JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 2951-2961 (1964)

Thermal Degradation of Fluorine-Containing Polymers. Part II. Degradation in Oxygen

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Synopsis

The thermal degradation in oxygen of a number of fluorine-containing polymers has been studied by using a weight loss technique. The relative thermal stabilities of the different polymers have been determined and, where possible, the overall activation energy and frequency factors for their breakdown. The results have been compared with those for samples of the same polymers degraded in vacuum. There is little change in the relative thermal stabilities observed under both conditions, the fully fluorinated structures being the most stable. The changes in the rates of breakdown in the presence of oxygen are difficult to interpret in the absence of mechanistic information.

INTRODUCTION

Although data on the weight loss of fluorine-containing polymers at high temperatures under inert conditions are fairly extensive, much less has been published on similar work under oxidizing conditions. Accordingly, polymers which had already been examined in vacuum (Part I of this paper)[1] were degraded in the presence of oxygen with the use of the same experimental technique and otherwise analogous experimental conditions in order to facilitate comparison of the results. Preliminary details of these experiments were given at the Society of Chemical Industry Symposium on thermal degradation of polymers.[2]

EXPERIMENTAL

Materials

Details of the polymers examined have been given in Part I.

Experimental

The apparatus used has been described previously.[2] It is illustrated in Figure 1.

RESULTS AND DISCUSSION

Form of Weight Loss Curves

With the exception of the fluorosilicone, where a residue of silicon dioxide could be formed during the oxidation, none of the polymers exhibited any

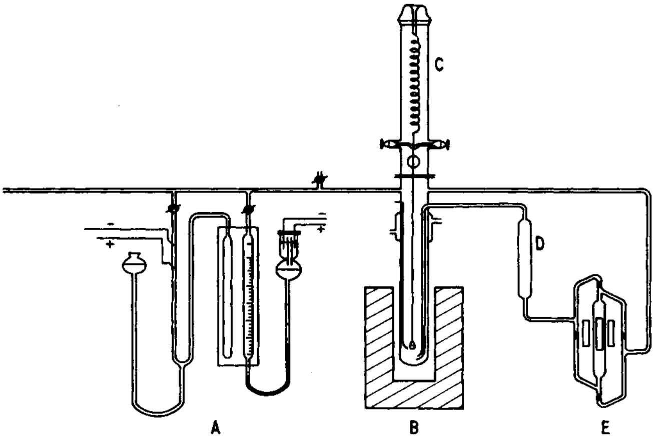

Fig. 1. Apparatus for study of degradation in oxygen: (*A*) system of measurement of oxygen absorption; (*B*) furnace; (*C*) quartz spring balance assembly; (*D*) absorption trap; (*E*) circulating pump.

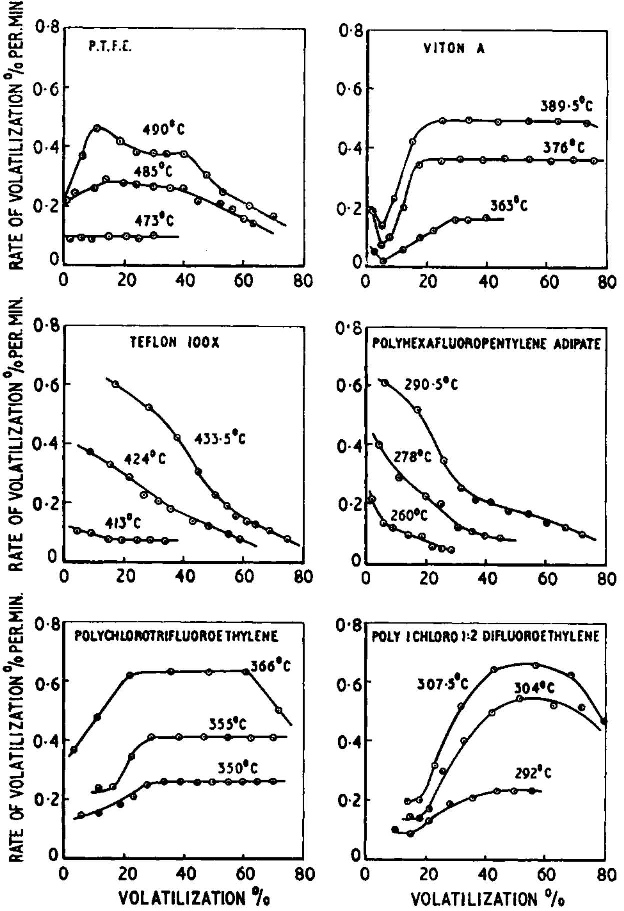

Fig. 2. Comparison of rates of volatilization of fluorine-containing polymers in oxygen

