EFFECTS OF CERTAIN TRANSITION METAL OXIDES ON THE CARBON–SILICA REACTIONS IN A GLASS-FILLED POLYMER COMPOSITE

J.B. HENDERSON and J.M. GUTKOWSKI

Department of Mechanical Engineering and Applied Mechanics, University of Rhode Island, Kingston, RI 02881 (U.S.A.)

(Received 13 September 1985)

ABSTRACT

The effects of two transition metal oxides on the kinetics of the carbon–silica reactions in a glass-filled phenolic resin have been studied. Samples containing 10 and 25% by weight of Fe_2O_3 or Cr_2O_3 were tested. The effects of the oxides on the reactions were evaluated from mass-loss data obtained using standard thermogravimetric techniques. The experimental data were obtained for heating rates of 10, 20, and 50°C min^{-1} over a temperature range of 30 to approximately 1700°C. The metals were found to lower the onset temperatures of the carbon–silica reactions up to 475°C.

INTRODUCTION

Glass-filled polymer composites are subject to two types of reactions when exposed to high temperatures. The first of these is the pyrolysis of the resin system which occurs in the temperature range 200–1000°C. At temperatures in excess of 1000°C, the possibility also exists for carbon–silica reactions to occur between the carbon residue from the pyrolysis reactions and the silica component of the glass filler. Both the pyrolysis and carbon–silica reactions are endothermic and heating-rate dependent.

As discussed by Henderson and Tant [1], the carbon–silica reactions are extremely heating-rate dependent and are highly endothermic. As a result, they can play a major role in the thermal performance of glass-filled composites at high temperatures. There has been much discussion, however, as to the advantages and disadvantages of these reactions. For example, since the reactions are highly endothermic, they result in the consumption of large amounts of energy which might otherwise result in additional surface removal. Gutman [2], on the other hand, pointed out that the char structure helps to insulate the virgin material from the high temperatures and that the carbon–silica reactions may reduce its structural integrity. Consequently, the

occurrence of these reactions could actually result in a decrease in the thermal performance of the material in applications where high shear forces exist.

Regardless of their effects on the strength of the char structure, the advantages of the carbon–silica reactions in low shear environments, which occur in many practical applications, are obvious. However, because of their high degree of heating-rate dependence, considerable doubt exists as to whether they occur in relatively short duration exposures to high temperatures. Therefore, it may be possible to improve the thermal performance of glass-filled composites, in certain applications, by altering these reactions so that they occur at lower temperatures. The purpose of this work was to investigate the effects of certain transition metal oxides on the kinetics of the carbon–silica reactions in a glass-filled composite. Standard thermogravimetric analysis techniques were employed.

BACKGROUND

The significance of the carbon–silica reactions in glass-filled composites has been discussed by Ladacki [3], Ruby et al. [4], and Beecher and Rosensweig [5], among others, and will not be repeated here. The effects of transition metals on the enhancement of these reactions in order to improve material performance was first studied by Seader et al. [6]. These researchers studied the effects of MnO_2, Cr_2O_3, Fe_2O_3, and Fe on the thermal performance of a silica phenolic. Test samples were fabricated by applying the metals, in powdered form, to the prepreg and then curing the samples in a laminating press. The samples were tested by exposing them to a heat flux of 45.0 cal cm^{-2} s^{-1} produced by an He–Xe lamp, for times ranging from 5 to 45 s. The effect of the metals was determined by measuring the reduction in char depth over that of a control sample containing no metal. All four metals resulted in significant improvements in thermal performance, with reductions in char depth ranging from 5 to 25%. The amount of metal contained in the samples was not reported.

EXPERIMENTAL

Approach

The approach adopted in this work was somewhat different than that of Seader et al. [6]. In this study, different percentages of the transition metals were added to samples of a glass-filled composite. The effect of the metals on the kinetics of the reactions was determined by measuring the mass loss

as a function of temperature and heating rate using standard thermogravimetric techniques. This same procedure was utilized by Henderson and Tant [1] to obtain the necessary experimental data to calculate the carbon–silica reaction kinetic parameters for a glass-filled composite.

