

THE PYROLYSIS BEHAVIOR OF MIXTURES  
OF COMMODITY PLASTICS  
WITH POLYVINYL CHLORIDE  
IN A THERMOGRAVIMETRIC ANALYZER

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Summary

Waste plastics make up approximately 20% of the volume of landfill material and almost 10% of the weight. These products contain substantial energy recovery value, and also represent a potentially valuable source of feedstock raw material for additional plastics production. Controlled pyrolysis offers a method of converting raw, mixed waste plastics back into feedstock grade liquids by the application of heat in the absence of oxygen. However, chlorine from the thermal degradation of polyvinyl chloride (PVC) can contaminate the reclaimed liquids making them more difficult and expensive for processing, and also produce a corrosive atmosphere which makes processing more expensive. This paper reports on a study of the impact of PVC on the thermal degradation rates other plastics including polypropylene (PP), polystyrene (PS), low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyethylene terephthalate (PET) in a thermogravimetric analyzer (TGA). Commodity plastics were mixed at various ratios with PVC and analyzed by means of their degradation rates to determine the kinetic rate constants which were compared to the rates obtained for the pure plastics. The values of the kinetic parameters for the pure compounds were all very close to, or within the ranges obtained from the literature. The results indicated that the decomposition behavior of the mixtures differed from those of the pure polymers. These deviations were greatest for mixtures of PVC with polyethylene terephthalate where it was determined that the dehydrochlorination step of PVC catalyzes the decomposition of PET. Pyrolysis of mixtures of PVC and polystyrene at temperatures between 200° C and 350° C result in incomplete dehydrochlorination. This results in more chlorinated compounds being released at higher temperatures.

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## INTRODUCTION

This paper reports on a study to investigate the pyrolysis behavior of mixtures of commodity plastics in a thermogravimetric analyzer. The investigation was focused on the interaction between polyvinyl chloride (PVC) and other polymers including polypropylene (PP), polystyrene (PS), low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyethylene terephthalate (PET). The objective was to determine if interactions which could affect the product yield exist during pyrolysis as a results of these mixtures. The reaction order, the activation energy and the preexponential coefficient for the pyrolysis reaction were experimentally determined. The sample mixtures were prepared by blending two components, PVC and one other polymer and comparing their decomposition behavior to the pure component decomposition behavior.

Recycling is becoming more and more important for the reduction of solid waste material. Recycling has two beneficial results: It reduces raw material needs through material recycling, and it can result in energy recovery. Both compete and complete each other. The implementation ratio for these options depends on a variety of technological and ecological criteria.

Material recycling should always be preferred since it involves both environmental protection and resource savings [10]. Approximately one fifth of the volume of municipal waste is plastics, which represents one tenth of the weight in the United States [2]. Of course the composition and the amounts of municipal solid waste vary widely with the season, the country and many local factors. The world consumption of plastics will grow  $\sim 5\%$  from 1997 till 2005. Therefore an extensive plastic recycling program presents an enormous economic potential of raw material. The recycling of plastics leads to new high-quality products only if a good separation to very pure fractions of single polymers can be reached. For instance this occurs in the recycling of polyvinyl chloride window-frames. The old used frames are collected, purified and ground. The ground particles can be directly admitted to the production of new frames [3]. Such so called mono-product recycling cannot be always used because unfortunately waste plastics are often a mixture of many different polymers and other impurities. Several coupled sorting processes can be used to separate this blend but it is very labor intensive and consequently, expensive. Compound materials, which are very popular, can hardly be separated mechanically. Furthermore, the waste plastics contain many additives that were added to give them properties appropriate for their original use. Thus a recycled feedstock of polymers gained in this way has a restricted purpose and is usually inferior to the original polymer [11]. Current research into plastics recycling is focused mainly on two techniques, pyrolysis and selective solvent extraction.

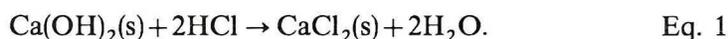
Selective solvent extraction is able to recover single polymers from miscellaneous, polluted plastics. Thereby the matrix polymer can be cleaned at the macromolecular level. It achieves an original re-utilization of the polymer. The process consists of selective dissolution of the desired macromolecules,

removing impurities from the solution and precipitating the target polymer. Problems with this method include regeneration of the solvent and the complexity of trying to isolate five or six or even more different types of plastics.

The basic principle of recycling by pyrolysis is to break apart the carbon-carbon bonds along the polymer backbone by heating under an inert gas atmosphere. This process forms monomers and short chained compounds in the form of gaseous and liquid fractions and leaves a residue char. The composition of the different pyrolysis products depends on the heating rate, residence time, composition of the waste and many other factors. A number of investigations have been carried out in order to study pyrolysis behavior of plastics and the resulting products in respect to all these parameters [18, 14, 13, 16]. But using this technology for treating plastic blends is still at an early stage of development. The countless interactions between the wide variation of substances makes it difficult to achieve a high value feedstock with low concentrations of impurities.

One of the most dramatic problems occurs if the feed into the pyrolysis unit contains polyvinyl chloride. The off-gas is contaminated by hydrochloric acid and other chlorinated compounds. These chemical substances are very corrosive to the facility. They also appear in the condensed liquid product, which is very problematic for further processing. Even small amounts of PVC causes problems. This disadvantage of PVC is not reflected in the production statistics because this polymer has also many exceptional advantages [3] including: Low energy input for production; the use of the huge inexhaustible resources of salt; coupled production of chlorine and caustic soda and hydrogen; and, a lower impact of oil prices on production costs due to the high inorganic content (57% chlorine) in contrast to other plastics.

A stepwise pyrolysis process has been investigated to overcome the problem of PVC contaminated wastes [8]. This technology is based on the knowledge that every single polymer decomposes at a particular temperature. Furthermore, it benefits from the unique ability of PVC to degrade in two steps. During the first step, the bound chlorine is converted mainly into hydrogen chloride and, to a much lesser degree, some chlorinated hydrocarbon and plain hydrocarbons. It is possible to release about 99,6% of the chlorine by heating to a temperature of 330°C [6]. The second step takes place at a temperature between 370°C and 470°C during which the polymer backbone of the PVC breaks apart along with the other polymers. This technology was implemented in a three reactor cascade in a laboratory plant, and performed well with polymer blends containing 10 to 15% PVC [5]. The polymers were pyrolyzed one after another at 330°C and 440°C. Every reactor produced a product flow whereby the first reactor removed 99,5% of the chlorine from the plastic mixture. Another way to handle very low PVC concentrations (> 2%) is to add some calcium hydroxide [17]. The hydrogen chloride produced from the pyrolysis of PVC is bound as follows:



However the drawback is that some chlorinated organics are formed which escape from the chemical scrubbing. Therefore pyrolysis might be a promising technique of converting all plastic simultaneously to a high value feedstock by a comparatively simple process, but a better understanding of the impact of PVC concentrations in the mix is needed in order to further develop the technology.

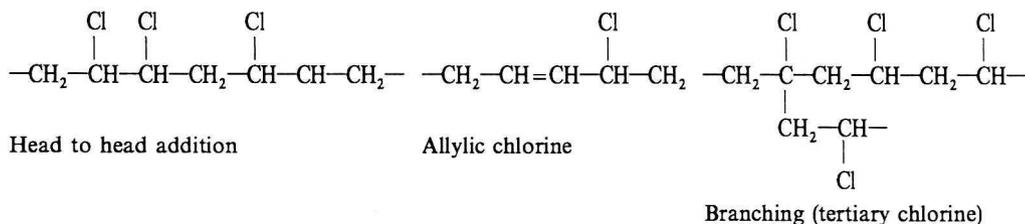
## BACKGROUND

### TYPES OF POLYMER DEGRADATIONS

Polymers can degrade by several mechanisms which vary depending on the environmental conditions in which the polymer is used, the manufacturing history and the structure of the polymers [1]. These mechanisms include thermal, mechanical, ultrasonic, hydrolytic, chemical, biological and radiation. When considering pyrolysis, only thermal and chemical degradation play an important role.

### GENERAL REACTION MECHANISM

Eq. 2



Thermal degradation itself is controlled by one of three general mechanisms or combinations of these three. Random scission, which is the predominant reaction in polyolefins, occurs through scission of bonds along the backbone chain. As the term implies, scission is a random event, and polymer molecules are first broken into large macro radicals. Depolymerization is the second general mechanism. This reaction is usually initiated at chain ends and monomer units are split off sequentially. Since only a small fraction of molecules react at the beginning, there is very little change in molecule weight. Once depolymerization has been initiated in a molecule, the reaction proceeds until the molecule has depolymerized completely. The third general mechanism is characterized by elimination of low molecular weight fragments. The splitting off of hydrogen chloride from polyvinyl chloride is a typical example.

