

KINETIC MODELING OF THE THERMAL DEGRADATION OF STABILIZED PVC PLASTISOLS

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Abstract

Thermogravimetric analysis (TG) was used in this work to study the degradation kinetics of industrial PVC plastisols. In order to model the pyrolytic degradation of plastisols in nitrogen, a kinetic model based on phenomenological considerations was developed. Two different processes were observed during the first degradation stage. The model parameters, such as activation energies and pseudo orders of reaction, were calculated using a non-linear regression analysis. The model developed was able to describe the degradation behaviour both in isothermal and in dynamic modes. The results of such analysis were applied to obtain long-term data from short-term experiments as an engineering approach to evaluate the thermal resistance of plastisols.

Keywords: degradation, kinetic model, plastisol, PVC, thermal stability

Introduction

Despite of the broad interest in the study of the degradation and stabilisation of PVC compounds, certain systematic investigations on the effect of additives on these reactions have recently started [1–5]. Most of PVC applications require the use of additives, which provide flexibility of processing and different properties to final products. One of the most common PVC compounds is plastisol, which consists of a mixture of pure PVC resin, and a plasticizer (mainly some long chain phthalates). During thermal degradation of such materials the plasticizer plays an important role, changing the main kinetic parameters and temperatures of reaction. The presence of the plasticizer introduces further variables that complicate the kinetic study, and therefore the effects of such additives must be taken into account.

The degradation of linear polymers is a complex phenomenon and although many authors [6–10] have studied it, many aspects are still unclear. The main reason can be attributed to the multiple aspects of this process. The degradation of a polymer can in fact be considered from several points of view, thermal degradation being only one aspect. Thermal degradation covers a wide field of useful processes, such as the development of heat resistant polymers, ablative materials, thermal stabilisation of

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polymers, and the characterisation of high-temperature composites for airplane and aerospace applications. It is evident that thermal degradation can cause serious damage to any polymeric material and can lead to the loss of functionality of a structure. It is therefore necessary to accurately control the processing and service life conditions of any polymeric system at elevated temperatures.

Generally, thermal degradation of polymers follows different mechanisms. The existence of more than one concurrent chemical reaction accompanied by other physical phenomena such as evaporation and ablation [11] contribute to complicate the modeling of the degradation kinetic. The development of affordable models, able to describe the degradation kinetic of polymeric materials, has been the concern of many authors [6–12]. Since the macroscopic phenomenon observed during the thermal degradation of polymers is the loss of mass caused by chain unzipping, or other phenomena such as plasticizer evaporation [13, 14], thermogravimetric analysis (TG) is the most indicated technique for this kind of studies. In fact, for a material system that loses material while reacting, using TG it is possible to relate the mass loss of a sample measured as a function of the temperature and/or the time with the extent of the degradation process. It should be considered that, the extent of reaction calculated by TG and its evolution with time and temperature takes into account all the possible degradation processes and, therefore, the degree of reaction should be considered as an overall value, which is not representative of the different single processes. It is out of doubt that coupled techniques, such as TG/FTIR or TG/MS may furnish more precise data to develop a mechanistic model of the degradation kinetic of linear polymers [15], nonetheless the use of TG alone is still a powerful tool to obtain engineering models of the degradation process.

The thermal degradation of PVC is substantially a two-step process. The first step (up to 330°C) mainly involves the zip-elimination of HCl and the simultaneous formation of sequences of conjugated double bonds in the polymer chain. This process yields a corrosive gas, HCl, and leads to highly reactive polyenes absorbing light in the UV and visible region. This absorption results in undesired coloration from yellow to nearly black, in some cases, and general loss of physical properties. Some evaporation of plasticizer may be also observed in this first step. At higher temperatures the material undergoes a partial carbonisation with the release of benzene and other aromatics.

