

Thermal Decomposition of Fluoropolymers and Firing Characteristics of Priming Compositions with Fluoropolymers

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ABSTRACT: Many pyrotechnics contain binders, such as nitrocellulose, Viton, and other plastics and elastomers. Most pyrotechnics are prepared by the dispersion of fuel/oxidizer ingredients in a liquid solution, which are then mixed well to form pyrotechnics. The thermal decomposition behavior of a binder is very important to pyrotechnics in a polymer. In this work, the thermal decomposition be-

haviors of three fluoropolymers have been investigated with differential thermal analysis/thermogravimetry and differential scanning calorimetry. The parameters concerning decomposition have been evaluated with a nonisothermal technique, and a suitable binder is suggested for the Zr/KClO₄ priming mixture. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2054–2059, 2005

INTRODUCTION

A fluorocarbon is an organic chemical composed of fluorine and carbon atoms; it is analogous to hydrocarbons. The structures of the monomers and polymers are comparable to those of hydrocarbons, with all the hydrogen atoms replaced with fluorine. Although polytetrafluoroethylene (PTFE) polymers are classified as thermoplastics, their behaviors are not similar to those of other thermoplastic materials because they do not become fluids at moderate processing temperatures, such as 300°C, or even at temperatures approaching 498°C. PTFE has the best chemical resistance of all polymeric materials, fairly good mechanical and physical properties for many special applications, and outstanding thermal and electrical properties. Viton is also an elastomer of a fluorinated copolymer, and it has the excellent thermal stability. Prolonged exposure to temperatures greater than over 200°C does not cause scission or halogen loss. However, one of their outstanding properties is their chemical resistance. They can withstand the attack and penetration of powerful oxidizing agents such as propellant-grade red-fuming nitric acid and 90% hydrogen peroxide. These elastomers have high tensile and tear strength and high extensibility. Their other properties are comparable to those of other fluorocarbons, including electrical properties, gas permeability, and

water absorption, and they come in a latex form for processing such as casting and dipping.

To increase the energy content of composite propellants and plastic-bonded explosives, more knowledge is needed concerning the thermal behaviors of the energetic ingredients, such as the binders, oxidizers, plasticizers, and composites composed of them. Increasing both the energy content and safety of gun or rocket propellants has become one of the major interests of researchers today. Azide polymers are a particularly important class of energetic materials. Of azide polymers, glycidyl azide polymer has been widely studied in recent years as an energetic binder. Many pyrotechnics contain binders^{1–7} such as nitrocellulose and Viton, which are usually dissolved in a solvent to make a concentrated solution and then mixed with pyrotechnics (powdered metal fuels and oxidizers); the advantage of such binders is that they can be easily mixed by agitation or extrusion. Therefore, pyrotechnics can be more safely embedded into the charge holder of electroexplosive devices (EEDs) by casting or pressing.

Mixing pyrotechnics with a binder can also change the sensitivities of the pyrotechnics^{1,5,6} and influence their properties drastically by small changes in the formulation of the pyrotechnics. PTFE, consisting of —C₂F₂—, is decomposed thermally, and an oxidizing gas is produced. The oxidizing gas reacts with metal particles and releases heat, specifically with magnesium. Typical examples of PTFE-containing pyrolants are magnesium/polytetrafluoroethylene (Mg/TF) and magnesium/polytetrafluoroethylene/Viton (MTV). They are used for igniters, gas generators, and fire-