A polymer is not normally an ideal string of monomers. Usually irregularities are always present and lead to different lower stabilities than for the pure polymer. Equation 2 shows a few examples of polyvinyl chloride's possible irregularities [12].

PVC usually starts to degrade at such structural defects like chain fragments of head to head additions, side branch and tertiary chlorine sites and

internal double bonds. The PVC degradation consists of two stages as mentioned previously. The first step is mainly a formation of carbon-carbon double bonds in macromolecules. Thereby, hydrochloric acid is formed in a nearly stoichiometric ratio. But formation of small amounts of benzene, toluene, naphthalene, chlorinated aromatic compounds etc., also happens in this stage. This dechlorination takes place mainly at a lower temperature than the depolymerization given in equation 3 as



This is because bond dissociation energy of a C-Cl bond (328 KJ/mol) is lower than that of a C-C bond (344 KJ/mol) [19]. Above 330°C the dechlorinated polymer undergoes further cracking and low molecular hydrocarbons of linear and cyclic structure are formed. As shown above during the degradation of polymers, several reactions take place simultaneously. In addition, other polymers have complex degradation behaviors which further complicate the problem of pyrolysis of mixtures.

## EXPERIMENTAL PROCEDURES

### DESCRIPTION OF THE EXPERIMENTAL SETUP

The thermogravimetric experiments are carried out with a DuPont Thermogravimetric Analyzer (TGA) thermobalance (Model #951) driven by a programmable thermal controller.

Nitrogen gas was used to purge the off-gas away from the reaction zone. The flow rate was always 20 ml/min. The reaction chamber was purged with a nitrogen flow rate of 500 ml/min for 5 min to eliminate any oxygen before any of the experiments were started. The sample thermocouple was calibrated after every tenth run.

### SAMPLE PREPARATION

Normal commercial plastics like those found in municipal solid waste were used for the experiments. The code marking for every plastic, as given in Table 1, helps to identify the polymer species.

Table 1. Plastic Identification Codes

Resin	Code*	Abbreviation
Polyethylene terephthalate	1	PET
High-density polyethylene	2	HDPE
Polyvinyl chloride	3	PVC
Low-density polyethylene	4	LDPE
Polypropylene	5	PP
Polystyrene	6	PS
Miscellaneous (usually mixed)	7	—

\* Number found within the „arrow” recycle triangle on the plastic.

The plastic products were cut into strips and thoroughly cleaned to remove any existing residue stemming from their former use. The pieces were cut into narrow strips which were ground into powder by a grindstone. Unfortunately not all of the plastics could be ground by using this method. These plastics were cut into small pieces (0.5 cm × 0.5 cm) and ground in a laboratory mill together with a little liquid nitrogen. The liquid nitrogen was necessary to cool the plastics and make them more brittle. The powdered plastics were sieved to obtain samples smaller than 0, 063 mm. After mixing the different plastic powders to the desired ratio, the powder mix was pressed into small discs to help minimize the electrostatic properties which made the powders difficult to handle. Prior to pressing the discs, the powder mix was softened by heating to 100°C. A mold with an inner diameter of 6.35 mm was used with a compression force of ~22 KN to produce discs of ~0.5 mm thickness. Each disc had a weight of ~15 mg. The resultant discs did not break apart while handling and were used in the TGA experiments.

#### EXPERIMENTAL MATRIX

Experiments were performed to determine the degradation rates and kinetic parameters for the pure compounds which were used in later tests for comparison purposes. The TGA conditions for these experiments are listed in Table 2.

Table 2. Pure Compound Experimental Matrix

RUN	SAMPLE	Sample disc	RAMP	Commercial	Pure
1	HDPE	pressed powder	8 K/min	+	
2	HDPE	pressed powder	5 K/min	+	
3	HDPE	pressed powder	2 K/min	+	
4	HDPE	pressed powder	1 K/min	+	
5	HDPE	pressed powder	0.5 K/min	+	
6	HDPE	pressed powder	2 K/min		+
7	HDPE	powder	2 K/min	+	
8	HDPE	punched disc	2 K/min	+	
9	PVC	pressed powder	2 K/min	+	
10	PP	pressed powder	2 K/min	+	
11	PS	pressed powder	2 K/min	+	
12	PET	pressed powder	2 K/min	+	
13	LDPE	pressed powder	2 K/min	+	

Detailed experiments were conducted on mixtures at a heating rate of 2°C/min (the effect of heating rate is discussed following this section). The composition of the samples are given in Table 3. Weight changes were detected at temperatures >225°C and <650°C. The temperature program of the TGA

was as follows; ramped to an initial starting temperature of 170°C, at which point the 2°C/min ramp was held until 650°C; the ramp rate was changed to 10°C/min was to 900°C to convert the remaining char and clean the sample pan. Every experiment was repeated at last once to verify the reproducibility.

Table 3. Mixture Experimental Matrix

RUN	COMPOSITION
14	30% PVC + 70% HDPE
15	50% PVC + 50% HDPE
16	70% PVC + 30% HDPE
17	30% PVC + 70% LDPE
18	50% PVC + 50% LDPE
19	70% PVC + 30% LDPE
20	30% PVC + 70% PP
21	50% PVC + 50% PP
22	70% PVC + 30% PP
23	30% PVC + 70% PS
24	50% PVC + 50% PS
25	70% PVC + 30% PET
26	30% PVC + 70% PET
27	50% PVC + 50% PET
28	70% PVC + 30% PET

## DATA ANALYSIS

### THE REACTION RATE EXPRESSION

As mentioned above, the mechanisms of pyrolysis include a wide range of different reactions. Not every reaction causes a release of a volatile molecule. Some only cause a change of mechanical properties. By the use of thermogravimetric analysis, only the weight loss is measured during heating, meaning only those reactions causing the weight loss are considered. Furthermore, because of the system complexity, all reactions are lumped together like an overall reaction. The following overall rate expression can normally be used to describe pyrolysis reactions [5].

$$\frac{d\alpha}{dt} = k(T) \cdot (1 - \alpha)^n \quad \text{Eq. 4}$$

In this equation  $\alpha$  is the dimensionless degree of conversion which is defined as  $\alpha = (m_0 - m)/(m_0 - m_\infty)$  where  $m_0$  is the initial mass,  $m$  is the mass reading at any time and  $m_\infty$  is the final mass;  $k$  is the rate coefficient which is a function of temperature ( $T$ ) only, and  $n$  is the apparent reaction order. The rate coefficient  $k$  often takes an Arrhenius type of temperature dependency shown in equation 5.

$$k(T) = k_0 \cdot e^{-\frac{E_A}{RT}}. \quad \text{Eq. 5}$$

$$\frac{d\alpha}{dt} = k_0 \cdot e^{-\frac{E_A}{RT}} \cdot (1-\alpha)^n. \quad \text{Eq. 6}$$

Here,  $k_0$  is the preexponential factor,  $E_A$  the activation energy and  $R$  the universal gas constant.

#### METHODS TO DETERMINE OVERALL KINETIC PARAMETERS OF DECOMPOSITION REACTIONS

##### Isothermal method

One method of determining overall kinetic parameters of decompositions is to perform several isothermal experiments in a thermogravimetric analyzer at different temperatures. The main advantage of this method is that changes in mechanisms are detectable because one can decomposition rates of the whole conversion range for single temperatures. However a few problems also occur. While the sample is being heated to the desired temperature, partial conversion takes place. Additionally, due to the various measurements required at different temperatures, a higher amount of sample is necessary and therefore the measurement method becomes extensive [7].

##### Dynamic method

Under the dynamic method, the sample is heated at a constant rate. Thereby, the weight loss and the decomposition rate are obtained as a function of temperature and conversion. The advantage of this method is that the kinetic parameters can be obtained from just one experiment. However, these parameters are able to describe the overall decomposition reaction only. It can not be used to study the reaction in detail like isothermal methods because the parameters are determined for the whole temperature range rather than at a specific temperature. Therefore the parameters have a temperature-average character. This method is more realistic when the experimental reaction conditions are similar to those of a practical application (e.g. a pyrolysis unit). Thus, it is more reasonable to predict the degradation behavior of plastics in a pyrolysis unit by performing experiments with dynamic measurements. Furthermore, this method is also very suitable for a fast overall characterization of decomposition behavior.

