

A Study on Thermal Behavior of a Poly(VDF-CTFE) Copolymers Binder for High Energy Materials

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ABSTRACT: This article describes a study on thermal behavior of poly(vinylidene fluoride-chlorotrifluoroethylene) [poly(VDF-CTFE)] copolymers as polymeric binders of specific interest for high energy materials (HEMs) composites by thermal analytical techniques. The non-isothermal thermogravimetry (TG) for poly (VDF-CTFE) copolymers was recorded in air and N₂ atmospheres. The results of TG thermograms show that poly(VDF-CTFE) copolymers get degrade at lower temperature when in air than in N₂ atmosphere. In the derivative curve, there was single maximum degradation peak (T_{max}) indicating one-stage degradation of poly(VDF-CTFE) copolymers for all the samples. The other thermal properties such as glass transition temperature (T_g) and degradation temperature (T_d) for poly(VDF-CTFE) copolymers were measured by employing differential scanning calorimeter (DSC) technique. The kinetic parameters related to thermal degradation of poly(VDF-CTFE) copolymers were investigated through non-isothermal Kissinger kinetic method using DSC method. The activation energies for thermal degradation of poly(VDF-CTFE) copolymers were found in a range of 218–278 kJ/mol. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Fluoropolymers are well known for their remarkable properties such as chemical, thermal, and electric stabilities, inertness of acids, and bases, low dielectric constant, low refractive index, lower or no flammability, high resistance to aging and to oxidation, and low surface energy.^{1–4} They are widely used in many industrial applications such as gaskets, seals, and O-rings in aerospace, petrochemical, automotive, medical, and electrical industries.⁵ They are also used as a polymeric binder in high energy materials (HEMs) composites such as plastic bonded explosives (PBXs) and propellants.

The most common polymeric binders used in current HEMs composites are Estane 5703P, a poly(ester urethane) block copolymer; Viton A, a vinylidene fluoride-hexafluoropropylene (VDF-HEP) copolymers and Kel-F, a vinylidene fluoride-chlorotrifluoroethylene (VDF-CTFE) copolymers.^{6–14} These binders play an important role in reducing the sensitivity as well as improving mechanical stability of HEMs composites. It is reported that fluoroelastomers are excellent polymeric binder

for HEMs composites due to their high density, better thermo-mechanical and chemical stabilities, longer shelf life and history of favorable performance.^{15–17} Vinylidene fluoride (VDF) based fluoroelastomers are the most successful commercial binders in the family of fluorocarbon elastomers and are still in use.^{18,19}

It is known that polymeric binder is mixed with HEMs to form molding compounds. These molding compounds are further processed to form molded components by processes such as pressing, injection moulding, extrusion, or hot pressing. In most cases, individual polymer materials must be processed to obtain solid samples for experimental studies, as they are often supplied in granular or pellets forms, and, so, studies of binders are limited compared with their HEMs composites. In preparation of binders for experimental studies, special care must be taken with choice of material, processing method, and control of thermal conditions, since polymer properties can vary widely with differences in temperature, thermal history, molecular weight, and percentage of crystallinity or phase separation. Thermal transitions, degradation and its kinetics are very

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important parameters for characterizing polymeric binders for formulation of PBXs, 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. The thermal degradation of HEMs has been studied by various researchers using thermal analytical techniques such as thermogravimetry (TG),^{21–23} differential scanning calorimeter (DSC),²¹ differential thermal analyzer (DTA).^{21,22} It is however observed that there are no systematic study published in the open literature linking the physical, thermal properties and kinetics of polymeric binders of specific interest for formulation of PBXs, propellants, and pyrotechnics.

The main aim of this work is to study thermal behavior of poly(VDF-CTFE) copolymers under air and N₂ atmospheres by applying thermogravimetry technique. The thermal transition, degradation, and kinetic parameters of poly(VDF-CTFE) copolymers are investigated under non-isothermal conditions using DSC technique. The kinetic of the thermal degradation of poly(VDF-CTFE) copolymers is studied by applying Kissinger kinetic method.