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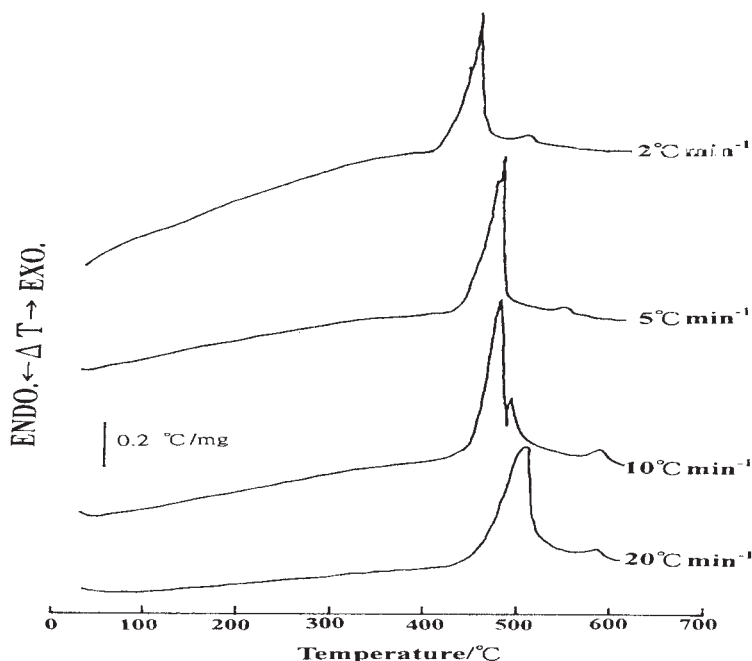


Figure 1 DTA curves of Viton A in a static air atmosphere with a 2–20°C/min heating rate.

works. The application of thermoanalytical techniques such as differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) to explosives and propellant ingredients is well established. Each individual technique has inherent value. In this work, the thermal decomposition properties of PTFE and two types of Viton were investigated with TG and DSC. Both sets of experiments were performed at various heating rates (5–30°C/min) in a static air atmosphere to determine the activation energy of the thermal decomposition.

EXPERIMENTAL

Fluoroelastomers Viton A and Viton E60C and fluorocarbon resin Teflon 7AJ are all products of E. I. du Pont de Nemours Co., Inc. Teflon 7AJ possesses a relative particle size (average, air sedimentation) of 35 μm and an apparent bulk density of 0.475 g/cm^3 . Because of their extremely high melt viscosity, all Teflon molding resins, including Teflon 7AJ, require special processing techniques similar to those used in powder metallurgy and ceramic molding. The Viton fluoroelastomers have excellent compounding and processing advantages, and their vulcanization properties are also good for acid, water, steam, heat, and fluid resistance. DSC and thermogravimetric analysis (TGA; model STD 2960), conducted with a TA Instrument TA 5000 thermal analyzer with the universal V2.5H program, were used to determine the kinetic parameters of the thermal decomposition of the fluoroelastomer and fluorocarbon resins; heating rates of

5°–30°C/min under a static air atmosphere were employed for the experiments. The surface microstructure of the fluoropolymer was observed with a JEOL JSM-6300 scanning electron microscope.

RESULTS AND DISCUSSION

DTA curves of Viton A and Viton E60C and DSC curves of Teflon 7AJ are shown in Figures 1 and 2 and Figure 3, respectively. In the Viton A curves, a broad but big exothermic peak with a maximum can be observed at 459–508°C, following a small exothermic peak from 508 to 585°C. The distribution of the small exothermic peak of Viton A in DTA curves with different heating rates shifted to a higher temperature than that of Viton E60C, and this indicates that residual Viton A is hard to remove when it is used as a binder. In the Viton E60C curves, a big, sharp exothermic peak can be observed from 460 to 503°C, following a small exothermic peak from 498 to 543°C, for Viton E60C samples heated at 2–20°C/min under a static air atmosphere. However, in the Teflon 7AJ DSC curves, a broad, small endothermic peak can be seen at 342–356°C, corresponding to the fusion of crystallization, following a big splitting exothermic peak with a maximum from 540 to 602°C. The decomposition kinetic parameters of the fluoroelastomers and fluorocarbon resin, calculated with dynamic DTA/DSC data, are listed in Table I. The activation energies of decomposition, calculated with a nonisothermal technique for the two fluoroelastomers and fluorocarbon resin, ranged from 225 to 266 kJ/mol .

