Thermal Degradation Kinetics of High Temperature Polymers for Aeronautic Cables Insulation

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Abstract – The perspective of increasing on board power on aircrafts leads to reconsider cable technologies, among which insulation processing. In this work, the thermal stability of three materials, Polyimide, Polytetrafluoroethylene and perfluoroalkoxy (PFA) is investigated. Based on a multi-step degradation model applied to thermogravimetric analysis curves, isothermal degradation curves are predicted. Outstanding thermal stability is anticipated for PFA on a chemical standpoint. With the advantage of being an extrusion-processable polymer, PFA constitutes therefore an excellent candidate for high performance cables with extruded insulation.

Keywords: high temperature insulation, aeronautic applications, thermal degradation, fluorinated polymers

1. INTRODUCTION

In recent years, with the development of electrical and electronic insulating applications to the trends of high power and high current, small and thin profile, high density, and high integrity, the demand to the high-thermal-class polymer dielectrics has been increasingly emphasized so as to maintain high reliability of the devices operating at "high temperatures" [1]. High temperature is usually defined as an operating temperature higher than 175°C. The service temperature in aeronautic applications can be as high as 250°C [1]. At such temperature, there are not so many candidate materials. For cables, once processability, flammability and security are taken into account, mainly polyimides and fluorinated polymers families remain. With taped insulation technologies, they are combined, polyimide bringing thermal and electrical endurance when fluorinated polymers have high performances for thermal and fire endurance and arc tracking. Increasing the power demand on aircrafts imposes to consider high voltage for on-board networks, with new challenges regarding design of power cables. In this context, taped cable technology, which may induce some void formation within the insulation, is reconsidered. Candidate materials for extrusion-processed insulation are explored, with as objective to fulfil thermal endurance performances already reached.

The most common tool for assessing thermal withstanding of polymers is monitoring mass loss using thermogravimetric analysis (TGA). TGA constitutes a very convenient way to analyse degradation. The kinetics of material degradation has been analysed in a number of works based on TGA under temperature ramp and then converted into a life model [1-5]. Drawbacks are on a degradation rate considerably fastened under ramped temperature and on ageing consequences viewed as a mass loss only.

Predictive kinetic models for degradation have been developed and parameterized by Hondred *et al* [6, 7] for Polytetrafluoroethylene (PTFE) and Polyimide (PI) among other polymers. The degradation was analysed as a multi-step reaction. In the present work, these kinetic data are exploited in order to establish the time dependence of mass loss in isothermal conditions at different temperatures in the range 250 to 350°C. It leads to a thermal life model based on mass loss criterion. Experimental data and analysis on perfluoroalkoxy (PFA), a high-end fluorinated thermoplastic co-polymer having the capability of being extrusion-processed, are included in the analysis. This provides a frame for the comparison of the relative merit of these materials as a function of temperature. The limitations of the approach for application to real cables in aerospace domain are discussed.

2. KINETIC MODEL AND APPLICATION

The degradation kinetics, analysed as a multi-step reaction, follows:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \quad (1)$$

in which $K(T)$ is the temperature dependent rate constant for the reaction, and $f(\alpha)$ is a function encompassing changes in the response of the material due to degradation: α is the material property that is being followed - mass loss here:

$$\alpha(t, T) = 1 - \frac{wt. \%}{100} \quad (2)$$

In case of thermal oxidation, $f(\alpha)$ contains an autocatalytic contribution to the rate constant. The subtlety in the model is in the form of the ageing function. Expanding the kinetic analysis from a single-step reaction to a multi-step reaction, the differential equations are separated based on each step of the reaction. The overall degree of degradation is constructed as follows:

$$\alpha(t, T) = \sum_j w_j \alpha_j \quad (3)$$

where α is the total fractional mass loss, α_j is the extend of conversion of a reaction step, w_j is the specific contribution of a reaction step into total mass loss, and j represents the given reaction step [5]. For each of the degradation steps, the rate constant is defined by its activation energy E_j and the pre-exponential factor A_j :

$$K_j(T) = A_j \cdot \exp\left(\frac{-E_j}{kT}\right) \quad (4)$$

A. Polyimide

From the analysis of TGA curves obtained at different heating rates, using a multivariate approach Hondred *et al* [6] obtained a set of kinetic parameters representing the different steps in the oxidation as given in Fig. 1 and Table 1. The apparent complexity of the process comes from the apparent double-step in the TGA curves at high heating rate.