Phthalate plasticizers are thermally degraded from 200°C on. However, when included in a polymeric matrix, the evaporation of plasticizers is shifted to higher temperatures. It has been suggested that their thermal degradation lead first to the formation of a monoester and olefins by a *cis*-elimination mechanism, and secondly to the cleaving of the monoester into phthalic anhydride and alcohol by a scission mechanism [16]. The study of the kinetic of plastisols degradation is further complicated by the fact that both processes indicated happen simultaneously.

This paper presents a study of the thermal degradation of PVC plastisols using TG tests to produce experimental data in terms of overall degree of reaction as a function of time and temperature. A general phenomenological kinetic model is developed in order to describe the plastisol degradation behaviour. In particular the activa-

tion energies of the degradation process will be determined from constant heating tests using the Friedman method [17]. The so obtained values of the kinetic parameters will be used as first guess in a non linear regression analysis method which exploits the results of isothermal and dynamic tests. The model equation used for the degradation of plastisols takes into account the presence of two simultaneous steps i.e. evaporation of plasticizer and thermal degradation of PVC.

Experimental

Dynamic thermal degradation measurements were performed using a SEIKO EXTAR 1000 TG-DTA system which allows heating rates from 1 to 200°C min⁻¹ up to a temperature of 1200°C. Tests were performed either in isothermal and dynamic modes in order to cover a wide range of thermal conditions in a nitrogen environment (flow rate 200 ml min⁻¹). Temperature programs were run from 30 to 900°C at different heating rates between 2 and 40°C min⁻¹ in 5°C min⁻¹ intervals. TG tests were performed in platinum crucibles where samples were placed without any previous treatment and experiments were run immediately. Data obtained from TG experiments were transformed in ASCII format and analysed using a statistics computer program. TG tests were carried out in nitrogen in order to remove all corrosive gases evolved in the degradation and to avoid thermoxidative degradation.

Vestolit 7021 (HULS, Germany) was used as PVC raw material. This is a suspension resin non-prestabilized and capable of forming low viscosity pastes easily. This resin, normally used in rotational moulding, was characterised by determining some properties mainly related to the molecular mass. One of them is the K value, which is related to the viscosity of the mixture between resin and plasticizer. This result was obtained by application of the DIN 53-726 standard and was 72.0. The molecular mass obtained by means of Gel Permeation Chromatography (Shimadzu LC-10AD) was $1.35 \cdot 10^5$.

Industrial grade DEHP was used. This plasticizer has been historically the most normally used in toys industry. Purity of DEHP was checked by using gas chromatography (Shimadzu GC-9A) with the obtainment of a single peak.

Plastisols were prepared by mixture of the adequate amounts of resin and plasticizer in a Brabender P-600 mixer during 20 min and 23±2°C. The paste obtained was then put in a vacuum dryer ($P < 7 \cdot 10^{-2}$ Pa) for 5 min. Once air was completely eliminated from pastes, they were ready for tests.

Three different samples were used in this work: Pure PVC and two different PVC/DEHP combinations, i. e. 50/50 and 70/30%. Samples were cut into small pieces weighing approximately 5 mg and inserted in the TG furnace in nitrogen environment. To ensure the reproducibility of the test, several runs were performed using different sample sizes. A variation between the runs of less than 1% of the mass loss was observed. TG experiments were performed either at constant heating rates (dynamic) and in isothermal conditions.

Results and discussion

A dynamic test in nitrogen at $10^{\circ}\text{C min}^{-1}$ of a PVC DEHP (70–30%) plastisol is reported in Fig 1. As it was previously indicated, the two different processes of the degradation of plastisols can be observed. The peak with two maximums, the first at 270°C and the second at 300°C approximately, represents the first degradation step, which includes the dehydrochlorination reaction. The second step of the degradation corresponds to the peak having a maximum at 450°C , which is related to the carbonisation process. Since the processing and use temperature of plastisols never exceed 400°C , and due to the sharp separation of the above mentioned peaks, which indicates that these two stages are kinetically independent, only the first stage of the plastisols thermal degradation was considered (1). Therefore, the models that are proposed in this paper are related to the study area indicated in Fig. 1. In order to perform the kinetic study and to characterise the thermal behaviour of the plastisol, different heating rates were used. All the dynamic tests showed a maximum mass loss of 63% in correspondence of the first stage of the overall degradation. Therefore the studied reaction was considered complete when this amount of residual material was obtained. In Fig. 2 an isothermal test at 220°C is shown; it is possible to notice that the mass loss obtained in isothermal conditions resembles the values obtained during the first step in dynamic tests.