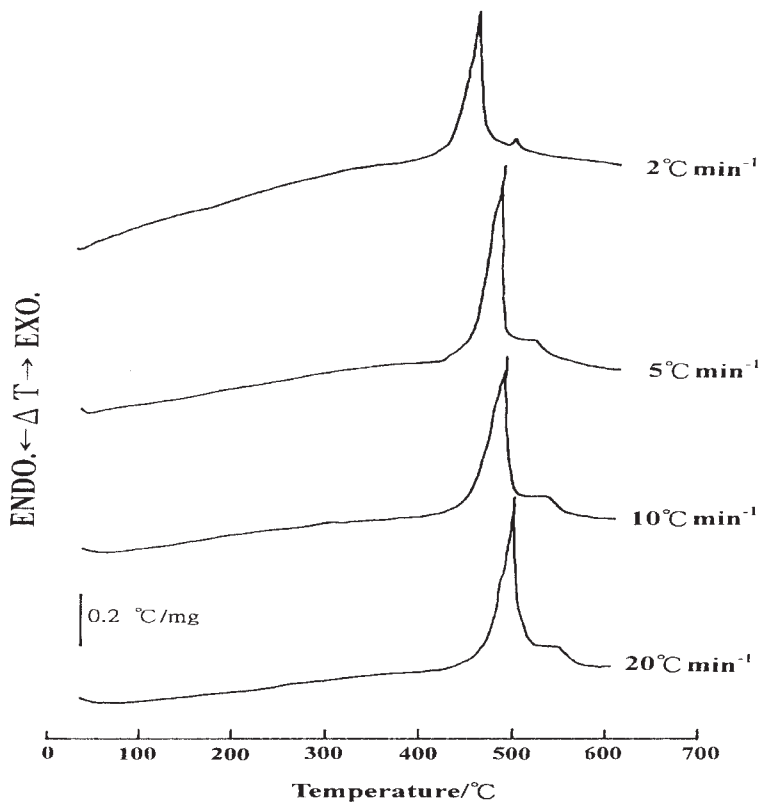


Figure 2 DTA curves of Viton E60C in a static air atmosphere with a heating rate of 2–20°C/min.

Figures 4 and 5 show the TG curves of the fluoropolymers under a static air atmosphere with a 5–30°C/min heating rate. Viton E60C and Viton A had

lower decomposition temperatures (400–500°C), and Viton A had a broad decomposition zone; this result was the same as that DTA indicated, but Teflon 7AJ

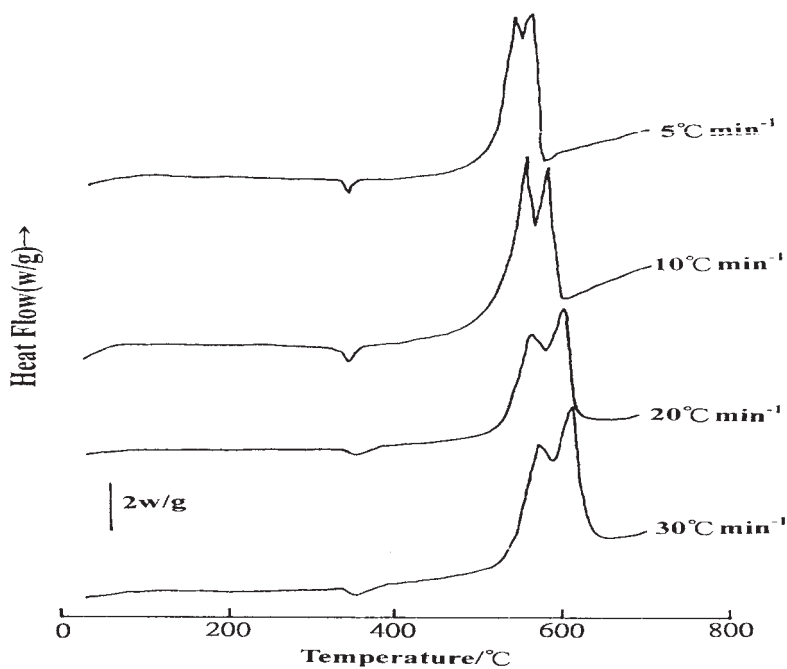


Figure 3 DSC curves of Teflon 7AJ powder in a static air atmosphere with a heating rate of 5–30°C/min.

