RELATING THERMAL ANALYSES TO THE FLAMMABILITY OF POLYMERS

RICHARD W. MICKELSON

*Department of Chemical Engineering and Material Sciences, Wayne State University,
Detroit, Mich. 48202 (U. S. A.)*

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ABSTRACT

Thermogravimetric and differential thermal analyses were made on an urethane polymer with and without a fire retardant added. These analyses were made at different heating rates and in different environments (argon and oxygen). The results of these tests were then used to show how they might help predict the response of a material to a fire.

INTRODUCTION

Literature describing tests on the flammability characteristics of materials frequently includes either a figure showing the thermogravimetric analysis or the differential thermal analysis of the materials investigated. Often these figures have such captions as "Effect of Fire Retardant on Foam Degradation (TGA)"[1], but no explanation is included to demonstrate how this analysis is related to either the flammability characteristics of the material or the prediction of these characteristics. Recently, Loehr and Levy[2] have measured the smoke evolved by different materials as they were heated in air at a rate of 20°C/min using the DuPont TGA. Unfortunately, the heating rates attainable with conventional thermal analyses instruments are far below those found in a fire, so, it is doubtful that the smoking characteristics of a material can be adequately established using TGA. However, thermal analysis can provide information on the mechanism and the kinetics of thermal decomposition which may provide insight as to how a material might react to a fire.

THERMAL ANALYSIS OF A SIMPLE URETHANE

An urethane polymer made of pure 2,4 toluene diisocyanate and a polyol of molecular weight 312 and a functionality of three was used by Mickelson and Einhorn[3] to evaluate their "ratio method" for determining the kinetics of thermal decomposition using TGA. In their initial work, they decomposed this material under an argon atmosphere at heating rates of 4°C/min and 10°C/min using a Mettler TGA. At these two heating rates, the activation energy was found to be 33,200 cals/gmole and quite reproducible. Subsequently, because researchers at

N.A.S.A.[4] have found that urethane polymers decompose by different mechanisms depending on the temperature to which they are exposed, additional runs have been made at heating rates of 15°C/min and 25°C/min.
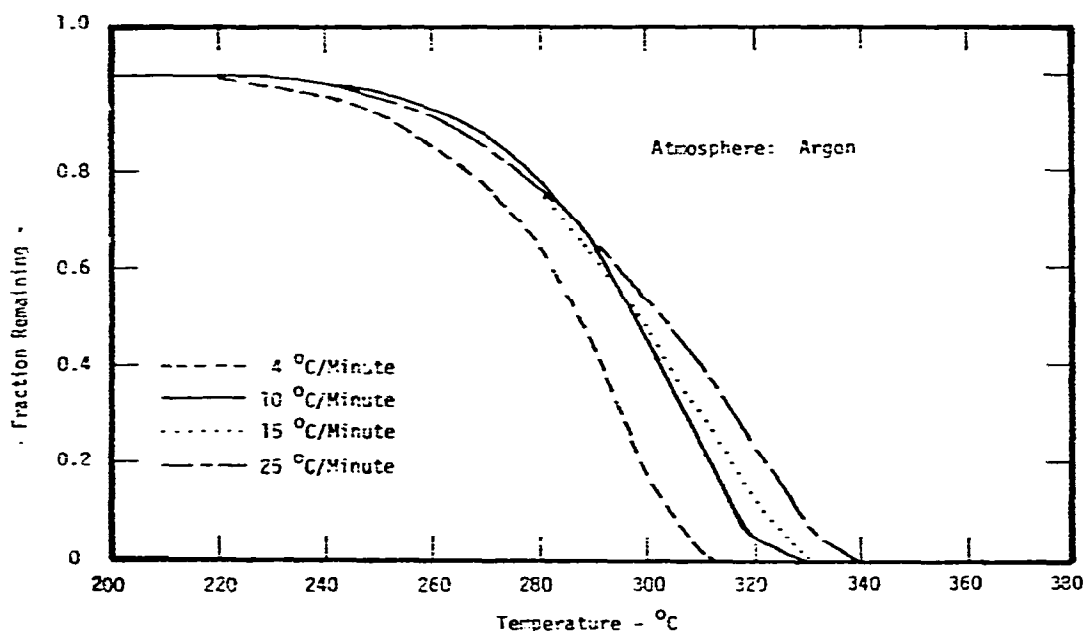

Fig. 1. TGA data for the decomposition of 2,4 TDI-polyol at various heating rates.