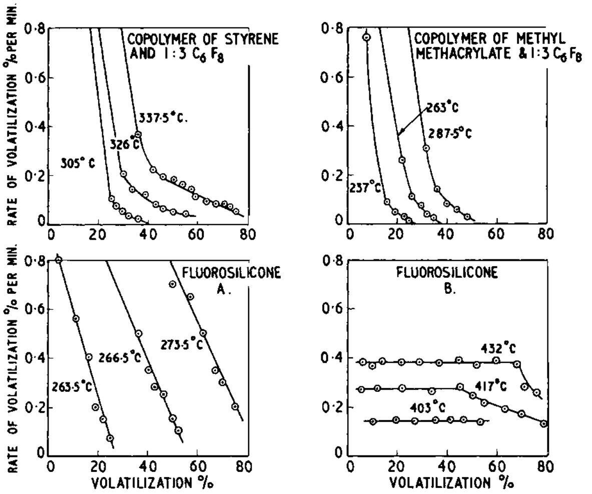

Fig. 3. Comparison of rates of volatilization of fluorine-containing polymers in oxygen.

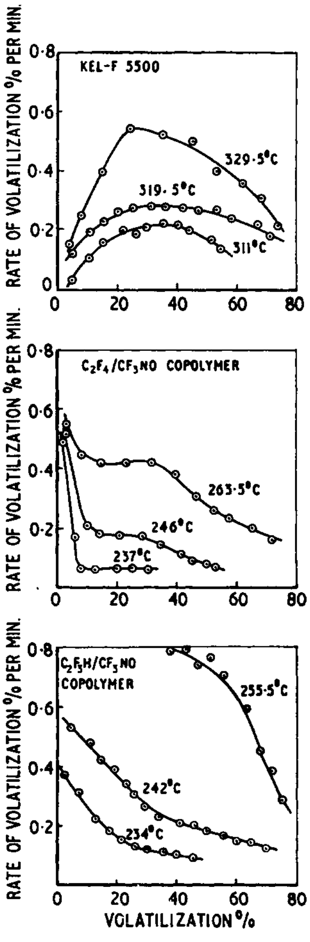

Fig. 4. Comparison of rates of volatilization of fluorine-containing polymers in oxygen

signs of stabilization at the temperatures used. The only differentiation between the curves was that in some cases the rate of volatilization decreased from the start of the reaction, whereas in others a maximum rate was attained after some degradation had occurred. This is illustrated in Figures 2–4, where the rate of volatilization has been plotted against the per cent volatilized. For the sake of clarity the results for three temperatures only are included on the graphs, though normally experiments were done at a minimum of five different temperatures. Results are not included for Viton A-HV and Viton LD-234, polyhexafluoropentylene adipate/isophthalate, Kel-F 800, and Kel-F 3700. The curves obtained were similar to those shown for Viton A, polyhexafluoropentylene adipate, and Kel-F 5500, respectively.

