

The thermal analysis of bismaleimide/graphite fiber composite by TG/FTIR¹

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Abstract

This study evaluates the thermal and oxidative stability of a specific polymer composite. A TG/FTIR combined technique was employed to characterize this polymer/graphite fiber composite. The polymer composite sample was pyrolyzed in nitrogen, air and 3% oxygen atmosphere, respectively, in a Seiko thermogravimetric analyzer. The use of a gas-cell Fourier transform IR spectrometer downstream from the TGA allowed for the identification of the evolved gas products.

The thermal oxidative stability (TOS) of this composite is compared to its thermal stability; also, comparison of the TOSs in different atmospheres is presented. In addition, the effects of specimen geometry in terms of sample thickness and surface area to volume ratio (A/V) were investigated and are discussed by relating gas diffusion into the specimen to its relative stability.

INTRODUCTION

The thermal oxidative stability (TOS) in an advanced polymer composite is an important material selection consideration for commercial aircraft applications. In this study, the TOS of a bismaleimide/graphite fiber composite, X5260/IM7, was investigated by dynamic thermogravimetric/gas-cell FTIR analysis [1]. BASF have reported wide processing capability, enhanced toughness and improved thermo-oxidative stability [2] for their newly developed BMI, Rigidite™ X5260. Hercules' IM7, an intermediate modulus and high-strength PAN-based carbon fiber, is the continuous reinforcing fiber used in this polymer composite [3]. In the present study, the TOS of X5260/IM7 was determined in terms of weight loss characteristics and evolved gas products. The difference in the TOSs in air and in 3%

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oxygen atmosphere is reported. The sample size effect on TOS was also examined and is discussed.

EXPERIMENTAL

A Seiko TG/DTA 200 was used to follow the composite weight change at a heating rate of $10^{\circ}\text{C min}^{-1}$ with a gas flow rate of 50 ml min^{-1} in nitrogen, air, and 3% oxygen. A Perkin-Elmer 1650 FTIR, coupled with the TG/DTA instrument by a connecting heated gas line (an insulated Teflon tube, its temperature being about 200°C) monitored the evolved gases. A Barnant thermocouple controller maintained the gas cell temperature at about 200°C to prevent condensation.

Composite test samples of varying thickness and surface area to volume ratio (A/V) were employed for sample size effect assessment. Table 1 lists the various sample dimensions used. Test samples were pre-dried for about three days at 93.3°C , with daily weighing until constant sample weights were attained.

TABLE 1

The dimensions of the samples

Sample no.	Approx. sample size	Dimensions $L \times W \times T$ in inches	A/V
1	20 mg	$0.15 \times 0.15 \times 0.042$	74
2	50 mg	$0.15 \times 0.15 \times 0.1$	47
3	80 mg	$0.15 \times 0.15 \times 0.172$	38
4	0.6 g	$1.0 \times 0.5 \times 0.042$	54
5	1.3 g	$1.0 \times 0.5 \times 0.1$	26
6	2.1 g	$1.0 \times 0.5 \times 0.172$	18

RESULTS AND DISCUSSION

At $10^{\circ}\text{C min}^{-1}$ heating rate in air, the composite started to lose weight at about 354°C regardless of its specific thickness or surface area to volume ratio. Its weight loss typically displayed three maximum weight change rates with respect to temperature. These three maxima occurred at 421 , 582 (as a shoulder) and 667°C , respectively (Fig. 1). The corresponding weight losses are 5%, 22%, and 45%. The third peak at about 45% weight loss is most probably associated with carbon fiber degradation. A typical FTIR spectrum of the evolved gases from X5260/IM7 at 420°C in air with IR band identification is presented in Fig. 2. The evolved gas products are composed of H_2O (1683 cm^{-1}), CO_2 (2359 cm^{-1}), CO (2110 cm^{-1}), NO (1920 cm^{-1}), CH_4 (3014 cm^{-1}), and other aliphatic hydrocarbons (2969 cm^{-1}) and aromatic hydrocarbons (3086 cm^{-1}) [4–6]. The evolved gas products also