##### Requirements for Dynamic Measurements

For more reliable results, experiments have to be performed with small sample amounts of only a few milligrams which is due to the continuous heating and limited heat conductivity (the interior of the sample is always cooler than the surface). As a result, the reaction in the outer layer is faster than in the inner layer. Low heat conductivity increases this negative effect. It is possible to limit this drawback by reducing the size of the sample and using

lower heating rates. Another problem is related to the technique of how the temperature is measured. Normally a small thermocouple is located beside the sample, not on the sample. Therefore, the thermocouple just measures the temperature of the gas flowing through the reaction chamber. However in reality, the temperature of the sample is always lower than the surrounding gas. Due to the continuous heating there is always a heat flux from the gas to the sample. This heat flux happens only if there is a temperature gradient. The result is that the sample temperature differs from the measured temperature.

#### True Sample Temperature

The change of the sample's temperature by heat transfer and heat release from the reaction is given by:

$$m \cdot c_p \cdot \frac{dT_s}{dt} = \dot{Q}_t - \dot{Q}_r. \quad \text{Eq. 7}$$

To simplify this equation, it is assumed that the mass of the sample and the contribution of the heat of reaction is insignificant because the sample pan has a 50 times higher weight than the sample and the reaction rates are very slow. In equation 7,  $c_p$  is the heat capacity of the sample pan and  $m$  is its weight.  $\dot{Q}_t$  is the heat flux to the sample pan and can be approximated by  $\dot{Q}_t = k' \cdot (T - T_s)$  where  $k'$  is the overall heat transfer coefficient. Equation 7 can then be rewritten as

$$m \cdot c_p \cdot \frac{dT_s}{dt} = k' \cdot (T - T_s), \quad \text{Eq. 8}$$

$$T(t) = T_0 + \beta \cdot t, \quad \text{Eq. 9}$$

$$\tau = \frac{m \cdot c_p}{k'}, \quad \text{Eq. 10}$$

$$\tau \cdot \frac{dT_s}{dt} = (T - T_s). \quad \text{Eq. 11}$$

Here,  $\beta$  is the heating ramp rate,  $T_0$  is the initial temperature or room temperature, and  $\tau$  combines the effect of the pan weight and pan heat capacity, and the heat transfer coefficient.

Equation 11 can be solved to give the sample temperature as a function of time.

$$T_s(t) = T_0 + \beta \cdot t - \beta \cdot \tau + \beta \cdot \tau \cdot e^{-\frac{t}{\tau}}. \quad \text{Eq. 12}$$

For  $t \rightarrow \infty$  the expression reduces to:

$$T_s(t) = T_0 + \beta \cdot (t - \tau). \quad \text{Eq. 13}$$

This simplified equation indicates how the heating rate influences the temperature divergence between the sample and the surrounding gas. The lower the heating rate, the lower the difference.

Experiments were performed at different heating rates to determine the magnitude of the temperature difference. It was experimentally determined that heating rates from 2–8 K/min gave results with minimal difference. These heating rates were used in subsequent experiments.

#### THE COMPUTATION OF THE KINETIC PARAMETERS

The derivation of the kinetic parameters from the dynamic thermogravimetric measurements can be performed by many different methods including differential, integral and isoconversional methods [4]. The principle is in each case to fit a model like equation 6 to the measured decomposition rates or conversions. In this research, two techniques were used to analyze the data. A multi-linear regression technique was used to approximate the kinetic parameters by taking the natural logarithm of equation 6 as shown in equation 14:

$$\ln \frac{d\alpha}{dt} = \ln k_0 - \frac{E_A}{R} \cdot \frac{1}{T} + n \cdot \ln(1-\alpha). \quad \text{Eq. 14}$$

which has the form

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2. \quad \text{Eq. 15}$$

The correlation of the variables is shown by establishing the linearity of equation 15. The statistical regression can be done with a statistics program. One problem with this method is that the whole range of conversion data can not be used, because small values for the conversion lead to a logarithm very closed to one and, the measured values just do not fit this mathematical model over the whole temperature and conversion range. Therefore, a more precise technique was developed. This method is a nonlinear regression technique which avoids the errors induced by the logarithm and the derivative of the weight loss which tends to be unstable. Equation 6 is modified by introducing the heating rate from equation 9 as shown in equation 16:

$$\frac{d\alpha}{dt} k_0 \cdot e^{-\frac{E_A}{R(T_0 + \beta \cdot t)}} \cdot (1-\alpha)^n. \quad \text{Eq. 16}$$

Equation 16 is numerically integrated to give the conversion values as a function of time. The sum of squares of the deviations (SSQ) between the calculated conversion values and the respective measured conversion is then calculated. For one set of parameters this sum of squares of deviations as determined by equation 17 has a minimum.

$$SSQ = \frac{1}{N} \sum_{i=1}^N [\alpha_{\text{meas},i} - \alpha_{\text{modcl},i}]^2. \quad \text{Eq. 17}$$

Where  $N$  is the number of data points used,  $\alpha_{\text{meas},i}$  is the measured value of conversion and  $\alpha_{\text{model},i}$  is the value of conversion calculated from equation 16 by assuming values of  $k_0$ ,  $E_A$  and  $n$ . This set presents the best fit for the kinetic parameters to the reaction. Initial values and ranges of  $k_0$ ,  $E_A$  and  $n$  are obtained from the multi-linear regression method of equation 15.

The steps for the determination of the kinetic parameters include determining the values of dimensionless conversion for the appropriate temperature range. To reduce the computation time, approximately 40 data points were used. The time correlates to the temperature by the heating rate. Therefore the time is reset to zero at the starting point of this temperature range. The multiple linear regression method is then used to obtain approximate values of the kinetic parameters. Then equation 16 and 17 are used to calculate the least square approximation for the assumed parameters. The problem is complicated by the fact it is sometimes difficult to find the global minima of the sum of squares of the deviation if three or more parameters have to be determined. Therefore the search for this minimum is split in two parts. For the first part, the sum of the squares are minimized for a specified reaction order. This is an easier and faster process because only two parameters are to be determined. The next step is to plot the sum of the square of the deviations against the reaction order for a given value of  $k_0$  and  $E_A$  as illustrated in Figure 1.

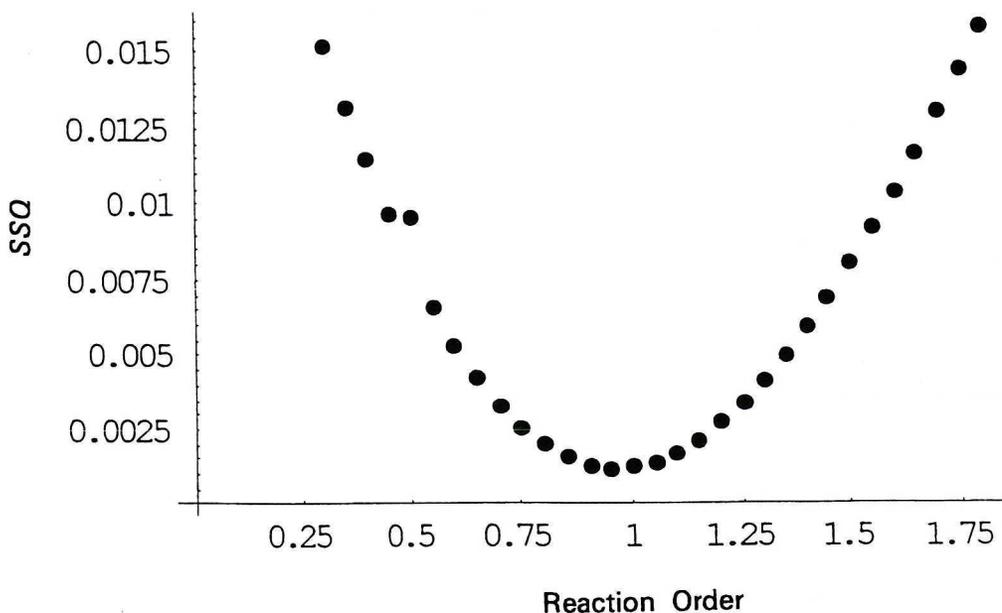


Fig. 1. Example of the Sun of the Squares of the Deviations versus Reaction Order (HDPE @ 2 K/min heating rate)

Additionally, it was assumed that the reaction order determination should show a minimum somewhere between 0.3 and 2. Any minimum outside this range may not be suitable. Subject to the condition that the graphical presentation suggests an existing minimum, an interpolation function is created. The minimum of this function gives the required reaction order. These computations were performed with the software program Mathematica<sup>®</sup>. Figure 2 illustrates visually that the model fits the experimental data with the determined parameters. Solid circles are for the experimental data and the continuous curve represents the calculated conversion.

