Kinetic Analysis of the Thermal Degradation of PVC Plastisols

A. JIMENEZ,¹ J. LOPEZ,² L. TORRE,³ J. M. KENNY³

¹ University of Alicante, Department of Analytical Chemistry, Alicante, Spain

² Institute of Toys Research (AIJU), Ibi, Alicante, Spain

³ University of Perugia, Institute for Chemical Technologies, Terni, Italy

Received 4 September 1998; accepted 12 January 1999

ABSTRACT: The thermal degradation of plasticized polyvinyl chloride (plastisol) is reported here. Plastisols used in the present work were prepared with the plasticizer diethylhexyl phthalate in different proportions. Thermogravimetric analysis has been applied to study the behavior of plastisols at high temperatures and to evaluate their degradation kinetics. Several tests were carried out at different heating rates and the variation of the degree of reaction with time and temperature was calculated. The influence of the heating rate in dynamic measurements $(5-40^{\circ}C/min)$ on kinetic parameters, such as activation energies and reaction orders, has also been studied. These parameters were calculated from dynamic thermogravimetric analysis tests using Friedman analysis and a kinetic model for the degradation of poly(vinyl chloride) and plastisols has been then developed. The obtained model was able to simulate the thermal degradation process of plastisols in dynamic conditions and was used to evaluate the effects of additives in the degradation. The results of this study can be used to optimize the concentration of plasticizers and stabilizers in poly(vinyl chloride) formulations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1069–1079, 1999

Key words: PVC; plastisols; kinetic analysis; thermal degradation; thermogravimetry

INTRODUCTION

The mechanism of poly(vinyl chloride) (PVC) degradation and stabilization remains one of the still unsolved problems in polymer science. Furthermore, since in many PVC applications the polymer is mixed with plasticizers, the study of the degradation must take into account the effects of such additives. In plasticized PVC (plastisol), in fact, the molecules of the plasticizer are intimately associated with the resin molecules and it has been shown that these additives not only modify the mechanical behavior, but can also have large influence on many of the polymer properties.¹ For instance, some recent studies on the influence of different plasticizers in the final products show that some additives change substantially the plastisol mechanical and electrical properties²; moreover they can modify the resin thermal degradation making it faster or slower.³ However, despite of the broad interest in such studies, systematic investigations on the effect of such additives in PVC thermal degradation have only recently started.

Correspondence to: J. M. Kenny.

Journal of Applied Polymer Science, Vol. 73, 1069–1079 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/061069-11

The degradation of polymeric materials has been studied mainly in relation with the reprocessability of thermoplastics after several processing cycles. The particular mechanisms of degradation are a function of the polymer structure and can follow different steps because of the complexity of the polymeric chains. Functional group transfer, chain unzipping with elimination of volatiles and the formation of intermediate compounds are the main decomposition mechanisms that contribute to complicate the development of a mechanistic kinetic model of the polymer degradation process.

In particular, the thermal degradation of PVC in a broad range of temperatures is substantially a two-step process.¹ The first step (up to 330°C) mainly involves the zip-elimination of HCl and the simultaneous formation of conjugated double bond containing sequences (polyenes) in the polymer chain. This process yields a corrosive gas, HCl, and leads to highly reactive polyenes absorbing light in the ultraviolet 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 product also undergoes a partial carbonization with the release of free carbon among other products, such as benzene and other aromatics.

On the other hand, the thermal degradation of phthalate plasticizers starts at 200°C. 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.³ The study of the kinetic of plastisols degradation is further complicated by the fact that the two indicated processes happen simultaneously.

Although degradation reactions can be, as in this case, very complex, the utilization of a material under critical temperature conditions requires, at least, the knowledge of its degradation kinetics that is related both to morphological changes and to chemical decomposition reactions. Polymer degradation is normally accompanied by different changes in polymer properties, such as increase of viscosity, crosslinking and weight loss. Experimentally, thermal degradation is typically detected by monitoring weight changes occurring to a polymer exposed to heat as a function of time and temperature, which is the basis of thermogravimetric analysis (TGA). Then, the degradation kinetics can be studied correlating the weight loss to time, temperature and a generic degree of degradation. Although TGA data may not give enough information about complex degradation mechanisms, it can be a very useful tool to analyze the overall behavior of the polymer in extreme conditions.