At these higher heating rates an anomaly in the thermograms appears which is shown in Fig. 1. At the higher heating rates, the polymer should not have decomposed until much higher temperatures had been attained, and activation energies of 28,200 cals/gmole for decomposition at a heating rate of 15°C/min and 23,900 cals/gmole for a heating rate of 25°C/min were obtained. Except for the much lower activation energies at the higher heating rates, the ratio method used for calculating the kinetic parameters did not indicate any abnormality as shown in Fig. 2. Thus, unlike many materials where thermogravimetric analysis at one heating rate would indicate a complex decomposition mechanism, this particular polymer would seem to have a simple mechanism governing its decomposition. It is only when this polymer is decomposed at several heating rates does thermogravimetric analysis suggest that the mechanism by which it decomposes is not simple.

Another thermal analysis technique must be used to both confirm the results obtained through TGA and provide additional data that might help predict a material's reaction to a fire. This TDI-polyol urethane was decomposed at the same four heating rates in a differential thermal analyzer under an argon atmosphere. All of the samples weighed 6.8 milligrams and the reference material was aluminium oxide. The results are shown in Fig. 3. If data had been obtained only at a heating rate of 4°C/min, the conclusion might have been that this was a simple polymer since
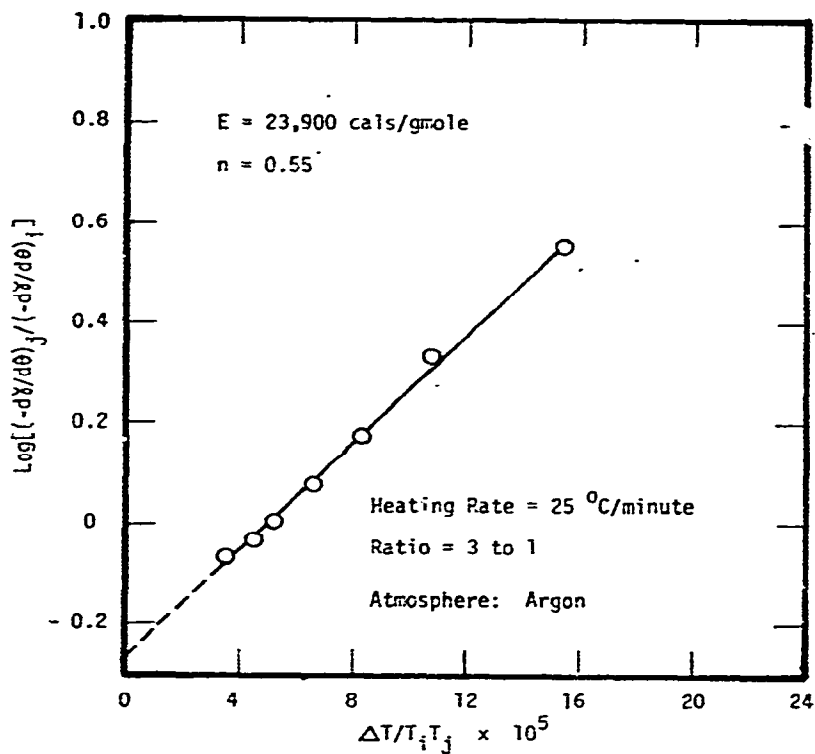
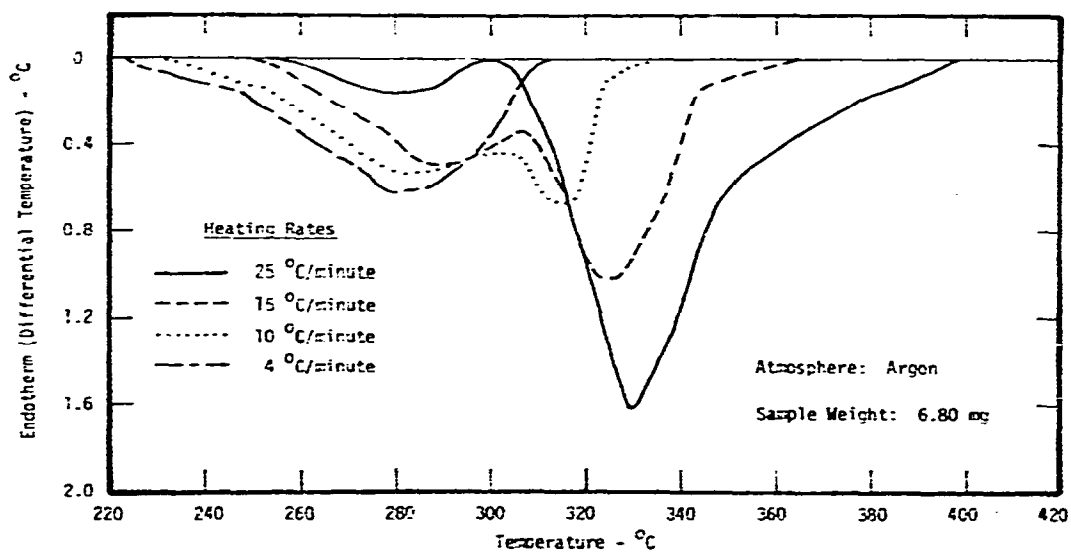Fig. 2. The ratio method applied to the decomposition of 2,4 TDI-polyol urethane.