The degree of reaction during both, the isothermal and the dynamic, tests was obtained applying the following equation, which assumes a linear relation between degree of reaction and mass loss:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad (1)$$

where α is the degree of reaction, W_0 is the initial mass, W is the actual mass and W_f is the residual mass obtained during each test. The value of α , calculated by Eq. (1), rep-

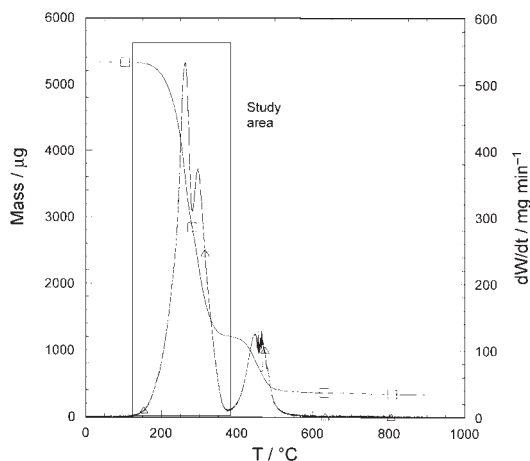


Fig. 1 Dynamic TG and DTG curves at $10^{\circ}\text{C min}^{-1}$ of a PVC:DEHP (100:70) plastisol

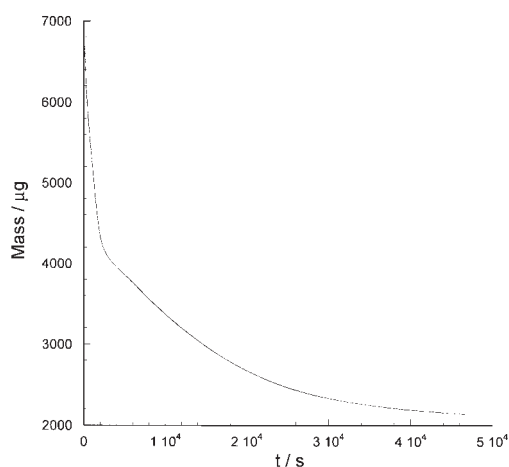


Fig. 2 Isothermal TG curve at 220°C of a PVC:DEHP (100:70) plastisol

resents the degree of degradation relative to the first reaction step, therefore W_f corresponds to the 63% of the actual mass loss.

A general kinetic model can be represented by the following expression:

$$\frac{\partial \alpha}{\partial t} = K(T) f(\alpha) \quad (2)$$

The term $K(T)$ is a function of the temperature, and its general form is an Arrhenius type expression:

$$K(T) = K_0 \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Depending on the mechanism of the degradation reaction, the function $f(\alpha)$ presents different forms. In general $f(\alpha)$ can be expressed as a simple function of α . The shape of the function $f(\alpha)$ was determined according with the following considerations:

The first stage of the degradation can be considered as an effect of the interrelation of two different processes. The first one is dominated by the evaporation of the plasticizer, while the second one is dominated by the dehydrochlorination reaction. This behaviour results in the two superimposed peaks shown in the study area of Fig. 1. Over these two processes, the first one, being an evaporation, can be considered as a first order process, while the second should be modelled using a different equation whose form is function of the shape of the derivative curves. By using a peak deconvolution software, the curves related to both processes were appropriately separated as can be seen in Fig. 3. Thus, the temperatures at which both processes are predominant can be calculated. It is possible to observe that at temperatures lower than 275°C, the evaporation is the dominating phenomena, while the dehydro-

chlorination is the predominant reaction at temperatures higher than 275°C. The sum of both peaks correlates the experimental results as shown in Fig. 4.