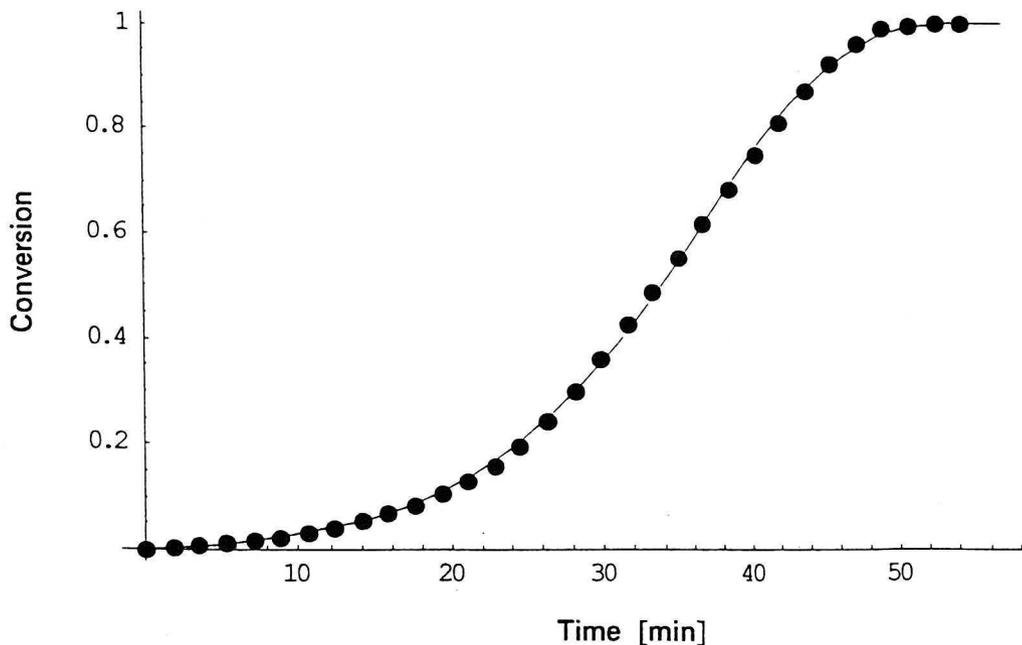


Fig. 2. Comparison of the Model and the Experimental Data (HDPE @ 2 K/min heating rate; ● data; — model)

## RESULTS AND DISCUSSION

### INFLUENCE OF THE HEATING RATE/GRINDING

Experiments with both ground samples and unground material showed that grinding had a negligible effect on the decomposition behavior of the polymers.

Different heating rates lead to significant differences in the conversion of the polymer. The lower the heating rate the further the conversion is shifted to lower temperatures as shown in Figure 3 for HDPE. The data in Figure 4 show that low heating rates cause a slower decomposition, and the reaction takes

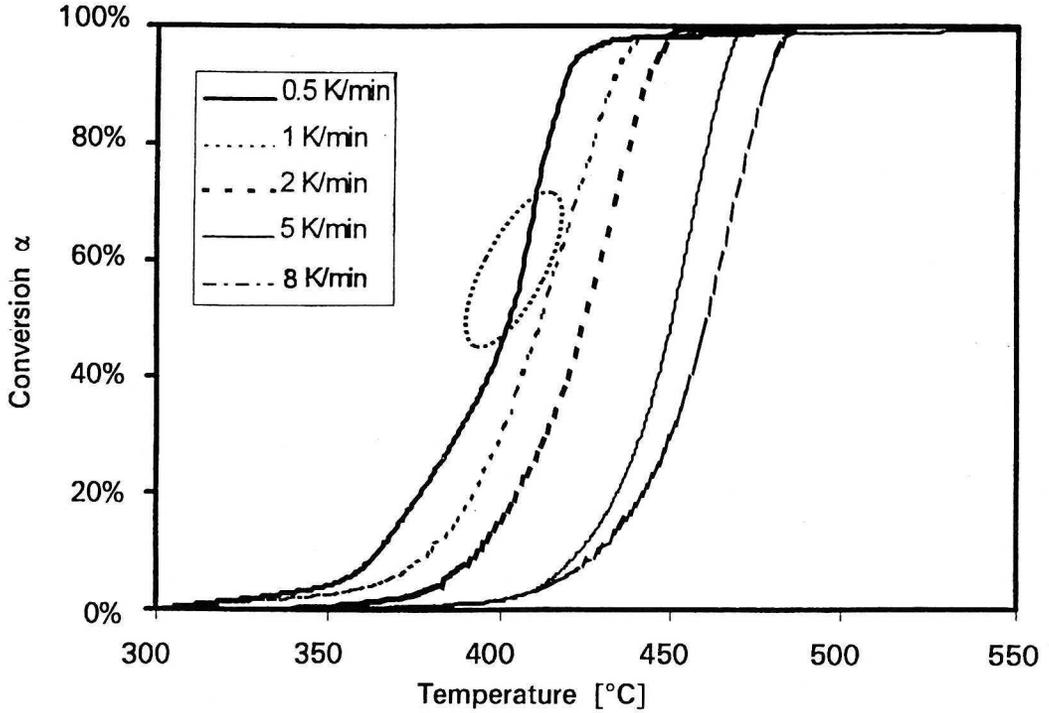


Fig. 3. Conversion versus Temperature for Different Heating Rates for HDPE

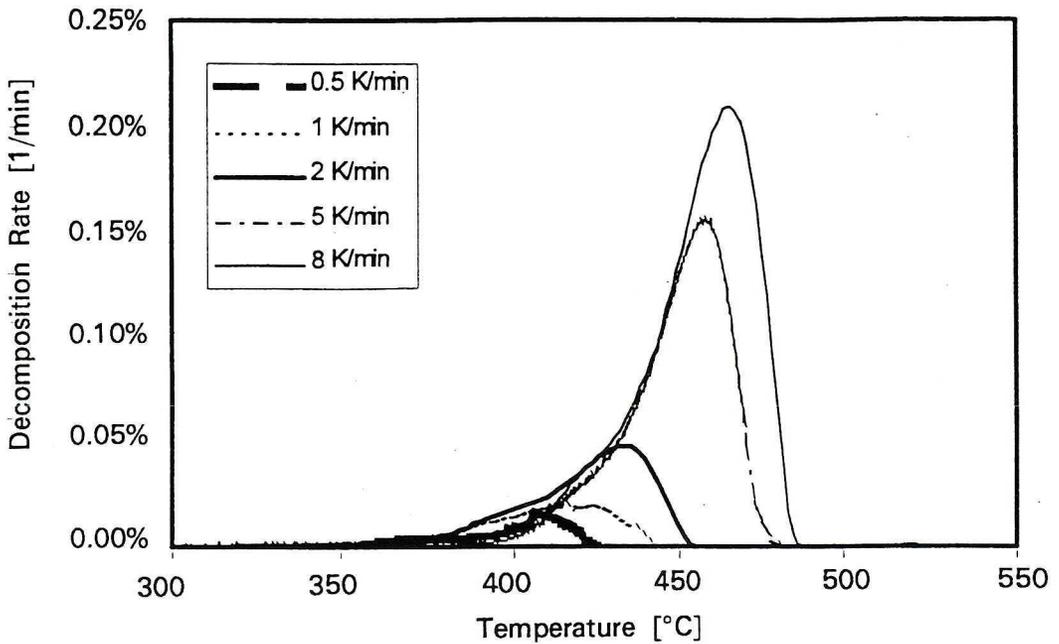


Fig. 4. Decomposition Rates versus Temperature for Different Heating Rates for HDPE

place in a more restricted temperature range than at higher heating rates. The consequence is that heat transfer limitations at low heating rates are much lower compared to higher heating rates, which leads to a more precise temperature measurement due to the condition mentioned previously.

Figure 5 shows that the apparent activation energy increases at higher heating rates, but approaches a constant value around  $2^\circ\text{C}/\text{min}$ . This effect is caused by the difference between the measured and actual temperature as discussed previously. For heating rates lower than  $2^\circ\text{C}/\text{min}$  a calculation of the kinetic parameter can not be performed because the trend of the weight loss graph contains discontinuities as indicated by a dashed oval in Figure 3. Therefore, a heating rate of  $2^\circ\text{C}/\text{min}$  was used for all subsequent experiments.