Fig. 3. Differential thermal analysis of 2,4 TDI-polyol urethane.

there was no drastic ambiguity in the data's appearance. But at the higher heating rates, a second peak appeared. The size of this peak increased for increasing heating rates and the first peak had almost disappeared at a heating rate of 25°C/min. It must be concluded that the decomposition mechanism of this polymer is not simple, giving strong support to the TGA data.

FLAMMABILITY TESTING

A device for measuring the flammability and smoking characteristics of polymers was constructed (Fig. 4). The basic premise governing its design was that the material must be subjected to a continuous energy source throughout the burning process. This heat source located above the sample provides the additional heat

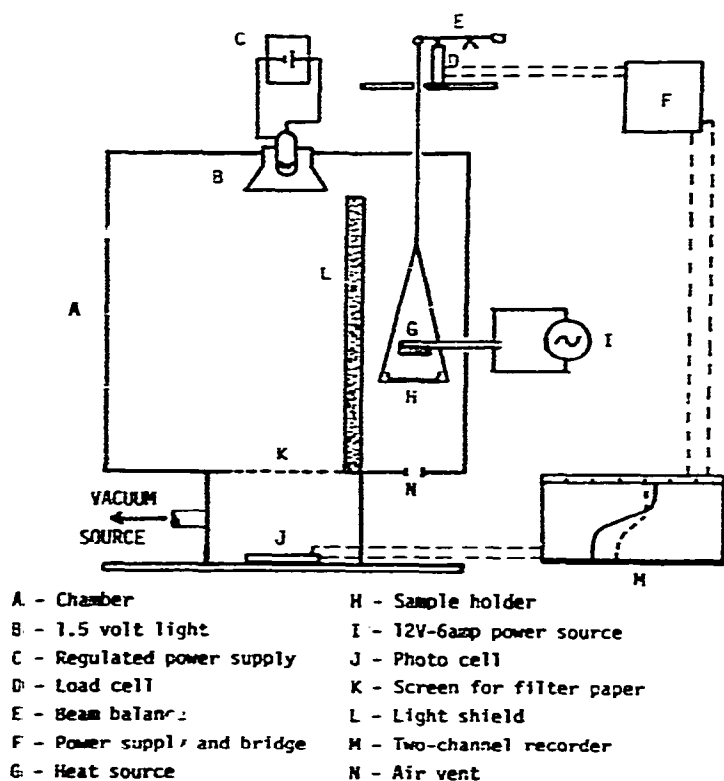| A - Chamber	H - Sample holder
B - 1.5 volt light	I - 12V-6amp power source
C - Regulated power supply	J - Photo cell
D - Load cell	K - Screen for filter paper
E - Beam balance	L - Light shield
F - Power supply and bridge	M - Two-channel recorder
G - Heat source	N - Air vent