An appropriate phenomenological kinetic model for the thermal degradation of plastisols should take this fact into account. Generally, the variation of the degree of reaction with time can be expressed as in Eq. (2), where the reaction rate K presents an Arrhenius dependence on the temperature [13]. The shape of the function $f(\alpha)$ is in general determined by the reaction rate curve obtained in isothermal mode.

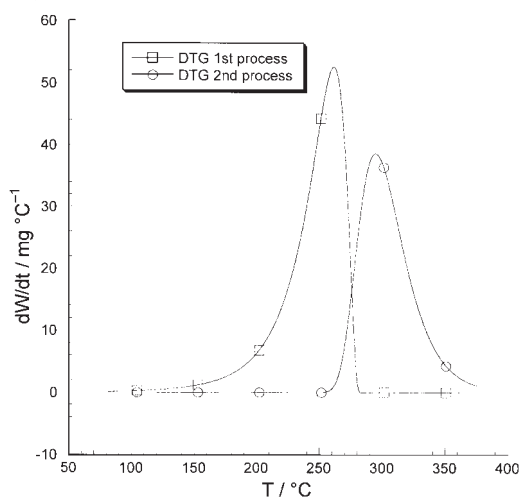


Fig. 3 DTG for the separation of peaks for the two reactions of the first thermal degradation step of a PVC plastisol

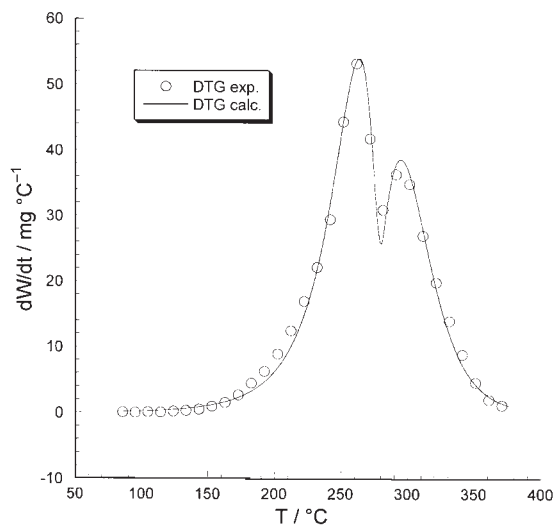


Fig. 4 Sum of DTG for both reactions

The shape of the reaction rate curves and the considerations about the maximum isothermal degree of reaction brought to a definition of the following models for the two indicated processes:

$$\frac{d\alpha}{dt} = K(T)(1-\alpha) \quad (4)$$

$$\frac{d\alpha}{dt} = K(T)\alpha^m (1-\alpha)^n \quad (5)$$

Equation (4) is related to the evaporation of the plasticizer, while Eq. (5) is related to the dehydrochlorination reaction. The overall kinetic equation proposed for the degradation of plastisols have to take into account the fact that these two processes occur simultaneously. Therefore a parallel kinetic model is proposed. In such model the degree of reaction, α is given by [18]:

$$\alpha = y\alpha_1 + (1-y)\alpha_2 \quad (6)$$

where α_1 and α_2 refers to the degrees of reaction of the processes represented by Eqs (4) and (5) respectively and y is a mass factor. It should be considered here that, since the first process, expressed by Eq. (4) is related to the evaporation, the maximum amount of material loss during this process should not exceed the amount of plasticizer not chemically linked to the PVC structure. Therefore this amount can be an indication of the excess of plasticizer in a plastisol formulation. The macroscopic representation of this phenomenon is represented in the model by the mass factor y , which, according to the experimental data, was set equal to 0.3.

