

Thermal Behaviour Prediction of Rigid Polyvinyl Chloride

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This work presents the results obtained from experiments of rigid PVC stabilization both lead stabilizer and earth alkaline carbonates as co stabilizer. Efficiency of stabilizers was tested by dynamic tests (roll mill processing or Brabender plastograph) and static test (thermogravimetric analysis). Both types of test were in concordance from point of view of stabilization efficiency and from thermal analysis can be predicted the thermal lifetime of PVC products. This is an important fact for durable usage or for recycling products made from PVC.

Keywords: PVC stabilizers, roll mill, Brabender plastograph, thermal analysis, lifetime prediction, isoconversional method

Polyvinyl chloride is the only polymer susceptible to rapid head degradation within narrow temperatures domain (160°C-190°C). Without a thermal stabilizer, it quickly evolves hydrogen chloride. Various metallic based heat stabilizers have been developed to provide thermal stability for rigid PVC products. Lead stabilizers are widely used in Europe but they present high toxicity and ecotoxicity level. From these reasons, the content of lead stabilizers in PVC products must be lowered without affect thermal stability of PVC.

From all earth alkaline carbonates, magnesium carbonate best helps prevent degradation of PVC during processing by acting as a scavenger for hydrochloric acid. It is an effective co-stabilizer when used with lead stabilizers [1].

There are many techniques for determination thermal stability for PVC such as: red Congo test dehydrochlorination, roll mill processing or Brabender plastograph [2]. One relative recent method, which has been incorporated into an American Society for Testing and Materials standard [3] is thermogravimetric analysis (TGA). This technique has proven to be useful and efficient technique of the estimation of lifetimes of polymers.

The aims of our paper are to estimate the lifetime of various rigid PVC additived with inorganic thermal stabilizers and compare the results with classical method for thermal stability determination.

Experimental part

Analyzed polymer was PVC type suspension (Oltvil Romania), with $K=70$ and content of humidity and volatile substances of maximum 0.5%. As thermal stabilizers, we have used high purity basic magnesium carbonate and tribasic lead sulphate containing 67.4% reactive lead oxide (both supplied by Aldrich Chemical Company). The particle size of PVC and inorganic salts ranged between 0.1 and 0.28 mm. The stabilized samples were prepared mixing mechanically the PVC with 4% tribasic lead sulphate (notated PVC-4%STPb), 4% basic magnesium carbonate (notated PVC-4%Mg) and 1.5% tribasic lead sulphate with 1.5% basic magnesium carbonate (notated PVC-1.5%STPb-1.5%Mg).

The thermal analysis was carried out on a Q-1500 D derivatograph, heating samples of 100 mg each, up to 500°C. The experiments were performed in air at three different heating rates of 5, 10 and 20 °C/min.

Samples of about 100 g were processed into a Brabender plastograph and heated up to 180°C by means of thermoresistant Shell oil and mixed between two rotors having a spinning speed of 50 rot/min.

Other samples, of same composition, were mixed in plastic state, for 5 min at 180°C, on a Berstoff roll mill. The distance between the cylinders was adjusted in order to obtain a sheet thickness of 0.3 mm. Every ten minutes, rectangles were cut out of the foil and visually examined.

Results and discussions

Thermogravimetric analysis

Thermogravimetry is the most widely used technique to characterize the thermal decomposition of polymer materials. Figure 1 shows typical thermogravimetry and derivative thermogravimetry curves as function of temperature for PVC without stabilizer, at a heating rate of 5°C min⁻¹ in air environment.