Fig. 4. Schematic diagram of equipment.

which would result upon the exposure of a material to the energy sources that are present during the combustion of other materials in a fire. Moreover, unlike the General Electric candle test where all of the heat is supplied to the sample by conduction and radiation back from the flame front, this added heat would correspond to the more severe convective heat transfer that occurs when the specimen is ignited at the bottom.

The weight of the sample under test was monitored continuously using a Statham load transducer. The material was prepared using the shredding technique described by Michelson and Einhorn and the samples all weighed close to 330 milligrams. For this experiment, the samples were exposed to a constant radiant energy source of 1.67 watts/cm^2. Future work at other fluxes is planned. A paper describing this instrument, its reliability, and the high degree of reproducibility that was obtained has been submitted to *Fire Technology*.

Because the smoke was removed continuously during burning, the fire could be photographed to determine if a correlation exists between the observed burning phenomenon and the rate of weight loss. Typical data on the burning of this urethane is shown in Fig. 5. For this polymer there is an initial rapid loss in weight followed by
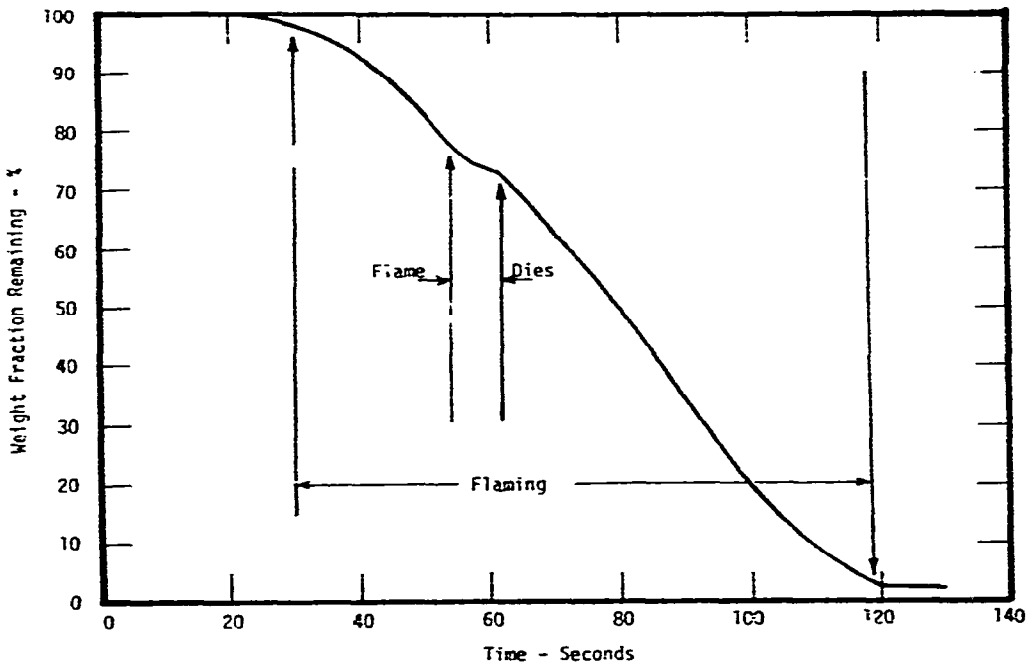

Fig. 5. Visual observations on the burning of an untreated urethane.

a lessened rate of weight loss and then a more rapid and longer sustained rate of loss. This corresponds well with the photographic evidence. Upon the application of the radiant heat source, the material starts to brown, begins to bubble, and after about 35 sec, the evolved gases ignite. The material burns strongly and then the flame dies down corresponding to the decline at which the material loses weight. After a short period, strong burning resumes and the flaming appears to be more intense than in the earlier burning period and lasts until the material is essentially consumed.