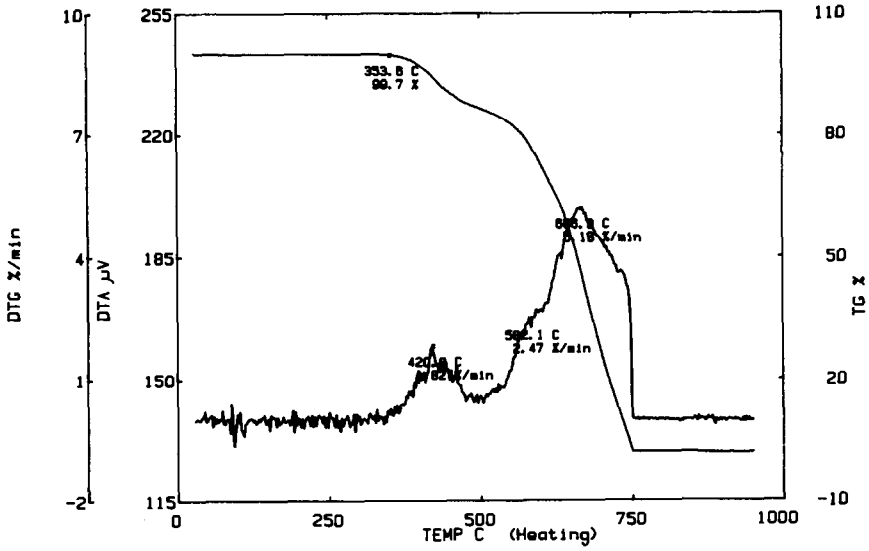


Fig. 1. TG/DTG curve for X5260/IM7 in air atmosphere.

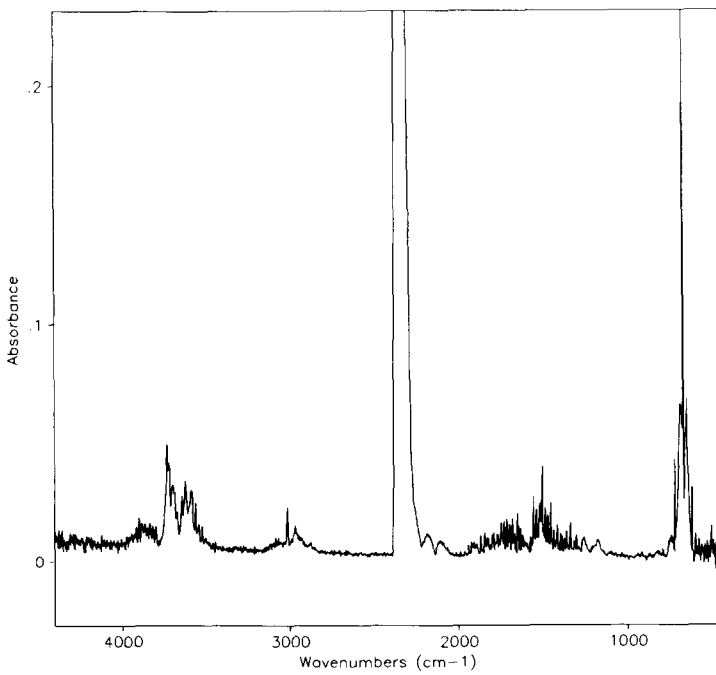


Fig. 2. FTIR spectrum of evolved gases from X5260/IM7 in air.