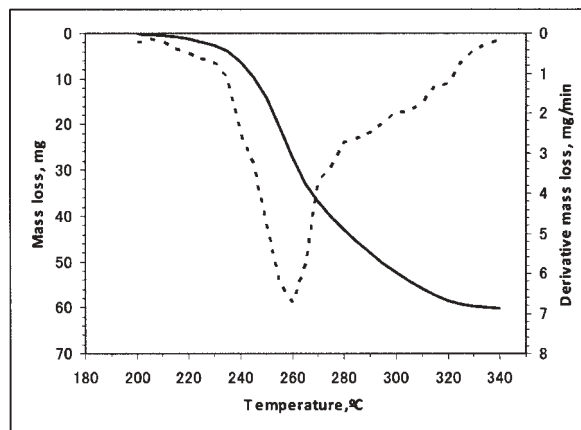


Fig. 1. Typical TGA data for PVC in air environment

It is clear that, between 197°C and 340°C, unadditived PVC mass loss is about 60% with a maximum rate of mass loss around 260°C.

Degradation kinetics

In thermogravimetry analysis, the conversion rate of reaction may be defined as ratio of actual mass loss to initial mass of sample:

$$\alpha = \frac{M_0 - M}{M_0} \quad (1)$$

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where, M_0 and M are the initial and actual masses of the sample.

The rate of degradation, $(d\alpha/dt)$, can be expressed as function of temperature and mass of the sample, i.e.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (2)$$

E is the apparent activation energy of the degradation reaction, often interpreted as the energy barrier opposing the reaction, A is the frequency factor measuring the probability that a molecule having energy E will participate in a reaction, n is the reaction order, R is the gas constant and T is the absolute temperature.

Upon introducing the heating rate, $\beta = dT/dt$, equation (2) can be modified to:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

Therefore equation (3) is the fundamental relationship to determine kinetic parameters on the basis of TGA data. The integral form of equation (3) can be written as:

$$g(\alpha) = \frac{A}{\beta} \int_0^\alpha \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p(x) \quad (4)$$

where $g(\alpha)$ is a conversion function having the following expressions: $-\ln(1-\alpha)$ for $n=1$

and $\frac{1-(1-\alpha)^{1-n}}{1-n}$ for $n \neq 1$, x is ratio E/RT and

$$p(x) = - \int_0^x \frac{\exp(-x)}{x^2} dx.$$

To describe the thermal degradation kinetics, Ozawa [4], Flynn and Wall [5] use Doyle's approximation [6] for $p(x)$ function:

$$\log p(x) = -2.315 - 0.457x \quad \text{for } 20 \leq x \leq 60$$

Introducing Doyle's approximation and taking the decimal logarithm both sides of equation (4) results the following equation:

$$\log g(\alpha) = \log \frac{AE}{R} - \log \beta - 2.315 - 0.457 \frac{E}{RT} \quad (5)$$

For a particular α value, $\log g(\alpha)$, A , and R are constants and equation (5) becomes:

$$\log \beta = C - 0.457 \frac{E}{R} \cdot \frac{1}{T} \quad (6)$$

where the constant C is $C = \log \frac{AE}{R \cdot g(\alpha)} - 2.315$

Hence, the value of E can be calculated from the slope of the most probable straight line obtained by drawing dependence of $\log \beta$ versus $1/T$ for at least three different heating rates.

Figure 2 shows relationships between $\log \beta$ and $1/T$ for different mass loss, during the thermal degradation of unadditived PVC in air environment.

The isoconversional plots from figure 2 are not parallel straight lines, which indicate that the PVC decomposition in air is a complex mass loss process with several changes in degradation mechanism.

The reaction order value, n , can be obtained directly from symmetrical index of derivative curve (DTG) peak based on Kissinger technique [7]:

$$n = 1.26 \cdot \sqrt{\left| \frac{d^2\alpha/dt^2}{d^2\alpha/dt^2} \right|_L / \left| \frac{d^2\alpha/dt^2}{d^2\alpha/dt^2} \right|_R} \quad (7)$$

Indices **L** and **R** correspond to the left and right peak ($d^2\alpha/dt^2$) values on second derivative curve (DDTG).