Isothermal or dynamic (constant heating rate) tests can be used to study the thermal decomposition of polymeric materials, such as PVC and plastisols, by TGA. With these techniques kinetic parameters, such as activation energy and reaction order as well as others such as the temperature at the maximum decomposition rate can be calculated. However, these two modes, dynamic and isothermal, present some advantages and drawbacks. The advantages of determining kinetic parameters by a dynamic method are mainly based on its fastness and reproducibility. There is no need of long runs to get the results and it is possible to obtain a lot of information from a single run. Mathematical models of thermal decomposition reactions make possible the understanding of the whole process and the obtainment of quantitative conclusions from apparent kinetic parameters.^{3–9} This is the main reason why a mathematical model would be helpful to get a clear vision of the mechanism of plastisols thermal degradation, a subject which has raised some interest during the last years.^{2,10–14}

The aims of the present work are the evaluation of the kinetic parameters as well as the characteristic temperatures of the thermal decomposition of plastisols based on PVC resins and plasticizers under different operating conditions. This evaluation will lead to the proposal of a mathematical model able to describe the thermal degradation of plastisols and to get an insight for the theoretical approach to the reactions involved in the degradation mechanism.

Degradation Kinetic Models

In the present work the following symbols will be used to describe the degradation kinetic models: E_a : apparent activation energy (kJ mol⁻¹); A: preexponential factor (min⁻¹); n and m: apparent order of reaction; R: gas constant (8.31 J mol⁻¹ °C⁻¹); T: temperature (°C); t: time (min); β : heating rate (°C min⁻¹); k: rate constant; α : degree of conversion or fractional mass loss.

In degradation studies the degree of conversion is typically calculated as

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{1}$$

Where W is the actual weight, W_0 is the initial weight, and W_f is the weight at the end of the TG test. The basic rate equation generally utilized to represent the reaction kinetics is expressed in the following way:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

This equation defines the rate of conversion, $d\alpha/dt$, as a function of the reactant concentration loss and of the temperature dependent rate constant.

The form of the function $f(\alpha)$ is dependent on the mechanism of the degradation reaction. Discussions of the form and of the validity of this approach have been the concern of many investigators.¹⁵ In the case of polymer degradation, the simplest form of the function $f(\alpha)$ assumes that the rate of conversion is proportional to the nth order of the material concentration:

$$f(\alpha) = (1 - \alpha)^n \tag{3}$$

A more complex form of the kinetic equation assumes an \ll autocatalytic \gg behavior as reported for the thermal degradation of PEEK^{16,17}

$$f(\alpha) = (1 - \alpha)^n \alpha^m \tag{4}$$

The combination of these equations and the Arrhenius expression for the temperature dependence of the rate constant gives the following relationship

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT$$
(5)

This is the fundamental expression for the development of the analytical methods used to calculate kinetic parameters based on TG data. One the most used methods to determine the activation energy from dynamic measurements was proposed by Friedman.¹⁶ The expression referred to this method, applied to a general kinetic equation is as follows:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + \ln(f(\alpha)) - \frac{E_a}{RT}$$
(6)

Thus, a plot of $\ln(d\alpha/dt)$ versus 1/T for a constant α allows to obtain the activation energy, reaction order and preexponential factor. It should be noticed that the use of the Friedman method does not require the specification of the kinetic model (like in eqs. 3 or 4). Any suitable kinetic model can be applied with the only condition that the contributions of temperature and degree of reaction may be uncoupled as in the kinetic models described above. Furthermore, in this work, the information of the Friedman analysis will be used to calculate the first guess of the other kinetic parameters of the degradation equation for plastisols.

An additional problem when long term data are needed is the test duration. This is the reason why some accelerated degradation experiments at high temperatures can be performed and the long-term behavior can be extrapolated at lower temperatures. This procedure may be applied assuming a simplified degradation process.¹⁸ Some works have been previously carried out in our research group with the obtainment of results for several TGA tests, performed under different conditions. These data are further used to analyze the thermal stability and to develop a kinetic model of the degradation process. The model can be also applied to extrapolate the degradation behavior of the materials studied.¹⁸

EXPERIMENTAL

Dynamic thermal degradation measurements have been performed using a Mettler TG-50 Analyzer coupled to a Mettler TC11-TA microprocessor. Tests were performed in dynamic mode at different heating rates in order to cover a wide range of thermal conditions. Temperature programs were run from 30 to 900°C at different heating rates between 5 and 40°C/min in 5°C/min intervals. Data obtained from TGA experiments were transformed in ASCII format and analyzed using a statistics computer program. TGA tests were carried out in aluminum crucibles (5.9×4.7 mm) where samples were placed without any pre-



Figure 1 TG and DTG curves at 10°C/min on pure PVC powder.

vious treatment and experiments were run immediately. Nitrogen flow was used in order to remove all corrosive gases evolved in the degradation and to avoid thermoxidative degradation.

