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# Degradation of contaminated plastics: a kinetic study*

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The thermal degradation of polypropylene (PP), polyacrylonitrile butadiene styrene (ABS), polyurethane (PU) and polyvinyl chloride (PVC) have been studied in the presence of copper, iron oxide and dirt. The rate constants and kinetic parameters for the degradation processes have been measured using the variable heating rate isoconversion method. The results suggest that the presence of metal contamination in these polymer systems can influence the degradation behaviour of the pure polymers. Generally it was found that certain metal contaminants could have a catalytic effect on the degradation processes of the polymers studied. This effect resulted in an increase in the measured rate constants and a lower onset temperature of their degradation. The largest effects were noted with PP, where substantial increases in the rate constant were noted as well as significant differences in the apparent activation energies.

## 1 INTRODUCTION

The thermal degradation of polymeric materials is a subject which has been pursued for many generations as scientists try to understand the processes responsible for the deterioration in physical properties of materials. Most of the earlier work centered on degradation and stabilization studies in which the major preoccupation was determining the decomposition mechanism with a view to preventing or retarding the processes involved in order to produce more thermally stable polymers. In recent years there has been a growing interest in pyrolysis (thermal degradation) for the recovery of valuable resources from post-consumer plastic wastes which are currently being landfilled.[1–5] This technology is perceived to offer several advantages for dealing with mixed and contaminated plastic wastes which cannot be easily recycled. One of these perceived advantages is that the polymers present in plastic waste can be thermally degraded back to basic hydrocarbons which can subsequently be reprocessed in a refinery to produce petrochemical streams for re-use in the petrochemical industry. However, whilst much is known about the thermal degradation and pyrolysis of individual polymers, little has been reported in the literature on the mechanisms and kinetics of the degradation of mixed polymer systems such as those found in typical waste streams.

One particular mixed plastic waste stream of interest is Auto Shredder Residue (ASR).[6] This material is a commingled waste stream produced by automobile shredding operations involved in the recovery of steel from old automobiles. It has been estimated that approximately three million tonnes of ASR is generated annually in North America[7] and this figure is anticipated to grow over the next few years due to the reduction in size and weight of automobiles which has resulted in many metal components being replaced by plastic. ASR is a complex mixture of plastics, foams, rubber, textiles, dirt, rust, glass, etc., contaminated with fluids and lubricants.[8] Because of this heterogeneous nature of the material, it is an ideal candidate for tertiary recycling because of the high costs associated with sorting and cleaning in order to separate the

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individual polymer types. However, for pyrolysis to be economically viable it is essential to produce marketable products at a saleable price, while at the same time producing them by an environmentally acceptable process. In order to assist this type of evaluation, it is essential to understand the chemical reactions taking place when mixed and contaminated polymers are pyrolysed. In a previous study, we investigated the interactions occurring when mixed polymers were thermally degraded and compared the results with the behaviour of the individual polymers.[9] This study clearly indicated that polymer/polymer interactions occurred when mixed polymers were degraded together, with the extent of interaction being greatly dependent upon the polymer types. In this current study we extend this investigation to determine the role of contaminants on the thermal degradation of the four major polymeric materials present in ASR. The contaminants examined include copper (electrical copper wire), ferric oxide (rust), and road dirt contained in ASR. Meanwhile the polymers selected for examination were: polypropylene (PP), polyurethane (PU), polyacrylonitrile butadiene styrene (ABS) and polyvinyl chloride (PVC).

## 2 EXPERIMENTAL

The four automotive grade polymeric materials employed in this study were:

(1) Himont PRO-FAX SV-152 polypropylene copolymer (PP)
(2) Dow Magnum acrylonitrile/butadiene/styrene polymer (ABS)
(3) BF Goodrich Geon polyvinyl chloride, (PVC)
(4) Curon Canada polyurethane seat cushioning foam, (PU)

All polymeric samples were cryogenically ground, using liquid nitrogen as coolant, to a size less than 20 mesh (1 mm) with a Wiley Laboratory Mill prior to use.

The four contaminants employed in the study were:

(1) Powdered metallic copper obtained from Amax
(2) Powdered ferric oxide ($Fe_2O_3$)
(3) Dirt less than 2 mm in size extracted from a sample of ASR by a sizing process

Each contaminant was added to each polymer at a concentration of 5% by weight. Blending was achieved by tumbling for 30 min.

The thermogravimetric weight-loss experiments were conducted using a TA Instruments 951 Thermogravimetric Analyser (TGA) coupled to a 2100 TA Instruments Thermal Analyser. Because of the known dependence of kinetic parameters on sample mass,[10] the sample size was standardized at $12.0 \pm 0.5$ mg. All experiments were performed in nitrogen which was maintained at a constant flow rate of 50 ml/min. Experiments were conducted at five heating rates of 0.5, 1, 2, 5 and 10 °C/min with the sample being heated from room temperature to 600 °C after a 20 min hold at room temperature to ensure that all traces of oxygen were removed from the apparatus. The sample holder, used in these experiments, was a single use top loading aluminum sample pan which was mounted in a special ring type quartz rod.