For each of the steps, the generic governing differential equation, presented in (1), defines the reaction model, $f(a_j)$, such that:

$$f(a_j) = (a_j)^n (1 + K_{cat-j} a_{j+1}) \quad (5)$$

where a_j represent the reactants (or products) concentrations in the different steps (A, B, C..) of the oxidation process, n represents the reaction order and K_{cat} the autocatalysis constant, i.e. the parameter reflecting kinetics changes with degradation.

Fig. 1. Schematic representation of the multistep reaction for the oxidation of Polyimide. From [6].

TABLE I. KINETIC PARAMETERS FOR PI DEGRADATION [6]

Step	Activation energy (eV)	A_i (s^{-1})	Reaction order	K_{cat}
1	1.983	2.15×10^8	0.77	8.71
2	1.981	2.40×10^8	0.75	8.51
3	1.765	5.37×10^7	0.89	1.23
4	1.05×10^{-3}	3.72×10^{-4}	3.17	44.7
5	0.102	6.76×10^{-4}	0.40	24.0

In order to predict isothermal mass losses, the time dependence of concentrations in the various processes was computed for different isothermal conditions. A missing information in the original paper is the mass loss contribution each of the steps represents in the thermal degradation. From an analysis of the degradation dependence of the mass loss activation energy based on either Ozawa's [3] or Friedman's analysis [2], it resulted that the activation energy was nearly unchanged for mass loss up to 20%, and corresponds to the one given by steps (1) and (2) [6]. Comparison of present output data to model and experimental isothermal data provided at 475°C in [6], reveal that the main contribution is from the $A \rightarrow B$ processes, i.e.

$$\alpha(t, T) = 1 - a(t) \quad (6)$$

Therefore, the degradation kinetics is supposed correctly accounted for by these two first steps.

$$\frac{d\alpha(t, T)}{dt} = \sum_{j=1,2} K_j(T) (1 - \alpha)^{n_j} (1 + K_{cat-j} \alpha) \quad (7)$$

$$\alpha(0, T) = 0, \alpha \leq 1$$

Results obtained on mass loss are consistent with those simulated by Hondred *et al* for isotherms at 475 and 450°C, which satisfactorily agreed with experimental results for 125 μm thick Dupont Kapton HN® films.

Fig. 2 shows isothermal mass loss curves obtained in this way. According to the model, the time for 5% mass loss at 250°C is 336 000 h (460 months). The lines drawn in Fig. 3 are with an activation energy of 1.98 eV, i.e. grossly the one for the first 2 steps in Table I. It fits correctly for the mass losses of 5 and 10% and underestimates the time for 50% loss. This provides a guideline for PI thermal stability, for free standing films in air, which represents a worse case compared to PI protected by a PTFE layer. Note that the resolution can be applied to arbitrary time dependence of the temperature, including ramp in TGA.

Fig. 2. Isothermal mass loss kinetics of PI obtained by simulation following (7).

Fig. 3. Temperature dependence of time for 5%, 10% and 50% mass loss.

B. PTFE

The test configurations consisted of single layer insulated cables either wound around a metal mandrel or with a section laid flat against a metal plate (ASTM methods) or by pulling a metal braid along them before testing (EN method). Below is a description of the methods with indication on the way it was implemented by the different labs, designated as A through D.