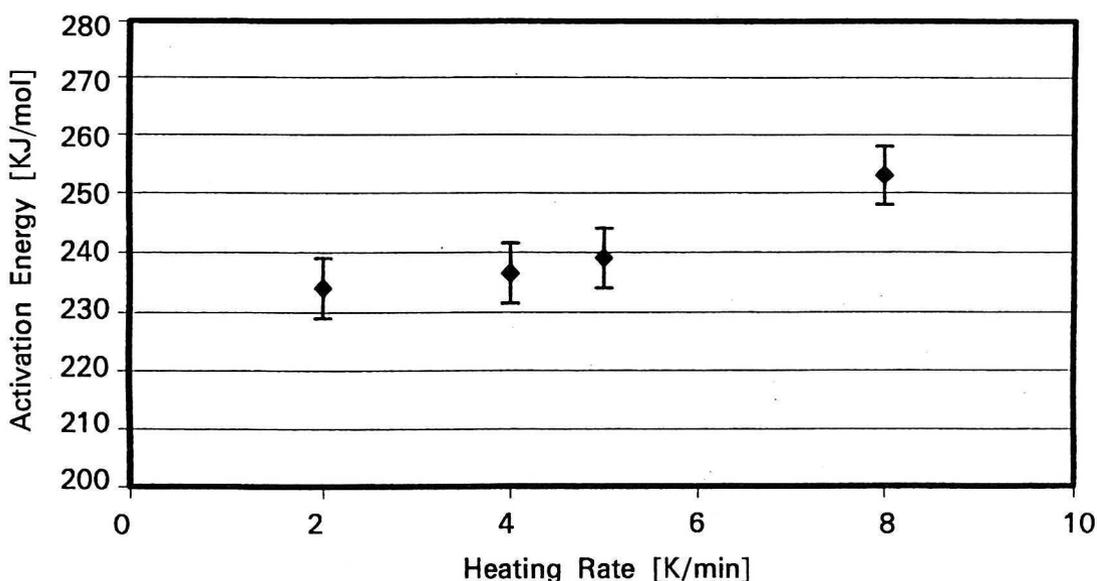


Fig. 5. Activation Energy versus Heating Rate for HDPE

#### EVALUATION OF THE EXPERIMENTS WITH PLASTIC MIXTURE

To find out if the presence of polyvinyl chloride has an influence on the decomposition behavior or other polymers, a composite model was created. This model consisted of the addition of the weight loss curves of the single polymers with regard to the composition of the mixture. The model represents the weight loss of the mixtures assuming no interactions among the individual polymers. These curves were then compared to weight loss values from the experiments taken with the discs produced with the polymer blends as given in Table 3. The relevant kinetic parameters determined from these experiments are given in Table 4, and are compared to those obtained from the literature.

Table 4. Kinetic Parameters of the Decomposition Reactions

	$\ln(k_0)$ [ $\text{min}^{-1}$ ] (from literature)	$E_a$ [ $\text{KJ mol}^{-1}$ ] (from literature)	$n$ (from literature)
PVC dehydrochlorination	30.8/(28.0–28.8)	152/(136–160)	1.3/(1.4–1.54)
PVC 2nd step degradation	42.5/(35.0–37.6)	265/(234–263)	1.85/(1.5–1.64)
Polystyrene	40.0/(24.8–56.7)	237/(172–322)	0.95/(0.5–1.09)
Polypropylene	33.1/(24.8–36.6)	192/(184–237)	1.15/(0.77–0.9)
High-density polyethylene	38.0/(32.2–41.5)	235/(233–262)	0.85/(0.74–0.83)
HDPE reference sample	40.2	247	0.8
Low density polyethylene	38.5/(27.8)	238/(206)	0.63/(0.9)
Polyethylene terephthalate	46.0/(41.5)	275/(238.7)	1.2/(1.15)
1st degradation step			
30% PS+70% PVC	32.3	162	1.6
50% PS+50% PVC	32.1	158	1.55
70% PS+30% PVC	30.7	152	1.6
30% PET+70% PVC	32.3	162	1.15
50% PET+50% PVC	33.2	166	1.1
70% PET+30% PVC	39.1	196	1.35
2nd degradation step			
30% PS+70% PVC	42.7	239	0.97
50% PS+50% PVC	46.3	261	0.82
70% PS+30% PVC	41.7	246	1.13
30% PET+70% PVC	39	245	1.35
50% PET+50% PVC	38.2	229	1.4
70% PET+30% PVC	41.4	245	1.3

The results of pyrolysis experiments of blends of PVC and polyethylene terephthalate (PET) showed that interactions occur. This is obvious as shown in Figure 6. The weight loss between 250°C and 350°C is much higher than the weight loss predicted by the model. This means the dehydrochlorination of the PVC catalyzes the decomposition of the PET. This phenomenon agrees with observations of other researchers [15] who have reported that a dramatic chain scission of the polyester occurs due to the presence of PVC. To further understand the influence of the PVC concentration, a mass balance was performed. This balance determined the percentage of PET which decomposed in the presence of PVC until reaching 350°C. The results are given in Table 5.

From the data in Table 5, the percentage of the degraded PET is higher at higher PVC concentrations. The activation energy and the reaction order of the first decomposition stage are plotted against the PVC concentration in Figure 7. The results indicate that the activation energies of the PET-PVC mixtures are bracketed by their pure component values and vary in an exponential manner

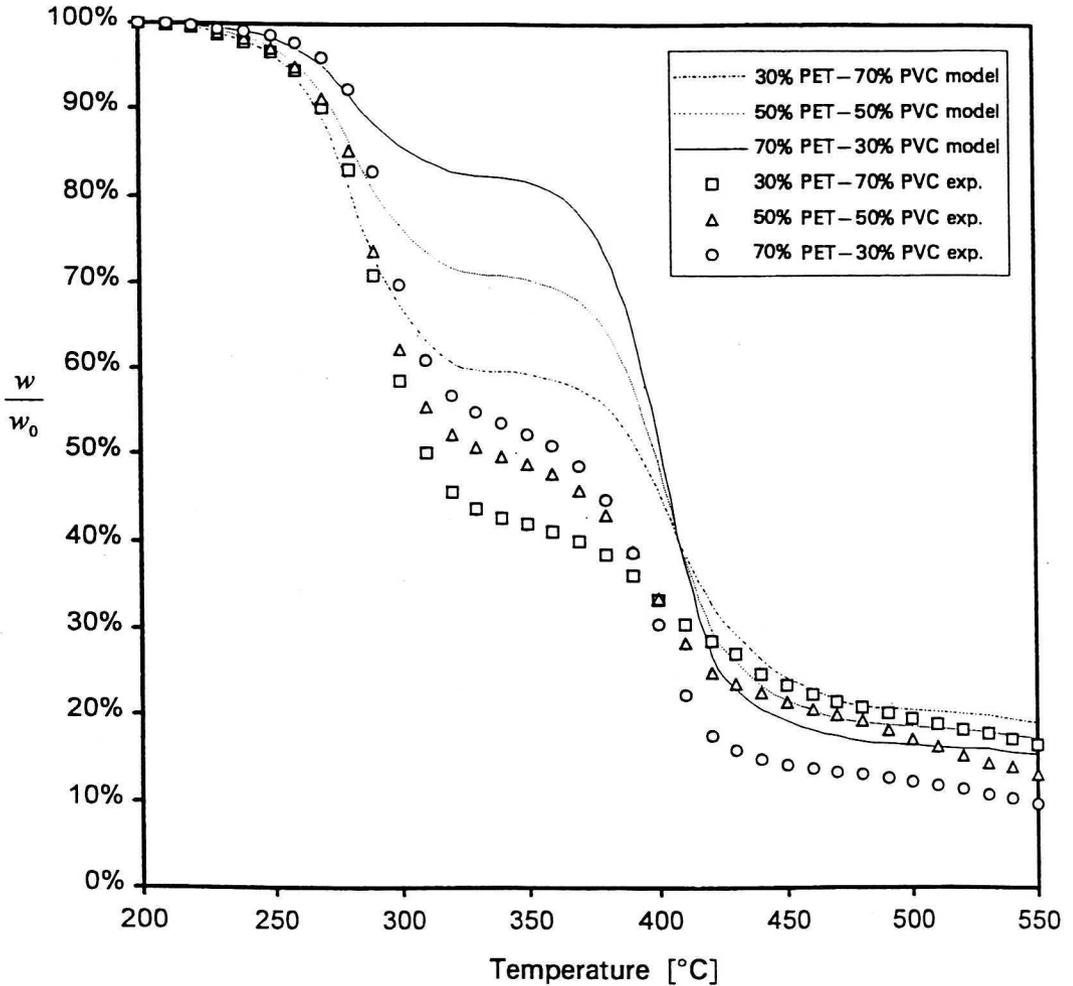


Fig. 6. Weight Loss Curves for Different PVC-PET Mixtures

Table 5. Mass balance of the PVC-PET system

15 mg sample	$w_{\text{PET, init}}$	$w_{\text{PVC, init}}$	$w_{\text{sample, model}}$	$w_{\text{sample, exp.}}$	$Dw_{\text{model-exp.}}$	$Dw_{\text{model-exp.}}/w_{\text{PET, init}}$
70% PET + 30% PVC	10.5	4.5	12.3	7.875	4.4	42%
50% PET + 50% PVC	7.5	7.5	10.6	7.365	3.2	45%
30% PET + 70% PVC	4.5	10.5	8.9	6.315	2.6	58%

from that of pure PET to that of pure PVC. After the second stage, there is almost no difference between the predicted and actual amounts of char.

