New Mathematical Model on the Thermal Degradation of Industrial Plastisols

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SYNOPSIS

The thermal degradation of some plastisols [poly(vinyl chloride) and plasticizer mixtures] normally used in the toy industry was studied using a nonisothermal thermogravimetric technique. Some kinetic parameters such as activation energies are calculated according to some methods reported in the literature. A mathematical model based on considerations of the plasticizer amount was proposed to foresee the thermal degradation behavior of plastisols mostly used in the toy industry. Activation energies calculated according to the proposed model agree reasonably well with experimental results in a broad range of plastisol composition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Investigation of the degradation and stabilization of poly(vinyl chloride) (PVC) products is one of the more active areas of research in polymer chemistry. During thermal degradation of PVC, dehydrochlorination is accompanied by rapid discoloration, chain scission, crosslinking, and general loss of physical properties.[1]

Dynamic thermogravimetry (with a linear temperature increase) is widely used as a tool to study the degradation of different polymeric materials, to elucidate the order of the reaction, and also to estimate other kinetic parameters such as the activation energy.[2] In a previous work,[3] thermogravimetric analysis (TGA) was used to determine the activation energy for the dehydrochlorination reaction of a PVC resin. This article presents the results applied to usual plastisols or plasticized PVC. Moreover, a new approach to understand the plastisol degradation mechanism was studied.

Plasticizers and other PVC additives have been shown to have a large influence on many polymer properties. For instance, they can modify the resin's thermal degradation, making it faster or slower. Recently, studies of the influence of different plasticizers in the final product were made.[4-6] Thus, it was observed that some additives change substantially the plastisol's mechanical and electrical properties.

But problems in the studies of the plasticized PVC thermal degradation are more important than are problems in the studies of rigid PVC. There are two basic possibilities:

- Degradation begins in the resin with the plasticizer being degraded afterward.
- Degradation begins in the plasticizer with a subsequent influence on the resin.

In most cases, previous studies in plastisol thermal stability have not found any difference between these two possibilities.

The first studies of the influence of plasticizer concentration in HCl release in some PVC pastes were made during the 1960s.[7] As there were no apparent color changes, it was considered that thermal degradation of different PVC pastes operates in a very similar way, not being dependent on the plasticizer amount. But it was also observed that thermal stability increased with the plasticizer content in some cases. Therefore, it was considered that some

plasticizers have an influence on the stabilization, but this influence has not been well explained.

In other studies,[8] investigations on the thermal stability in mixtures were combined with the oxidation capabilities of plasticizers normally used. It was observed that the plasticizer with the slowest oxidation rate made the most stable mixture, even when some stabilizers were used.

One of the most important studies of plastisol degradation was made by Dunn and Ennis.[9] They studied PVC, diethylhexyl phthalate (DEHP or DOP), and their mixtures using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in an inert atmosphere. In that work, the authors compared thermograms of a number of PVC/DOP formulations and observed that a progressive increasing of plasticizer amount led to more stable mixtures. This fact seems to indicate that the resin degradation starts before the plasticizer degradation. It was also observed that there was no DOP boiling for PVC pastes in a resin concentration higher than 16%, indicating that DOP had already been combined with PVC. In the present work, we tried to confirm this behavior in a broader range of plasticizer concentrations and using PVC pastes of a different formulation.

The aim of the present work was the study of the influence of formulations on the two types of plastisols mostly used in the toy industry, with diethylhexyl phthalate (DEHP or DOP) and dibuthyl phthalate (DBP). Dehydrochlorination activation energies of these PVC products were calculated and compared with those of resin and plasticizer.