Materials

The base composite material used in this study was supplied by Ametek, Haveg Division. The material, designated H41N, contained approximately 39.5% phenol-formaldehyde resin and 60.5% glass and talc filler. H41N was selected because it is used in a large number of thermal protection applications. It is also ideal for this study since it undergoes carbon–silica reactions which result in significant mass loss. Details of the kinetics of both the pyrolysis and the carbon–silica reactions for this material have been discussed previously by Henderson et al. [7] and Henderson and Tant [1].

Preliminary screening tests were conducted to evaluate the effects of several transition metal oxides on the carbon–silica reactions in H41N. Fe_2O_3 and Cr_2O_3 were found to be the most effective and, therefore, were used exclusively in this study. The samples were tested in powdered form. The H41N powder was obtained by machining larger blocks of the material. The test samples were prepared by mixing 10 and 25% by weight of the transition metal powders with H41N. After thorough mixing, the samples were filtered through a No. 20 sieve and stored overnight in a vacuum desiccator maintained at 35°C to remove traces of moisture.

Apparatus and procedure

A Netzsch Instruments model 409/6 simultaneous thermal analyzer (STA) capable of operation to 1750°C was used for the measurements. Temperature control of the STA was provided by a Netzsch model 413 programmer and model 413 controller. The analog signals output by the STA control system were digitized at specific time intervals using a Monitor Labs model 9302 data logger. The data were processed by an Apple IIe microcomputer and stored on disk for later use. The data acquisition system has been described by Henderson and Mendelsohn [8]. Prior to testing, the STA temperature calibration was checked using Curie standards.

Test samples weighing 48.0 ± 1.0 mg were heated from approximately 30 to 1700°C at heating rates of 10, 20, and 50°C min^{-1}. In order to prevent the resin system from thermo-oxidatively degrading, the samples were maintained in an argon atmosphere with a purge rate of 145 ml min^{-1}. The mass loss, the derivative of mass loss, and the temperature were monitored throughout the experiment.

RESULTS AND DISCUSSION

The mass loss, rate of mass loss, and temperature were digitized at 60-, 30-, and 15-s intervals for the 10, 20, and 50°C min^{-1} heating rates, respectively. These data were then interpolated to 0.01 intervals of fraction of mass remaining. The figures were reproduced from these data. Figure 1 depicts the fraction of mass remaining as a function of temperature and heating rate for both the low temperature pyrolysis reactions and the high temperature carbon–silica reactions for pure H41N. This figure shows the relative mass loss and heating-rate dependence between the two sets of reactions. Clearly the carbon–silica reactions result in a larger mass loss and are far more heating-rate dependent.

Figures 2 and 3 show the fraction of mass remaining as a function of temperature and percent Fe_2O_3 for the 50 and 10°C min^{-1} heating rates, respectively. Several points regarding the effects of the Fe_2O_3 on the reactions should be made. First, the pyrolysis reactions were unaffected. The shift in the mass loss curve occurred because the Fe_2O_3 acted as an inert filler during these reactions. Secondly, as shown by Fig. 2, the onset temperatures of the carbon–silica reactions at the 50°C min^{-1} heating rate were lowered by approximately 60 and 475°C for the 10 and 25% mixtures, respectively, from that for pure H41N. It is, however, interesting to note that although the onset temperatures were lowered, the reaction rates were actually slowed. That is, the final mass ratio remained essentially unchanged, while the reactions occurred over a wider range of temperatures. Finally, the addition of Fe_2O_3 significantly reduced the heating rate effect on the onset temperatures of the carbon–silica reactions. For example, the difference in the onset temperatures between the 10 and 50°C min^{-1} heating rates for
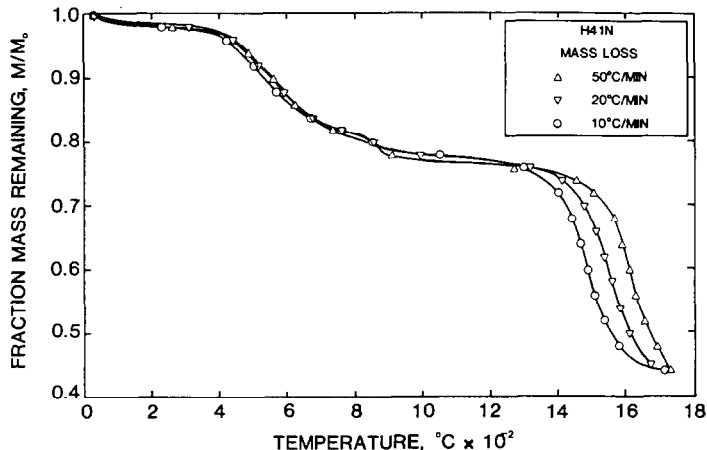