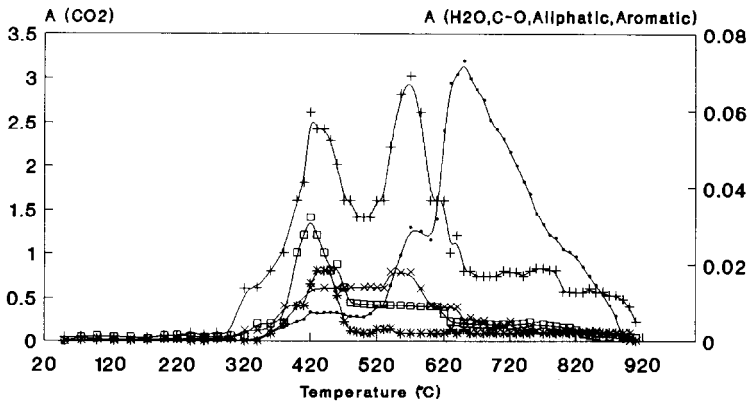


Fig. 3. Gas release profiles during combustion of X5260/IM7: •, CO₂ (2359 cm⁻¹); +, H₂O (1683 cm⁻¹); *, aliphatic (2969 cm⁻¹); □, C–O (1176 cm⁻¹); ×, aromatic (3086 cm⁻¹).

exhibited peak amounts at around T_{\max} , the temperature of the maximum weight loss rate (Fig. 3). For instance, the amounts of H₂O, CO₂, aliphatic hydrocarbons, and aromatic hydrocarbons given off are relatively high at the first peak temperature of 420°C. The temperatures at 5% and 10% weight losses determined for samples 1–6 are given in Table 2. It can be seen that the temperature for 5% weight loss increases slightly with increasing sample thickness above 0.042" and decreasing sample A/V ratio below 74. The temperature at 10% weight loss follows a similar trend. The sample size and thickness effects shown in Fig. 4 are indicative of a gas-diffusion-controlled oxidation and degradation process.

The weight loss in test specimens 4–6 was measured at the specific temperature with the sample placed in a quartz tube. Their total weight losses were 100%, 64%, and 51%, respectively. Thus the thickest and smallest A/V ratio, sample (No. 6) gave the least weight loss; again this suggests a gas-diffusion-controlled mechanism.

At 10°C min⁻¹ heating in a 3% oxygen atmosphere, the composite also began to lose weight at about 354°C. Even though its initial weight loss

TABLE 2

Temperatures for 5% and 10% weight loss

Sample no.	A/V	Thickness in inches	T for 5% loss/°C	T for 10% loss/°C
1	74	0.042	421	459
2	47	0.100	427	475
3	38	0.172	429	485
4	54	0.042	425	470
5	26	0.100	450	510
6	18	0.172	480	530

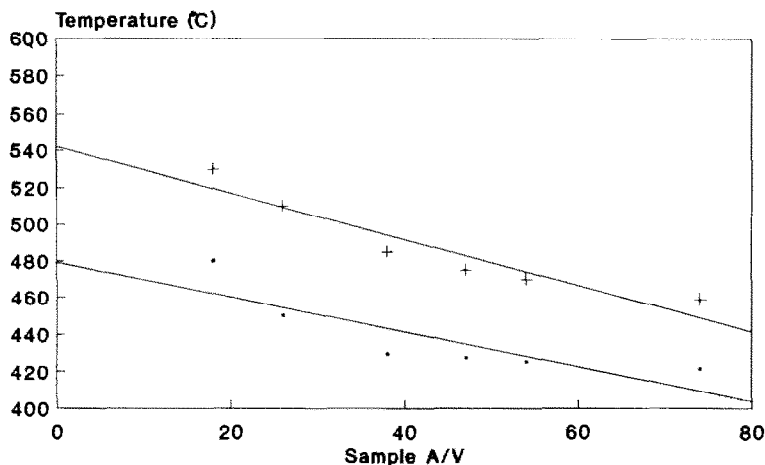


Fig. 4. Temperature vs. sample surface area to volume ratio: •, T at 5% weight loss; +, T at 10% weight loss.

temperature is the same as that in air, its weight loss rate is relatively smaller. In the end, it only lost 50% of its weight (Fig. 5). Hence, this TG run confirmed that the expected composite TOSs are greater in an atmosphere of reduced oxygen content (Fig. 6).