As a PVC raw material, Vestolit 7021 (HULS, Germany) was used. This is a suspension-produced polymer nonprestabilized and capable of forming low viscosity paste easily. This resin, normally used in rotational molding, was characterized by determining some properties mainly related to the molecular weight. The molecular weight obtained by means of Gel Permeation Chromatography (Shimadzu LC-10AD) was 1.35 $\times 10^5$. A K value equal to 72.0, related to the viscosity of the resin and plasticizer mixture was obtained by application of the DIN 53-726 standard.

Industrial grade DEHP was used. This plasticizer has been historically the most used in the toy 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 $23 \pm 2^{\circ}$ C. The paste obtained was then put in a vacuum dryer ($P < 7 \times 10^{2}$ Pa) during 5 min. Once air was eliminated from pastes, they were ready for tests.

Three different formulations were analyzed in this work: Pure PVC and two different PVC/ DEHP blends, i.e., 50/50% wt and 70/30 % wt.

RESULTS AND DISCUSSION

Dynamic thermogravimetric curves obtained on neat PVC at 10°C/min are shown in Figure 1. Weight loss derivatives are also reported in the same plot; it can be noticed that the polymer is thermally stable up to 200–220°C. Above this temperature interval, the polymer undergoes the first step of the thermal degradation, which lasts up to the temperature of 380°C when the second degradation step starts. The exact values of the onset temperatures of the degradation processes depend on the previous thermal history of the



Figure 2 Degree of reaction versus temperature at 10°C/min of different plastisols.

polymer and on the heating rate of the DSC test. These two steps are evident in the derivative curves shown in the same figure, which present two different peaks associated to each of the two steps, respectively. Because the working temperatures of PVC and plastisols barely overcome 200°C and never reach 380°C, this work will focus on the study the first reaction step, which mainly corresponds to the dehydrochlorination.¹ Therefore, in the calculation of the degree of degradation α from eq. 1 the term of the final weight (W_f) corresponds to the weight at the end of the first step, i.e., in correspondence of the baseline of the first peak of the derivative curve.

Curves of α versus T, for a dynamic test at 10°C/min, calculated according to these assumptions, are shown if Figure 2 where data corresponding to three different samples have been plotted. The effects of the plasticizer on the thermal degradation can be observed in this figure. The curves relative to plastisols are in fact shifted to lower temperatures. This behavior is in agreement with the two different reactions that characterize the first step of the degradation of plastisols. It was, in fact, previously indicated that during this step the evaporation of plasticizer and dehydrochlorination of PVC proceed simulta-

neously and therefore it is very difficult to observe a sharp distinction of these two phenomena from the thermograms and their derivatives.² It is very difficult, then, to separate the effects of each reaction on the overall mechanism of the thermal degradation of plastisols. Since the goal of this work was to develop a phenomenological model to be used to evaluate the effect of the plasticizer on thermal stability of plastisols, a complete elucidation of the mechanism of the reaction was not considered.

The apparent activation energy was calculated using the Friedman analysis applied to the general kinetic model (eq. 2) without supposing any form for the function $f(\alpha)$. According to eq. 6, a plot of $\ln\left(\frac{d\alpha}{dt}\right)$ versus 1/T at fixed α , should give a straight line whose slope gives the apparent activation energy. The results of such analysis are presented in Figure 3 for one of the samples analyzed (DEHP 30%) where the curves corresponding to five different values of α , ranging from 0.1 to 0.9, are shown. Each data point on a single curve was extracted from a single dynamic run at a different constant heating rate. Straight lines fitting the data of Figure 3 are practically parallel indicating constant activation energy in the range



Figure 3 Application of Friedman method to the degradation of the sample DEHP 30% in correspondence of different degrees of reaction.

of α analyzed and confirming the validity of the approach applied. It should be reminded that this analysis corresponds only to the first degradation process. A different and independent value can be expected for the second degradation process not analyzed in this work. The same procedure was used to compute the apparent activation energy relative to the other two samples. The obtained values, shown in Table I, were used as starting points for the regression analysis of the full model.

In order to obtain a phenomenological model for the thermal degradation of plastisols, an explicit expression for $f(\alpha)$ in the kinetic equation is needed. Following the same approach already applied to the degradation of other polymers¹⁸ a behavior represented by eq. 4 was considered.