On completion of the weight-loss experiments, the weight-loss curves were normalized to 100% by correcting for the 5% contaminant present in each sample. The normalized data from each experiment was then converted and evaluated by a Pascal written program to extract temperature values for fractional conversion values of 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9. The resulting data was then used to determine the kinetics of the weight-loss process and apparent activation energies, $E_a$, using the approach of Ozawa[11] and Flynn and Wall.[12]

## 3 RESULTS AND DISCUSSION

The thermogravimetric weight-loss curves for the four automotive polymers used in this study were presented in previous studies in which the influence of polymer/polymer interactions was considered.[9,13] The weight-loss curves for the single polymers were relatively simple and straightforward and showed no significant differences from data previously reported in the literature. For example, PP and ABS degraded by an apparent single stage process while PVC and PU appeared to degrade in a two stage process. These weight-loss curves obtained for the pure polymers form the basis from which the influence of contaminants, on the degradation process, can be evaluated.

### 3.1 The role of copper contamination

The influence of copper on the weight-loss curves of these four polymers is presented in Figs 1 and 2. Figure 1 presents the standard weight-loss data while Fig. 2 provides the derivative information. It should be noted that while only the data obtained at a heating rate of 5 °C/min. are presented in these figures, similar curves were obtained at all heating rates examined in this study.

Examination of this data clearly indicates that the presence of copper does appear to be influencing the weight-loss of all four polymers although the magnitude of the effect does appear to be dependent to some extent on the polymer type. For example, in the case of PP, the 10% weight-loss temperature measured at a heating rate of 5 °C/min., is reduced by 26.2 °C in the presence of copper (Table 1). While lower 10% weight-loss degradation temperatures were also noted with the other polymers, the magnitude of the differences were not as large (see data in Tables 1–4).

While a direct comparison of weight-loss curves can give some information on the role of additives and, in this case the influence of contaminants; analysis of kinetic data from several experiments, conducted at a variety of heating rates, can sometimes be much more informative. The resulting apparent activation energies ($E_a$) calculated for these polymers in the presence and absence of copper are presented in Figs 3–6 for the polymers PP, ABS, PU and PVC, respectively.

In the case of the PP, it is evident that the values for $E_a$ in the presence and absence of copper are significantly different. For example at a fractional weight-loss of 10% the measured $E_a$ values are 113.6 ± 7.7 and 138.1 ± 3.8 kJ/mol in the presence and absence of copper. When these $E_a$ values are coupled with log $A$ values of 10.15/s and 11.60/s, calculated assuming first order rate constants, it can be readily seen that at 400 °C the rate of decomposition of the copper containing sample was 2.8 times faster than that of the pure PP (Table 1). This observation is not too surprising in view of the information[14–16] on the kinetics of the thermal oxidation of PP in the presence of metals, such as copper, used in electrical copper wiring.[17]

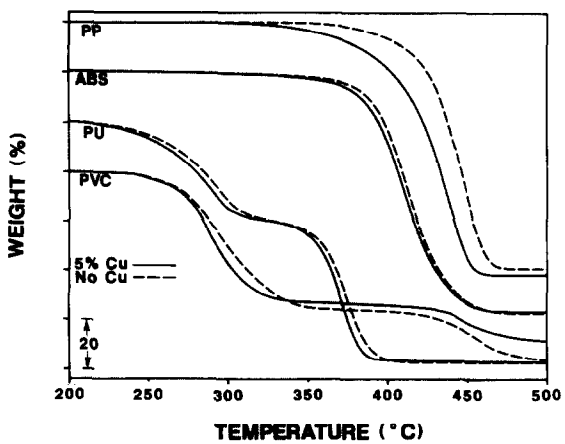


**Fig. 1.** Weight-loss curves for PP, ABS, PU and PVC in the presence (solid line) and absence (dashed line) of copper, determined at a heating rate of 5 °C/min in nitrogen.

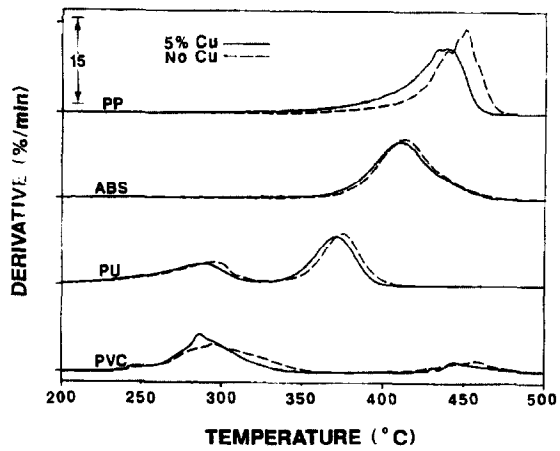


**Fig. 2.** Derivative weight-loss curves for PP, ABS, PU and PVC in the presence (solid line) and absence (dashed line) of copper, determined at a heating rate of 5 °C/min in nitrogen.

