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# Thermal degradation, kinetic and correlation models of poly(vinylidene fluoride–chlorotrifluoroetheylene) copolymers

Arjun Singh [a,b,*], P.K. Soni [a], Manjit Singh [a], Alok Srivastava [b]

[a] *Terminal Ballistics Research Laboratory, DRDO, Ministry of Defence, Explosive Division, Sector 30, Chandigarh (UT) 160 030, India*
[b] *Department of Chemistry and Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh 160 014, India*

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ABSTRACT

In this paper, thermal degradation and degradation kinetic of a poly(vinylidene fluoride–chlorotrifluoroethylene) (poly(VDF–CFTE)) copolymers are investigated by thermogravimetry (TG) under non-isothermal conditions. Thermal degradation of poly(VDF–CFTE) copolymers namely $FKM_1$, $FKM_2$, $FKM_3$ and $FMK_4$ samples is carried out at different heating rate under nitrogen atmosphere. The activation energies of poly(VDF–CFTE) samples are calculated from Kissinger–Akahira–Sunose (KAS) and Friedman kinetic methods. To investigate the kinetic model of thermal degradation for poly(VDF–CTFE) copolymers, Criado method is employed. The results showed that the probable model for the degradation of poly(VDF–CTFE) copolymers agreed with a power law and diffusion ($D_1$) model. The activation energies of $FKM_1$, $FKM_2$, $FKM_3$ and $FKM_4$ samples are found to be 196, 197, 198 and 207 kJ mol$^{-1}$, respectively.

## 1. Introduction

The first commercially available fluoroelastomer (FKM) was KeL-F developed by the M.W. Kellog Co. in the late 1950s. Subsequently 3 M Company was developed original poly(VDF–HFP) copolymers a family of FKM under the Viton trade name. The demand for high performance elastomers like FKM having high temperature and oil resistance is ever growing [1,2]. FKMs are increasingly used in high performance seal material in many industrial and space applications due to their excellent thermal, oil, and chemical resistance arising from their C—F bonds (i.e. C—F bond, 485 kJ mol$^{-1}$). The introduction of fluorine atoms into the elastomeric macromolecule generally produce materials exhibiting excellent chemical, thermal electric stabilities, inertness to acids, bases, and solvents, low dielectric constant, low refractive index, low or no flammability, high resistance to ageing and to oxidation besides interesting surface properties [3–6]. They are widely used in the many industrial applications such as gaskets, seals, and O-rings in the petrochemical, automotive, medical and electrical industries [7]. VDF based elastomers has been commercially most successful among fluorocarbon elastomers and they are still in use [8,9]. Currently, seven major manufacturers AGC Chemicals, Daikin Industries Ltd., Dupont Performance Elastomers CLC, Dyneon LLC, Kiroro-Chepetsk Chemical Plant, Precision Polymer Engineering Ltd., and Solvery Soxlers S.A have produced thermoplastics, fluoroelastomers or thermoplastic elastomers [1,10–12] according to properties and application required.

The kinetic analysis is essential for designing any kind of device, in which thermal degradation takes place. On the other hand, kinetic study is intrinsically related with the degradation mechanism. The knowledge of the mechanism allows the postulation of kinetic equation or vice-versa and kinetic is the starting point to postulate mechanisms for thermal degradation [13].

A common technique for obtaining kinetic thermal degradation parameters for polymers is thermo-gravimetric analysis (TGA). Overall kinetics can be easily obtained by measuring the change in mass of the sample with time based on isothermal or non-isothermal thermo-gravimetric data [14–19]. Thermal degradation, kinetic and degradation mechanism are very important parameters for characterizing fluoropolymers as polymeric binders for formulation of plastic bonded explosives, propellants and pyrotechnics [20]. The data collected from thermal characterization and its kinetics provide useful information in the form of prediction of safety features of the future formulations. Several researchers have evaluated a variety of analysis techniques over the years by knowing how a model can justify experimental data [11,21,22].

From the perspective of FKMs degradation, many researchers have published studies on both thermal and irradiative degradation [23–31] where attempts have been made to establish degradation kinetics. Generally, fluoropolymers are among the

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* Corresponding author at: Terminal Ballistics Research Laboratory, DRDO, Ministry of Defence, Explosive Division, Sector 30, Chandigarh (UT) 160 030, India. Tel.: +91 172 26551824 26; fax: +91 172 2657506.
*E-mail address:* arjunsngh@yahoo.com (A. Singh).

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organic materials with highest resistance to thermal degradation. Even in order to further improve the performance, the fluoroelastomer–nanocomposites were synthesized and their mechanical, morphological and swelling behaviors were extensively reported in literature [32–35]. So, far no investigation in the form of publications exists which systematically explained and analyzed thermal degradation, kinetics and mechanism of poly(VDF–CTFE) copolymers.

The main aim of this study is to investigate the thermal degradation, kinetics and reaction kinetic model of poly(VDF–CTFE) copolymer using thermogravimetric method. Two Kissinger–Akahira–Sunose (KAS), and Friedman kinetic methods are applied to study degradation kinetics. The kinetic model for degradation process is investigated by Criado method by applying different solid state process mechanisms.

## 2. Experiment and materials

### 2.1. Material

Poly(VDF–CTFE) copolymers are prepared from chlorotrifluoroethylene (CFTE) and vinylidene fluoride (VDF) by varying their molar ratios using suspension polymerization technique. The poly(VDF–CTFE) copolymers designated as $FKM_1$, $FKM_2$, $FKM_3$, and $FKM_4$ samples were prepared from VDF and CTFE at Indian Institute Council and Technology Hyderabad, India and these samples are used for study of thermal behavior as received.

