JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, PP. 973-981 (1975)

Thermal Degradation of Polymers. VIII. Ablation Studies on a Series of Fiber-Reinforced Phenolic Resin Composites

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Synopsis

The use of a laboratory ablation test rig for the assessment of tubular fiber-reinforced composites is described. Ablation resistance, char depth, smoke, and flash measurements have been made on a series of composites based on a standard phenol–formaldehyde resin incorporating various fibrous reinforcing agents. The results have been compared with those obtained from a standard asbestos-reinforced composite prepared from the same resin. Results are discussed in terms of the properties of the composite and of the fibrous reinforcing agent.

INTRODUCTION

In a previous paper,[1] we described a laboratory ablation test rig for use with tubular composite specimens. Composites based on asbestos and commercially available high-temperature resins were assessed for use in rocket motor applications. Ablation resistance, smoke, and flash measurements were made and correlated with composite structure.

We now report studies on a series of composites based on a standard phenolic resin with different fibrous reinforcing agents. Ablation resistance, smoke, flash, and char depth measurements have been made and correlated with the properties of the composite and the fibrous reinforcing agent.

EXPERIMENTAL

Apparatus

The apparatus, operating procedure, and specimen preparation is as described previously,[1,2] with minor modification as indicated in the text.

Materials

A standard asbestos/phenolic compound, Durestos RA51, was used as the control material, supplied by Turner Brothers Asbestos Ltd., as a preblended molding material containing a nominal 59% asbestos by weight. The material

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was passed once through a Christy and Norris grinding machine, and then the required weight was made into a preform in order to reduce the high bulk factor. Molding was carried out at 150°C for 30 min.

The standard phenolic resin without asbestos was supplied by Turner Brothers Asbestos Ltd., and composites based on this resin (resin RA51) with a variety of fibrous reinforcing materials were prepared. All fibers were used in short-length form of less than $^1/_8$ in. Details of the premixing processes and the materials used are shown below.

Silica fiber (Refrasil ex The Chemical and Insulating Co. Ltd.) (200 g) was mixed with the standard phenolic resin (133 g) in a Z-blade mixer over a period of 20–30 min. After grinding, the material was preformed. Aluminum silicate fiber (Kaowool ex Morganite Ceramic Fibres Ltd.) (200 g) and the standard phenolic resin (133 g) was similarly mixed, ground, and preformed.

High-modulus carbon fiber (Grafil HM-S ex Courtaulds Ltd.) (175 g) and the standard phenolic resin (140 g) were premixed and then tumble-mixed for 2 hr, ground, and preformed. Nongraphitic carbon fiber (Grafil A ex Courtaulds Ltd.) (160 g) and standard phenolic resin (140 g) were treated similarly to Grafil HM-S.

E glass fiber (ex Deeglass Ltd.) (200 g) was mixed with the standard phenolic resin (133 g) in a Z-blade mixer, ground, and then preformed. Polyacrylonitrile fiber (PAN) (ex Courtaulds Ltd.) (140 g) and the standard phenolic resin (115 g) were mixed together in a Z-blade mixer, ground, and preformed. Molding was carried out on the preforms as for Durestos RA51.

Fiber content, specific gravity, char depth, and weight loss measurements were made as previously reported.[1]

RESULTS AND DISCUSSION

In Table I are shown the fiber content, specific gravity, and weight loss data obtained for the samples under test. It can be seen that the fiber contents, where determined, vary considerably. The mixing formulations were designed to give a fiber content of 44% by volume. The differences found may be ascribed to two basic factors: (a) the shape of the fiber and its ability to pack into the composite, and (b) the specific gravity used for the resin in the calculations. The specific gravity used was 1.31 that quoted for the monolithic cast material.[3] That this may not be the same as that of the resin in the composite is a distinct possibility due to the internal strains imposed on the resin by the fibers.