A better representation of this burning process is shown in Fig. 6 where the rate at which the material burns is plotted against the time of burning. When this figure is compared to Fig. 3 showing the DTA, the remarkable similarity between
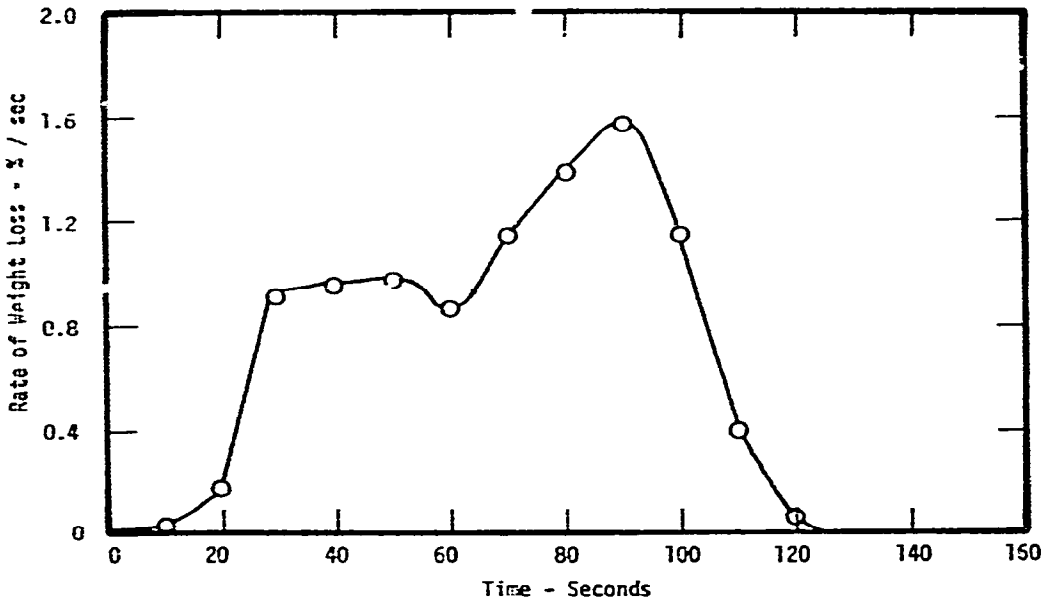
Fig. 6. The rate of burning for a non-fire retarded urethane.

these data is seen. The DTA suggests that the material will decompose at two different rates, that there will be a period when the decomposition rate will be very slow and then increase in intensity corresponding well with the visual observations of the fire.

This evidence certainly indicates that thermal analyses can be related to burning; however, much more can be learned if these tests are also performed in an oxygen atmosphere. Unfortunately, not as much data were obtained for the decom-
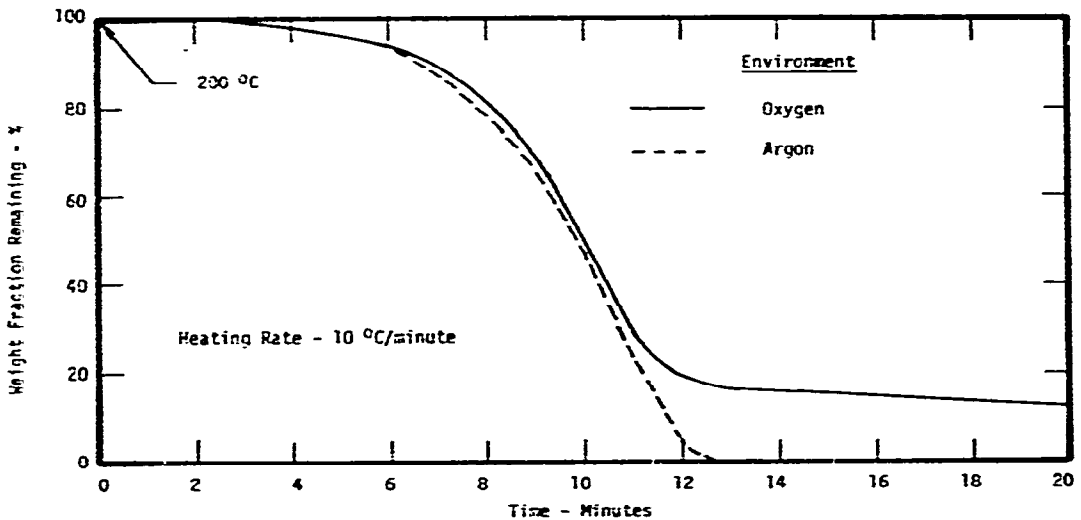