In a nitrogen atmosphere, the composite started to lose weight at about 345°C. Two T_{max} temperatures at 425 and 546°C are noted (Fig. 7). Their corresponding weight losses are 5% and 15%. The gas release profiles in Fig. 8 also exhibited two major peaks around these two temperatures. A typical FTIR spectrum of the evolved gases during pyrolysis at 430°C is

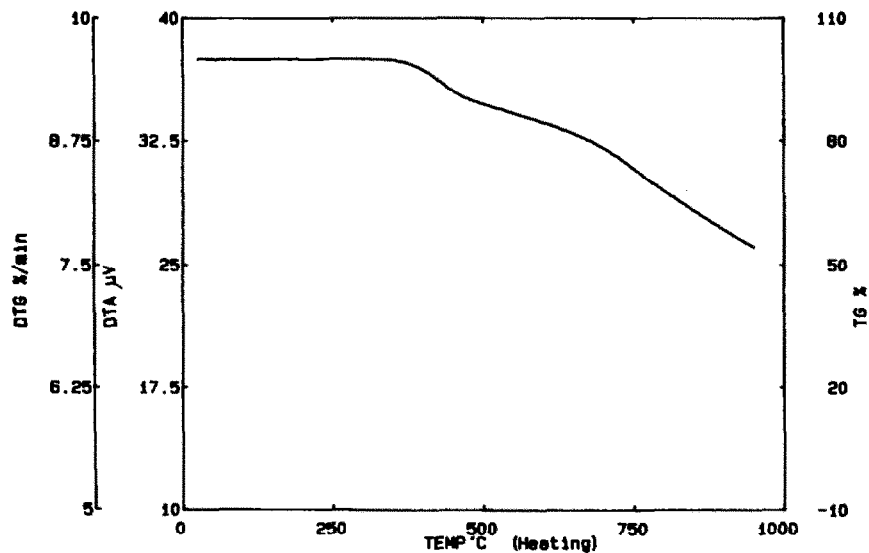


Fig. 5. TG curve for X5260/IM7 in a 3% O_2 atmosphere.

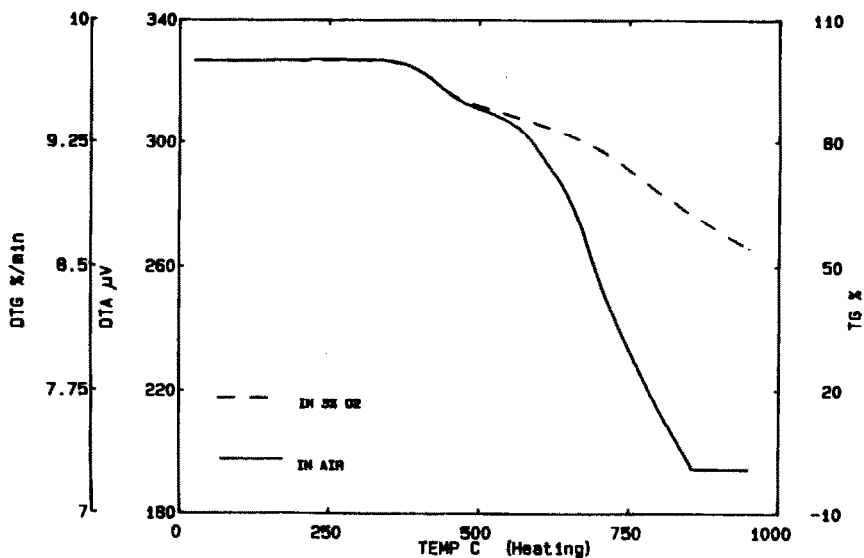


Fig. 6. TG curves for X5260/IM7 in air and a 3% O₂ atmosphere.

shown in Fig. 9. The evolved gas products are identified as CO₂, CO, CH₄, phenol, *para*-cresol, maleimide, succinimide [7], and other aliphatic and aromatic hydrocarbons. Table 3 lists the wavenumbers of some functional groups in organic compounds [4] selected to identify the species in the evolved gases during pyrolysis.