TABLE I
Fiber Content, Specific Gravity, and Weight Loss Data for Fiber-Reinforced Composites

Material	Fiber content, %	sp. gr.	Weight loss after standard ablation test, %
Durestos RA51 control	58.4	1.74	28.0
Resin RA/51/Refrasil	58.0	1.67	18.8
Resin RA51/Kaowool	68.4	1.84	19.5
Resin RA51/E glass	66.8	1.84	19.7
Resin RA51/Grafil HM-S	—	1.55	20.8
Resin RA51/Grafil A	—	1.50	25.7
Resin RA51/PAN	—	1.23	54.9

No data were obtained for the fiber content of the three samples based on carbon fibers and PAN which were not amenable to the burn-off technique applied to the other samples. Other methods are available for assessment of fiber content of such systems, notably the removal of the resin component by sulfuric acid/peroxide.[4] The poor performance of these materials on the test rig, however, did not warrant their further examination.

Comparison of the weight loss data for the composites reveals that, with the exception of the resin RA51/PAN and resin RA51/Grafil A composites, there is a significantly improved weight retention compared with the Durestos RA51 composite. These figures arise in part because the asbestos fiber initially contains 13.5% by weight water of crystallization which is lost at high temperature, a feature which is absent with the other fibers. In addition, in the case of resin RA51/Kaowool and resin RA51/E glass, the higher fiber content and consequent lower resin content also favors weight retention.

The higher weight losses of the resin RA51/Grafil A and the resin RA51/PAN composites can be attributed to their (a) higher resin content (resin RA51/Grafil A, sp. gr. 1.50, resin RA51/PAN, sp. gr. 1.23 cf. Durestos RA51, sp. gr. 1.74), (b) the lower thermal stability of the reinforcing fiber, and (c) the absence of endothermic cooling reactions derived from the fibrous reinforcing phase. PAN, in contrast to asbestos, shows a highly exothermic "cyclization" reaction at 220–250°C.[5]

The difference in behavior of the two carbon fiber composites can be similarly attributed to the higher resin content of the resin RA51/Grafil A composite and to the lower inherent thermal stability of the Grafil A reinforcing fiber.

Char thickness measurements on samples after the ablation test are shown in Table II. It is apparent that in all cases more resin is charred as compared with the Durestos RA51 control specimen, as shown by the very low virgin material thickness results obtained for all other fiber-reinforced systems. The major factor responsible for this behavior is the absence of the cooling effect of the loss of water from the asbestos reinforcing material which is only present in the Durestos RA51 control sample.

The chars produced during the ablation tests had significantly different properties. The resin RA51/Refrasil sample gave a dense char having a smooth inside surface, white in places, indicating the presence of uncoated silica, i.e., total removal of the resin from the silica surface. Resin RA51/Kaowool showed a less dense char with evidence of surface melting. Resin RA51/E glass gave a material from which the fiber reinforcement effect was lost by melting of the reinforcing component. These tubes on cooling cracked and broke into small segments, and char depth measurements could not be made. A similar effect was observed with the resin RA51/PAN composite which was prepared in order to assess the potential of possible "in situ" formation of a "carbon fiber" type reinforced composite. Its failure may in part be ascribed to the highly exothermic nature of the "cyclization" reaction which is known to occur with polyacrylonitrile.[5] This would result in an enhanced rate of char formation around the PAN fiber and the loss of its reinforcing ability. These two effects lead ultimately to the total disruption of the composite making char thickness measurements impossible.