Table I Results of the Kinetic Analysis

Sample	$E_a \ ({\rm kJ/mol})$	$\ln(A)$ (\min^{-1})	т	n
PVC	249 ± 7	52	0.25	2.7
DEHP 50%	174 ± 6	44	0.25	2
DEHP 30%	169 ± 7	35	0.2	1.8

This specific selection and the elimination of eq. 3 model are supported by the particular results obtained in isothermal tests. It can be noticed in the isothermal thermogram reported in Figure 4 that the maximum of the curve does not correspond to the starting point ($\alpha = 0$) as predicted by eq. 3. A maximum of the curve after the beginning of the reaction is typical of autocatalytic models as the one represented by eq. 4. The full model adopted was then the following:

$$\frac{d\alpha}{dt} = A \, \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n(\alpha)^m \tag{7}$$

The kinetic parameters of eq. 7 were calculated by regression analysis using as starting point the results of the Friedman method previously obtained.

While the activation energy is a parameter that can be directly calculated from dynamic tests as described above, reaction orders n, m, and the pre-exponential factor A typically require information given by isothermal tests. In this research an alternative method to determine such parameters using only dynamic experiments has been developed and applied.



Figure 4 Degree of reaction and its derivative, as a function of time, during an isothermal test on pure PVC at 210°C.

In the Friedman analysis, the first two terms of the right hand side of eq. 6 are not function of the heating rate and temperature. The value of the sum S, of these two terms, represents the intercept with the y-axis of each isoconversion curve shown in Figure 3. Then, using as function $f(\alpha)$ the one described by eq. 4, the following yields:

$$S = \ln A + n \, \ln(1 - \alpha) + m \, \ln(\alpha) \tag{8}$$

Plotting the term S, calculated at different values of α , versus α and performing a nonlinear regression analysis on the data, the values of A, n, and m can be easily calculated. The results of such analysis in terms of S versus α are shown in Figure 5 for the formulation DEHP 50%. The agreement with the model proposed is shown in the same figure; a correlation coefficient of 0.98 was obtained giving a good fit of the data.

Once the values of the kinetic constants of the eq. 7 model were calculated according with the procedure described above, plots of α versus temperature were obtained for different heating rates by numerical integration of the model. Parameter values were subsequently improved by using a regression analysis on the integrated model.

The results of the complete procedure are reported in Table I where an overall reaction order 2 is reported for the plastisols while is close to 3 for the pure PVC. Also the activation energy and the preexponential factor decrease with the plasticizer content, compared with results for pure PVC. The values of the apparent activation energy of PVC and plastisols obtained here cannot be fully compared with those reported in literature,^{2,12} as ours refer to eq. 7 model not considered in the previous investigations. In any case, an apparent activation energy of the same order has been obtained.²⁰

The decrease of the apparent activation energy obtained in plastisols, with respect to the values observed in the PVC resin, is coherent with the decrease of the temperature of maximum weight loss observed in the TGA tests. These two phenomena, which result in a faster start of the degradation reaction, can be explained taking into account the interactions between plasticizer and PVC during mixing and cooling. Thus, one of the consequences of the mixture between the plasticizer and the resin may be the separation of chains in the 3-dimensional structure of PVC. Because of this, the interactions between macro-



Figure 5 Representation of eq. 8 versus degree of degradation for the sample DEHP 50%.

molecules become less strong and therefore the beginning of the degradation reaction is more favorable energetically. Furthermore, a small increase in apparent activation energy is observed for a DEHP 50 plastisol, compared to DEHP 30 in agreement with previously reported results which indicate that a PVC/DEHP (70:30) combination has the lower activation energy.² In fact, it has been previously suggested that the higher thermal degradation resistance of the PVC/DEHP (70 : 30) formulation can be attributed to the maximized interaction between the PVC and the plasticizer, who acts as a protection coating of the PVC macromolecules. This explanation is in agreement with the extensive industrial use of this compound taking also advantage of its higher processability and workability.

The final results obtained by the integration of eq. 7 model, using the kinetic parameters reported in Table I, are shown in Figures 6, 7, and 8; model results are well compared with experimental data at different heating rates for PVC, DEHP 50% and DEHP 30% respectively. As it can be observed, results obtained from the application of the proposed model fit with the experimental for every sample. This is a sign of the good agreement between the model proposed here and the results obtained from the TGA experiments. An additional point to be noticed is related to the influence of the heating rate on the experimental results. As it is indicated in Figure 6, results obtained at 5 and 10°C/min fit well with the experimental data, but this is not true at 50°C/min. This may be caused by the thermal lag between the furnace nominal temperature and the actual sample temperature. It has been also indicated that some problems related to heat and/or mass transfer may be important at high heating rates, affecting the temperature control and the uniformity of temperature inside the sample.⁸ Moreover, some additional errors can be caused by the intrinsic thermal conductivity of the sample, mainly PVC, because the sample used was a fine powder respect the use of a continuous fluid as in the case of plastisols. Therefore, the use of heating rates lower than 10 to 15°C/min is highly recommended in order to avoid such problems.