EXPERIMENT AND MATERIAL

Material

Fluoro-monomers like CTFE and VDF are generally used as raw materials for the preparation of poly(VDF-CTFE) copolymers. A series of poly(VDF-CTFE) copolymers was prepared from CTFE and VDF of different molar ratio by suspension polymerization technique.²⁴ The powdered poly(VDF-CTFE) copolymers designated as FPB₁, FPB₂, FPB₃, and FPB₄ samples were used for study of thermal behavior as received from Indian institute of Chemical Technology (Hyderabad, India). Methyl ethyl ketone (MEK) extra pure was used as received from MERCK.

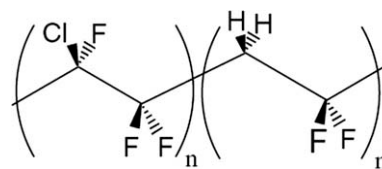
Characterization of Poly(VDF-CTFE) Copolymers

Particle density of poly(VDF-CTFE) samples was determined by using Ultracycrometer 1000 instrument (from M/s Quantachrome), which is measured the volume of poly(VDF-CTFE) copolymers. This method is based on Archimedes' principle of fluid displacement and Boyle's law for determining volume by comparing the change in pressure when the sample is introduced in the measurement chamber which has a reference standard having pre-determined volume. The displaced fluid is an inert gas (Helium) that can penetrate all but the finest pores, thereby assuring maximum accuracy. Here, Helium gas was used due to its small atomic dimensions approaching 0.25 nm in diameter. The volume of the samples was calculated using the following equation:

$$V_s = V_c - \frac{V_{\text{exp}}}{\frac{P_1}{P_2} - 1}$$

where V_s is volume of the sample, V_c is sealed cell volume, V_{exp} is expansion volume, P_1 is initial pressure, and P_2 is pressure after expansion.

Number average molecular weight (M_n) and weight average molecular weight (M_w) of FPB₁, FPB₂, FPB₃, and FPB₄ samples were determined by size exclusion chromatography using poly-



Scheme 1. The molecular structure of poly(VDF-CTFE) copolymers.

styrene as calibration standard. Size exclusion chromatography was carried out at 303 K with Shimadzu Prominence apparatus equipped with Polymer Laboratories column (PL Gel 1110-6550) and an evaporative light scattering detector (PL ELS2100) for determination of molecular weight of poly(VDF-CTFE) copolymers. Tetrahydrofuran was used as eluent at rate 0.5 mL/min and a series of narrow molecular weight polystyrenes were used as standards.

The thermal characterization of poly(VDF-CTFE) copolymers was carried out using thermal analytical techniques. The non-isothermal thermogravimetry and its derivative thermogravimetry (TG/DTG) of poly(VDF-CTFE) samples were recorded by using TGA manufactured by Mettler Toledo 851° instrument. Samples weighing 4.5 ± 1.0 mg were taken in an alumina crucible and were scanned from ambient temperature to 600°C employing a heating rate 10°C/min under N₂ and air atmospheres.

The other thermal properties such as glass transition temperature (T_g) and thermal decomposition temperature (T_d) were obtained using a differential scanning calorimeter (DSC) equipped with an intra-cooler TC100 system manufactured by a Mettler-Toledo DSC823°. The samples were accurately weighed on the Mettler micro-analytical balance, directly placed into the aluminium sample pan and sealed with lid over the sample. The weight of samples $\sim 3.5 \pm 0.5$ mg were taken for each experiment. The T_g s of poly(VDF-CTFE) copolymers were recorded in the range -50 to 100°C at heating rate of 10 K/min under N₂ atmosphere, whereas for kinetic study, the samples were scanned from ambient 550°C for each experiment at different heating rates; 5, 10, 20, and 30°C/min under N₂ atmosphere. The temperature and enthalpy of DSC apparatus were calibrated using the onset melting point of In and Zn.

