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Prediction of thermoplastic flammability by thermogravimetry [1]

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Abstract

The novel aspect of this work is that it examines relationship between the amount of thermogravimetry (TG) char measured at various sample degradation temperatures and the limiting oxygen index (LOI) at elevated sample temperatures. Analysis of experimental results indicates the amount of TG char is directly proportional to the LOI value of most thermoplastics evaluated. The higher the amount of TG char of a thermoplastic material, the higher will be its LOI value, i.e. lower flammability. The LOI value decreases, however, with higher sample temperatures. Statistical relationships for predicting LOI values of thermoplastics at various temperatures are provided.

INTRODUCTION

Objective

The objective was to demonstrate that thermoanalytical techniques can predict flammability properties of polymers.

Background

The Survivability and Fire Research Laboratory of Carderock Division, Naval Surface Warfare Center (CDNSWC) conducts research to reduce flammability of Navy shipboard materials. Owing to the fact that the necessary sample sizes are not always available and may be prohibitively expensive, the ability to screen small sample sizes is needed. As more sophisticated and complicated small scale fire test methods, such as the Factory Mutual fire test apparatus [1,2] and the cone calorimeter [3] are developed, the time and associated cost for assessing candidate materials will continue to rise.

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A useful small scale method available to those involved with polymer flammability research is thermogravimetry (TG). TG is used through its display of the thermal degradation profile of minute samples, to obtain fundamental information about burning material. One fire parameter that the TG profile displays is char residue. Char formation in the combustion process moderates or curtails fire growth by limiting heat transfer to unburned material [4] and limits the availability of oxygen for reaction with additional fuel. TG offers a fast reproducible bench scale technique for measurement of char residue of small samples.

The limiting oxygen index (LOI) is the minimum concentration of oxygen in an oxygen–nitrogen atmosphere that is sufficient to ignite and support combustion for at least three minutes or to support flame spread of 50 mm. It is a test method for evaluating the relative flammability (ignition and flame propagation) of materials. This report examines the correlation of TG char residue and flammability of polymers as measured by the LOI test.

Approach

A correlation between TG char residue and LOI had been suggested by a previous study [7]. The study indicated that formation of char minimizes flammability and hence increases LOI. Flammability of polymeric materials is a key issue in shipboard fire safety, so experiments were performed at CDNSWC to verify the relationship. The hypothesis that a correlation exists was verified for thermoplastic polymers. The LOI experiments in the earlier work had been conducted at 25°C. CDNSWC experiments were conducted to determine whether a relationship also held at elevated LOI temperatures of 50°C and 100°C.

Although TG is a tool for measuring char, the amount of char produced depends upon the chosen experimental conditions. For example, the lower the rate of heating, the lower will be the char yield. In this case, a heating rate of 20°C min^{-1} was selected for the experiments. The purge gas is another experimental condition effecting char yield. Char undergoes oxidation in air, so TG runs were conducted in an inert nitrogen atmosphere [5].

Most char-forming polymers, when exposed to TG nitrogen atmospheric conditions, lose weight in two stages (see Fig. 1). The first weight loss transition occurs between 400 and 600°C and is characterized by a rapid weight loss. Beyond this temperature range, the material undergoes a gradual weight loss. The second stage usually terminates above 1000°C. Char yield, therefore, was measured at three separate points along the TG degradation curve: at the end of the first major weight loss transition; at 800°C; at 900°C (see Fig. 1). Experiments included char measurements above and below 850°C, the temperature utilized in previous work [7].

The TG experiments were made with a Du Pont 9900 computer/thermal analyzer and 951 thermogravimetric analyzer (TGA). TG samples were cut