TABLE I
Kinetic Parameters of Decomposition for
Fluoroelastomers and the Fluorocarbon Resin

	Viton A	Viton E60C	Teflon 7AJ
Activation energy of decomposition (kJ/mol^{-1}) ($-\gamma_a$)	225.8 (0.997)	255.3 (0.999)	266 (0.996)
Frequency factor $\times 10^{17}$	6.83	987	72.5

$-\gamma_a$ = correction coefficient for linear regression.

decomposed at a higher temperature (500–600°C). Table II summarizes the kinetic parameters of decomposition for the three fluoropolymers evaluated by dynamic TG techniques. The activation of decomposition for the three fluoropolymers obtained by dynamic TG techniques was close to the results of the dynamic DTA/DSC technique.

Figure 6 shows the surface morphology of the fluoropolymers after a heat-treatment procedure; for Viton E60C and Teflon 7AJ, there were no changes in the

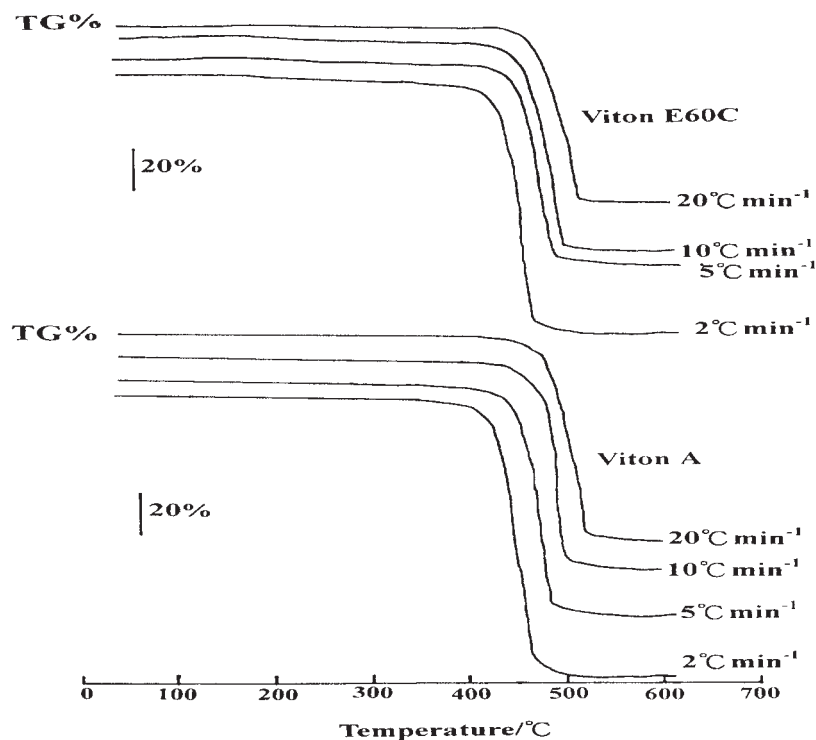


Figure 4 TG curves of Viton A and Viton E60C in a static air atmosphere with a heating rate of 2–20°C/min.