The two carbon fiber-reinforced composites showed good resistance to erosion although again the absence of endothermic cooling reactions and the high thermal

TABLE II
Char Thickness Measurements

Material	Position	1	2	3	4	5	6	7	8
Durestos RA51	Initial thickness	0.276	0.280	0.283	0.284	0.283	0.283	0.282	0.281
	Final thickness	0.265	0.284	0.308	0.343	0.327	0.354	0.354	0.354
	Thickness change	−0.011	+0.004	+0.025	+0.059	+0.044	+0.071	+0.072	+0.073
	Virgin material	0.043	0.051	0.075	0.102	0.106	0.106	0.108	0.103
	Char thickness	0.222	0.233	0.283	0.241	0.221	0.248	0.246	0.251
	Comments	fairly dense char showing some cracking and smooth inside surface							
Resin RA51/Refrasil	Initial thickness	0.293	0.295	0.297	0.297	0.294	0.292	0.290	0.287
	Final thickness	0.387	0.332	0.332	0.320	0.332	0.316	0.324	0.332
	Thickness change	+0.094	+0.037	+0.037	+0.023	+0.038	+0.024	+0.034	+0.045
	Virgin material	0	0	0	0	0.008	0.016	0.020	0.055
	Char thickness	0.387	0.332	0.332	0.320	0.324	0.300	0.304	0.277
	Comments	dense char; very smooth inside surface showing a white coloration							
Resin RA51/Kaowool	Initial thickness	0.269	0.270	0.272	0.270	0.271	0.272	0.272	0.272
	Final thickness	0.312	0.292	0.288	0.311	0.298	0.305	0.313	0.311
	Thickness change	+0.043	+0.022	+0.016	+0.041	+0.027	+0.033	+0.041	+0.040
	Virgin material	0	0	0	0	0	0	0	0
	Char thickness	0.312	0.292	0.288	0.311	0.298	0.305	0.313	0.311
	Comments	fairly open porous char; surface uneven; melting obvious							

Resin RA51/Grafil HM-S	Initial thickness	0.310	0.313	0.312	0.312	0.312	0.313	0.312	0.310
	Final thickness	0.346	0.340	0.346	0.382	0.390	0.370	0.375	0.367
	Thickness change	+0.036	+0.027	+0.034	+0.070	+0.078	+0.057	+0.063	+0.057
	Virgin material	0	0	0	0	0	0	0	0
	Char thickness	0.346	0.340	0.346	0.382	0.390	0.370	0.375	0.367
	Comments	char contained numerous small cracks; smooth inside surface							
Resin RA51/Grafil A	Initial thickness	0.295	0.296	0.293	0.289	0.288	0.286	0.283	0.277
	Final thickness	0.304	0.304	0.324	0.320	0.315	0.311	0.296	0.315
	Thickness change	+0.009	+0.008	+0.031	+0.031	+0.027	+0.025	+0.013	+0.038
	Virgin material	0	0	0	0	0	0	0.035	0
	Char thickness	0.304	0.304	0.324	0.320	0.315	0.311	0.296	0.315
	Comments	char contained numerous small cracks; smooth inside surface							
Resin RA51/E glass	no measurements taken								
	very poor char structure; very badly cracked transversely into small segments, obvious signs of melting having occurred								
Resin RA51/PAN	no measurements taken								
	specimen totally destroyed; char cracked transversely and broken up into small segments								

conductivity of the fiber resulted in the resin component being completely charred. This behavior is again highlighted in the next section dealing with specimen time–temperature profiles.

Specimen Temperature Profiles

In Figures 1 and 2, the time–temperature profiles for Durestos RA51 control specimens and the various fiber-reinforced resin RA51 composites are compared. The reproducibility of the results has already been discussed elsewhere[2] and has been shown to be excellent, considering the severity of the test conditions. In addition, it should be noted that with this apparatus it is possible to maintain a controlled reproducible ablation environment over a period of time.

The time–temperature profiles for the Durestos RA51 control samples show a slow rate of temperature rise over the first 60 sec. The rate of temperature rise then becomes more rapid as the char–virgin material interface moves through the thermocouple position toward the backface of the tube. The temperature finally levels out at 700–900°C as pseudosteady-state ablation is achieved.

The various fiber-reinforced composites show interesting differences in behavior as can be seen from Figures 1 and 2. The resin RA51/E glass composite profile is very similar to that of the Durestos RA51 control sample. This behavior arises as a result of the temperature being maintained at the same level as with asbestos by melting of the E glass fiber rather than by loss of water.