In the case of the ABS/copper system (Fig. 4) however, the kinetic data are similar to that of ABS alone throughout the whole weight-loss range. For example using the kinetic data for 10% weight-loss, the relative rate with copper and without copper was 1.23 at a temperature of 400 °C (Table 2). This data would appear to confirm the weight-loss data presented in Figs 1 and 2 which shows only a slight enhancement of the degradation in the presence of copper.

With PU the degradation proceeds in a two stage process, the first stage results in the production of cyanates and substituted amines, while the second stage produces low molecular weight nitrogen containing species.[18] In terms of the first stage degradation process, it appears that there is little difference between the kinetics of the degradation of pure PU with that of the copper containing sample (Fig. 5). This was confirmed by comparing the relative rates at

**Table 1. Kinetic data for PP samples**

| | Uncontaminated | Copper | $Fe_2O_3$ | Dirt |
|---|---|---|---|---|
| 10% weight-loss temperature at 5 °C/min (°C) | 410.4 | 384.2 | 386.3 | 367.3 |
| $E_a$ at 10% weight-loss (kJ/mol) | 138.1 | 113.6 | 108.8 | 128.2 |
| Log $A$ at 10% weight-loss ($s^{-1}$) | 11.60 | 10.15 | 9.65 | 11.40 |
| Rate constant at 400 °C using 10% data | 7.56 | 21.4 (2.80)[a] | 16.0 (2.11)[a] | 28.0 (3.70)[a] |

[a]Values in parentheses are relative rates to those for the uncontaminated sample.

250 °C using the kinetic data from the 10% conversion, where the value was found to be 1.17 for the copper containing sample with respect to the sample without copper (Table 3). The kinetic data for the second stage degradation process was similar. Although the $E_a$ values were $152.7 \pm 7.4$ and $181.6 \pm 2.1$ kJ/mol for the copper and non-copper samples, respectively, at a conversion of 60%; when the rate constants were calculated a relative rate of 1.15 at 350 °C was obtained. This value is comparable to the value obtained at the lower degree of conversion. Thus like ABS and PP, copper also appears to enhance the degradation of PU.

PVC is generally accepted as not having good thermal stability and metal compounds have been extensively investigated as heat stabilizers[19,20] and smoke suppressants[21] to improve thermal processing and fire performance. In this study while it appears that the copper is influencing the weight-loss curve for PVC (i.e. a sharper HCl evolution) an evaluation of the kinetic weight-loss data (Fig. 6) suggests that copper has little influence upon the apparent activation energy, $E_a$, up to a weight-loss of about 50%. This, once again, is reflected in a relative rate for the copper containing sample of 1.35 at 250 °C when using the 10% conversion kinetic data (Table 4). Although there appears to be large differences in the calculated $E_a$ values above 50% these values were found to incorporate a great deal of scatter and statistical variability. For example, the 60% weight-loss $E_a$ value for the copper containing sample which was calculated to be 142.2 kJ/mol had a calculated standard deviation of 54.1 based upon a correlation coefficient of 0.835, while the 70% weight-loss value had a correlation coefficient of 0.558.

### 3.2 The role of ferric oxide contamination

Ferric oxide ($Fe_2O_3$) was chosen to be representative of rust, a major contaminant in the mixed plastic waste derived from recycling old automobiles.[22] The weight-loss and derivative curves for the four polymers with 5% $Fe_2O_3$ are shown in Figs 7 and 8, respectively.

Examination of these weight-loss curves indicates that the presence of $Fe_2O_3$ influences the onset of degradation, with all polymers showing lower initial 10% weight-loss temperatures in the presence of $Fe_2O_3$ than in its absence (Tables 1–4). A quick comparison of the data presented in Figs 7 and 8 with data contained in Figs 1 and 2 would also suggest that the observed effect was also slightly larger in the presence of $Fe_2O_3$ than copper.

However, when the apparent activation energies were calculated and compared for each polymer system (Figs 9–12) the results were similar to those obtained with copper as an additive. For example in the case of PP (Fig. 9) once again a significant difference in $E_a$ was obtained for PP in the presence of $Fe_2O_3$ than in

**Table 2. Kinetic data for ABS samples**

| | Uncontaminated | Copper | $Fe_2O_3$ | Dirt |
|---|---|---|---|---|
| 10% weight-loss temperature at 5 °C/min (°C) | 386.4 | 382.6 | 380.9 | 383.8 |
| $E_a$ at 10% weight-loss (kJ/mol) | 190.4 | 178.1 | 173.6 | 179.4 |
| Log $A$ at 10% weight-loss ($s^{-1}$) | 16.22 | 15.35 | 14.99 | 15.42 |
| Rate constant at 400 °C using 10% data | 27.4 | 33.6 (1.23)[a] | 32.5 (1.19)[a] | 31.0 (1.13)[a] |

[a]Values in parentheses are relative rates to those for the uncontaminated sample.