The interaction between polystyrene (PS) and PVC shows an opposite effect than that of PET and PVC discussed above. It has been reported that radical

intermediates from the decomposition of polyvinyl chloride and polystyrene stabilize one another [9]. This results partly in lower weight loss during the first degradation step, especially in the mixture of 30% PVC+70% PS as shown in Figure 8. This means less hydrochloric acid is released in the first degradation step. Figure 9 shows the activation energies and reaction orders for mixtures of PS with PVC. The activation energies of these mixtures are all approximately the same as pure PVC.

When polyethylene or polypropylene are pyrolyzed with polyvinyl chloride, interactions are not detectable by thermogravimetric analysis as shown in

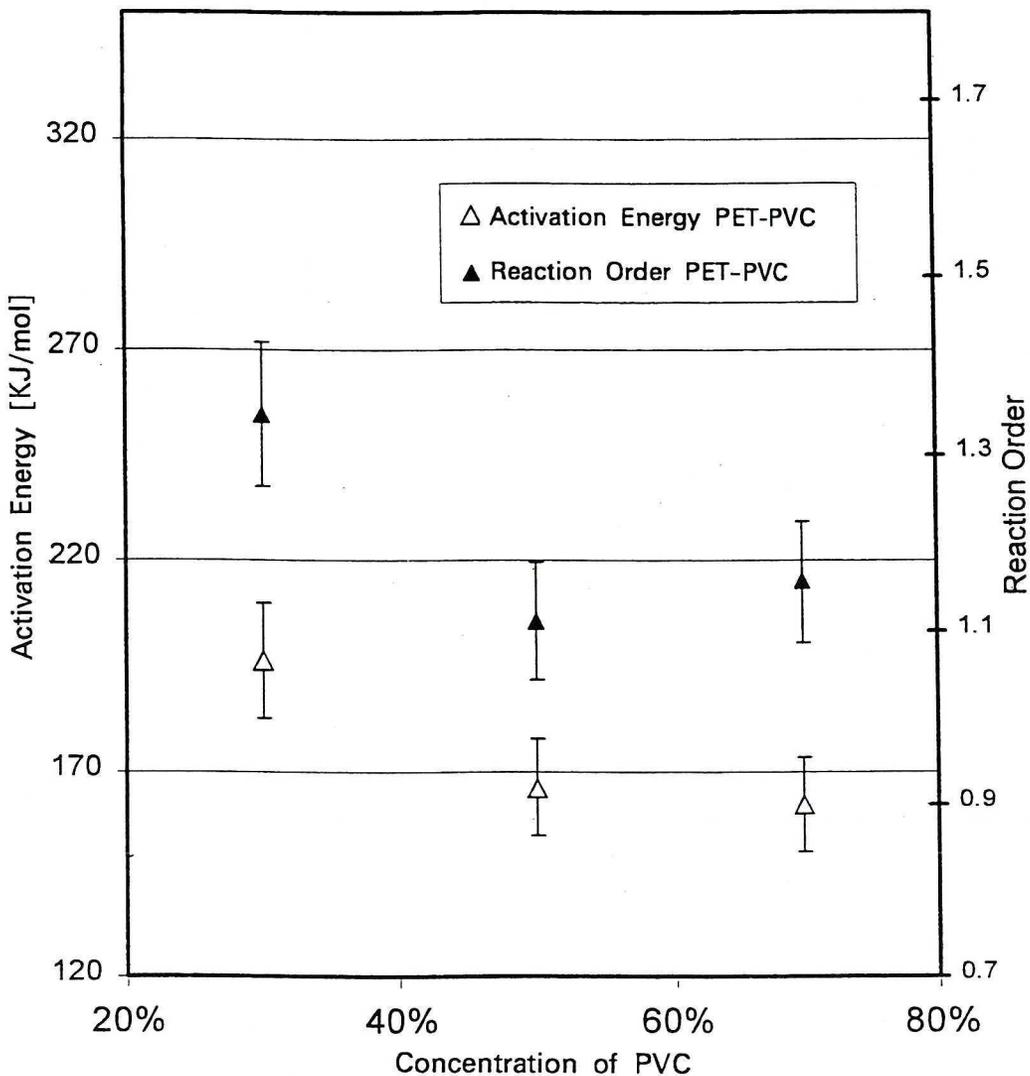


Fig. 7. Activation Energy and Reaction Order for Mixtures of PERT and PVC

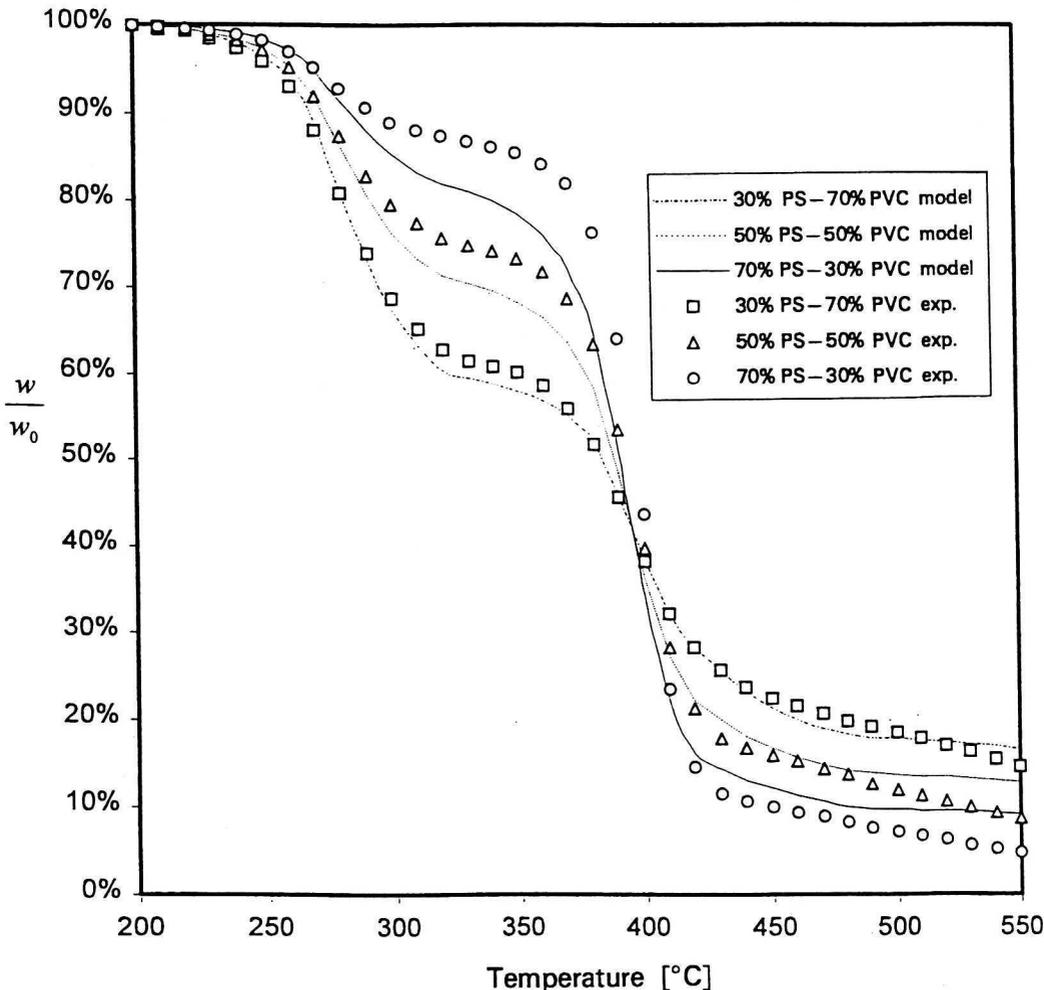


Fig. 8. Weight Loss Curves of Different PVC-PS Mixtures

Figures 10–12. As shown in these figures, a variation of the PVC content does not result in a significant difference from the predicted weight loss curves for the addition of pure compounds. A very small exception is the small deviation at the upper temperature of the temperature range. The char weight appears to be slightly lower than that predicted. A reason could be that the plastic mixture, after overcoming both degradation steps, yields a char with a higher porosity. When single polymers were pyrolyzed, all degraded without any significant amounts of char except PVC, which always resulted in ~15% char by weight. Therefore immediately after the second degradation step the polymer admixture results in extra pores in the PVC residue. This can support the transport of reaction products out of the reaction zone what leads to a further weight loss.