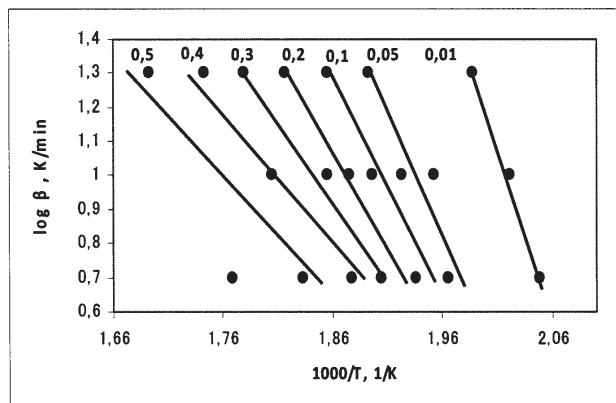


Fig. 2. Dependence $\log \beta - 1/T$ for various conversions of simple PVC at three β -values (5, 10 and 20 K/min)

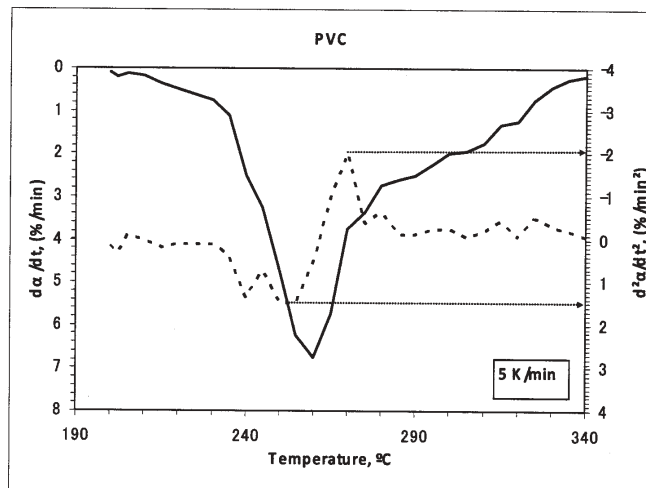


Fig. 3. DTG and DDTG curves of simple PVC at 5K/min heating rate in air.

Figure 3 shows DTG and DDTG curves for PVC at 5 K/min heating rate in air environment.

At this heating rate it can be observed that ratio $|(d^2\alpha/dt^2)_L| / |(d^2\alpha/dt^2)_R| = 1.5/2.05$ and n become 1.08.

With values of E obtained at every conversion rate by Flynn-Wall-Ozawa method it can be determined frequency factor A . Taking natural logarithm and rearrange equation (2) result:

$$\ln A = \ln \frac{d\alpha}{dt} - \ln(1-\alpha)^n + \frac{E}{RT} \quad (8)$$

From equation (8) for same α value, obtained at three β values, results values for $\ln A$ if n is calculated for every β value by Kissinger technique. Temperature T , corresponds be every α value.

In table 1 are listed the n values for decomposition of simple PVC at various heating rates β in air, as well as $\ln A$ values calculated from equation (8) based on activation energies at mass losses of 5% and 10%.

Lifetime prediction

Lifetime estimations using TGA technique are useful in the processing and in development or selection of polymers for different applications where long-term usage is essential. The estimated thermal lifetime t_f of polymer to failure can be defined as time when the mass loss reaches a certain value at temperature T . The principal problem in the data analysis process is the choice of level of decomposition. Typically, an early value in the decomposition profile is more likely to be that of the actual

Table1
THERMAL DEGRADATION KINETIC PARAMETERS OF SIMPLE PVC AT MASS LOSSES OF 5% AND 10%

$\beta, ^\circ\text{C}/\text{min}$	$\alpha=0,05$			$\alpha=0,1$		
	$E, \text{J} \cdot \text{mol}^{-1}$	n	$\ln A, \text{min}^{-1}$	$E, \text{J} \cdot \text{mol}^{-1}$	n	$\ln A, \text{min}^{-1}$
5	132890	1.08	32.04	117280	1.08	28.58
10		1.21	32.65		1.21	28.46
20		1.78	32.15		1.78	28.80
Average		1.36	32.28		1.36	28.61

Table1. Thermal degradation kinetic parameters of simple PVC at mass losses of 5% and 10%.