Another cause of the discrepancy between the experimental data and the model observed for pure PVC may be attributed to the effect of DEHP. While it is evident the effect of DEHP on the apparent activation energy, which results in a clear decrease for every sample, the presence of this plasticizer could also influence the form of the kinetic curve resulting in a different kinetic expression. The values of the reaction orders re-



Figure 6 Comparison between model results and experimental data on pure PVC.

ported in Table I for the degradation of pure PVC are in fact different from the ones of the two plastisols. This behavior may be attributed to the fact that the evaporation of plasticizer and the dehydrochlorination may not happen simultaneously, but at different stages that superimpose



Temperature (K)

Figure 7 Comparison between model results and experimental data on DEHP 30%.



Figure 8 Comparison between model results and experimental data on DEHP 50%.

in correspondence of a certain temperature and conversion range. Therefore it can be considered that the first reaction, i.e. evaporation of DEHP, influences the second process, changing the overall mechanism of the reaction. Nevertheless the approach used in this work keeps its validity and allows the comparison of the effects of plasticizer and other additives on the thermal degradation of plastisols.

CONCLUSIONS

A new phenomenological model was developed in order to explain the kinetics of the thermal degradation of DEHP based plastisols. This model has shown a good agreement with experimental data. The kinetic parameters—activation energy $(E_a = 179 \text{ kJ/mol})$ and reaction orders (n = 2, m = 0.2)—were calculated using the Friedman method and a modification of it. The model was then integrated numerically to obtain the conversion curves. Some clear differences in parameters have been observed when the model was applied to thermal degradation of pure PVC compared to plastisols. These discrepancies were attributed to the existence of two simultaneous reactions in the thermal degradation of plastisols. One of the two

reactions involved in the mechanism is the evaporation of plasticizer, which influences the kinetics of the other reaction, i.e., dehydrochlorination of PVC macromolecules. The apparent activation energy decreased with the DEHP content according to the theory. 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, mainly thermal stabilizers.

REFERENCES

- Minsker, K. S.; Kolesov, S. V.; Zaikov, G. E. Degradation and Stabilization of Vinylchloride Based Polymers, Oxford: Pergamon Press, 1988.
- Jiménez, A.; Berenguer, V.; López, J.; Vilaplana, J. J Appl Polym Sci 1996, 60, 2041.
- Wu, C. H.; Chang, C. Y.; Hor, J. L.; Shih, S. M.; Chen, L. W.; Chang, F. W. Can J Chem Eng 1994, 72, 644.
- 4. Tanaka, H. Thermochim Acta 1995, 267, 29.
- 5. Simon, P. Polym Degrad & Stab 1995, 47, 265.
- McNeill, I. C.; Memetea, L.; Cole, W. J. Polym Degrad & Stab 1995, 49, 181.

- Bockhorn, H.; Hornung, A.; Hornung, U.; Teepe, S.; Weichmann, J. Combust Sci & Tech 1996, 116– 117, 129.
- Carrasco, F.; Pagès, P. J Appl Polym Sci 1996, 61, 187.
- 9. Pielichowski, K.; Hamerton, I. Polymer 1998, 39, 241.
- Biggin, I. S.; Gerrard, D. L.; Williams, G. E. J Vinyl Technol 1982, 4, 150.
- Bublick, A. T.; Bogomolova, L. K.; Paufner, O. E.; Tsirkun, R. R. Plast Massy 1985, 11, 17.
- 12. Jiménez, A.; Berenguer, V.; López, J.; Sànchez, A. J Appl Polym Sci 1993, 50, 1565.
- Jiménez, A.; López, J.; Vilaplana, J.; Dussel, H. J. J Anal & Appl Pyrolysis 1997, 40–41, 201.

- 14. Hollande, S.; Laurent, J. L. Polym Degrad & Stab 1997, 55, 141.
- 15. Schneider, H. A. Polym Eng Sci 1992, 32, 1309.
- 16. Friedman, H. L. J Polym Sci C 1964, 6, 183.
- Kenny, J. M.; Torre, L. in High-Temperature Properties and Applications of Polymeric Materials, Tant, M. R.; Conell, J. W.; McManus, H. L. N., Ed., Am Chem Soc, 1995, 140.
- Kenny, J. M.; Torre, L.; Nicolais, L. Thermochimica Acta 1993, 227, 97.
- 19. Hawkins, W. L. Polymer Degradation and Stabilization; Springer–Verlag: Hamburg, 1983.
- 20. Carberry, J. J. Chemical and Catalytic Reaction Engineering; McGraw Hill: New York, 1976.