Modelling Kinetic Parameters of Poly(vinyl chloride) Binder Filled with Ammonium Perchlorate

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Summary: In the study of the ageing of solid combustibles we present some results dedicated to the non-isothermal analysis of a binder of polyvinylchloride filled with ammonium perchlorate. The thermal degradation of these components under the optical microscope has assisted with an image processing software. The determination of the activation energies using the reaction surface evolution process and the evolution of number of germs. The Ozawa [1], Freeman and Carroll [2] methods are used to determine the kinetic parameters of the thermal decomposition of these materials. A mathematical model based on Arrhenius law has been established. The result shows a good correlation with experimental data.

1 – Introduction

The thermal analysis by optical microscopy assisted with an image processing and analysis, has become a tool of characterization in a frequently scientific and technological discipline. The image analysis gives a qualitative and quantitative description and permits recognition of forms. It is particularly adapted to the microscopic phenomenon study. The application consists in counting and measuring sizes of germs in function of time, or temperature, during the reaction of degradation of the polymer. The technique has allowed establishing the evolution of the conversion rate with temperature. This relationship is necessary for the calculation of the activation energy. The statistical analysis of variance over activate energy has shown that the operative conditions such as the surrounding, the films thickness and the speed of heat, have no influence on the degradation process. Some operating parameters such as the pressure, the time and the mode of ageing as well as the rate of loading in NH_4ClO_4 have been fixed in order to simplify the mathematical equation [3]. The theoretical model that describes best this mechanism is based on the Arrhernius law [4]. The Fundamental kinetic law used is defined by the relationship (1).

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \qquad (1)$$

Freeman and Carroll [2] use a kinetic law of the form $f(\alpha) = (1-\alpha)^n$, where α represents the conversion rates and n the reaction order. The conversion rate in the case of the recovery of the interface is calculated from the surface S_G of germs at the instant t as

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compared to the unit surface of the sample, the relationship that will serve to calculate the conversion rate [5] is:

$$\alpha_G = \frac{S_G}{S_U} \qquad S_G \text{ : Total germ surface} \quad S_U \text{ : Unit surface}$$

The invariability of the preexponential factor appears as being an essential parameter for the confirmation of the good choice of the kinetic law [6]. The methods of determination of kinetic parameters are very numerous and depend on the experimental methods used. In this study the methods used are:

- integer method of Ozawa [1]
- differential method of Freeman and Carroll [2]

The qualitative analysis by optical microscopy has allowed establishing the evolution of the reactant interface between the different operating conditions [3].

2 – Equipment

In addition to the quoted optical microscopy, this work has needed the use of the differential scanning calorimeter (Perkin Elmer DSC 7) to determine the activated energy, the frequency factor and the reaction total order, these parameters have been used for the model. The optical reflection microscope is made essentially of four parts, as shown in figure 1.

The reactive cell shown in figure 2 is composed:

* a heated cell in which the sample is submitted to operating conditions ;
* a temperature control and program device ;
* a gas flow control device ;
* a water cooling system.

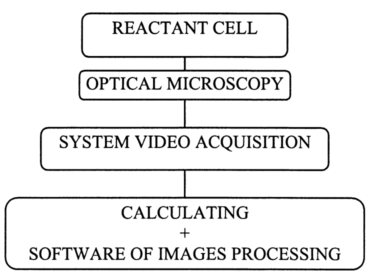

Figure 1: Tabular diagram for an experience of image processing

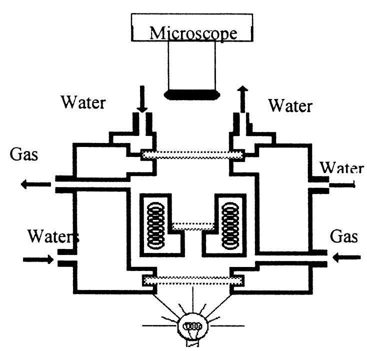

Figure 2: Reactant cell

3 - Operating conditions and experimental procedure

The samples used (polymer - new and old) are studied under nitrogen atmosphere or air. The speed of heating varies as follows: β = 10 - 20 - 40 °C/mn. The loading of NH_4ClO_4 is fixed to 4 % and the thickness of the films is included between 0.07 and 0.25 mm. The adopted image processing is illustrated in figure 3. The raw image is improved by filters, then binarized in two figures, zero for the black and one for the white. After the step of binarizing, we proceed to the extraction of contours it consists in drawing the perimeter of each germ. Finally, the last step consists in the sample characteristic extraction such as the size and the position of germs, as well as their number.