Kinetic Methods

As in a previous work,[3] in these methods the following symbols are usual:

E_a apparent activation energy (kJ mol^{-1})
A preexponential factor (min^{-1})
n apparent order of reaction
R gas constant (8.3136 J mol^{-1} K^{-1})
T temperature (K)
α degree of conversion or fractional mass loss
t time (min)
β heating rate (K min^{-1})
k rate constant

As has been stated,[3] the most useful kinetic method to determine the activation energies of PVC products was by Friedman,[10] which is based on the comparison of mass loss rates ($d\alpha/dt$) for a fractional

mass loss, α, determined using different heating rates:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n \ln(1 - \alpha) - \frac{E_a}{RT} \qquad (1)$$

The other method used in this study was by Flynn and Wall,[11] which needs several curves measured at different heating rates. Thus, the next expression can be obtained:

$$-\frac{d \lg \beta}{d\left(\dfrac{1}{T}\right)} = 0.457 \frac{E_a}{R} \qquad (2)$$

EXPERIMENTAL

Materials

The PVC resin used was Vestolit B 7021 (HULS), which was characterized in a previous work.[3] Plasticizers used were dibuthyl phthalate (DBP) (Vestinol C, HULS) and diethylhexyl phthalate (DEHP) (Vestinol AH, HULS), which are the most commonly used plasticizers in the toy industry.

Equipment

Thermogravimetric analysis was performed using the same instrument as in the previous work.[3] To prepare the pastes, a Brabender P-600 mixer coupled with a Brabender Plastograph/Plasti-Corder register unit was used. This instrument was built according to German Standard DIN 54 802.

Operating Procedure

In the present work, four different formulations were mainly studied, two of them using DOP as a plasticizer and the other two using DBP. Relationships between resin and plasticizer amounts were 100 : 70 and 100 : 50 in every case. These relationships were selected because they are the ones most commonly used in the toy industry.

To obtain a complete study, a series of pastes with different formulations were prepared using DOP and DBP and formulations of the following: 100 : 30, 100 : 40, 100 : 50, 100 : 60, 100 : 70, 100 : 80, 100 : 90, 100 : 100, 100 : 110, 100 : 120, 100 : 130, 100 : 140, and 100 : 150 (resin : plasticizer). PVC pastes used in the present work were prepared according to Spanish Standard UNE 53-462-90,

equivalent to ISO 4612-79. Thus, pastes were prepared by mixing defined amounts of the resin and the selected plasticizer, according to the conditions of shaker rotation frequency, temperature, and mixing time. Working conditions were as follows:

- Temperature: 23 ± 2°C
- Rotation frequency: 120 min^{-1}
- Mixing time: 20 min

The paste was then stored in a vacuum dessicator (7×10^{-2} Pa) to eliminate foams. At that moment, the pastes were ready for TGA. The plastisol degradation process was followed by monitoring weight loss according to temperature in a controlled atmosphere.[3]

RESULTS AND DISCUSSION

A typical thermogravimetric curve of these compounds is given in Figure 1 for a PVC : DOP (100 : 50) paste, with a heating rate of 20 K min^{-1} and using an inert atmosphere. It can be noted that the first step ($\sim$ 600 K) presents a dehydrochlorination process resulting in the formation of C═C bonds. This study is focused on this stage. The second step

corresponds to pyrolysis of carbonaceous compounds previously formed. Finally, the third step corresponds to the change of atmosphere when air is introduced into the oven ($\sim$ 1000 K).

Application of Kinetic Methods

The obtained data were analyzed by applying the above methods and calculating kinetic parameters. As indicated in a previous work,[3] the Friedman method is the more adequate because it works with the basic rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (3)$$

This method was applied to the four pastes which were formulated as above. The slope values obtained are different. Therefore, activation energies will also be different.