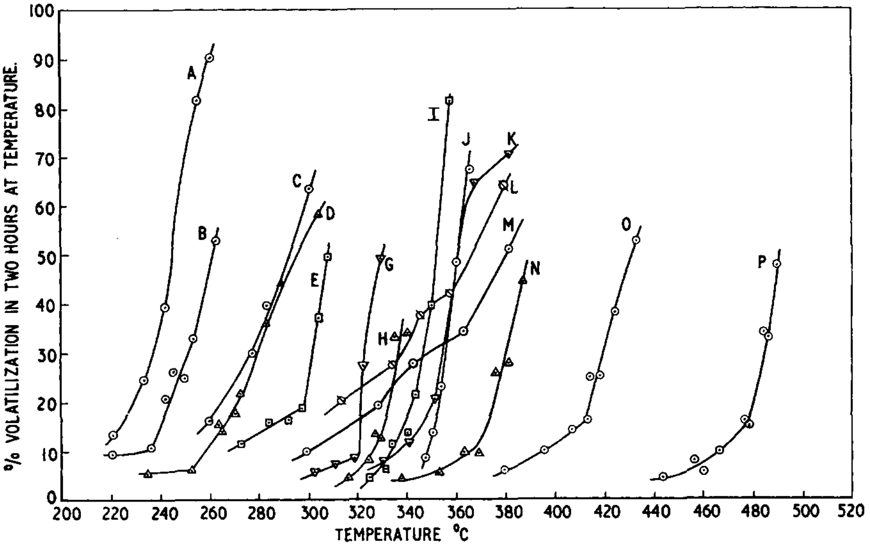

Fig. 5. Comparison of thermal stabilities of various fluorine-containing polymers in oxygen: (*A*) CF_3NO/CF_2CFH copolymer; (*B*) CF_3NO/CF_2CF_2 copolymer; (*C*) polyhexafluoropentylene adipate; (*D*) fluorosilicone A; (*E*) $[CHFCFCl]_n$; (*G*) Kel-F 5500; (*H*) Kel-F 3700; (*I*) Kel-F 800; (*J*) $[CF_2CFCl]_n$; (*K*) $[CF_2CH_2]_n$; (*L*) terephthalyl chloride/octafluorohexane-1,6-diol polymer; (*M*) butadiene/octafluorocyclohexa-1,3-diene copolymer; (*N*) Viton A; (*O*) Teflon 100X; (*P*) $[CF_2CF_2]_n$.

As has been pointed out by Wall et al.[3–5] this type of plot can yield information on certain aspects of the degradation mechanism. The point of immediate interest is the general similarity between the types of curve obtained for the same polymer in oxygen and vacuum, i.e., either a falling rate curve or one containing a maximum, was obtained in both cases. This may be taken to indicate that for these fluorine-containing polymers, regardless of the method of initiation of the breakdown of the chains (purely thermal or oxidative), the subsequent course of the reaction is very much the same kinetically.

Relative Thermal Stabilities

The relative thermal stability of the different polymers has been compared by plotting the loss in weight after an arbitrary time (2 hr.) at temperature against temperature. The time taken to attain constant temperature varied slightly from run to run and the amount of material lost during the heating-up period depended upon the temperature used. In consequence the loss in weight after 2 hr. at constant temperature was expressed as a percentage of the amount of polymer remaining when the desired temperature was first attained. The results are shown in Figure 5. In the main, the relative thermal stabilities already observed in vacuum were maintained in the oxidation experiments. The fully fluorinated poly-

TABLE I
Relative Thermal Stabilities of Polymers in Oxygen and Vacuum

Polymer	Temperature for 25% weight loss in 2 hr., °C. In vacuum	Temperature for 25% weight loss in 2 hr., °C. In oxygen	Temperature difference, °C.
Polytetrafluoroethylene	494	482	−12
CF_2CF_2/C_3F_6 copolymer, Teflon 100X	481	417	−64
Fluorosilicone B	407	289 (285)[a]	−118 (−122)[a]
Polyvinylidene fluoride	403	354	−49
Terephthalyl chloride/octafluoro-*n*-hexane-1,6-diol	401	328	−73
CF_2CH_2/C_3F_6 copolymers			
Viton A	389	378	−11
Viton LD-234	389	378	−11
Viton A-HV	382	368	−14
CF_2CH_2/CF_2CF Cl copolymers			
Kel-F 3700	365	336	−29
Kel-F 5500	362	322	−40
Kel-F 800	351	345	−6
Polychlorotrifluoroethylene[b]			
Sample 1	349	355	+6
Sample 2	346	350	+4
Sample 3	345	352	+7
Butadiene/C_6F_8 copolymer	340	338	−2
Fumaryl chloride/octafluoro-*n*-hexane-1,6-diol	320	288	−32
Poly 1-chloro-1,2-difluoroethylene	304	301	−3
Hexafluoropentylene adipate	290	272	−18
Hexafluoropentylene adipate/isophthalate	290	272	−18
Fluorosilicone A	262	276 (268)[a]	+14 (+6)[a]
CF_3NO/C_2F_4 copolymer	246	247	+1
CF_3NO/C_2F_3H copolymer	221	234	+13