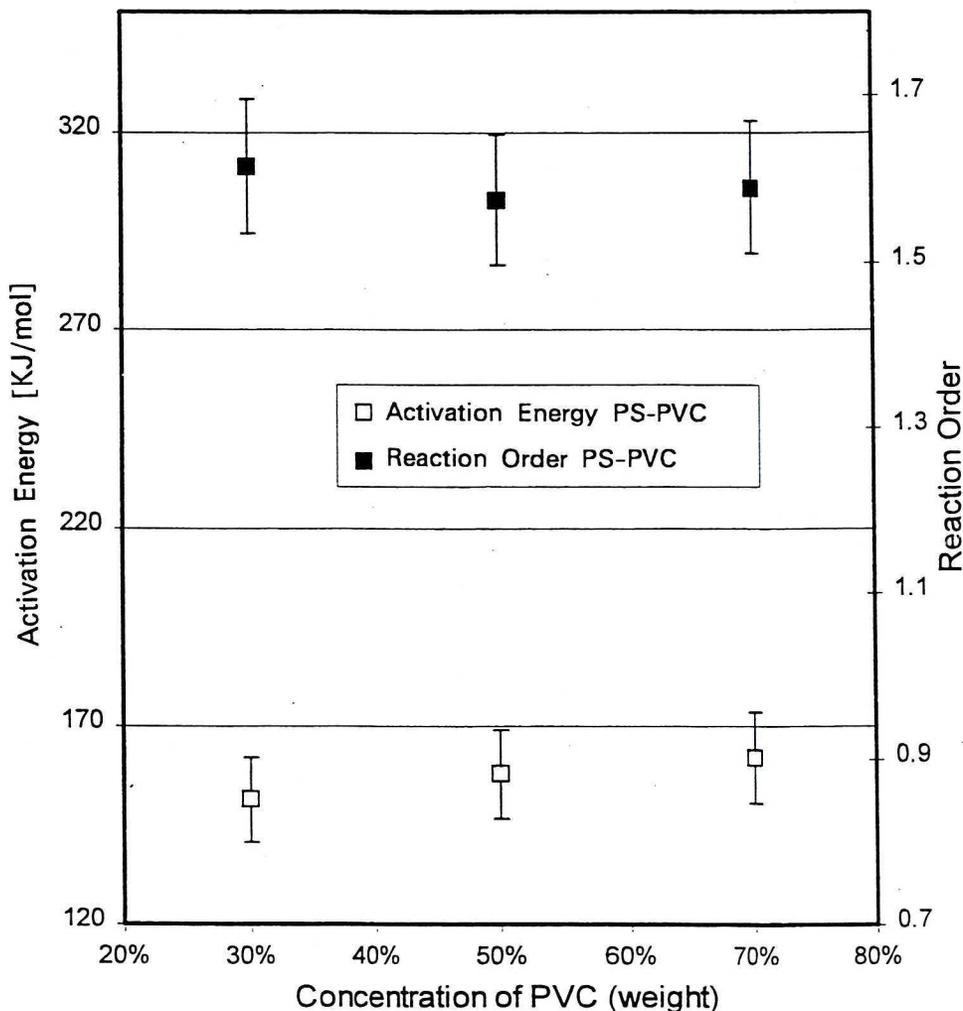


Fig. 9. Activation Energy and Reaction Order for Mixtures of PS and PVC

No attempt was made to obtain the kinetic parameters of the decomposition of polyolefins and the polypropylene mixed with PVC because the overall decomposition reaction can easily be obtained by adding two single reactions of known parameters.

## CONCLUSIONS

Pyrolysis of waste plastics offers a potential energy saving method for reclaiming the organic material of these materials for use as feedstock. However, polyvinyl chloride in the input stream has the potential of contaminating the resulting products. Pyrolysis might be a promising technique of converting

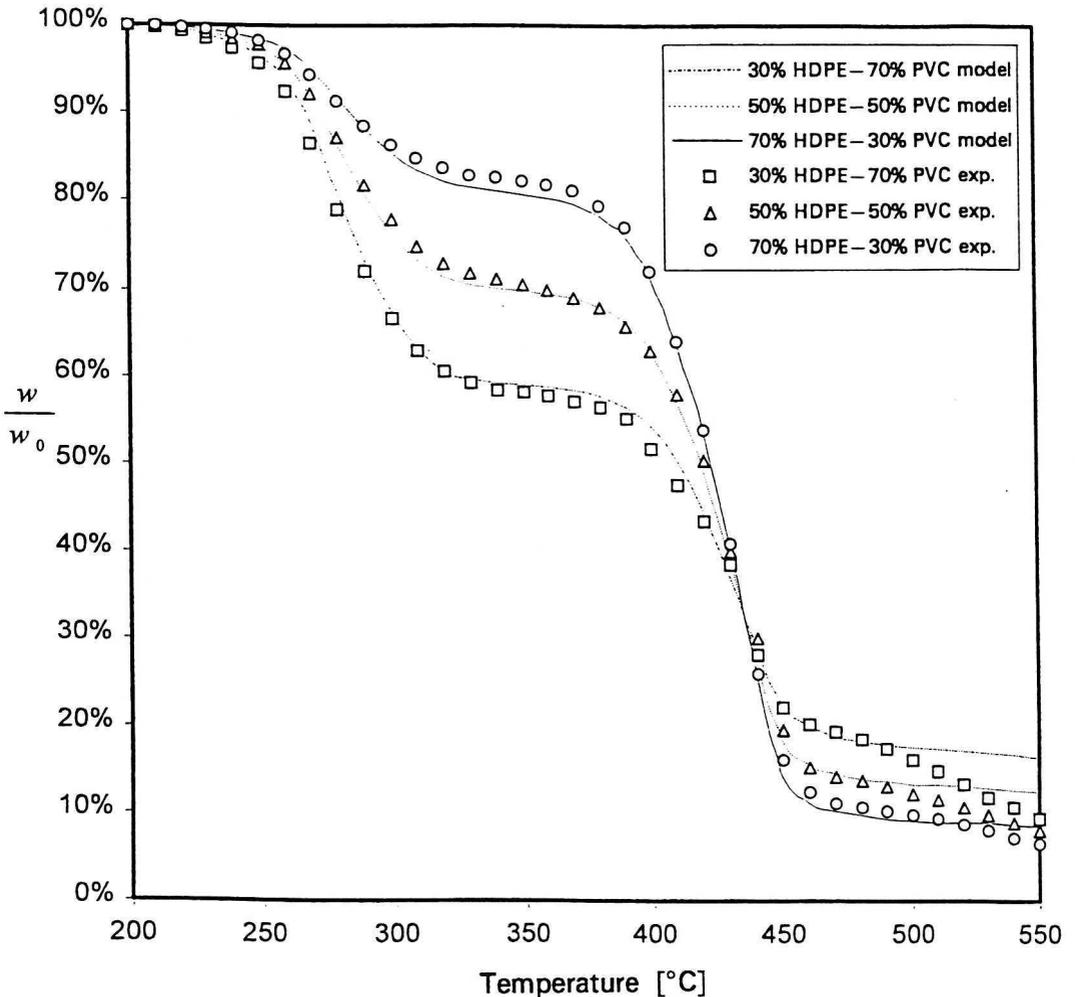


Fig. 10. Weight Loss Curves of Different PVC-HDPE Mixtures

all waste plastics simultaneously to a high value feedstock by a comparatively simple process, but a better understanding of the impact of PVC concentrations in the mix is needed in order to further develop the technology.