RESULTS AND DISCUSSION

Physical Properties

The molecular structure of poly(VDF-CTFE) copolymers is given in Scheme 1. The solubility of polymeric binders in low molecular weight organic solvent is a primary requirement for formulating of HEMs composites. The solubility of FPB₁, FPB₂, FPB₃, and FPB₄ samples were determined by suspending 1g polymer in 10 mL of methyl ethyl ketone (MEK) and refluxing the solution for 3 h at ambient temperature. The solubility values of FPB₁, FPB₂, FPB₃, and FPB₄ samples are presented in Table I. It was observed that FPB₁ was partially soluble whereas FPB₂, FPB₃, and FPB₄ samples were completely soluble in low molecular weight organic solvent MEK thereby indicating that FPB₂, FPB₃, and FPB₄ samples can be utilized as a polymeric binder for HEMs application as far as solubility is concerned.

Table I. Particle Density, Molecular Weight, and Solubility of Poly(VDF-CTFE) Copolymers FPB₁, FPB₂, FPB₃, and FPB₄ Samples

Polymer samples	VDF:CTFE monomer (By mole)	Molecular weight (g/mol)			Particle density (g/cm ³)	Solubility (%)
		$M_n \times 10^3$	$M_w \times 10^3$	M_w/M_n		
FPB ₁	1 : 3.0	56.1	132.2	2.3	2.17	65
FPB ₂	1 : 2.5	77.5	130.4	1.68	2.02	93
FPB ₃	1 : 2.25	503.6	982.5	1.95	1.92	95
FPB ₄	1 : 2.0	785.5	801.2	1.02	2.18	97

The particle densities of poly(VDF-CTFE) copolymers were measured by pycnometer instrument in Helium gas and the results are shown in Table I. The results show that FPB₁ and FPB₄ samples have higher particle density compared to the remaining samples. It is known that higher the particle density of a polymeric binder, higher will be the performance of HEMs composites. The results of M_n and M_w FPB₁, FPB₂, FPB₃, and FPB₄ samples are also listed in Table I.

Thermal Degradation of Poly(VDF-CTFE) Copolymers

To understand the effect of environment on thermal degradation of poly(VDF-CTFE) copolymers, TG measurements were carried out from ambient temperature to 600°C under N₂ and air atmospheres. The TG and DTG profiles related to poly(VDF-CTFE) copolymers namely FPB₁, FPB₂, FPB₃, and FPB₄ samples are shown in Figure 1 under N₂ atmosphere. Similarly, Figure 2 showed TG and DTG profiles of poly(VDF-CTFE) copolymers in air atmosphere. The data obtained from these curves are listed in Table II. The TG thermograms of FPB₁, FPB₂, FPB₃, and FPB₄ samples showed that weight loss occurred in a single step in a range of 380–430°C. Although, the overall profile of weight loss by thermal degradation of FPB₁, FPB₂, FPB₃, and FPB₄ samples were almost similar up to 370°C in both N₂ and air atmospheres, the thermal degradation temperature of poly(VDF-CTFE) copolymers samples showed a drastic change at higher temperature under air and N₂ atmospheres. The TG data indicated that the thermal degradation for all samples occurred earlier in air atmosphere as 387–416°C, whereas

thermal degradation in N₂ atmosphere occurred at higher temperature in range of 411–430°C. This indicated that air oxidation may be playing an important role in bringing about degradation of the copolymeric materials. A similar observation for single degradation peak has been reported by other researchers on thermal degradation of fluoropolymers.²⁵ It was observed that FPB₄ samples had shown a higher thermal degradation temperature than other samples. The DTG results also showed low maximum temperature peak (T_p) values in air than T_p in N₂ atmosphere for all samples.

DSC Analysis

The thermal properties such as T_g and T_d of poly(VDF-CTFE) copolymers were measured by DSC technique. The DSC curves and data obtained from DSC instrument are presented in different sets to demonstrate the thermal behavior.