[a] Figure for 15% loss of original weight, i.e., the equivalent of 25% loss in weight of organic fraction assuming all the available silicon is converted to silicon dioxide.

[b] Sample 1 prepared with ferrous sulfate/citric acid recipe; sample 2 prepared by γ-irradiation; sample 3 prepared with a silver nitrate recipe.

tetrafluoroethylene and the copolymer of tetrafluoroethylene and hexafluoropropylene were still the most stable and the copolymers containing trifluoronitrosomethane the least stable of the polymers examined. The effect of change of conditions is more clearly shown in Table I, which quotes the temperatures at which 25% loss in weight would occur in 2 hr. either in vacuum or under 300 mm. oxygen pressure. The polymers are arranged in descending order of stability according to the vacuum results. As can be seen, with the exception of fluorosilicone sample B, the use of the oxygen results would effect only minor rearrangements and that among the large number of polymers which degrade in the 320–380°C. temperature range. The effect of oxygen was more marked for some polymers, though on the basis of the weight loss figures alone it is very difficult to find any logical explanation of the results. The polymers may be divided arbitrarily into three groups: (A) those apparently relatively unaffected by oxidizing conditions (temperature difference less than −10°C.); (B) those slightly affected (temperature difference −10 to −20C°.); and (C) those more adversely affected (temperature difference greater than −20°C.) The polymers so grouped are listed in Table II.

TABLE II

Group A	Group B	Group C
Kel-F 800	Polytetrafluoroethylene	Teflon 100X
Polychlorotrifluoroethylene	Viton A, A-HV, LD-234	Fluorosilicone B
Butadiene/C_6F_8 copolymer	Hexafluoropentylene adipate	Polyvinylidene fluoride
Polychlorodifluoroethylene	Hexafluoropentylene adipate/ isophthalate	Terephthalyl chloride/ octafluoro-*n*-hexane-1,6-diol
Fluorosilicone A		Kel-F 3700
CF_3NO/C_2F_4 copolymer		Kel-F 5500
CF_3NO/C_2F_3H copolymer		Fumaryl chloride/octafluoro-*n*-hexane-1,6-diol

Leaving aside considerations of the actual chemical structure, if the temperatures for 25% weight loss in 2 hr. in vacuum for the polymers in each group are averaged, the figures 293°C., 366°C., and 391°C. are obtained for groups A, B, and C, respectively. It therefore appears as a first approximation that the effect of oxygen is relatively more deleterious on those polymers which possess higher inherent thermal stability simply because of the higher temperatures necessary for their breakdown.

Some features of the results, which would not have been apparent by inclusion in Figure 5, are illustrated in Figure 6. From this it is evident that, as in vacuum, there is little difference in the stability of the three samples of polychlorotrifluoroethylene prepared by different methods.

Variation of the composition of the vinylidene fluoride–hexafluoropropylene copolymers between narrow limits did not greatly affect the stability, but once again the higher molecular weight copolymer was less stable at the higher temperatures than its lower molecular weight analogue.