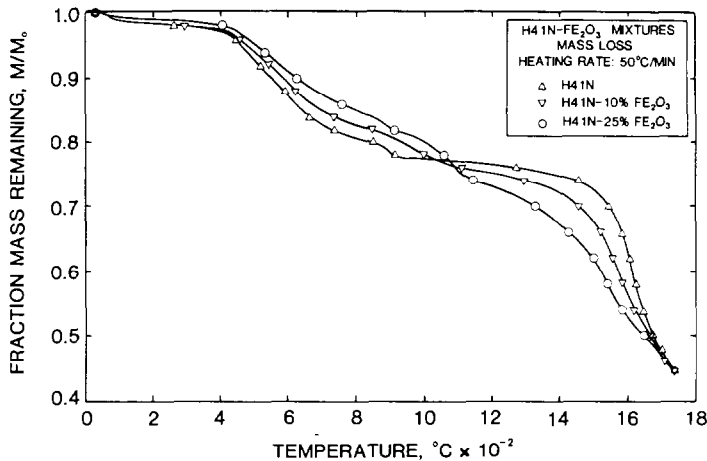Fig. 1. Fraction of mass remaining for H41N.

Fig. 2. Fraction of mass remaining for H41N–F_2O_3 mixtures for 50°C min^{-1} heating rate.

pure H41N was approximately 135°C. The addition of Fe_2O_3 compressed this difference to approximately 115 and 50°C for the 10 and 25% mixtures, respectively.

The fraction of mass remaining as a function of temperature and percent Cr_2O_3 for the 50 and 10°C min^{-1} heating rates is depicted by Figs. 4 and 5, respectively. The same trends as those displayed for Fe_2O_3 are evident. Cr_2O_3, however, was somewhat less effective at lowering the onset temperatures of the reactions. As shown by Fig. 4, at the 50°C min^{-1} heating rate the onset temperatures were lowered approximately 25 and 300°C for the 10 and 25% mixtures, respectively, over that for pure H41N. Also, a similar reduction in heating rate effect on the onset temperatures of the reactions
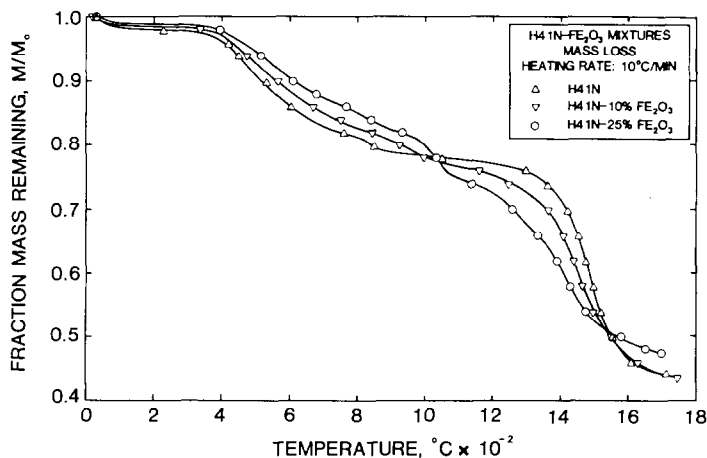