The resin RA51/Kaowool composite shows similar behavior over the first 60 sec, after which time the temperature slightly exceeds that of the control. This material would be expected to show this type of temperature–time profile because of the increased melting temperature of the fiber as compared to E glass. This would result in less melting of the fiber and consequently a lower endothermic contribution as compared to E glass.

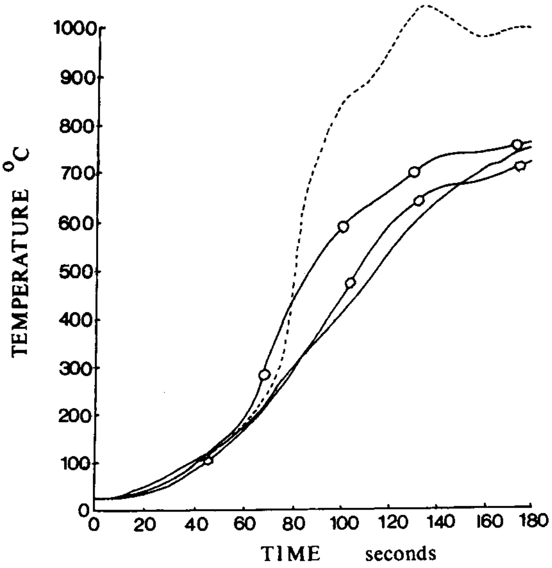

Fig. 1. Time–temperature profiles. Fiber specimens: (———) Durestos RA51 control (- - - - - -) resin RA51/Refrasil; (—O—) resin RA51/Kaowool; (—O—) resin RA51/E glass.

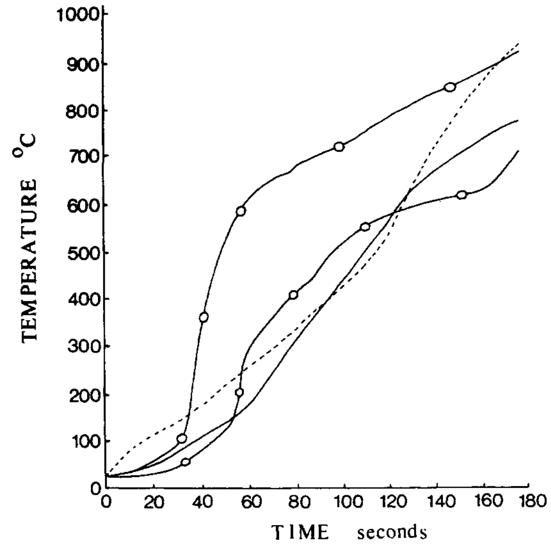

Fig. 2. Time–temperature profiles, Fiber specimens: (———) Durestos RA51 control; (– – – – – –) resin RA51/carbon fiber Grafil HM-S; (—O—) resin RA51/carbon fiber Grafil A; (—O—) resin RA51/polyacrylonitrile.

The resin RA51/Refrasil composite shows strikingly different behavior to that of the other materials in Figure 1. A very rapid increase in temperature occurs after 60 sec, indicating a high thermal conductivity of the fiber–char matrix. The resin phase in this system provides the only endothermic cooling reactions since the silica fibers do not melt under the test conditions, as shown by visual examination.

In Figure 2, the Durestos RA51 control sample is compared with the "carbon fiber" based composites. In all cases the behavior was inferior to that of the control specimen. The high thermal conductivity of carbon fibers[6] (which have values measured along the fiber axis of 80×10^{-3} cal per cm per sec per °C) is apparent from the high initial temperature rise of the resin RA51–Grafil HM-S specimen.

The effect is less pronounced in the case of the resin RA51–Grafil A composite which maintains a lower temperature for the first 40 sec by virtue of the degradation reactions caused by the environment which do not occur with Grafil HM-S. It does, however, show a poor ablation performance overall due to its inherent high thermal conductivity and low thermal stability.