Table2
ESTIMATION VALUES OF LIFETIME OF SIMPLE AND ADDITIVED PVC BASED ON MASS LOSSES OF 5% AND 10% AT VARIOUS TEMPERATURES

Sample	Lifetime t_f (min)							
	Flynn-Wall-Ozawa method						Roll mill processing at 180°C	Brabender plastograph test at 180°C
	$\alpha=0,05$			$\alpha=0,1$				
	25°C	160°C	180°C	25°C	160°C	180°C		
PVC	$9.5 \cdot 10^7$	5.26	1.03	$1.4 \cdot 10^7$	5.62	1.33	-	-
PVC+4%STPb	$1.4 \cdot 10^9$	16.2	2.73	$9.47 \cdot 10^8$	22.63	4.1	10	20.5
PVC+4%Mg	$8.04 \cdot 10^5$	1.71	0.48	$8.24 \cdot 10^4$	1.12	0.38	5	2
PVC+1,5%STPb +1,5%Mg	$1.61 \cdot 10^9$	16.05	2.66	$6.52 \cdot 10^9$	45.7	7.33	20	21.5

product failure. On the other hand, taking the value too early on the curve may result in the measurement of some volatilization (e.g. moisture) which is not involved in failure mechanism. A value of 5% [8, 9] or 10% [10] decomposition level (conversion) is a commonly chosen value. Other values may be selected to provide correlation with other types of lifetime testing [11].

From the integration of equation (2), the lifetime (min) can be estimated by the following two equations:

$$t_{f(\alpha)} = \frac{[1 - (1 - \alpha)^{1-n}]}{A(1-n)} \exp \frac{E}{RT} \quad \text{for } n \neq 1 \quad (9)$$

or

$$t_{f(\alpha)} = \frac{-\ln(1 - \alpha)}{A} \exp \frac{E}{RT} \quad \text{for } n=1 \quad (10)$$

where: T (K) is temperature imposed to estimate life/time prediction of polymer, α is conversion rate of prediction (usually small i.e. 0.05 or 0.1), A (min^{-1}) is average frequency factor, n is average value for reaction order (evaluated by Kissinger technique) and R is the gas constant ($8,314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

Using kinetic data and equation (9), the estimation results of lifetime values for all PVC samples in air at 5% and 10% mass losses and various temperatures are listed in table 2. For comparison this table contains also values of lifetime obtained by two classical methods.

It is apparent that lifetime of all PVC samples decreases dramatically from 10^5 - 10^9 min to ten or few minutes as temperature increases from 25°C to 180°C. These lifetime parameters clearly suggest that magnesium carbonate alone could not stabilize PVC but in mixture with lead sulphate is a synergetic stabilizer compound. This fact allows to decrease the content of lead stabilizer in PVC with the same results or better in stabilizing process.

Conclusions

All the methods give results in concordance from point of the order decreasing thermal stability of PVC samples: $PVC+1,5\%STPb+1,5\%Mg > PVC+4\%STPb > PVC+4\%Mg$. The differences between values obtained by different methods are due to the techniques used (roll mill and plastograph being dynamical tests from mechanical point of view in comparison with TGA statically test where difficult diffusion of hydrochloric acid has influence on the prediction values).

The isoconversional methods have advantage of estimation lifetime at service temperature (i.e. 25°C) for PVC product. This is an important fact for a durable usage or for recycling products made from PVC.

Also, isoconversional methods allow to mark out the moment when operate one of the stabilizers. At $\alpha=0.05$ lead stabilizer seem to be in action and at $\alpha=0.1$ both stabilizers seem to play an important role as scavengers for hydrochloric acid.

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