At 425°C, relatively high amounts of evolved CO₂, aliphatic hydrocarbons, and aromatic hydrocarbons are apparent; the amount of evolved CH₄

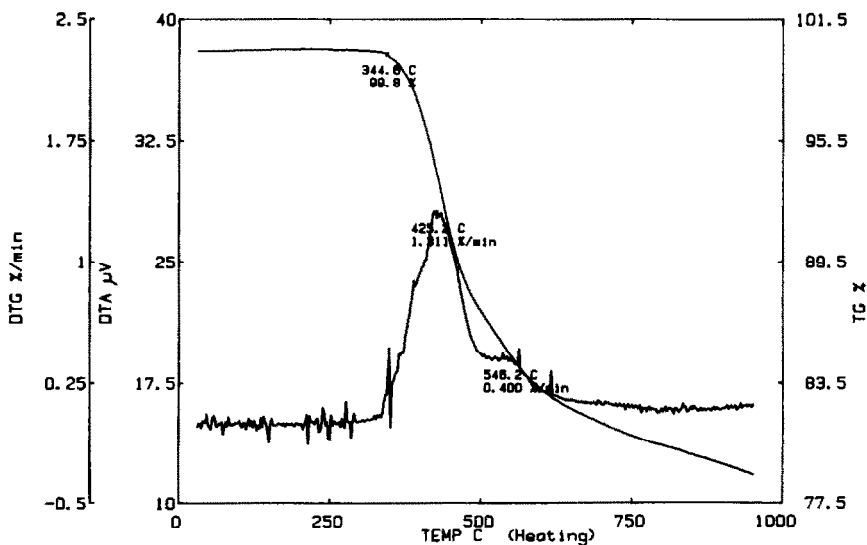


Fig. 7. TG/dTG curve for X5260/IM7 in N₂ atmosphere.

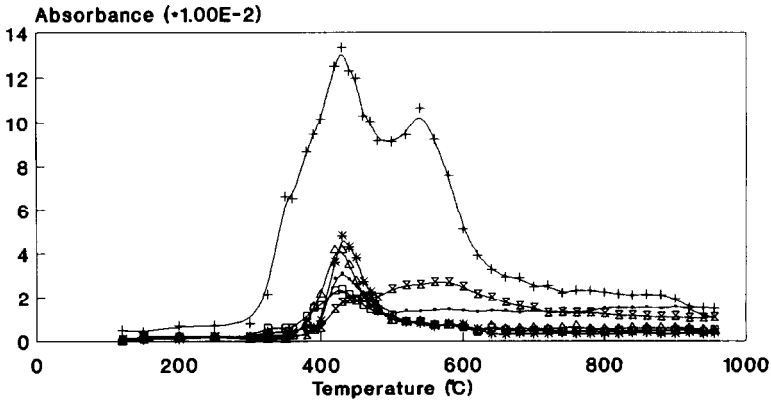


Fig. 8. Gas release profiles during pyrolysis of X5260/IM7: •, aliphatic (2968 cm^{-1}); +, CO_2 (2360 cm^{-1}); *, C=O (1713 cm^{-1}); □, aromatic (1609 cm^{-1}); Δ, C-O (1175 cm^{-1}); ⌘, CH_4 (3015 cm^{-1}).

is relatively high at 550°C . Thus, the TG results are independent of the sample size and geometry.

The overall weight losses in samples 4–6 were measured at the end of the pyrolysis in nitrogen. Their amounts are 20%, 18% and 18%, respectively. Evidently, these weight changes are independent of their sample size and geometry.

