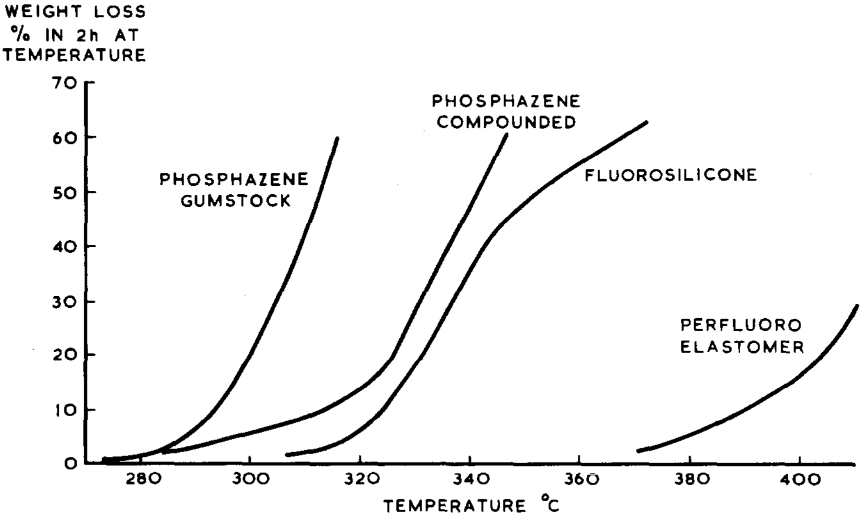


Fig. 6. Comparison of the thermal stabilities of fluorosilicone, perfluoro and phosphazene elastomers.

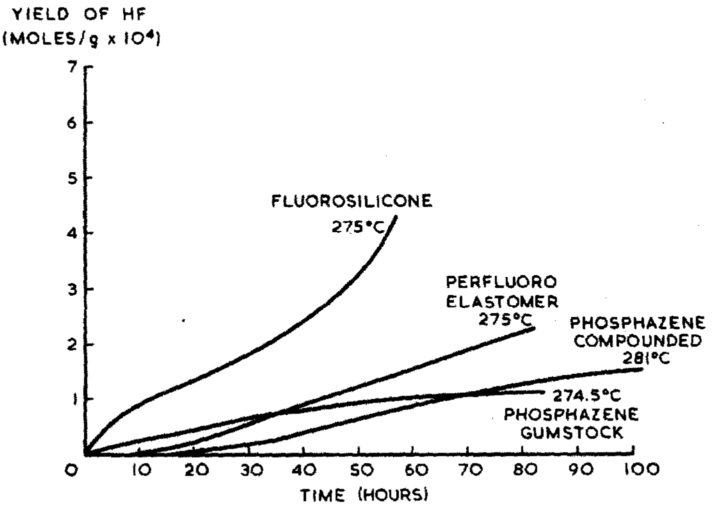


Fig. 7. Isothermal HF results for fluorosilicone, perfluoro and phosphazene elastomers.

less stable than any of the hydrofluoro elastomers already referred to above. It should be emphasised that these curves are mainly for compounded, crosslinked materials as the perfluoro elastomer was only supplied commercially in that form. The three samples also had quite different fluorine contents; the perfluoro elastomer contained about 53% F, the phosphazene elastomer about 51% F and the siloxane only 25% F. The HF yields for the three elastomers at 275°C are shown in Fig. 7. The values were lower than those obtained for diamine-cured hydrofluoro elastomers, although a peroxide-cured material was superior to the poly(methyltrifluoropropylsiloxane) sample at least up to 60 h at temperature.

On the basis of the results, the perfluoro elastomer is the most thermally stable of those examined and also gives very low yields of HF. The phosphazene is the least stable of the elastomers and also gives the lowest HF yields. The siloxane has a relatively low thermal stability and gives a surprisingly high HF yield considering that the fluorine is present only at the end of a side chain.

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