The resin RA51–PAN sample temperature is lower initially, but after 60 sec there is a sudden, rapid increase in temperature. This occurs in the temperature range in which PAN is known to undergo a highly exothermic cyclization reaction.[5] The behavior of the composite is then similar to the control material indicative of resin cooling reactions and further endothermic structural changes occurring in the fibrous reinforcement.

Smoke Obscuration Measurements

Figures 3 and 4 show the smoke obscuration traces obtained from the Durestos RA51 control sample and composites from the six fibers under test. With the exception of the resin RA51/PAN composite, all the fibers show lower levels of

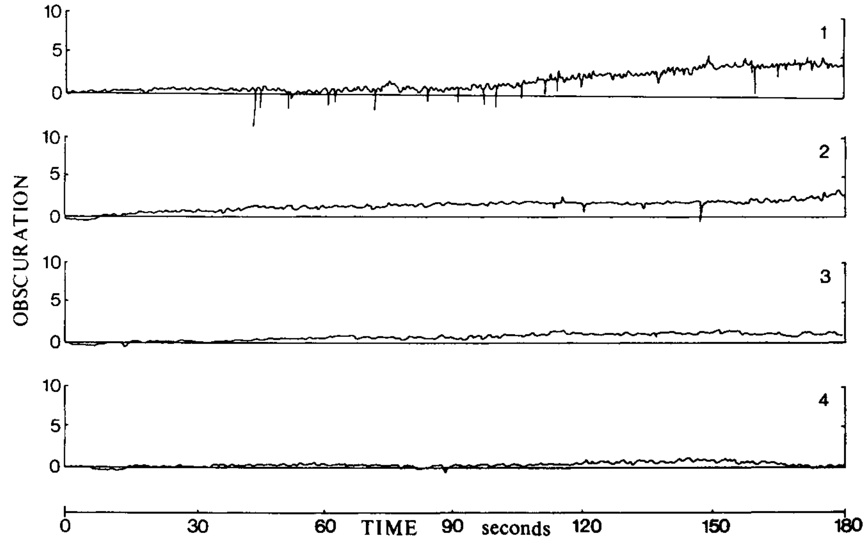

Fig. 3. Smoke obscuration traces: (1) Durestos RA51 control; (2) resin RA51/Refrasil; (3) resin RA51/Kaowool; (4) resin RA51/E glass.

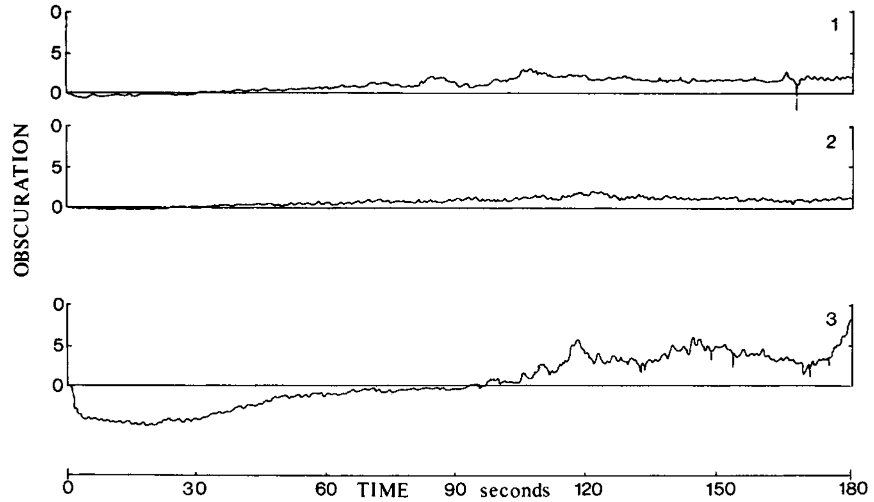

Fig. 4. Smoke obscuration traces: (1) resin RA51/carbon fiber Grafil HM-S; (2) resin RA51/carbon fiber Grafil A; (3) resin RA51/polyacrylonitrile.