Glass Transition Temperature. T_g is a very important parameter of the fluoroelastomer samples used as polymeric binders for HEMs composites. The mechanical properties of HEMs composites are significantly influenced by their thermal transitions. It is reported that T_g affects both the rheological properties of HEMs as well as basic parameters of polymeric binders obtained from them.^{26–28} T_g s of FPB₁, FPB₂, FPB₃, and FPB₄ samples were measured in the range –50 to 100°C and DSC curves are shown in Figure 3. The T_g data obtained from DSC curves are listed in Table III. The measurements showed that T_g values for FPB₁, FPB₂, FPB₃, and FPB₄ samples increased with

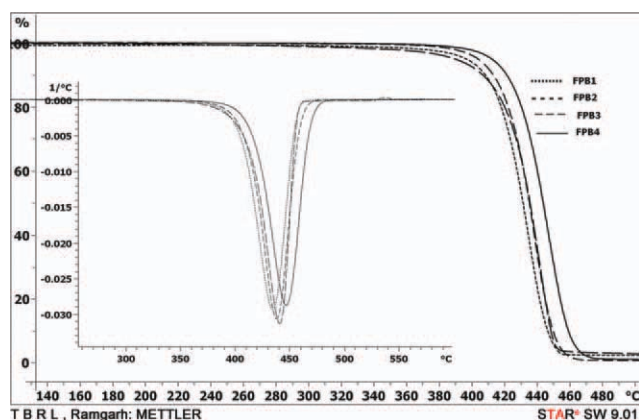


Figure 1. TG and DTG curves of poly(VDF-CTFE) FPB₁, FPB₂, FPB₃, and FPB₄ samples at heating rate of 10 °C/min under N₂ environment. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

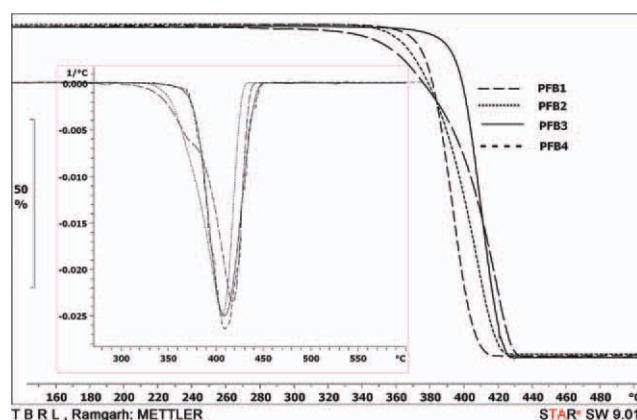


Figure 2. TG and DTG curves of poly(VDF-CTFE) FPB₁, FPB₂, FPB₃, and FPB₄ samples at heating rate of 10°C/min in air environment. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

Table II. TG Data of T_{onset} , T_{endset} , and T_{max} of Poly(VDF-CTFE) Copolymers Obtained from TG Curve

Samples	Decomposition temperature (°C) (in N ₂)			Residue (%)	Decomposition temperature (°C) (in O ₂)			Residue (%)
	T_{onset}	T_{endset}	T_{max}		T_{onset}	T_{endset}	T_{max}	
FPB ₁	415.4	446.7	434.0	2.3	403.9	444.9	433.4	1.7
FPB ₂	420.4	449.4	437.4	1.3	389.6	420.0	409.7	2.4
FPB ₃	420.1	448.8	440.1	1.4	400.7	437.6	414.1	1.6
FPB ₄	426.5	459.7	446.0	2.4	394.5	424.9	413.3	2.4

increasing CTFE to VDF molar ratios. The T_g of a polymer is a most important property because it determines the range of temperatures for processing and the range for applications.²⁹ This temperature is the boundary between a low temperature stiff, glassy state, and a high temperature rubbery state.³⁰

Thermal Degradation by DSC. DSC curves of FPB₁, FPB₂, FPB₃, and FPB₄ samples copolymers obtained at different heating rates 5, 10, 20, and 30 °C min⁻¹ are depicted in Figure 4. The data derived from these DSC curves are listed in Table IV. The DSC curves representing FPB₁, FPB₂, FPB₃, and FPB₄ samples showed a single-step decomposition and well defined initial (T_{onset}), final decomposition temperatures (T_{endset}), and T_p . The temperature for the maximum degradation rate was found to increase with increasing heating rate. The DSC results indicated that the thermal decomposition for all samples occurred at higher temperature in a range of 394–439°C. The DSC data is further supported for TG/DTG results where poly(VDF-CTFE) copolymers exhibited almost the same thermal degradation pattern. The results indicated that poly(VDF-CTFE) copolymers showed a better thermal stability as compared to reported fluoropolymer.²⁵ The enthalpy (ΔH) of the endothermic processes for poly(VDF-CTFE) copolymers is listed in Table IV.