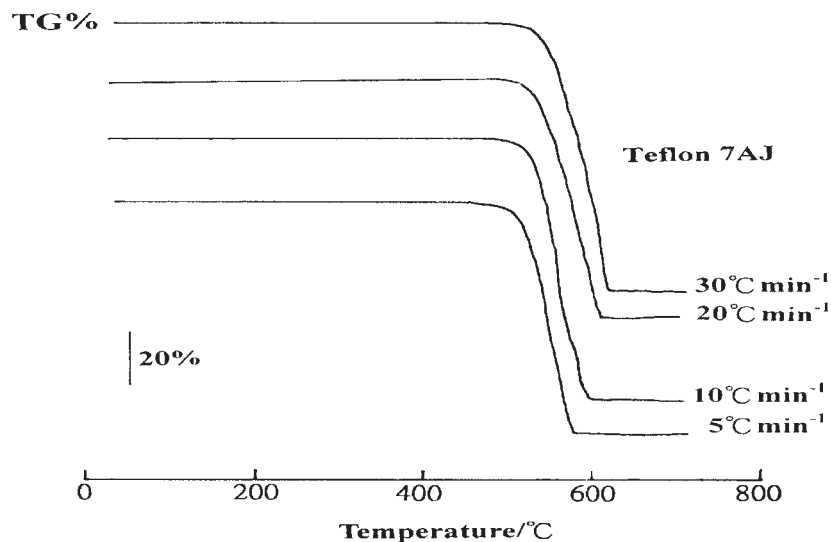


Figure 5 TG curves of Teflon 7AJ powder in a static air atmosphere with a heating rate of 5–30°C/min.

TABLE II
Kinetic Parameters of Decomposition for Three Fluoropolymers

Mass loss (%)	Viton A		Viton E60C		Teflon 7AJ	
	Activation energy (kJ/mol)	$-r_a$	Activation energy (kJ/mol)	$-r_a$	Activation energy (kJ/mol)	$-r_a$
1	45.31	0.9932	100.40	0.9749	283.9	0.9936
3	141.48	0.9934	156.40	0.9843	306.42	0.9986
5	181.76	0.9965	299.20	0.9974	312.19	0.9992
7	195.67	0.9982	289.27	0.9850	316.22	0.9998
9	198.69	0.9990	296.83	0.9926	314.11	0.9994
15	206.62	0.9986	294.31	0.9936	332.59	0.9993
20	208.16	0.9987	289.27	0.9946	332.59	0.9993
30	210.60	0.9991	287.54	0.9960	325.12	0.9987
40	213.50	0.9989	274.72	0.9966	296.83	0.9997
50	216.96	0.9994	267.94	0.9988	257.09	0.9989
60	221.17	0.9998	264.73	0.9992	244.10	0.9988
70	224.15	0.0024	253.69	0.9994	250.30	0.9998
80	228.76	0.9965	252.16	0.9985	264.34	0.9995