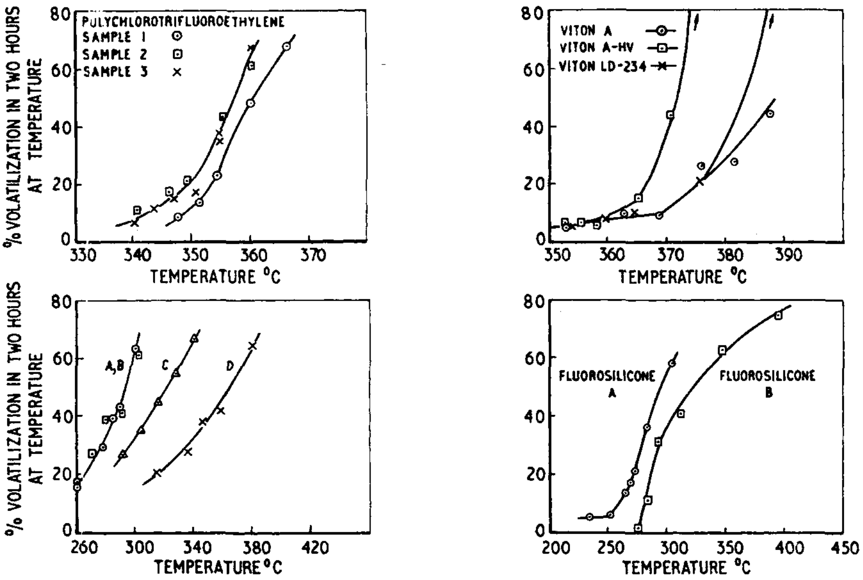

Fig. 6. Comparison of thermal stabilities of sets of polymers of related structure: (*A*) polyhexafluoropentylene adipate; (*B*) polyhexafluoropentylene adipate/isophthalate; (*C*) fumaryl chloride/octafluorohexane-1,6-diol polymer; (*D*) terephthalyl chloride/octafluorohexane-1,6-diol polymer.

Incorporation of 25 mole-% of isophthalate in the hexafluoropentylene adipate polymer had no effect on the stability observed. Substitution of the tetramethylene grouping by the vinylene and especially by the phenylene grouping caused an increase in stability. This was by no means as marked as in the vacuum experiments, the difference between the terephthalyl chloride/octafluoro-*n*-hexane-1,6-diol polymer and hexafluoropentylene adipate being reduced from approximately 110°C. to 60°C.

The two nominally identical fluorosilicones showed a slight difference in stability (10–20°C.) in contrast to the very large differentiation (approximately 150°C.) observed in vacuum. From the similarity in the rate curves for weight loss of the two samples in oxygen, compared with the apparent first-order and zero-order plots in vacuum, and from the comparable values of the overall activation energy for breakdown in oxygen (see later), it would appear that the mode of degradation for both samples in oxygen is the same, despite the presence of residual catalyst in sample A. (The difference in stability of the two samples in vacuum was ascribed to the presence of residual basic catalyst in sample A, leading to an ionic rather than a free radical mechanism of breakdown.)

Overall Activation Energies for the Degradation Processes

The overall activation energy determined by weight loss studies is a complex one, depending upon initiation, depropagation, termination,

TABLE III

Overall Activation Energies for Oxidative Thermal Breakdown of Fluorine-Containing Polymers

Polymer	Activation energy E, kcal./mole	Derivation of E	Activation energy from specific rate plot at various per cent volatilization, kcal./mole				
			10%	20%	30%	40%	50%
Polytetrafluoroethylene	78	First-order plot	78	79	82	88	96
CF_2CF_2/C_3F_6 copolymer, Teflon 100X	66	First-order plot	87	74	66	60	77
Fluorosilicone B	—	—	—	27	31	28	—
Polyvinylidene fluoride	28	Maximum rates	37	29	29	29	30
Terephthalyl chloride/octafluoro *n*-hexane-1,6-diol	—	—	21	26	34	43	—
CF_2CH_2/C_3F_6 copolymers							
Viton A	—	—	41	43	Arrhenius plot curves		
Viton LD-234	—	—		No satisfactory results obtained			
Viton A-HV	—	—	56	Arrhenius plot curves			
CF_2CH_2/CF_2CF Cl copolymers							
Kel-F 3700	36	Zero-order plot	44	37	36	37	45
Kel-F 5500	35	Zero-order plot	33	36	36	35	40
Kel-F 800	Arrhenius plot curves (41)	Zero-order plot	41	32	36	46	40
Polychlorotrifluoroethylene							
Sample 1	65	Zero-order plot	72	65	66	66	66
Sample 2	65	Zero-order plot	80	61	66	66	66
Sample 3	63	Zero-order plot	66	61	62	62	62
Butadiene/C_6F_8 copolymer	(21)	First-order plot	41	40	38	—	—
Fumaryl chloride/octafluoro *n*-hexane-1,6-diol	—	—	18	36	36	35	37
Poly-1-chloro-1,2-difluoroethylene	38	Maximum rates	—	33	38	42	39
Hexafluoropentylene adipate	37	Second-order plot	31	37	43	41	—
Hexafluoropentylene adipate/isophthalate	—	—		Arrhenius plot curves at all per cent			
Fluorosilicone A	31	First-order plot	35	31	37	36	—
CF_3NO/C_2F_4 copolymer	37	First-order plot	44	35	35	38	39
CF_3NO/C_2F_3H copolymer	45	First-order plot	43	52	53	50	47