Degradation Kinetics. Kissinger's method is one of the differential methods that have been used by researchers to determine the activation energy of solid state reactions from plots of the

logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate. The advantage of this method is that even without a precise knowledge of the reaction mechanism and reaction order, the activation energy of solid state reaction can be determined using the following equation:

$$E_a \beta \left(RT_p^2 \right) = A e^{-E_a/RT_p} \quad (1)$$

where A is the frequency factor and β is the heating rate, which is expressed as $\beta = dT/dt$. Taking the logarithm of the above equation, we obtain:

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \left(\frac{AR}{E_a} \right) - \frac{E_a}{RT_p} \quad (2)$$

where T_p is top peak temperature at maximum reaction rate, E_a is the activation energy, and R is the universal gas constant (8.314 J/mol/K). Therefore, if Kissinger's assumptions are correct, a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ gives linear slope ($-E_a/R$) for evaluation of activation energy. It is interesting to note that Kissinger's method though initially developed for first-order reactions holds good for any kinetic model.^{31,32}

The Kissinger eq. (2) was employed to determine activation energy of FPB₁, FPB₂, FPB₃, and FPB₄ samples from DSC data by Kissinger's plots $\ln(\beta/T_p^2)$ versus $1000/T$ at maximum reaction rate of decomposition. The Kissinger plots of $\ln(\beta/T_p^2)$ against $1000/T$ of FPB₁, FPB₂, FPB₃, and FPB₄ samples are shown in Figure 5. The E_a s calculated from the slope are shown in Table V. It is observed that the activation energies for thermal degradation of FPB₁, FPB₂, FPB₃, and FPB₄ samples were 247, 238, 219, and 278 kJ/mol, respectively.

Comparing the obtained data with literature shows that the kinetic parameters are unique to each individual type of fluoropolymers. Prasad et al.³³ reported thermal degradation

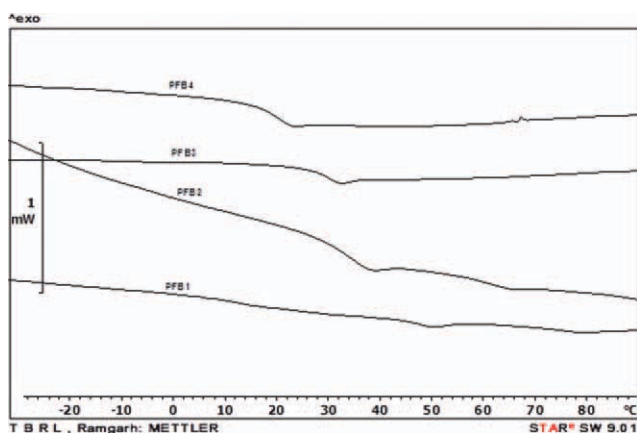


Figure 3. DSC curves of poly(VDF-CTFE) FPB₁, FPB₂, FPB₃, and FPB₄ samples at heating rate of 10°C/min in N₂ environment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. The T_g and T_p of Poly(VDF-CTFE) FPB₁, FPB₂, FPB₃, and FPB₄ Samples Using DSC Technique