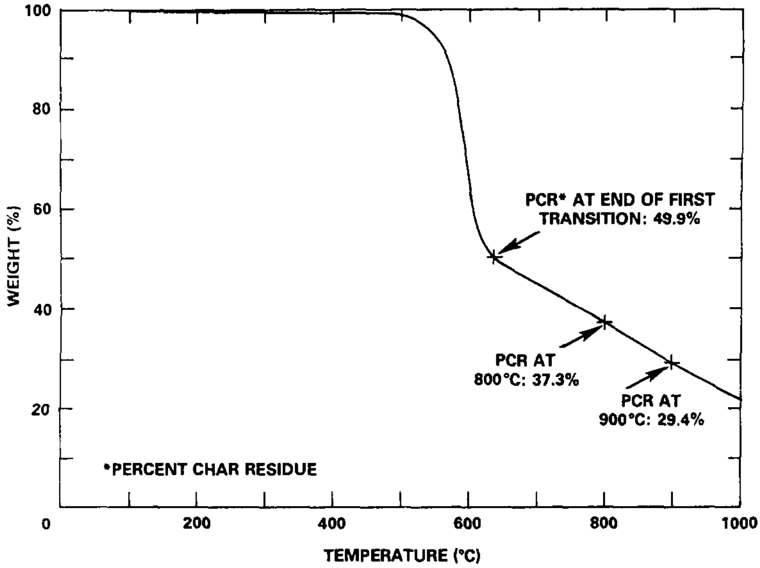


Fig. 1. TG run of polysulfone. Heating rate, 20°C min^{-1}; weight, 7.14 mg; atmosphere, nitrogen.

from commercial 3.2 mm (1/8 in) thick sheets into 6–10 mg pieces. LOI measurements were made with a Stanton and Redcroft hot flammability test apparatus (HFTA); 25°C measurements were obtained using the conventional chimney and the heated chimney was used for elevated temperature measurements of 50°C and 100°C. LOI sample dimensions were 3.2 × 6.5 × 70–100 mm^3.

RESULTS

TG char and LOI relationship

Correlation analysis indicates that the performance of some thermoplastics under room temperature and elevated LOI conditions can be predicted from knowledge of the associated TG char residue. Regardless of the position along the TG curve at which char yield was measured, the data show that the higher the TG char yield of a thermoplastic, in general, the greater is its LOI (Table 1 and Fig. 2 show examples). Finally, higher LOI preheating temperatures resulted in a lower LOI value (see Fig. 3).

Statistical assessment of data

TG char yields and LOI measurements are tabulated in Table 1 for the various experimental conditions. The data as illustrated in Fig. 2 suggest a straight line relationship, so the correlation between char and LOI for each

TABLE 1

TG percent char residue and LOI test results for representative thermoplastic materials

Material	TG [a] percent char residue			LOI		
	End of first transition	800°C	900°C	25°C	50°C	100°C
Polytetrafluoroethylene	0	0	0	> 95	90.3	82.1
Polyethylene	0	0	0	17.7	17.1	15.2
Polypropylene	0	0	0	17.6	16.6	16.0
Polymethyl methacrylate	0	0	0	17.3	16.7	15.7
Polyoxymethylene	1.1	1.1	1.1	14.9	13.2	12.1
Polystyrene	5.8	4.8	4.8	18.2	17.6	16.6
Polydimethylphenylene oxide	30.0	14.2	6.1	31.8	29.4	28.3
Polycarbonate	30.2	19.4	12.4	24.8	24.4	23.2
Polyethersulfone	41.1	34.2	29.5	30.8	29.6	25.5
Polyvinyl chloride	42.6	9.8	9.6	46.5	43.1	41.4
Polysulfone	49.9	37.3	29.4	36.9	36.4	34.5
Graphite sample	– [b]	89.7	71.8	65.0	64.8	63.5

[a] Nitrogen purge; heating rate 20°C.

experiment was determined using the method of least-squares and is provided in Table 2. A 95% prediction interval for LOI (25°C) for any given TG percent char residue value is shown in Fig. 2.

The coefficient of determination r^2 is also shown in Table 2 for the various experiments. The coefficient r^2 measures the percentage of the