smoke obscuration. This is indicative of the asbestos fiber contributing markedly to the smoke evolution effect. The sensing method utilized to measure smoke does not differentiate between "carbonaceous" particulate material as in smoke and water droplets in a fog. Asbestos is unique among the fibers studied in that is loses 13.5% by weight of water, which can condense outside the heated zone of the test rig. In a rocket motor, this may yield a water droplet fog which contributes adversely to the "signature problem."

The resin RA51/PAN composite yielded an unusual trace similar to that previously discussed for the asbestos-reinforced composites based on Xylok 210 and epoxy 154/NMA/BDMA.[1] The anomalous behavior of the smoke trace falling below the zero obscuration axis may be explained by the "char growth"

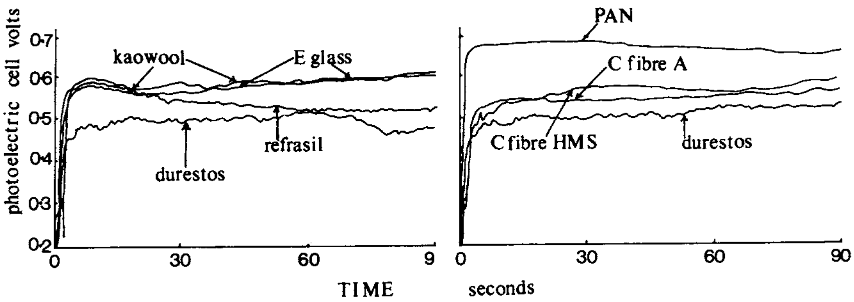

Fig. 5. Flash measurements.

effect. This effect reduces the bore diameter of the tube which causes elongation of the test flame, which then affects the photoelectric cell output. From the smoke obscuration trace, Figure 4, it can be seen that the erosion of the sample takes place at that period of time (40–90 sec into the ablation test) when a very rapid increase in sample temperature occurs (see Fig. 2). Aromatization and loss of condensable volatile materials together with erosion result in the high smoke obscuration values obtained in the latter half of the ablation test.

Flash Measurements

The results shown in Figure 5 indicate that all fiber-reinforced composite resins under test exhibit inferior behavior as compared to the control material. This is not unexpected on the basis of the complete charring observed in these systems.

CONCLUSIONS

Considering the ablative insulation properties only, it is apparent that asbestos fibers offer the best performance due to the cooling effect of the loss of water of crystallization. All other fibers where the composite remains structurally sound show inferior insulation behavior.

However, two systems (resin RA51/Refrasil and resin RA51/Kaowool) show improved weight retention coupled with improved smoke obscuration properties.

These systems could find application in rocket motors requiring low "signature" characteristics.

The authors thank Imperial Metal Industries, Summerfield Research Station, for a Research Studentship (to D.K.) and for a grant. The authors also thank Mr. M. J. Chase for useful discussions.

References

1. D. Kershaw, R. H. Still, and V. G. Bashford, *J. Appl. Polym. Sci.*, **19**, 959 (1975).
2. D. Kershaw, R. H. Still, V. G. Bashford, and S. J. Hurst, *Chem. Ind.*, 95 (1973).
3. *Materials in Design Engineering.* Materials Selector Issue, Reinhold, Stamford, Conn., October 1966/67.
4. Ministry of Defençe (Aviation Supply) D. MAT/Aviation, Provisional Spec. NM. 547, Issue, 3, May 1971.
5. N. Grassie and R. McGuchan, *Eur. Polym. J.*, **6**, 1277 (1970).
6. Courtaulds Ltd. Tech. Bull. G.12, April 1972.

Received July 25, 1974
Revised September 23, 1974