The approach presented above for PI was applied to the case of PTFE [7]. The degradation kinetics in PTFE could be described by a single step kinetics with:

$$f(\alpha) = (1 - \alpha)^n(1 + K_{cat}X) \quad (8)$$

where X represents the 'step of the reaction', normally the reaction result, assimilated to α here.

Then the reaction kinetics obeys:

$$\frac{d\alpha}{dt} = K(T) \cdot (1 - \alpha)^n(1 + K_{cat}\alpha) \quad (9)$$

with activation parameters given in Table 2. Fig. 4 and 5 show isothermal mass loss curves obtained using (9). According to this model, the time for 5% mass loss at 250°C is 63 000 h, being shorter than for PI by a factor of 5. At 260°C, the 5% mass loss is for 30 000 h. The lines drawn in Fig. 5 are with an activation energy of 1.77 eV. It fits the process for all mass loss fractions as the kinetics is simpler than for PI. Also, the drop in mass is faster than for PI.

The above analysis has to be tempered by the fact that PTFE is a semi-crystalline polymer with high degree of crystallinity. So, the kinetics that holds at temperature beyond the melting point may be different, expectedly faster than under it: in the analysed TGA curves, degradation is above 450°C, whereas the melting point is at 330°C. Therefore, the thermal withstanding at 300 or 250°C can be better than predicted.

TABLE II. KINETIC PARAMETERS FOR PTFE DEGRADATION [7]

Step	Activation energy (eV)	A_i (s^{-1})	Reaction order	K_{cat}
1	1.77	1.78×10^7	0.74	14.45

Fig. 4. Isothermal mass loss kinetics of PTFE obtained by simulation following (9).

Fig. 5. Temperature dependence of the time for 5% mass loss for PI, PTFE and PFA.

3. THERMAL DEGRADATION OF PFA

There are far less literature data about PFA compared to PI or PTFE. Main data are with product datasheets without much detail on the way it was obtained [8]. PFA has similar performances and application fields as PTFE and the properties are often compared. A main advantage of PFA is the processability through extrusion process. It is a semi-crystalline polymer with typical crystallinity of 60% [9]. Commercial grades of PFA melt typically in the temperature range from 300 to 315°C.

A. TGA data

As no TGA data similar to those presented for PI and PTFE are available for PFA, measurements were achieved on Daikin Neoflon® PFA AP-210 material. Experiments were performed in air atmosphere, on samples having 15 mg typical mass using TQ500 TA instrument.

Fig. 6 shows the TGA curves obtained at heating rates of 2, 5, 10 and 20°C/min. Comparatively to PTFE, the curves for PFA show much less heating rate dependence: the shift is by about 40°C for PFA and about 80°C for PTFE when changing the heating rate from 2 to 20°C/min. Obviously, this is reflected by a much larger activation energy in case of PFA.

Fig. 6. TGA curves at different heating rates for PFA.

B. Kinetic Analysis

The analysis developed for PI and PTFE [6, 7] was applied to the case of PFA. By plotting the following quantity for isoconversion (iso- α) condition, it can be assessed whether several processes contribute to the degradation and if the kinetics depends on the progress of the reaction:

$$\ln \left[\beta_i \left(\frac{d\alpha}{dT} \right)_{\alpha,i} \right] = \ln(A_\alpha f(\alpha)) - \frac{E_\alpha}{kT_{\alpha,i}} \quad (10)$$

Here the relation is taken for a particular value of the conversion degree α , and β_i represents the heating rate for the TGA thermogram i . Fig. 7 shows the Friedman's plot, i.e. a representation of (10), for the 4 heating rates obtained using $d\alpha/dT = -1/m_0 \cdot dm/dT$ where m is the sample mass. The lines correspond to isoconversion lines. If parallel lines are found as the conversion progresses, it tends to mean that a single process is in operation, with unchanged activation energy. From the progression of the lines with the conversion degree [10], it can be deduced that degradation of PFA is rather a slightly retarded process.