and transfer reactions. The largest contribution to the overall energy is made by the initiation reaction, though the other factors may also be of considerable importance. A comparison of the activation energies for reactions in vacuum and oxygen may therefore give some indication as to whether a change in the method of initiation of breakdown has occurred. An analysis of the results of experiments in vacuum showed that treatment of the figures on the basis of apparent zero-order or first-order reactions gave values for the activation energies which were within experimental error of those obtained by treating the results by more refined techniques. The simpler plots have therefore been used here. For hexafluoropentylene adipate a second-order plot (i.e., the reciprocal of the amount of residue versus time) gave good straight lines, and second-order reaction constants were calculated from these. Some of the results could not be analyzed satisfactorily by either a zero-, first-, or second-order plot, by use of maximum rates, or by attempting to extrapolate the rate of volatilization against percentage volatilization curves to give an apparent initial rate. In these cases the rates of volatilization were taken for a definite fixed conversion (10, 20, 30, 40, or 50%) at a series of temperatures and used as reaction constants for calculation of an overall activation energy provided a satisfactory Arrhenius plot was obtained. Variation of the values with per cent volatilization may be taken to indicate a change in the predominant mode of initiation or breakdown. For purposes of comparison this method of calculation has also been applied to the results, which would be treated satisfactorily by one of the other methods. Details are given in Table III.

For most of the polymers there is a reasonable or even good agreement between the two sets of figures. The only glaring exception is that of the butadiene/perfluorocyclohexa-1,3-diene copolymer. The difference here may be ascribed to the fact that the first-order plot was based on results from approximately 30% volatilization onwards.

Table IV gives what are considered to be the most reasonable figures for the activation energies, together with the Arrhenius factors and rates of weight loss at 350°C. calculated from these figures. For polytetrafluoroethylene, the Viton copolymers, polychlorotrifluoroethylene, polychlorodifluoroethylene, and the trifluoronitrosomethane/trifluoroethylene copolymer there were increases or relatively little change in the activation energies for oxidizing as compared with vacuum conditions. The 350°C. rates did not differ by more than a factor of two. The Kel-F copolymers showed a large drop in activation energy for degradation in oxygen compared with vacuum and the 350°C. rates were increased by a factor of five to ten. The most deleterious effects were observed for fluorosilicone B, polyvinylidene fluoride, the tetrafluoroethylene/hexafluoropropylene copolymer, and the polymer from terephthalyl chloride and octafluoro-*n*-hexane-1,6-diol. For these compounds the rates at 350°C. in oxygen were approximately 10^2–10^3 times as great as in vacuum.

The result for the trifluoronitrosomethane/tetrafluoroethylene copolymer was somewhat anomalous, in that while there was a considerable drop in

TABLE IV
Activation Energies, Arrhenius Factors, and Calculated Rates of Weight Loss at 350°C. for Fluorine-Containing Polymers in Oxygen