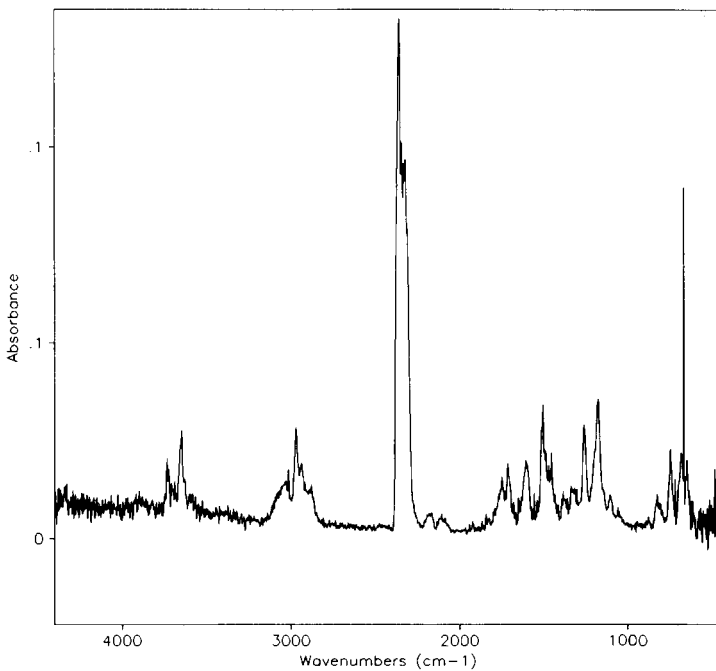


Fig. 9. FTIR spectrum of evolved gases from X5260/IM7 in N_2 .

TABLE 3

Wavenumber of selected functional groups

Functional group	Wavenumber/cm ⁻¹
O–H (stretching)	3647
Aromatic C–H, aliphatic C–H (stretching)	2880–3060
C=O (stretching)	1715, 1748
Aromatic ring (C=C vibrations)	1507, 1607
Alkane CH ₂ (scissoring) and CH ₃ (asymmetric bending)	1460
CH ₃ (symmetric bending)	1373
C–H (bending), O–H (bending)	1340, 1176
C–N, C–O, C–OH (stretching)	1100–1300
Aromatic C–H (out-of-plane bending)	747, 828

CONCLUSIONS

In an air atmosphere, the dynamic TGA study of X5260/IM7 indicated that the weight loss characteristics depend on the test specimen thickness and surface area to volume ratio, due to gas diffusion.

In nitrogen, the weight loss characteristics were observed to be independent of sample thickness and surface area to volume ratio.

The TOS of this composite in the 3% oxygen atmosphere, which was applied to simulate aircraft flight environment, displayed a greater thermal oxidative stability than that in air, as expected.

Gas-cell FTIR showed that the gas products were CO₂, CO, NO, H₂O, CH₄, phenol, and other aliphatic and aromatic hydrocarbons. It was interesting to note that these gas products also exhibited peak amounts of evolution at the weight-loss-rate peak temperatures.

REFERENCES

- 1 M.E. Brown, Introduction to Thermal Analysis Techniques and Applications, Chapman and Hall, New York, 1988.
- 2 J.D. Boyd, Glenn E. C. Chang, V. Altstädt, D. Gerth and W. Heckmann, SAMPE Proceeding, Society for the Advancement of Material and Process Engineering, Covina, CA 1990, pp. 994–1006.
- 3 Hercules product bulletin on Hercules Graphite Fibers and Prepregs, Wilmington, DE.
- 4 R.T. Conley, Infrared Spectroscopy, Allyn and Bacon, Boston, 1966.
- 5 J. Khorami, A. Lemieux, H. Menard and D. Nadeau, Usefulness of Fourier Transform Infrared Spectroscopy in the Analysis of Evolved Gas from the Thermogravimetric Technique, ASTM Spec. Tech. Publ. 997, Compos. Anal. Thermogravim., Philadelphia, PA, 1988, pp. 147–159.
- 6 P.L. Hanst and S.T. Hanst, Gas Measurement in the Fundamental Infrared Region, Infrared Analysis, Inc., Potomac, MD, 1991.
- 7 H.D. Stenzenberger, K.U. Heinen and D.O. Hummel, Thermal degradation of poly(bismaleimides), J. Polym. Sci. Chem. Ed., 14(12) (1976) 2911–2925.