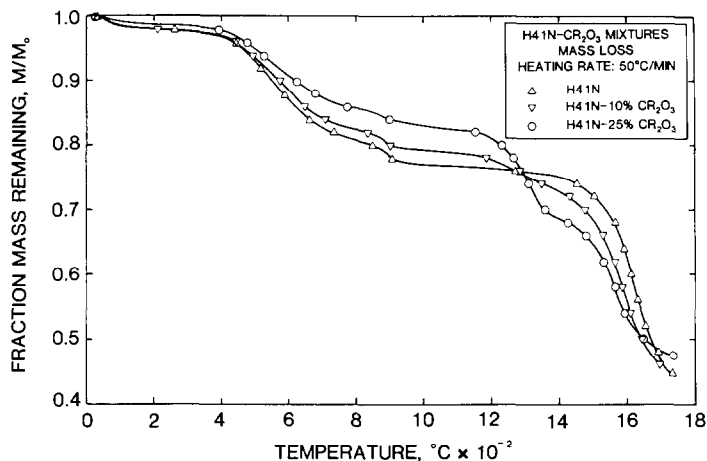Fig. 3. Fraction of mass remaining for H41N–Fe_2O_3 mixtures for 10°C min^{-1} heating rate.

Fig. 4. Fraction of mass remaining for H41N–Cr_2O_3 mixtures for 50°C min^{-1} heating rate.

was observed. The difference in onset temperatures between the 10 and 50°C min^{-1} heating rates for the 10 and 25% mixtures was compressed to approximately 130 and 55°C, respectively. It is also worth noting that the carbon–silica reactions for the 25% mixture occurred in two distinct stages, indicating that all of the individual reactions were not affected to the same extent.

Finally, Figs. 6 and 7 give a direct comparison of the effects of Fe_2O_3 and Cr_2O_3 on the reactions for the 10 and 25% mixtures, respectively, at the 50°C min^{-1} heating rate. As can be seen, Fe_2O_3 was more effective for both percentage mixtures.
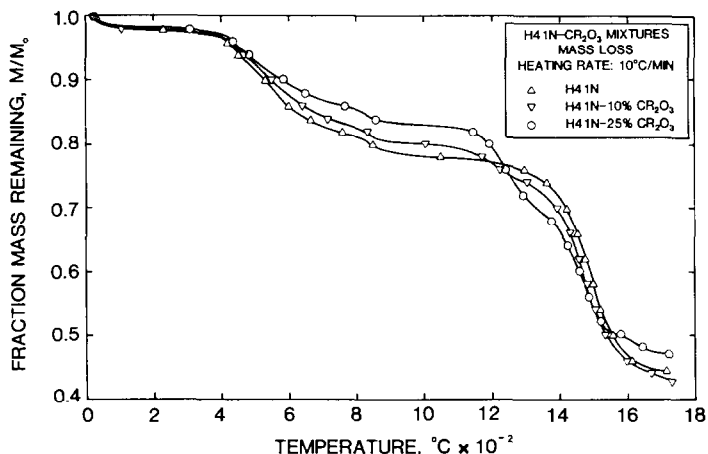