**Table 3. Kinetic data for PU samples**

| | Uncontaminated | Copper | $Fe_2O_3$ | Dirt |
|---|---|---|---|---|
| 10% weight-loss temperature at 5 °C/min (°C) | 263.0 | 256.6 | 257.1 | 255.5 |
| 60% weight-loss temperature at 5 °C/min (°C) | 367.4 | 263.0 | 357.4 | 361.6 |
| $E_a$ at 10% weight-loss (kJ/mol) | 122.0 | 120.2 | 121.6 | 124.1 |
| Log $A$ at 10% weight-loss ($s^{-1}$) | 13.09 | 12.98 | 13.18 | 13.45 |
| $E_a$ at 60% weight-loss (kJ/mol) | 181.6 | 152.7 | 149.4 | 159.5 |
| Log $A$ at 60% weight-loss ($s^{-1}$) | 16.93 | 14.57 | 14.47 | 15.22 |
| Rate constant at 250 °C using 10% data | 7.99 | 9.72 (1.17)[a] | 10.8 (1.35)[a] | 11.3 (1.41)[a] |
| Rate constant at 350 °C using 60% data | 50.1 | 58 (1.15)[a] | 87.2 (1.74)[a] | 69.7 (1.39)[a] |

[a]Values in parentheses are relative rates to those for the uncontaminated sample.

its absence (i.e. 108.8 ± 17.6 and 138.1 ± 3.8 kJ/mol at 10% weight-loss). This translates into a relative rate of 2.11 at 400 °C (Table 1) comparable to that obtained for the copper contaminated PP (2.8). A similar effect was noted for ABS. While ABS has a lower $E_a$ value at 10% weight-loss in the presence of $Fe_2O_3$ (173.6 ± 8.1) in comparison to its absence (190.4 ± 4.1), the calculated relative rate using 10% data was 1.19 at 400 °C (Table 2).

In the case of PU, however, while the relative rate for the $Fe_2O_3$ containing sample in comparison to the standard PU is only 1.35 at 250 °C based on the kinetic values for 10% weight-loss, the value at 350 °C using 60% weight-loss kinetic data has increased to 1.74 (Table 4). This latter value appears to be in keeping with the shift noted in Figs 7 and 8 for the second weight-loss zone.

In the case of the PVC/$Fe_2O_3$ system, the weight-loss curves (Fig. 7) clearly indicate a more sudden and sharper evolution of HCl around 280 °C in the presence of $Fe_2O_3$ than in its absence. However, in terms of the kinetic data, the 10% weight-loss values for $E_a$ of 135.1 ± 2.8 and 141.8 ± 2.7 kJ/mol, with and without $Fe_2O_3$, are similar and translate into a relative rate of 1.29 at 250 °C (Table 4), similar to that noted with the copper contamination. Thus it appears that both Cu and $Fe_2O_3$ produce similar effects on the polymers PP, ABS, PU and PVC in that there appears to be decreases in the 10% weight-loss temperatures, some reduction in the $E_a$ values and increased rates of reaction.

### 3.3 The role of dirt contamination

It has been shown that the polymeric waste stream generated from the recycling of old automobiles, in addition to containing copper and rust ($Fe_2O_3$), is also contaminated with relatively large quantities of dirt. This dirt accumulates both inside and outside the automobile during normal usage and has characteristics similar to conventional road dirt.[23] Although of unknown and variable composition, this mixture usually contains a variety of inorganic contaminants that could influence the degradation of polymeric materials. The influence of this contamination upon the four polymers: PP, ABS, PU and PVC are presented in Figs 13 and 14. Once again the appearance of the weight-loss

**Table 4. Kinetic data for PVC samples**

| | Uncontaminated | Copper | $Fe_2O_3$ | Dirt |
|---|---|---|---|---|
| 10% weight-loss temperature at 5 °C/min (°C) | 274.6 | 273.0 | 271.9 | 270.6 |
| 60% weight-loss temperature at 5 °C/min (°C) | 431.2 | 445.7 | 416.6 | 425.9 |
| $E_a$ at 10% weight-loss (kJ/mol) | 141.8 | 142.2 | 135.1 | 142.3 |
| Log $A$ at 10% weight-loss ($s^{-1}$) | 14.73 | 14.90 | 14.17 | 14.88 |
| Rate constant at 250 °C using 10% data | 3.67 | 4.95 (1.35)[a] | 4.72 (1.29)[a] | 4.62 (1.26)[a] |

[a]Values in parentheses are relative rates to those for the uncontaminated sample.