Polymer	Activation energy, kcal./mole	*A* factor, sec.$^{-1}$	Rate at 350°C., %/min.
Polytetrafluoroethylene	79	10^{20}	3.3×10^{-6}
CF_2CF_2/C_3H_6 copolymer, Teflon 100X	66	10^{18}	1.2×10^{-3}
Fluorosilicone B	29	10^{11}	3.2
Polyvinylidene fluoride	29	10^{10}	0.34
Terephthalyl chloride/octafluoro-*n*-hexane-1,6-diol	20–40	—	~0.57
CF_2CH_2/C_3F_6 copolymers			
Viton A	(42)	(10^{11})	0.03
Viton LD-234	—	—	~0.07
Viton A-HV	(56)	(10^{17})	0.07
CF_2CH_2/CF_2CF Cl copolymers			
Kel-F 3700	37	10^{11}	0.69
Kel-F 5500	36	10^{11}	1.3
Kel-F 800	39	10^{12}	0.67
Polychlorotrifluoroethylene			
Sample 1	66	10^{21}	0.18
Sample 2	66	10^{21}	0.26
Sample 3	62	10^{19}	0.26
Butadiene/C_6F_8 copolymer	40	10^{12}	0.54
Fumaryl chloride/octafluoro-*n*-hexane-1,6-diol	36	10^{11}	2.8
Poly-1-chloro-1,2-difluoroethylene	38	10^{12}	5.5
Hexafluoropentylene adipate	40	10^{14}	21
Hexafluoropentylene adipate/isophthalate	—	—	—
Fluorosilicone A	34	10^{11}	10
CF_3NO/CF_2CF_2 copolymer	37	10^{13}	60
CF_3NO/CF_2CF_3H copolymer	48	10^{18}	1800

the overall activation energy it was accompanied by a decrease in the 350°C. rate in oxygen as compared with vacuum. It should be noted that the calculation of the 350°C. rate in this case was based on results obtained approximately 100°C. lower, and hence the drop in the value of the activation energy has a considerable effect on the calculated rate.

The differences observed are difficult to explain in the absence of mechanistic studies. For example it might appear that oxidative stability is reduced by the presence of vinylidene fluoride ($CF_2{=}CH_2$) but not by trifluoroethylene ($CF_2{=}CFH$) or chlorodifluoroethylene ($CHF{=}CFCl$). The vinylidene fluoride/hexafluoropropylene copolymers, however, do not differ in stability in oxygen and vacuum. This might be ascribed to some stabilizing influence of the hexafluoropropylene units under oxidizing conditions, but the stability of the hexafluoropropylene/tetrafluoroethylene copolymer is considerably less than that of polytetrafluoroethylene. Other examples might be quoted, and it follows that no firm conclusions can be drawn regarding the cause of these changes in stability without analytical evidence of the mode and products of breakdown.

Thanks are given to Dr. J. Burdon (Birmingham University), du Pont de Nemours Co., Professor R. N. Haszeldine (Manchester College of Science and Technology), Mr. W. Hopkin (Imperial Smelting Corporation), and Midland Silicones Ltd. for polymer samples.

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Résumé

On a étudié la dégradation thermique sous oxygène d'une série de polymères contenant du fluor en utilisant une technique par perte de poids. On a déterminé les stabilités thermiques relatives des différents polymères, et quand cela a été possible, l'énergie d'activation totale et les facteurs de fréquence de leur décomposition. On a comparé ces résultats avec ceux obtenus sur des échantillons des mêmes polymères décomposés sous vide. On a observé une légère variation dans les stabilités thermiques relatives dans ces deux conditions, les structures complètement fluorées étant les plus stables. Il est difficile d'interprêter les variations dans les vitesses de décomposition en présence d'oxygène si l'on n'est pas informé sur le mécanisme.

Zusammenfassung

Der thermische Abbau einer Reihe fluorhältiger Polymerer wurde in Sauerstoff unter Verwendung einer Gewichtsverlustmethode untersucht. Die relative Stabilität der verschiedenen Polymeren und, wenn möglich, die Bruttoaktivierungsenergie und die Frequenzfaktoren für die Abbaureaktion wurden bestimmt. Die Ergebnisse wurden mit denen für dieselben Polymeren im Vakuum verglichen. Unter beiden Bedingungen ist nur eine geringe Änderung der thermischen Stabilität bemerkbar, die gänzlich fluorierte Struktur ist die stabilste. Die Änderung der Abbaureaktionsgeschwindigkeit in Gegenwart von Sauerstoff ist ohne mechanistische Information nur schwer zu beurteilen.

Received January 7, 1964