Fig. 7. Thermogravimetric analysis of an untreated urethane.

position of this material in an oxygen atmosphere; but nevertheless, the results are significant. The thermograms for this urethane obtained in both argon and oxygen atmospheres at a heating rate of 10 °C/min are presented in Fig. 7. The slight deviation between these thermograms over most of the decomposition range is not thought to be significant since variations of this magnitude have been observed for the decomposition of a number of samples of the same material at this heating rate in argon. The important observation is that the material decomposes entirely in an inert atmosphere whereas, in oxygen, it is not entirely consumed, but reacts to form a char.
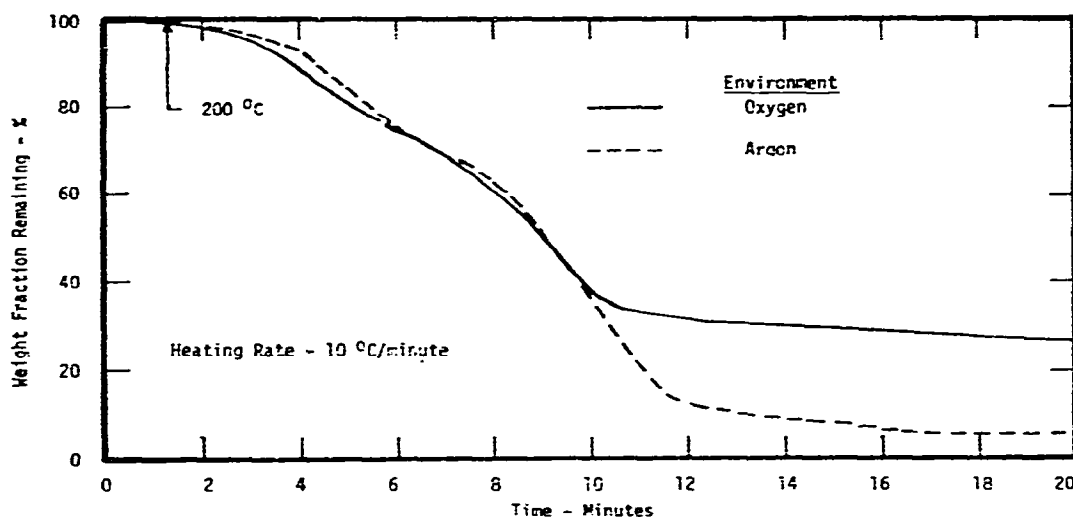

Fig. 8. Thermogravimetric analysis of a fire-retarded urethane.

A better indication of the use of TGA to predict char formation is shown in Fig. 8. In this case, the polymer contained 30 percent of a non-reactive fire retardant. The weight fraction remaining at the end of this TGA agrees exactly with the amount of char left after burning this same material. The shape of this thermogram is typical of thermograms where two different materials are present each having different kinetics of decomposition. Only in this case, the non-reactive fire retardant is not decomposing, but rather, subliming away from the polymer.