Activation energies and pre-exponential factors were obtained from the slopes and intercepts of the lines shown in Fig. 7. Activation energies in the range from 3.44 to 4.29 eV were obtained, which represent much less variation than reported for PTFE (50% in Friedman's plot [7]). The same kinetic model as for PTFE is adopted here. In order to avoid fluctuations in pre-exponential factor due to fluctuation in activation energy, the latter was set to 3.6 eV, and the pre-exponential factor was recalculated as to give the same value of $\beta \cdot d\alpha/dT$ at the average temperature over the 4 heating rates. Finally, a fit on pre-exponential factor vs. α was achieved to obtain the kinetic parameters A , n and K_{cat} of (9). The fitting curves for the TGA thermograms are given as dashed lines in Fig. 6 and kinetic parameters in Table III.

TABLE III. KINETIC PARAMETERS FOR PFA DEGRADATION

Step	Activation energy (eV)	A_i (s^{-1})	Reaction order	K_{cat}
1	3.60	2.01×10^{20}	1.23	-0.71

Fig. 7. Friedman's plot (mass variation rate vs. reciprocal temperature according to (10)) applied to TGA data on PFA.

Some deviations occur at the beginning and end of each curve; however, the overall shift is correctly accounted for. Here the autocatalytic parameter is negative, meaning that the reaction tends to be slower when progressing. Intuitively it could correspond to a situation where oxygen is diffusion limited. Obviously the activation energy for PFA is significantly higher than for PTFE, which is appealing. Large differences in activation energy was found between that report by Hondred *et al* for PI (less than 2 eV in Table 1) and that reported in a different study on the same material (Kapton HN®), being 2.6 to 3 eV [11]. As a consequence, the estimated time for 5% mass loss in isothermal conditions at 350°C is 3-6 years when it is to only a few days in here.

Fig. 8 shows isothermal conversion curves obtained for different temperatures. As expected due to the high activation energy, the stability is strongly temperature dependent. Considering Fig. 5, it comes out that at low temperature PFA would be more stable than PTFE whereas at the highest temperature, it would be less. Other models for analysing TGA curves exist, including the one consisting in maintaining a activation energy depending on conversion degree [11, 12]. However, irrespective of the model, the main trends will be maintained. Indeed, if TGA curves are weakly dependent on the heating rate, then the activation energy will be high. Besides what is important for the application is the kinetics for the first steps of degradation, not that at play at advanced conversion degree.

Fig. 8. Isothermal mass loss kinetics of PFA obtained by simulation following (9).

Perhaps what is more disputable in the exercise achieved here is the sampling on the one hand, which may affect degradation kinetics according to sample mass, and most importantly the extrapolation. Indeed, fast degradation forced in TGA may not be transposable to the isothermal behaviour at substantially lower temperature because materials undergo thermal transitions and because other competing chemical processes not dominant at high heating rate (involving for example oxygen diffusion) may become effective at lower temperature/longer time.

For these reasons, monitoring physicochemical properties as a function of isothermal ageing time is necessary. Said that, the thermal performances of PFA appear very promising. With reported breakdown field similar to that of PTFE [8], with very low losses, these features make PFA an excellent candidate for extruded insulation of high performances cables.

4. CONCLUSION

A multi-step degradation model was used to convert mass loss obtained by thermogravimetric analysis into isothermal degradation curves. The stability of three materials used as electrical insulation in aerospace applications, PTFE, PI and PFA was compared. Literature data on PTFE and PI were used whereas new data were produced for PFA. The degradation of PFA appears to obey simple kinetics, with an activation energy substantially higher than for the other two materials. A better thermal withstanding of PFA at moderate temperatures is forecasted. Notably, according to the model, the exposure temperature giving an equivalent mass loss as for PTFE at 250°C is 333°C for PFA. PFA appears therefore as a promising material and offers an invaluable advantage which is the possibility of being processed by extrusion.

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