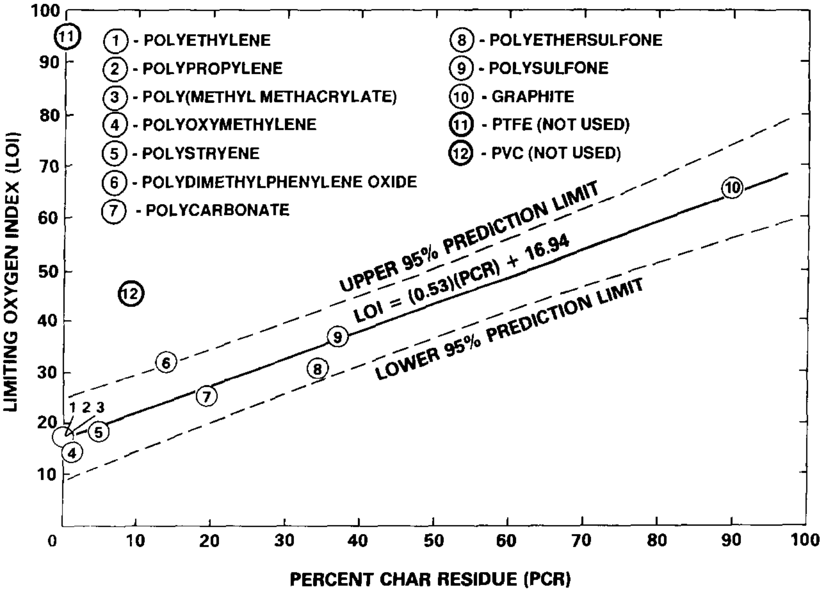


Fig. 2. LOI (at 25°C) vs. TG percent char residue (at 800°C).

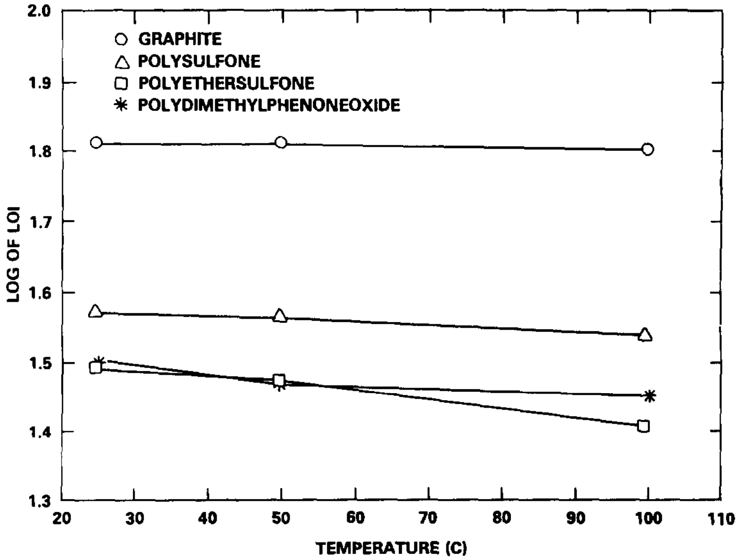


Fig. 3. Dependence of preheating temperature on LOI of selected materials.

total variation in LOI explained by variation in TG percent char residue. Although the values of r^2 are high for the experimental categories, the coefficient corresponding to curves generated with TG char values measured at the end of the first weight loss transition and 900°C are not as high as the correlation coefficient for the curves using TG percent char residue at 800°C.

TABLE 2

Correlation analysis for TG percent char residue (PCR) versus LOI measurements

LOI and char conditions	Linear prediction equation LOI = m(PCR) + b	Coefficient of determination r^2
LOI 25°C		
Char at 1st weight loss	LOI = 0.38 PCR + 16.61	0.93
Char at 800°C	LOI = 0.53 PCR + 16.94	0.96
Char at 900°C	LOI = 0.64 PCR + 17.60	0.92
LOI 50°C		
Char at 1st weight loss	LOI = 0.38 PCR + 15.64	0.94
Char at 800°C	LOI = 0.53 PCR + 15.85	0.96
Char at 900°C	LOI = 0.65 PCR + 16.64	0.93
LOI 100°C		
Char at 1st weight loss	LOI = 0.35 PCR + 14.61	0.90
Char at 800°C	LOI = 0.53 PCR + 14.52	0.95
Char at 900°C	LOI = 0.64 PCR + 15.18	0.91