### 2.2. Characterization of poly(VDF–CTFE) copolymers

Non-isothermal thermo-gravimetric of the $FKM_1$, $FKM_2$, $FKM_3$, and $FKM_4$ samples were carried out by simultaneous thermal analyzer (STA) manufactured by Mettler Toledo $851^e$ instrument. The mass of samples approximately 4 mg ± 1.0 mg was taken in alumina crucible (70 μl) and these samples were heated from ambient temperature to 600 °C for each experiment at different heating rates under nitrogen atmosphere. The data runs were fitted to KAS and Friedman. In this work, we employed five heating rates for KAS and Freidman kinetic methods to calculate activation energies at different conversion. However, Criado method was employed to evaluate reaction model at heating rate of 5 °C/min$^{-1}$ under nitrogen atmosphere.

### 2.3. Theoretical approach for kinetic study

Solid-state kinetics can be studied with thermal analytical methods [36,37] by measuring a sample property as it is heated or held at a constant temperature. The majority of kinetic methods used in the area of thermal analysis considers the rate to be function of the rate constant and a function of the conversion.

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$k$ is the reaction constant, the temperature dependence of the rate constant ($k$) is usually given by the Arrhenius equation [38]:

$$k = A\,e^{-\frac{E_a}{RT}} \tag{2}$$

where, $A$ is the pre-exponential (frequency) factor, $E_a$ is activation energy, $T$ is absolute temperature and $R$ is the gas constant. $\alpha$ is the degree of conversion, which is defined as following:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{3}$$

where, $m_0$ is the initial sample weight, $m_t$ is the sample weight at time, $t$, and $m_\infty$ is the final sample weight. The conversion dependence of the process rate can be expressed by using a wide variety of reaction models; $f(\alpha)$, some of which are presented in Table 1. Combining Eqs. (1) and (2) we have

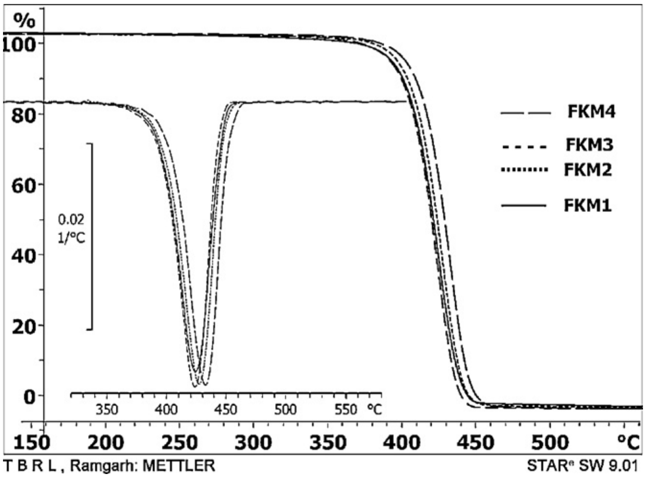

**Fig. 1.** TG curves of $FKM_1$, $FKM_2$, $FKM_3$ and $FKM_4$ samples (i) and their derivative (DTG) (ii) at heating rate 5 °C/min using STA instrument under $N_2$ atmosphere.

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} f(\alpha) \tag{4}$$

Model free kinetics is based on an isoconversional method [39–42] where the activation energy is a function of the conversion degree of a chemical reaction. Kissinger–Akahira–Sunose (KAS) method determines the activation energies without a precise knowledge of the reaction mechanism [43].

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(x)} - \frac{E}{RT} \tag{5}$$

By plot $\ln\beta/T^2$ vs. $1/\mathrm{T}$ for a constant value of $\alpha$ should be a straight line whose slope can be used to evaluate the activation energies. Freidman's method [44] is probably the most general of the differential isoconversional technique and utilizes the following natural logarithmic equation:

$$\beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{6}$$

From this equation, it is easy to obtain value for $E$ over a wide range of conversions by plotting $\ln[\beta(d\alpha/dT)]$ against $1000/T$ for a constant $\alpha$ value.

## 3. Results and discussion

### 3.1. Thermal degradation

Thermal degradation of poly(VDF–CTFE) copolymers such as $FKM_1$, $FKM_2$, $FKM_3$, and $FKM_4$ samples is studied by determining its weight loss during heating. The TG curves of $FKM_1$, $FKM_2$, $FKM_3$ and $KM_4$ samples obtained in $N_2$ atmosphere at heating rate 5 °C/min are shown in Fig. 1. These TG curves of $FKM_1$, $FKM_2$, $FKM_3$, and $FKM_4$ samples show single-step degradation with well-defined initial ($T_{\mathrm{onset}}$), final degradation temperature ($T_{\mathrm{endset}}$) and maximum degradation temperature ($T_{\max}$) and data obtained from TG curves at different heating rates are listed in Table 2. The $T_{\mathrm{onset}}$, $T_{\mathrm{endset}}$ and $T_{\max}$ values for $FKM_1$, $FKM_2$, $FKM_3$, and $FKM_4$ samples are found to increase with increasing heating rate. The weight loss of samples during thermal degradation is a function of degradation rate and time. The degradation of polymer materials has been previously studied by many researchers [45,46]. Baker and Kasprzak [47] have studied the degradation and nature of products of fluoropolymers in air.