4 – Qualitative analysis

The qualitative analysis of thermal curve consists in showing the analogy that exists between a TGA thermal curve and optical microscopy images. The curve, in figure 4, gives some characteristics described hereafter. The degradation begins by a renewal of the reactive interface represented by figure 5 and figure 6. An initial period (I) concerning only a weak value of the degree of evolution such as α is $0.01< \alpha < 0.05$. The evolution during this period is due to the desorption of gas or to a thermal decomposition concerning only some atomic layers near to the surface of the reactive solid; in optical microscopy we observed the appearance of the first germ, figure 7. The zone (II) is the period of induction while the development of the reaction is limited. The increase of the germs volume appears in figure 8. Figure 9 shows the appearance of other germs. After a critical time t_c (corresponding to a critical temperature T_c). From this stage the growth in number and volume of germs evolves rapidly the rate of the reaction increases rapidly until the zone (III). The zone (III) is an accelerated period, during which is reached, a maximal value of the conversion called "point of inflection α_i corresponding to a time t_i". This evolution is shown in figure 10. According to E. Turi [7] and Bircumshaw [8], the point of inflection of the curve corresponds to $\alpha_i = 0.5$. The optical microscope we have this value, as shown in figure 11. For $t > t_i$, the speed of reaction decreases rapidly. The zone IV is called where the degree of evolution $\alpha_f = 1$, figure 12. This evolution of the number and the surface of germs have allowed to follow the evolution of the reactive interface.

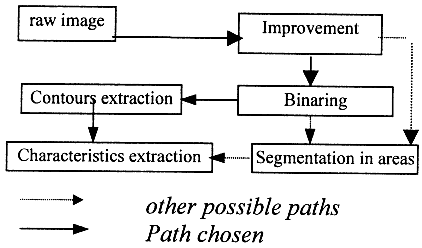

Figure 3: Different possible paths of the image processing experience

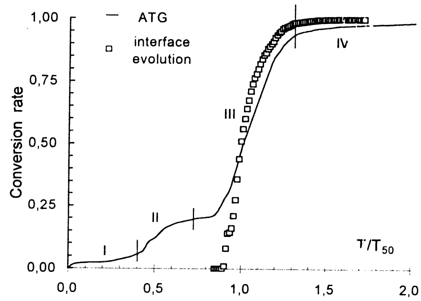

Figure 4: Typical Thermal curve $\alpha = f(t)$

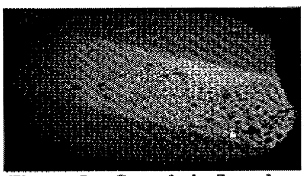

Figure 5 : Sample before the start degradation.

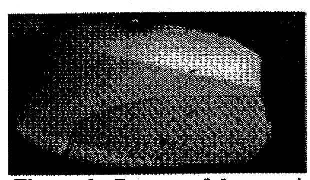

Figure 6 : Renew of the reactive interface.

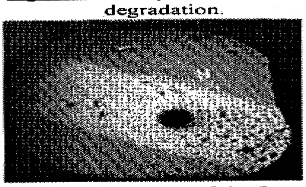

Figure 7 : Appearance of the first germs

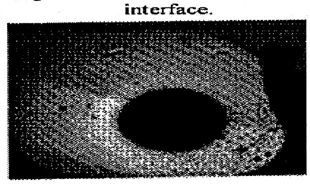

Figure 8 : Appearance others germs

Figure 9 : Increase of volumes and The number of germs

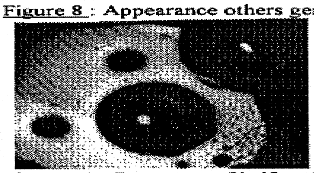

Figure 10 : Recovery of half surface

Figure 11 Recovery for a conversion Rate superior at 0.5

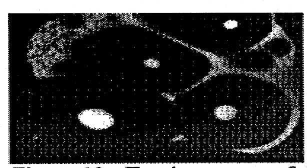

Figure 12 : Total recovery of the surface

5 – Influence of the operative conditions [4]

The thermal degradation is undertaken in relation with the following parameters:

- the surrounding : nitrogen or air
- the speed of heat : 10-20 and 40 °C/mn
- the rate of NH_4ClO_4 of : 4 % and 10 %
- the thickness : 0.07 and 0.25 mm
- the ageing : the simulation of the artificial ageing has been undertaken in a steamer at a temperature of 50 °C in an inert atmosphere and in the dark.