Another very informative test is the DTA in oxygen of this urethane with and without fire retardant added. These tests (Fig. 9) show that strong exotherms result when these materials are decomposed at 10 °C/min suggesting that they are burning. There are two interesting features in the data shown in Fig. 9. First, the material containing no fire retardant exhibits a trace of the double hump again indicating that the material will burn at two different rates. Secondly, the DTA of the fire-retarded material exhibits a much stronger exotherm that starts much sooner than does the one for the untreated material. This suggests that the presence of a fire retardant could cause the burning to be more severe. Evidence obtained during the burning of this fire-retarded polymer exhibits a similar behavior as shown in Fig. 10. The rate of
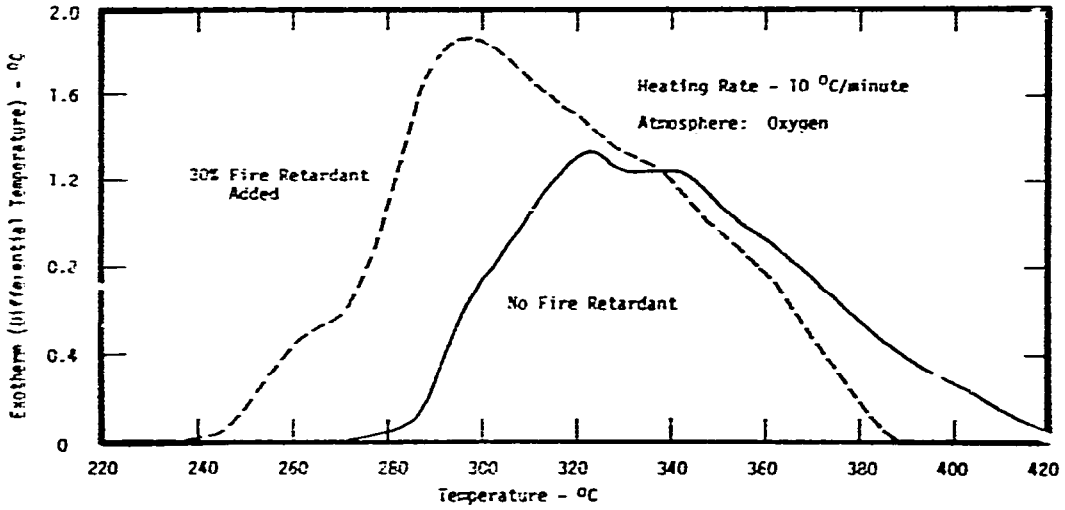
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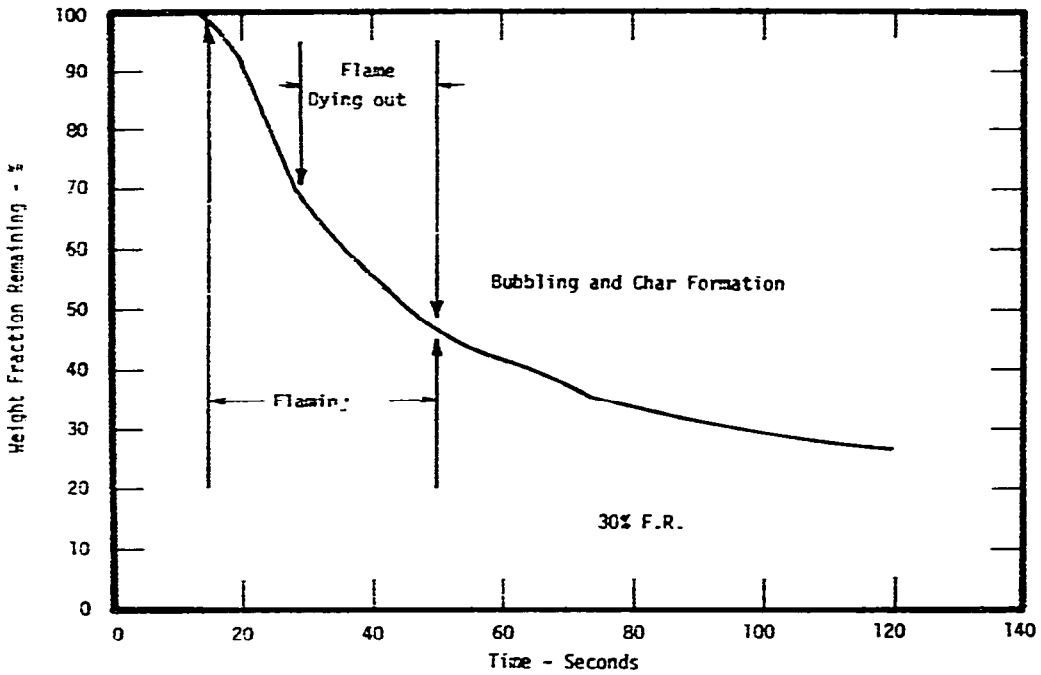Fig. 9. Differential thermal analysis of urethanes in oxygen.