S. No.	Samples	T_g (°C)	T_p (°C)
1.	FPB ₁	48.6	438.3
2.	FPB ₂	34.7	446.3
3.	FPB ₃	28.9	439.7
4.	FPB ₄	20.3	451.2

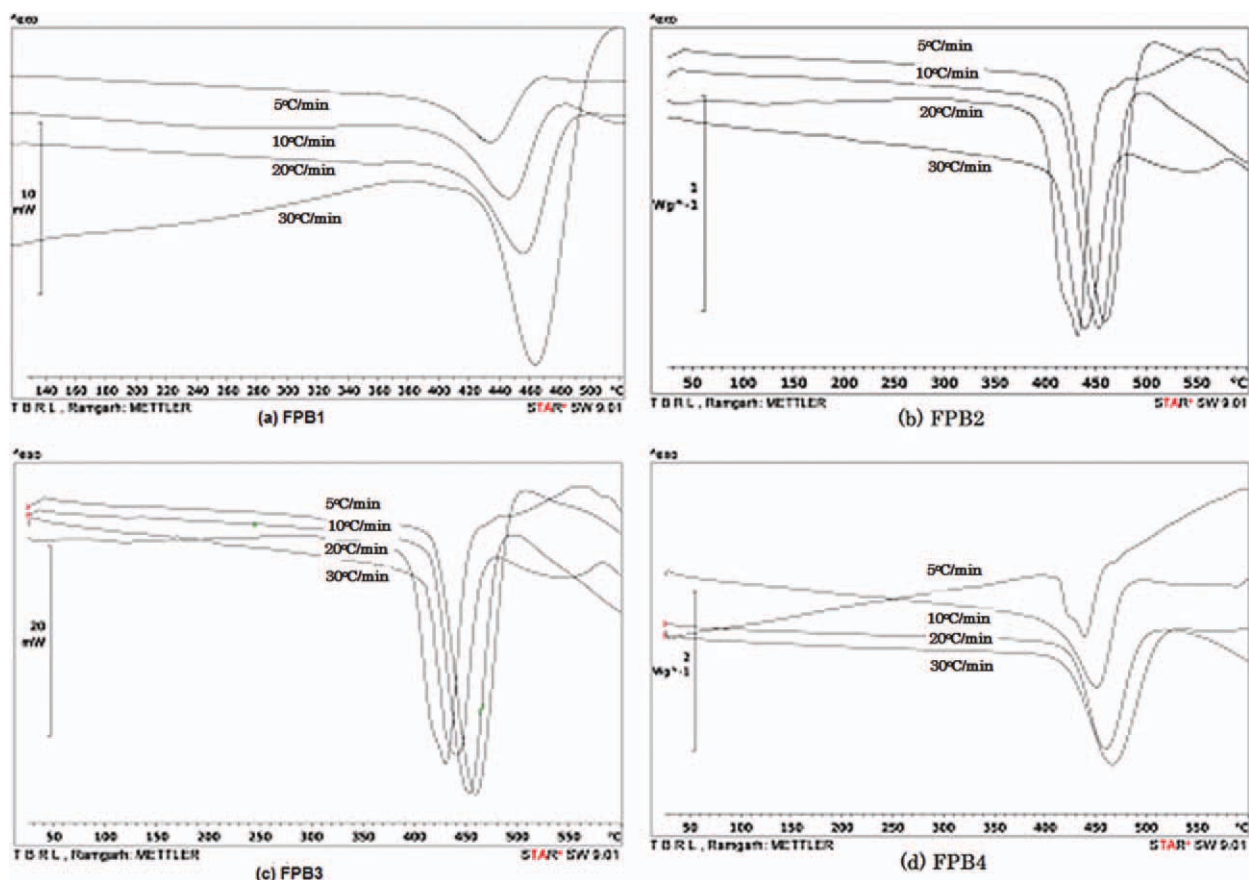


Figure 4. Thermal decomposition of poly(VDF-CTFE) (a) FPB₁, (b) FPB₂, (c) FPB₃, and (d) FPB₄ samples at four heating rates: 5, 10, 20, and 30 °C/min in N₂ environment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. The Data of T_{onset} , T_{endset} , and T_{max} Obtained from DSC Curves of FPB₁, FPB₂, FPB₃, and FPB₄ Samples