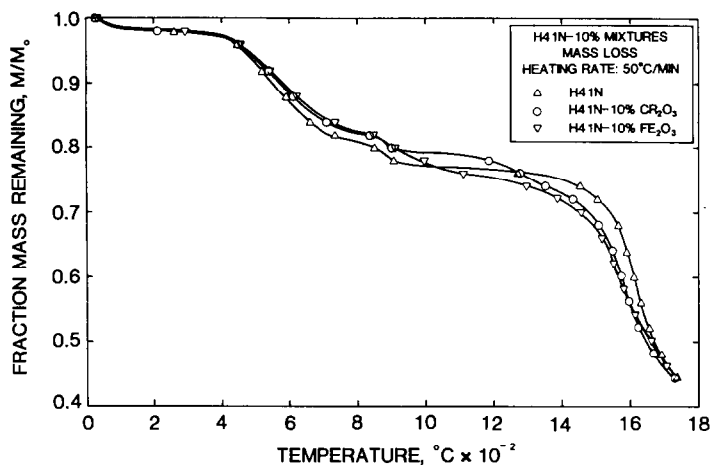Fig. 5. Fraction of mass remaining for H41N–Cr_2O_3 mixtures for 10°C min^{-1} heating rate.

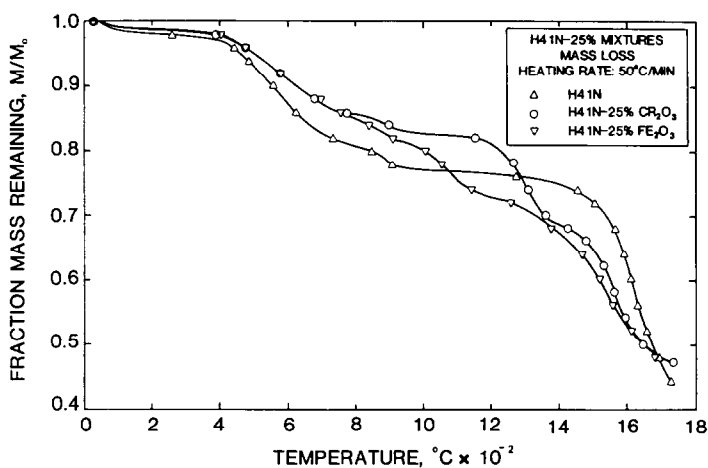Fig. 6. Fraction of mass remaining for H41N–10% mixtures for 50°C min^{-1} heating rate.

Fig. 7. Fraction of mass remaining for H41N–25% mixtures for 50°C min^{-1} heating rate.

CONCLUDING COMMENTS

The addition of both Fe_2O_3 and Cr_2O_3 resulted in lower onset temperatures of the carbon–silica reactions for all the heating rates and percent mixtures studied. Fe_2O_3 was the more effective of the two. Samples treated with 25% Fe_2O_3 experienced a reduction in onset temperature of the carbon–silica reactions of approximately 475°C for the 50°C min^{-1} heating rate, as compared to approximately 300°C for the samples containing Cr_2O_3. The addition of the metals also resulted in a significant reduction in the reaction rates and reduced the heating-rate dependence of the onset temperatures.

The results of the study indicate that it is possible to partially control the temperature range over which carbon–silica reactions occur. Since these

reactions have a large effect on the overall thermal behavior of glass-filled polymer composites, this could lead to the ability to alter the material to match certain specific applications. In turn, this would result in improved thermal performance of existing glass-filled composites.

ACKNOWLEDGMENT

REFERENCES

1 J.B. Henderson and M.R. Tant, Polym. Comp., 4 (1983) 233.
2 V.R. Gutman, AIAA J., 5 (1967) 1053.
3 M. Ladacki, in R.F. Landel and A. Renbaum (Eds.), Chemistry in Space Research, Elsevier, New York, 1972, p. 253.
4 S. Ruby, J.B. Cohen and F.K. Ward, Planet. Space Sci., 3 (1961) 68.
5 N. Beecher and R.E. Rosensweig, ARS J., 31 (1961) 532.
6 J.D. Seader, J.V. Larsen, R.W. Thompson and J.D. Chidley, J. Spacecr. Rockets, 5 (1968) 1362.
7 J.B. Henderson, M.R. Tant, G.R. Moore and J.A. Wiebelt, Thermochim. Acta, 44 (1981) 253.
8 J.B. Henderson and D.L. Mendelsohn, Thermochim. Acta, 75 (1984) 151.