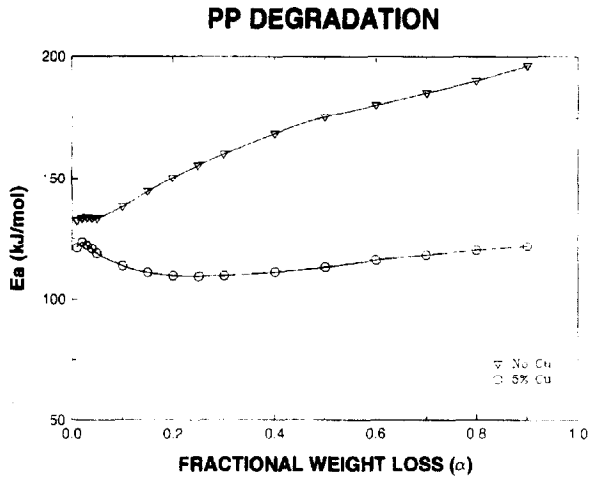


**Fig. 3.** Apparent activation energies as a function of fractional weight-loss for PP in the presence and absence of copper.

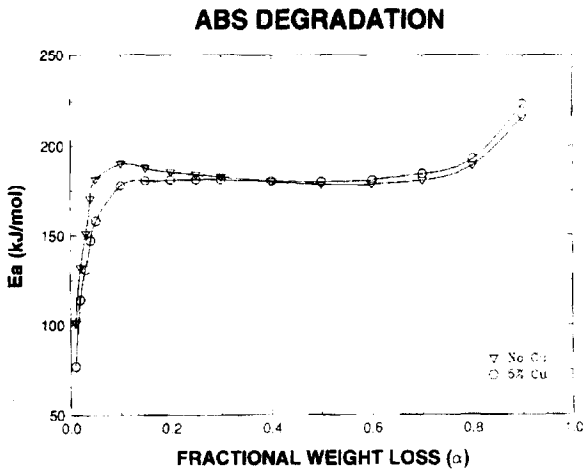


**Fig. 4.** Apparent activation energies as a function of fractional weight-loss for ABS in the presence and absence of copper.

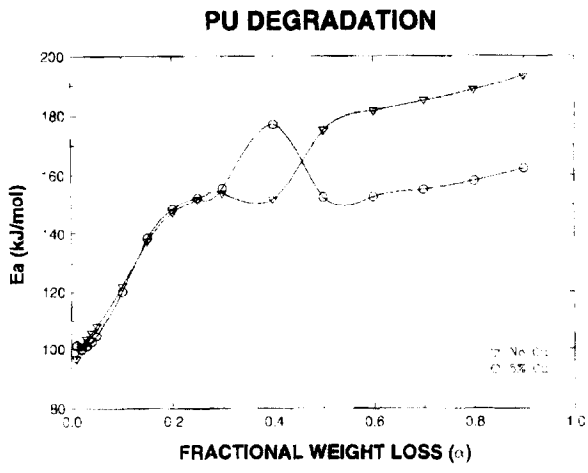


**Fig. 5.** Apparent activation energies as a function of fractional weight-loss for PU in the presence and absence of copper.

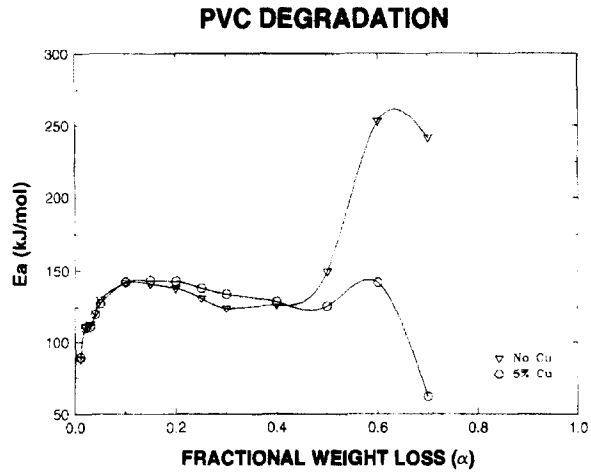


**Fig. 6.** Apparent activation energies as a function of fractional weight-loss for PVC in the presence and absence of copper.

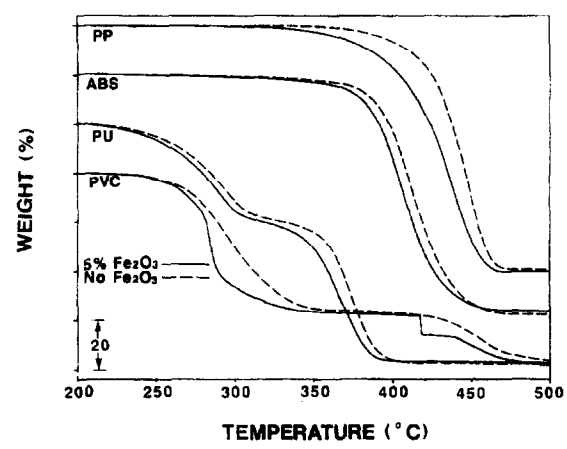


**Fig. 7.** Weight-loss curves for PP, ABS, PU and PVC in the presence (solid line) and absence (dashed line) of $Fe_2O_3$, determined at a heating rate of 5 °C/min in nitrogen.