The heating rate has a direct influence on the obtained data of activation energies. Thus, the most reproducible results are obtained in a range between 15 and 40 K min^{-1}. Out of this interval, some important variations caused by the thermal lag in the instrument can be observed. The same behavior was proved for the resin.[3]
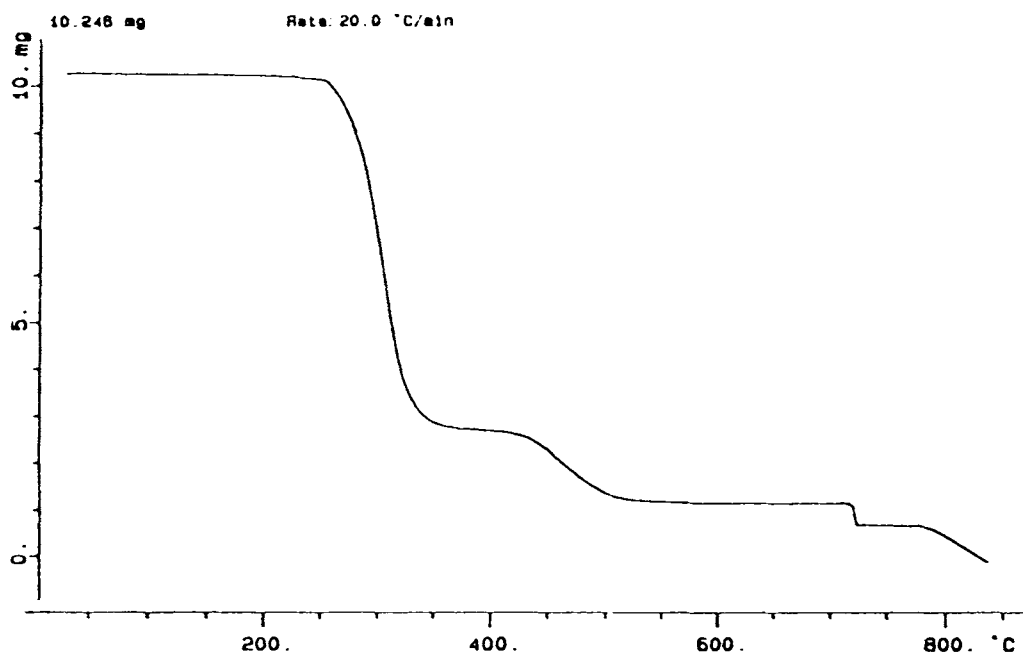

Figure 1 TG curve for a plastisol sample heated in N$_2$ atmosphere.

The activation energy results for the plastisol dehydrochlorination reaction at different heating rates and every formulation used is shown in Figure 2. Thus, it can be seen that different results are obtained with every formulation. Activation energies with DOP are clearly higher than are the DBP values. This behavior is observed for every heating rate in the range between 15 and 40 K min^{-1}. This fact indicates that plastisols with DBP present a favored thermal degradation process in terms of energy. On the other hand, it can be seen from Figure 2 that 100 : 70 pastes have lower activation energy values than those of 100 : 50 pastes.

This situation can be explained according to observed differences between the boiling process of these two plasticizers, which are presented in Figure 3. There are differences in boiling because DBP vaporizes at a lower temperature than does DOP (DOP bp, 323.3°C, DBP bp, 268.3°C). Therefore, the activation energy for a PVC:DBP paste must be lower than the values for a PVC : DOP paste.

A complete series of pastes were prepared to measure activation energies at a given temperature and using the Friedman method.[10] A plot of the results and activation energy values of the resin and plasticizers separately used in the present study is shown in Figure 3. It can be observed that there is a great drop in activation energy values of the obtained pastes in both cases. This behavior suggests the existence of a point in the activation energy from pastes 100 : 70, whose results can be considered very similar with a small increase in plastisols with a higher plasticizer amount. This result indicates that the most favored thermal degradation process is given by the 100 : 70 paste, which is the most recommended and used formulation in the PVC transformation industry.[12]

On the other side, activation energies for every formulation used were calculated by using Flynn and Wall method.[11] This kinetic method, which, in spite of their differences, presents similar results to those of Friedman in PVC resins,[3] was applied with a degree of conversion $\alpha = 0.50$. The obtained activation energy results are shown in Figure 4.

This different behavior in activation energy values when the resin : plasticizer relationship is changed seems to indicate that the plasticizer's final concentration in the paste is an important factor. It can be thought that this influence is caused by plasticizer evaporation during the first step of the thermal degradation in the same way as has been proposed with other plasticizers.[5]

Thus, if it is supposed that a close mixture between resin and plasticizer during the gelation process has been reached, it can be thought that this compound's molecules will be in the internal area of a 3-dimension net which gives the resin primary structure. When thermal degradation starts, the only associated process is solvent evaporation. Therefore, it will be the only stage which determines the reaction rate.