An expression for the rate of reaction is obtained by the time derivative of Eq. (6):

$$\frac{\partial\alpha}{\partial t} = y\frac{\partial\alpha_1}{\partial t} + (1-y)\frac{\partial\alpha_2}{\partial t} \quad (7)$$

In this equation each α is calculated from the TG data obtained by the integration of the peaks represented in Fig. 3, which yield to the two TG curves of Fig. 5. The values of the activation energies and the order of reactions for Eqs (4) and (5) were calculated using the Friedman analysis [19]. The order of reaction and the pre-exponential factor of both equations were obtained using a non-linear regression program and are reported in Table 1.

Table 1 Results of the kinetic analysis

	$E_a/\text{kJ mol}^{-1}$	n	m	$\ln K$
Evaporation	111±10	1.00	0	21.7
Degradation	145±2	1.73	0	25.8

The results of the kinetic analysis, in terms of degree of reaction vs. temperature are reported in Fig. 6. The agreement between the model and the experimental data, confirm the validity of the approximations proposed.

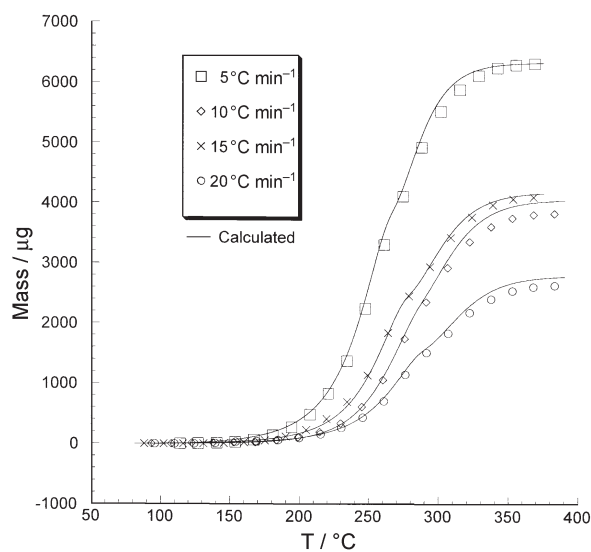


Fig. 5 Integration of DTG curves for the calculated and experimental data

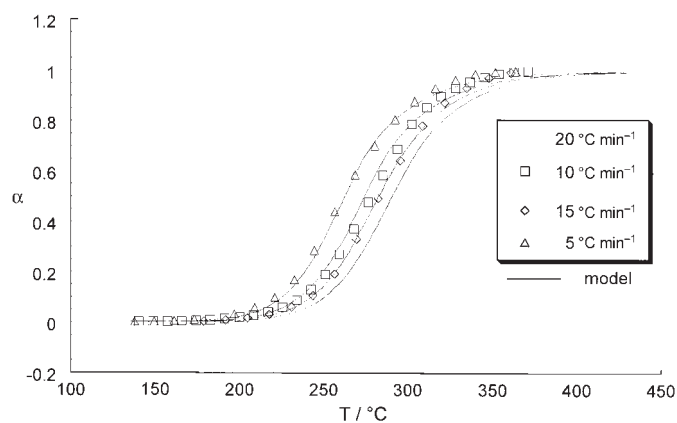


Fig. 6 Comparison between the model and the experimental data on DEHP 30%

Conclusions

The thermal degradation of PVC plastisol was analysed in this paper on the basis of a new phenomenological model that describes the kinetics of the first stage of the reaction. The kinetic parameters were calculated utilizing the Friedman method and the model was integrated numerically to obtain the conversion curves. The first step of the thermal degradation reaction of these samples can be considered as the superposition of two simultaneous processes, the evaporation of the plasticizer and the dehydrochlorination of PVC macromolecules. As both processes influence the kinetics

of the process, a parallel expression was used to model the overall reaction. The mass factor introduced took into account the maximum amount of evaporable plasticizer in the plastisol. The proposed model can be used as a tool to evaluate the thermal stability and to understand better the effect of concurrent reactions during thermal degradation. The procedure here developed can be suitable for application to the study of degradation kinetics of other kind of plastisols containing more than one additive.

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