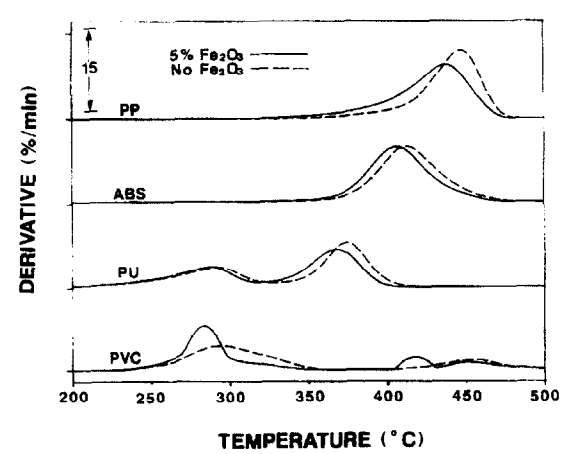


**Fig. 8.** Derivative weight-loss curves for PP, ABS, PU and PVC in the presence (solid line) and absence (dashed line) of $Fe_2O_3$, determined at a heating rate of 5 °C/min in nitrogen.

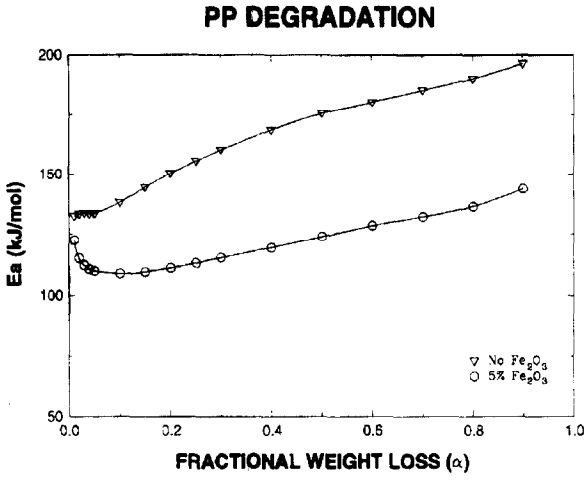


**Fig. 9.** Apparent activation energies as a function of fractional weight-loss for PP in the presence and absence of $Fe_2O_3$.

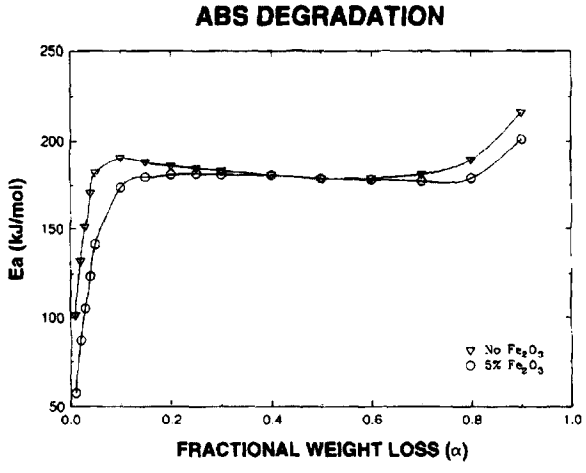


**Fig. 10.** Apparent activation energies as a function of fractional weight-loss for ABS in the presence and absence of $Fe_2O_3$.

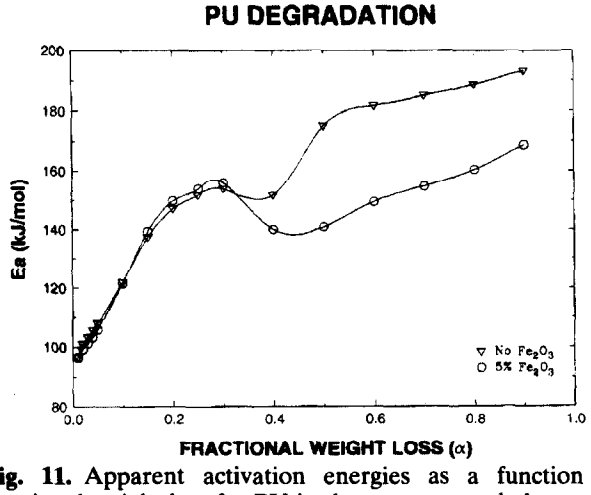


**Fig. 11.** Apparent activation energies as a function of fractional weight-loss for PU in the presence and absence of $Fe_2O_3$.