In the beginning, when the whole process is kinetically controlled by evaporation, plasticizer concentration must be homogeneously distributed in the polymer and every mass loss must involve a plasticizer concentration reduction. Therefore, it seems to be clear that it will have the result of free holes in the plastisol structure. These holes can be considered as initiation centers (or active centers) of the dehydrochlorination process and make this reaction faster, as has been previously proved.[13]

In addition, as is well known, the whole dehydrochlorination process results in a hydrogen chloride release, which can be considered as a catalyst of this own reaction. Thus, reaction rate increases and activation energy decreases.[14-17]

MATHEMATICAL MODEL OF THERMAL DEGRADATION

Plasticizer addition to PVC resins changes their degradation mechanisms. Two situations must be considered:

1. The PVC dilution effect in the plasticizer.
2. The interaction between chlorine atoms in PVC and the plasticizer. This point has a major influence because

- The plasticization mechanism involves a plasticizer–chlorine interaction caused by the polar character of bonds.
- PVC degradation starts in the chlorine atom, acting as a self-catalyst.

One possible explanation of the PVC degradation mechanism could be as follows:

1. As the PVC–plasticizer interaction is weak, a temperature increase must have as a consequence an unplasticization and plasticizer evaporation.
2. Plasticizer evaporation involves the creation of holes around the chlorine atoms making
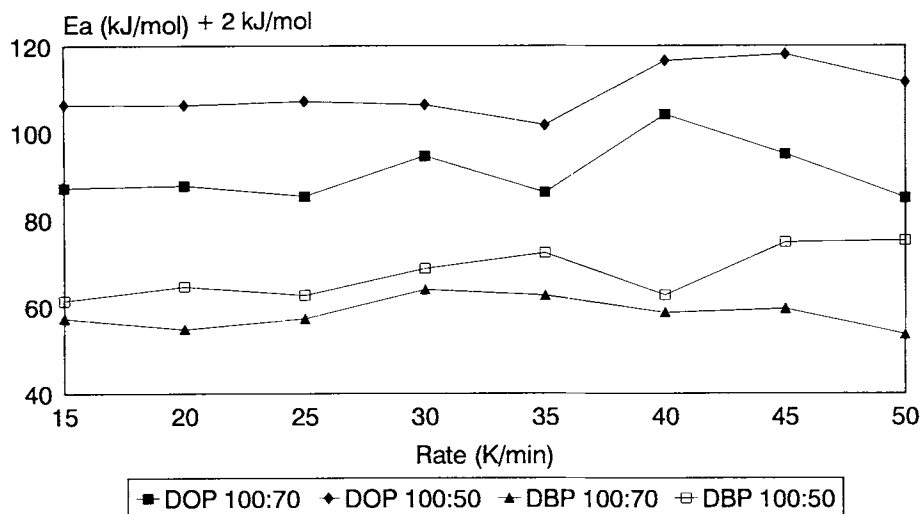
Ea VS. HEATING RATE

Figure 2 Activation energies variation with heating rates.

their release easier and the degradation re-
action faster.

Therefore, the activation energy, E_a, would be
dependent on two different factors: plasticizer evap-
oration (E_{ev}) and PVC activation (E^*):

$$E_a = E_{ev} + E^* \qquad (4)$$

To calculate E_{ev}, it could be considered that the
unplasticization process must be much smaller than
the evaporation. Considering the dilution factor,