Mixtures of commodity plastics were prepared with polyvinyl chloride to determine if possible chemical interactions existed when these mixtures were pyrolyzed. The investigation focused on the interactions between PVC and other polymers including polypropylene, polystyrene, low-density polyethylene, high-density polyethylene and polyethylene terephthalate. The experiments were conducted in a thermogravimetric analyzer under controlled conditions. Experimental procedures were developed to produce uniform samples for analyses, and analytical evaluation methods were developed to help in the interpretation of the data.

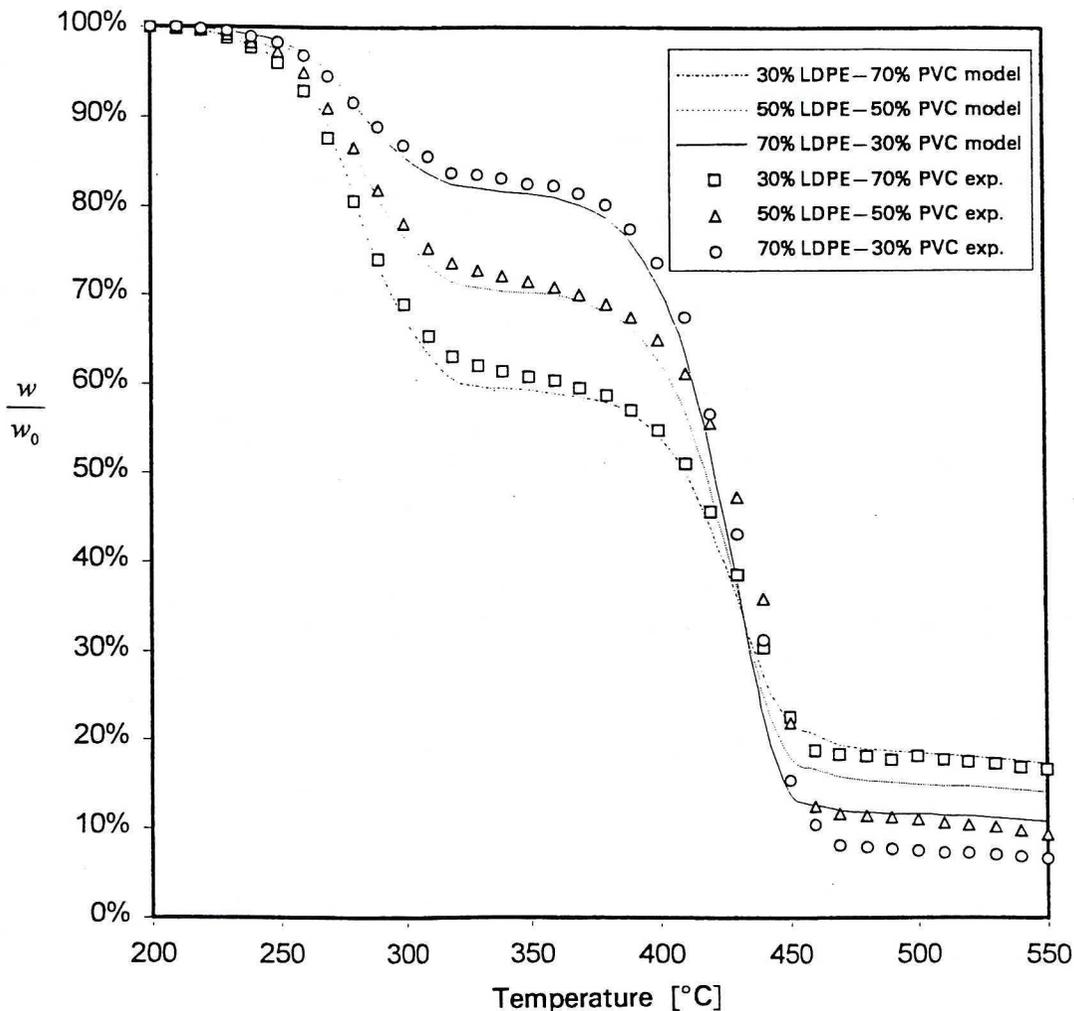


Fig. 11. Weight Loss Curves of Different PVC-LDPE Mixtures

Activation energies and reaction orders for selected mixtures and for the pure polymers were obtained. The values of the kinetic parameters for the pure compounds were all very close to, or within the ranges obtained from the literature.

The results indicated that the decomposition behavior of the mixtures differed from those of the pure polymers. These deviations were greatest for mixtures of PVC with polyethylene terephthalate where it was determined that the dehydrochlorination step of PVC catalyzes the decomposition of PET.

Pyrolysis of mixtures of PVC and polystyrene at temperatures between 200°C and 350°C result in incomplete dehydrochlorination. This results in more chlorinated compounds being released at higher temperatures.

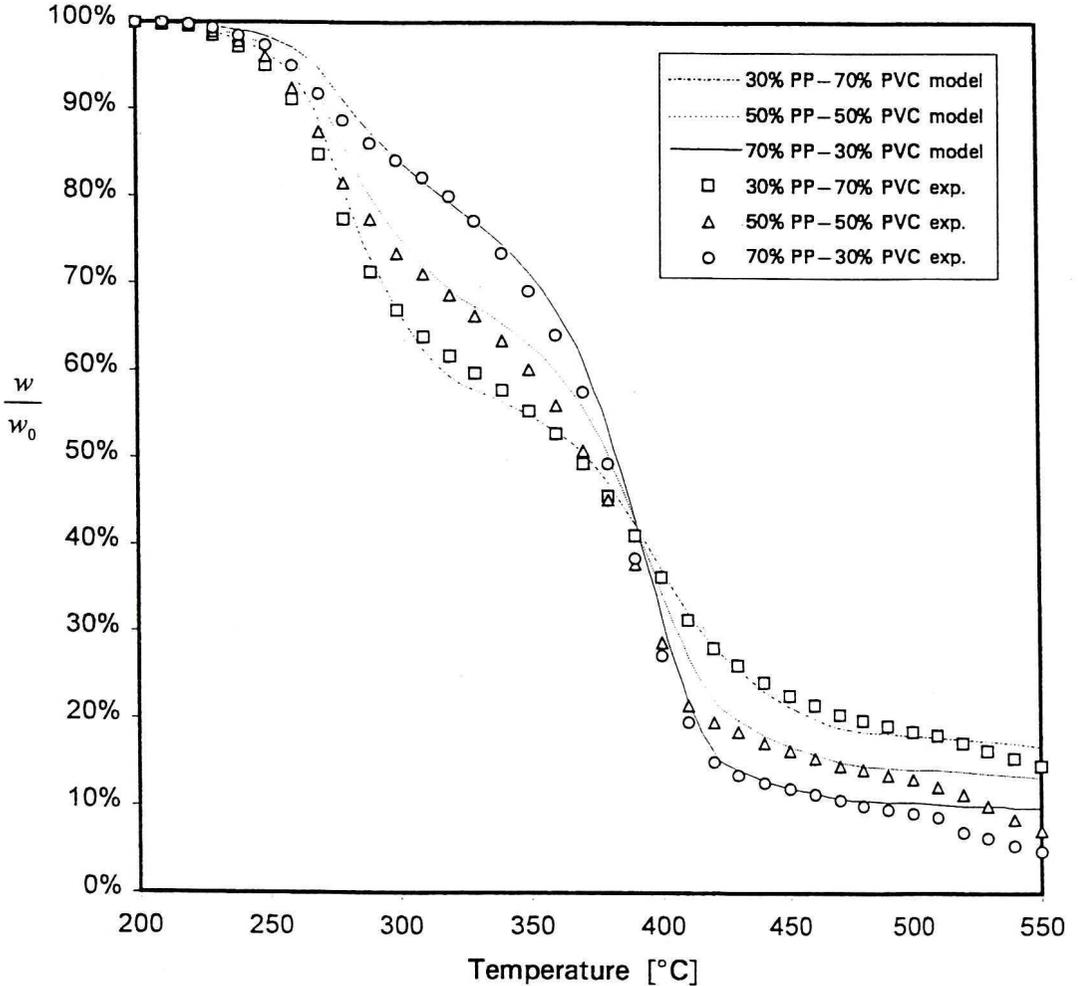


Fig. 12. Weight Loss Curves of Different PVC-PP Mixtures

The overall results suggest that commercial pyrolysis units should consider the potential effect that the composition of the input mixtures of waste plastics can have on the product quality in order to minimize the effects of PVC contamination.

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