To estimate the differences observed, an analysis of the variance [9] on values of activated energies is undertaken. It has allowed observing that these differences have been estimated as negligible with a confidence degree of 90%. The kinetic parameters describing the degradation process, then:

For the free polymer

Ea = 19 kcal/mole
$n = 1$; $m = 0.2$; $p = 1$
$A = 9.1013\ s^{-1}$

For the filled polymer with 4% NH_4ClO_4

Ea = 32 kcal/mole;
$n = 1$; $m = 0.2$; $p = 1$
$A = 5.1024\ s^{-1}$.

The conclusion is that in the solid phase, the degradation process is essentially based on the chemical reaction. The gas phase and the diffusion in the solid phase are negligible.

6 - Model

It would be advantageous to use the Arrhenius model corrected by the kinetic law represented by the equation (2) with n, m and p of partial orders corresponding to the different stages of the degradation process. The equation that will be used as a basis for the calculation of kinetic parameters is represented by the next expression [5].

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{Ea}{RT}\right)\left[(1-\alpha)^n \alpha^m Log\left(\frac{1}{1-\alpha}\right)^p\right] \qquad (2)$$

We first calculate the conversion rate in function of to the temperature, by using the algorithm presented by figure 13. Once the profiles of the conversion rate determined, the problem consists in calculating iteratively the activated energy, the reaction orders and the frequency factor, in accordance with the algorithm of figure 14. Some tests have been used to estimate the sensitivity of the model. Figure 15 represents results and the curves drawn from the model.

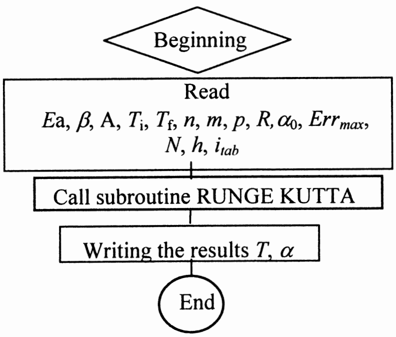

Figure 13: Algorithm of calculation of the conversion rate according to the temperature.

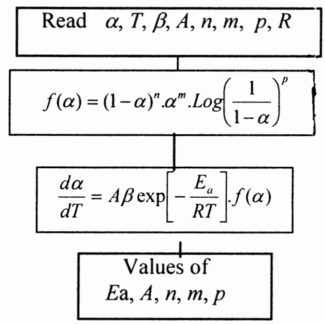

Figure 14: Algorithm of kinetic parameter calculation

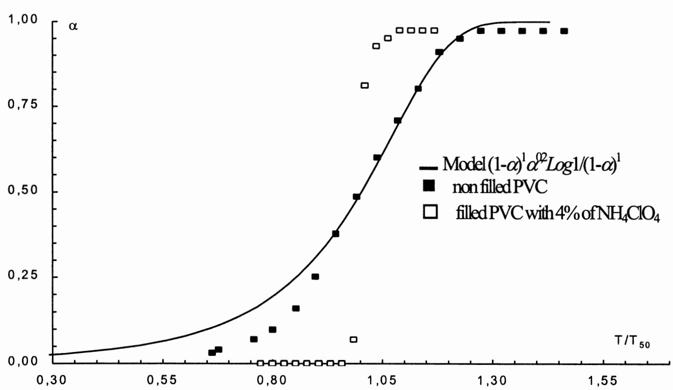

Figure 15: Test of sensitivity of mathematical model

7 – Conclusion

Activated energies calculated by the OZAWA method, from curves giving the evolution of the reactive interface are for the free PVC Ea= 19 kcal/mole, for the filled PVC of 4% of NH_4ClO_4 Ea= 32 kcal/mole. The Kinetic Parameters determined by the optical microscopy represent only a part of the process of degradation. The kinetic model depends especially on the invariability of the frequency factor. The equation of the model represents only the chemical reaction, while all the other phenomena, diffusion essentially seems to be negligible. The superposition of the experimental curves of the recovery of the reactive interface, for the free filled PVC and the filled PVC with 4 % NH_4ClO_4 with the theoretical curve shows a great similarity in the zone of rate conversion between 0.25 and 0.75. The application of methods of kinetic parameter calculation has to be done only in the zone where the conversion rate increases linearly with the temperature.

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