DISCUSSION

Material characteristics

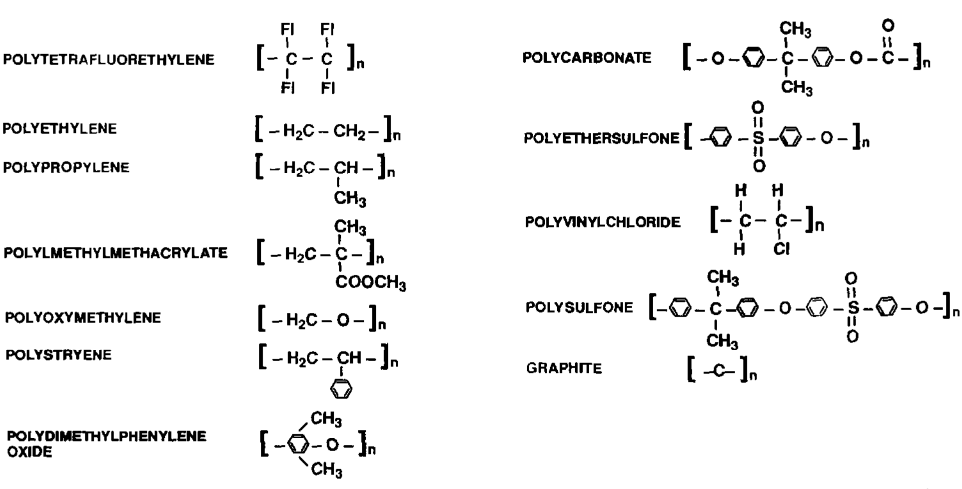
Fire retardant mechanisms

The relationship between char and LOI applies only to thermoplastics that suppress burning predominantly by formation of char. As shown in Fig. 2, data points for polytetrafluoroethylene (PTFE) and polyvinylchloride (PVC) fall above the curve and were not used to determine equations representing the relationship between TG char residue and LOI in Table 2. PTFE has a LOI of almost 100 but exhibits virtually no char formation because fluorine is lost from the polymer and operates to suppress flaming in the vapor phase. PVC, in contrast, forms some char, but (like PTFE) is commonly thought to reduce the formation of flame, predominantly in the vapor phase [5,7].

The behavior of PTFE under high temperature conditions demonstrates that LOI measurements alone cannot be used as a measure of the fire performance of a polymer. Although the polymer has a high LOI and high decomposition temperature, once degradation is initiated by the high temperature conditions of the TGA furnace it proceeds rapidly to completion. There is no char residue left to minimize the production of fuel. Indeed, the correlation of TG char yields with LOI values may not be as important as the ability of TG techniques to measure carbonaceous residue.

TABLE 3

Structure of polymers evaluated



Structure

Examination of the polymer structures shown in Table 3 confirms a relationship between structure and char [5,7]. Polymers with an aromatic structure in the backbone promote char formation. Polydimethylphenylene oxide, polycarbonate, polyethersulfone, and polysulfone all contain an aromatic structure in their backbone, and upon thermal degradation yield the most char, except for graphite. Polymers with bulky side chains such as polymethyl methacrylate and polystyrene or those without aromatic backbone structures such as polyethylene and polypropylene yielded approximately zero percent char.

The coordinates for polydimethylphenylene oxide shown in Fig. 2 are slightly above the curve and it is the only polymer among those tested that produces char and deviates from the least-squares curve. This polymer has an LOI (at 25°C) of about 30 and a TG percent char yield (at 800°C) of approximately 15, which is lower than other char-forming materials with similar LOI values. During the LOI test, polydimethylphenylene oxide produced char, but this was carried away as soot. Soot was also probably deposited onto the walls of the TGA chimney. Therefore, adding the increase in chimney weight might improve the accuracy of TG percent char residue measurements.

High temperature LOI

As shown in Fig. 3, the samples evaluated exhibited a lowering of LOI value at higher LOI temperatures. All materials showed a reduction in LOI value at approximately the same graduated rate. Although materials evaluated showed no erratic LOI performance, it was anticipated that some materials may rapidly decrease in LOI value with higher preheating temperatures [8].

CONCLUSIONS

Thermoplastics that degrade from the heat of a TG furnace producing carbonaceous char exhibit certain characteristics. In general, the higher the TG char yield, the higher the LOI value. Thermoplastic LOI values can be predicted from 20°C min^{-1} nitrogen TG experiments by using the equations

$$\text{LOI}(25^\circ\text{C}) = 0.5(\%\text{TG char residue at } 800^\circ\text{C}) + 16.9$$

$$\text{LOI}(50^\circ\text{C}) = 0.5(\%\text{TG char residue at } 800^\circ\text{C}) + 15.9$$

$$\text{LOI}(100^\circ\text{C}) = 0.5(\%\text{TG char residue at } 800^\circ\text{C}) + 14.5$$

Curves for TG char residue and LOI display a least-squares fit in the LOI range 25–100°C. An aromatic structure in the polymer backbone promotes the formation of TG char.

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