$-r_a$ = correction coefficient for linear regression

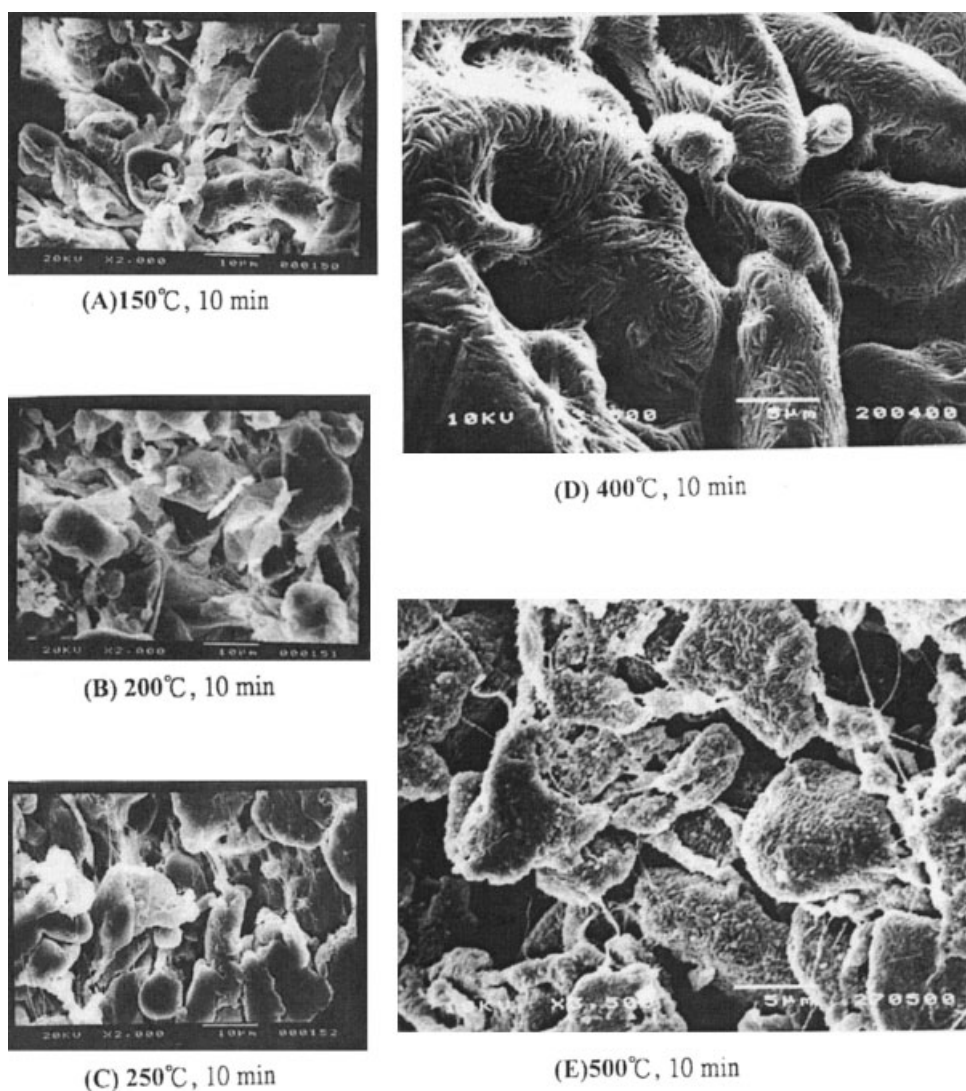


Figure 6 Microscopic images of Teflon 7AJ at different heat-treatment temperatures: (A) 150° for 10 min, (B) 200°C for 10 min, (C) 250°C for 10 min, (D) 400°C for 10 min, and (E) 500°C for 10 min.

morphology when the heat-treatment temperature was under 400°C for 10 min. However, both fluoropolymers decomposed when the heat-treatment temperature was 500°C for 10 min. These results are in agreement with the DSC results. Binders, such as Viton and nitrocellulose, can be imbedded into pyrotechnics with a solution of polymer binders. Fluoroelastomers are dissolved in ketones and lacquer solvents easily, and the thermal decomposition properties are also important in the preparation of pyrotechnics. Teflon, consisting of $-\text{C}_2\text{F}_4-$, decomposes thermally, and an oxidizing gas is produced. The oxidizing gas reacts with metal particles, and this is accompanied by the release of heat; typical examples are Mg/TF and magnesium/polytetrafluoroethylene/viton (MTV) pyrolants. The results measured by DSC/DTA and TGA indicate that the fluoroelastomers and Teflon decompose exothermically at about 460 and 540°C, respectively, under static air conditions and produce gaseous products; this thermal decomposition process provides very important information on the firing characteristics of pyrotechnics. Viton A and Viton E60C were added to a Zr/KClO₄ priming composition with a solvent method, and then the priming composition was pressed into the charge holder of EEDs to evaluate the direct-current (dc) sensitivity by the Bruceton test.⁸ Table III shows the firing characteristics of three groups of EEDs that were determined from the Bruceton test results and associated statistical calculations. Imbedding pyrotechnics in a polymer can change the firing characteristics of the priming composition drastically.

CONCLUSIONS

The thermal decomposition properties of fluoroelastomers and PTFE have been examined by using DSC/DTA and TGA, and information on the release of

TABLE III
Threshold Firing Current and Maximum No-Fire Current Within 5 min for Pressure Cartridges of Various Priming Compositions

Composition of the primer mixture	Threshold firing current (A)	Maximum no-fire current within 5 min (A)	Minimum all-fire current (A)
50/50 Zr/KClO ₄	1.82	1.63	2.30
49/49/2 Zr/KClO ₄ /Viton A	1.53	1.14	2.05
48/48/4 Zr/KClO ₄ /Viton A	1.92	1.75	2.34

energy and gaseous products were also obtained. The decomposition of fluoroelastomers occurs from 400 to 500°C for PTFE. Although the decomposition mechanism of fluoroelastomers and PTFE is not yet understood in detail, the results obtained in this study provide very important information on the firing characteristic of pyrotechnics.

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