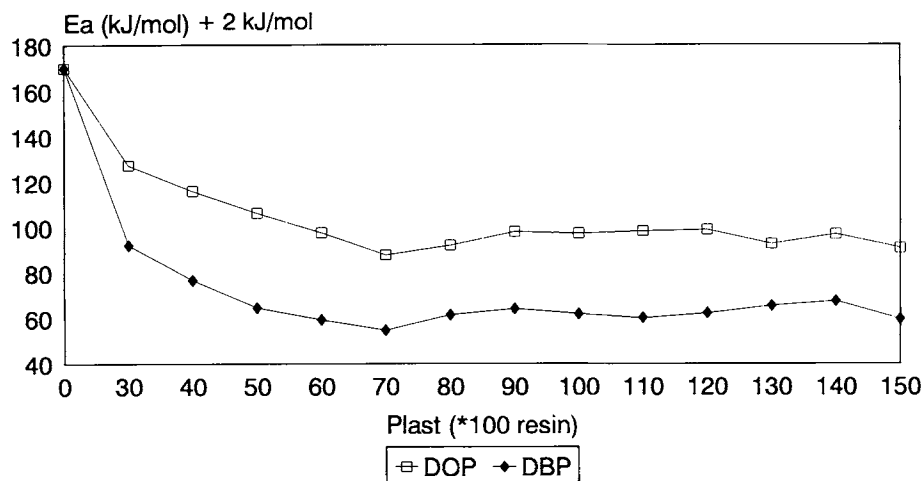# Ea VS. PLASTICIZER AMOUNT

FRIEDMAN METHOD

Figure 3 Activation energy vs. plasticizer amount (Friedman method).
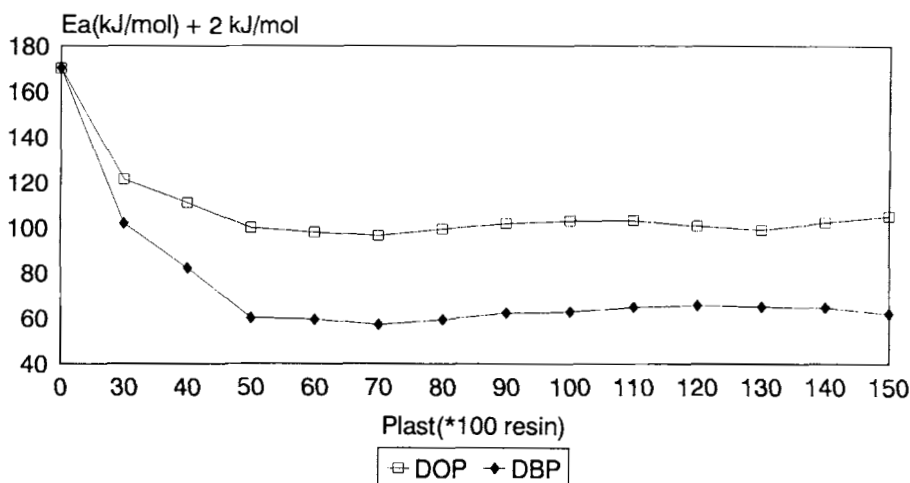
Ea VS. PLASTICIZER AMOUNT
FLYNN-WALL METHOD.

Figure 4 Activation energy vs. plasticizer amount (Flynn and Wall method).

$$E_{ev} = E_{pl}\left(\frac{m_{pl}}{m_{PVC} + m_{pl}}\right) = E_{pl}\left(\frac{m_{pl}}{m_T}\right) \quad (5)$$

where m_{pl} is the plasticizer mass; m_{PVC}, the resin mass; and m_T, the total mass. E_{pl} in eq. (5) is the energy needed to evaporate the plasticizer.

Evaluation of the second term in eq. (4) is made difficult by the evaluation of the PVC plasticization degree, which is dependent on the plasticizer amount in the mixture, so that plasticized PVC (PVC$_p$) and nonplasticized PVC (PVC$_n$) should be considered separately in terms of activation energies (E_{PVC-p} and E_{PVC-n}, respectively):

$$E^* = E_{PVC-p}\frac{m_{PVC-p}}{m_T} + E_{PVC-n}\frac{m_{PVC-n}}{m_T} \quad (6)$$

where m_{PVC-p} is the plasticized PVC mass, and m_{PVC-n}, the nonplasticized PVC mass.

To obtain simpler expressions, it is better to work with plasticizer parts per resin unit (n). According to the resin amount, two different situations can be considered (n_e being the stochiometric amount of plasticizer per resin unit), and eq. (4) can be written as follows:

(a) $n < n_e$:

$$E_a = E_{pl}\frac{n}{1 + n} + E_{PVC-p}\frac{n}{n_e}\left(\frac{1}{1 + n}\right)$$
$$+ E_{PVC-n}\left(1 - \frac{n}{n_e}\right)\frac{1}{1 + n} \quad (7)$$

(b) $n > n_e$:

$$E_a = E_{pl}\frac{n}{1 + n} + E_{PVC-p}\left(\frac{1}{1 + n}\right) \quad (8)$$

Thus, by plotting $E_a(1 + n)$ vs. n, E_{pl}, E_{PVC-n}, and E_{PVC-p} can be calculated.