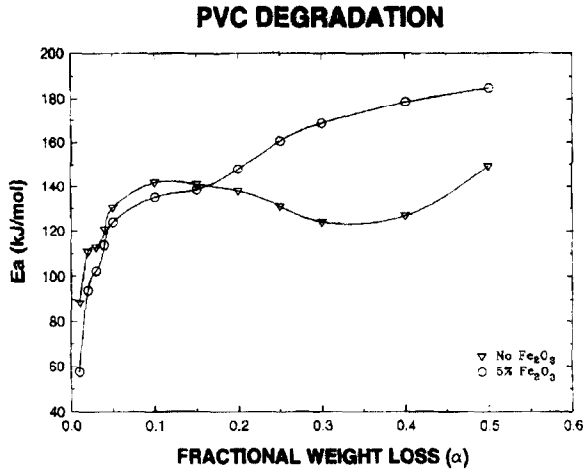


**Fig. 12.** Apparent activation energies as a function of fractional weight-loss for PVC in the presence and absence of $Fe_2O_3$.

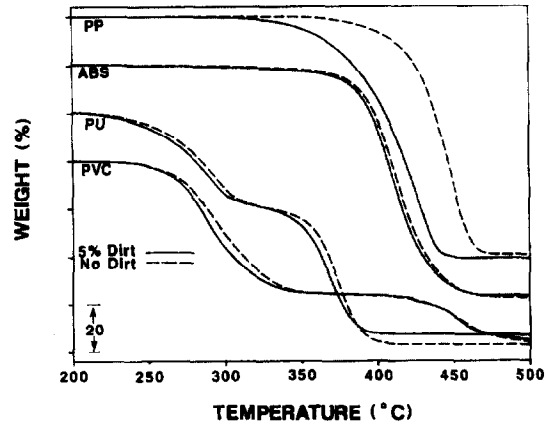


**Fig. 13.** Weight-loss curves for PP, ABS, PU and PVC in the presence (solid line) and absence (dashed line) of dirt, determined at a heating rate of 5 °C/min in nitrogen.

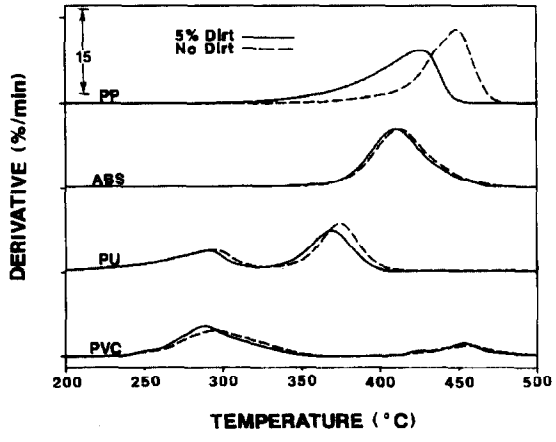


**Fig. 14.** Derivative weight-loss curves for PP, ABS, PU and PVC in the presence (solid line) and absence (dashed line) of dirt, determined at a heating rate of 5 °C/min in nitrogen.

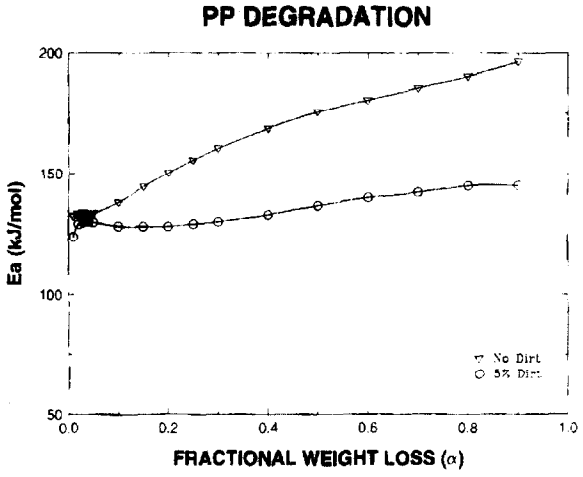


**Fig. 15.** Apparent activation energies as a function of fractional weight-loss for PP in the presence and absence of dirt.

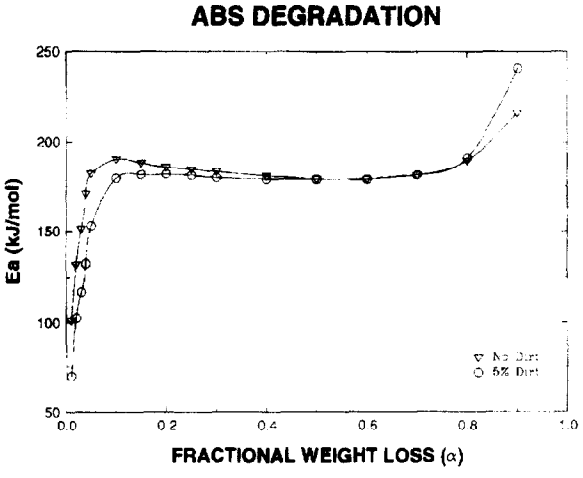


**Fig. 16.** Apparent activation energies as a function of fractional weight-loss for ABS in the presence and absence of dirt.