S. No	Sample	Heating rate (°C/min)	Temperature (°C)			ΔH (J/g)
			T_{onset}	T_{endset}	T_{max}	
1.	FPB ₁	5	398.1	464.4	431.4	484
		10	411.8	465.4	439.5	724
		20	418.6	476.0	451.3	723
		30	424.2	481.6	460.5	705
2.	FPB ₂	5	398.5	463.4	432.2	369
		10	407.0	472.1	439.7	393
		20	417.1	480.4	454.7	415
		30	437.5	490.6	463.8	461
3.	FPB ₃	5	394.6	451.1	430.3	345
		10	398.7	464.7	444.9	310
		20	414.0	477.2	454.8	346
		30	425.1	492.8	463.7	392
4.	FPB ₄	5	399.7	478.6	437.7	410
		10	434.6	484.2	449.5	577
		20	435.9	494.0	457.4	517
		30	438.1	495.1	463.9	578

kinetic for a Tefzel fluoropolymer in the range 359–550 °C by TG and 235–270 °C by DSC under nitrogen flux by using Fuoss’s relationship. The activation energy for decomposition was 53.3 kcal/mol in TG, whereas it was 9.5 kcal/mol in DSC. Other researcher³⁴ also reported pyrolysis kinetic of Kel-F polymer and found the activation energies in the range of 209–285 kJ/

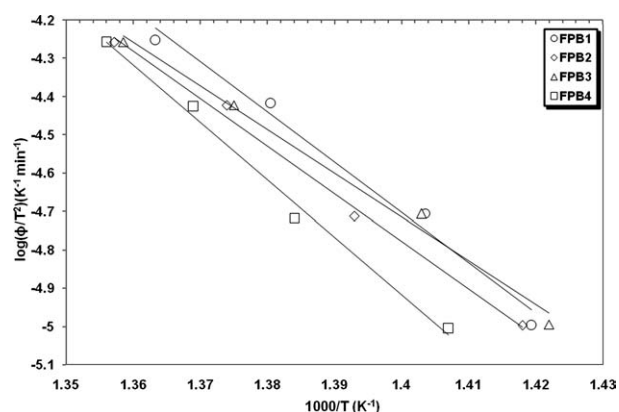


Figure 5. Kissinger’s plots of poly(VDF-CTFE) polymers (a) FPB₁, (b) FPB₂, (c) FPB₃, and (d) FPB₄ samples applied at the top of the peak in N₂ environment using DSC method.

Table V. Kinetic Parameters of Poly(VDF-CTFE) FPB₁, FPB₂, FPB₃, and FPB₄ Copolymers by Kissinger's Method

Polymer samples	Activation energy (kJ/mol)	γ_a
FPB ₁	247.4	0.983
FPB ₂	237.6	0.994
FPB ₃	218.6	0.990
FPB ₄	277.5	0.992

γ_a = correlation coefficient for linear regression.

mol. The difference in the results obtained in our study and those found by other workers are probably due to the differences in types of fluoropolymer, synthesis conditions and rates of pyrolysis.

CONCLUSION

According to results presented in this article, it is concluded that solubility of poly(VDF-CTFE) copolymer seems to increase in common solvents with decreasing CTFE to VDF molar ratio, which is due to increase polar nature of vinylidene unit in poly(VDF-CTFE) copolymers. The poly(VDF-CTFE) copolymers are less stable in air than in N₂ atmosphere which indicating that air is oxidizing the fluoropolymer samples. Comparing the thermal degradation of poly(VDF-CTFE) copolymers samples in N₂ atmosphere, FPB₄ sample seems to better thermal stability than other samples. Thermal property, i.e., T_g of poly(VDF-CTFE) could be tailored by varying CTFE to VDF molar ratio for application of HEMs binder. The kinetic study shows that the activation energies of FPB₁, FPB₂, FPB₃, and FPB₄ samples are 247, 238, 219, and 278 kJ/mol, respectively. These studies clearly indicate that poly(VDF-CTFE) copolymers with higher particle density, soluble in organic solvent, higher thermal stability, and higher activation energy can be considered as a potential candidate for use as polymeric binder for HEMs applications.

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