Experimental results are plotted in Figure 5. As shown in this figure, experimental results fit reasonably well with straight lines in every case above and below the plasticizer equilibrium point ($r > 0.996$). A clear drop in energy results is observed in plasticizer amounts lower than 0.6 and the slope changes for $n > 0.7$. Therefore, energy values can be calculated as indicated in eqs. (7) and (8). The obtained results and comparison with expected parameters are shown in Table I. As can be seen in the table, the obtained results according to eqs. (7) and (8) fit reasonably well with expected parameters as reported in the literature.[3,18]

The differences in energy values between DOP and DBP pastes are in the same order as are differ-

Activation energies.
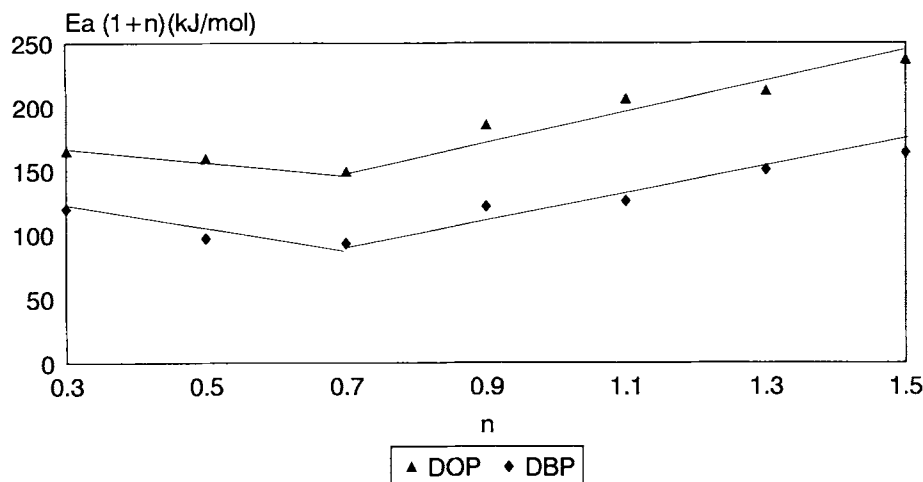
Ea (1+n)(kJ/mol)

Figure 5 Energy calculation according to proposed model: DOP and DBP plastisols.

ences in vaporization energy of plastisols obtained with these plasticizers [$E_{vp(DOP)}$ = 111.0 kJ/mol, $E_{vp(DBP)}$ = 80.6 kJ/mol],[18] so that it could be considered that the plasticizer content is mainly responsible for these differences, as has been suggested above. Moreover, these results indicate the importance of the plasticizer vaporization process in plastisol thermal degradation.

In the interval corresponding to $n < n_e$, it can be seen from Figure 5 that the straight lines have their intercept with the y axes near 170 kJ/mol values. This result was obtained during a previous work[3] and was calculated for n = 0.

CONCLUSIONS

It can be stated that DOP is a much better plasticizer than is DBP to obtain plastisols because DOP pastes

present higher activation energy values, they have a better behavior at high temperatures, and their thermal degradation will be more difficult. This point means a clear advantage because, as it is well known, the main dehydrochlorination product (HCl) is a hazardous gas to humans, animals, and the environment.

In addition, plastisol thermal degradation can be considered as a two-stage process. First of all, there will be a plasticizer evaporation which will be more important according to the excess of this product in the paste. It will mean that the plastisol 3-dimension structure will present some holes which can be considered as active centers in the dehydrchlorination reaction. The whole process will result in an activation energy drop, as has been observed. Finally, a mathematical model to explain this process has been suggested in order to foresee the thermal degradation behavior of plastisols easily.

Table I Comparison Between Obtained and Expected Energy Results (kJ/mol)

	Obtained Results		Expected Results	
	DOP	DBP	DOP	DBP
E_{PVC-n}	177.8	153.6	170.0	170.0
E_p	107.1	90.9	111.0	80.6
E_{PVC-p}	85.8	33.2	90.6	40.1
n_e	0.68	0.58	0.44	0.32

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