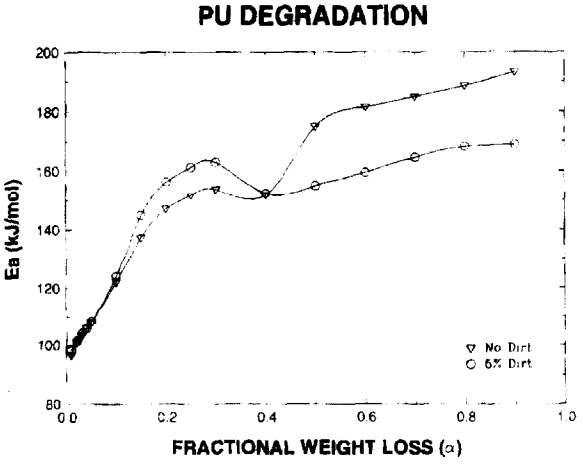


**Fig. 17.** Apparent activation energies as a function of fractional weight-loss for PU in the presence and absence of dirt.

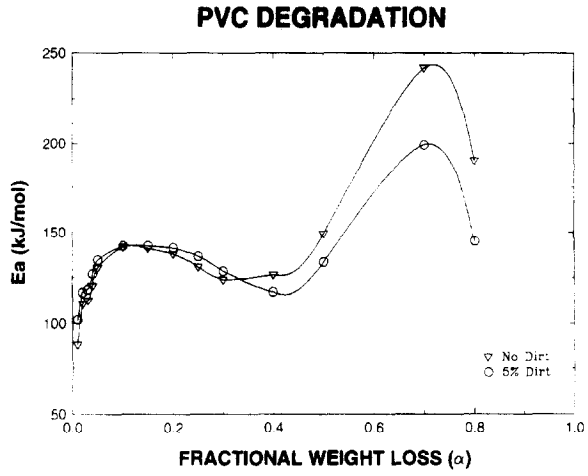


**Fig. 18.** Apparent activation energies as a function of fractional weight-loss for PVC in the presence and absence of dirt.

curves reflects those already noted for the copper and $Fe_2O_3$ experiments. These results are not unexpected when it is realized that dirt contains relatively large quantities of $Fe_2O_3$ in addition to some copper. However, a more noticeable change was noted for the PP sample than was seen in the case of the copper and $Fe_2O_3$ experiments. This was clearly evident from the 10% weight-loss temperatures at 5 °C/min heating rate which were: 367.3 °C, 386.3 °C, 384.2 °C, and 410.4 °C in the case of dirt, $Fe_2O_3$, copper and uncontaminated samples, respectively (Table 1).

The influence of dirt on the kinetics of the weight-loss, is presented in Figs 15–18. Once again the largest differences in the $E_a$ values were noted for PP with 10% weight-loss values of $128.2 \pm 12.6$ and $138.1 \pm 3.8$ kJ/mol (Fig. 15) in the presence and absence of dirt, respectively. However, when these values were used to calculate relative rates at 400 °C (Table 4), the dirt contaminated sample had a rate constant 3.70 times that of the uncontaminated PP sample. The data confirms the acceleration effect caused by the presence of dirt in PP. The behaviour of the ABS sample (Fig. 16) meanwhile reflects the data obtained with copper and $Fe_2O_3$ in that, while there is a reduction in the $E_a$ value to 179.4 kJ/mol at 10% weight-loss, the relative rate in comparison to the contaminated sample was only 1.13 (Table 2).

Not surprisingly the two stage degradation of PU contaminated with dirt (Fig. 17) behaved similarly to that observed with the copper and

$Fe_2O_3$ with $E_a$ values of 124.1 and 159.5 kJ/mol, respectively, for the 10% and 60% weight-loss values. These values translate into relative rates of 1.41 and 1.39 at temperatures of 250 °C and 350 °C, respectively (Table 3). Likewise, the dirt contaminated PVC with an $E_a$ value of $142.3 \pm 3.0$ kJ/mol at 10% weight-loss had a relative rate of 1.26 at 250 °C (Table 4). This behaviour was similar to the copper and $Fe_2O_3$ contaminated PVC samples.

## 4 CONCLUSIONS

Based upon the results of this study it is clear that the presence of metal contamination, such as copper, $Fe_2O_3$ and dirt found in recycled automotive plastics, will produce a decrease in the decomposition temperature of polymers such as PP, ABS, PU and PVC typically found in automobiles. Although all four polymers studied showed slightly different behaviour in the weight-loss experiments, the kinetic data were similar for the three contaminants examined. Applying first order kinetics to the Arrhenius parameters, suggests that the degradation process was accelerated about 20% (13–74%) for the polymers ABS, PU and PVC while a much larger increase of over 100% was noted for the PP sample. This data suggests that if pyrolysis is to be used as a resource recovery option for plastic components contained in automobiles, the degradation behaviour is likely to be affected by the presence of contamination such as copper, rust and dirt. The influence of these components on the pyrolysis products and degradation mechanisms was beyond the scope of this study and still needs to be addressed.

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