Fig. 10. Visual observations on the burning of a fire-retarded urethane.

weight loss is much more rapid for this polymer than for the untreated material. Moreover, an examination of the photographic data showed that flaming occurred much earlier, at about 15 seconds after the application of the heat source. The flaming, although lasting for a shorter time, did appear to be more intense. After about 20 more seconds, the flame died down, eventually going out. The material continued to bubble while a dense char was formed.
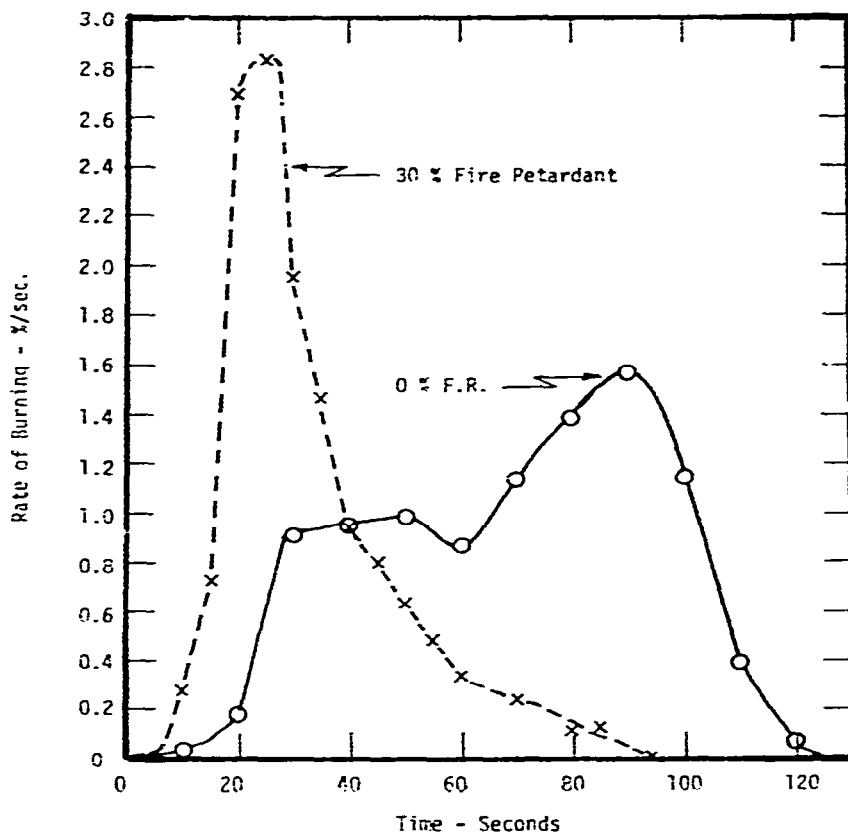
Fig. 11. A comparison between the rates of burning for a treated and untreated urethane.

A comparison of the data showing how much faster the rate of burning is for the fire-retarded material than for the untreated material is shown in Fig. 11. For the fire-retarded material, the two phases of burning exhibited by the untreated material have virtually disappeared. All of this evidence that a fire-retarded polymer could, in the presence of other burning materials, make a fire worse must certainly be investigated further.

CONCLUSIONS

This discussion has demonstrated the importance of thermal analyses as a tool for predicting and providing confirmation as to the reaction of a material to a fire. It must be re-emphasized that for certain materials many tests must be applied. A single thermogram at one heating rate is virtually useless in providing any satisfactory information as to how a material might burn.

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NOMENCLATURE

T_i	temperature at point i on a thermogram
T_j	temperature at point j on a thermogram
ΔT	$T_j - T_i$
γ	weight fraction remaining
θ	time
$(-d\gamma/d\theta)_i$	rate of disappearance of material at point i on the thermogram
$(-d\gamma/d\theta)_j$	rate of disappearance of material at point j on the thermogram

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