Computer-Aided Molecular Design of Fire Resistant Aircraft Materials

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ABSTRACT

Molecular dynamic simulations and Cone Calorimeter measurements were used to assess the effects of electron beam irradiation and heat treatments on the flammability of the honeycomb composites used in the sidewalls, ceilings and stowage bins of commercial aircraft. The irradiation of this material did not result in any measureable changes. A dramatic reduction in the peak rate of heat release, however, was observed in samples that had been heated overnight at 250 °C.

INTRODUCTION

Synthetic polymers comprise a significant fraction of the fire load borne by commercial aircraft interiors. The flammability, smoke and toxicity characteristics of these materials may impact passenger survivability in the event of an in-flight or postcrash fire. In recent years, the FAA has issued improved fire test standards for aircraft seat cushions, panels, cargo liners and evacuation slides. The goal of an "all-fire resistant aircraft cabin interior," however, will require significant breakthroughs in fire retardant chemistry and materials design.

In previous studies, molecular dynamics modeling was used to identify factors which contribute to the flammability of polymeric materials. This research focussed on the mechanistic aspects of char formation during thermal degradation [1-4]. Charring increases the fraction of the fuel retained in the condensed phase so that less combustible gases are evolved. The presence of a surface char also insulates the unburnt polymer from the external heat source, while at the same time, obstructing the outward flow of combustible products from the degradation of the interior. Computer movies based on molecular dynamics simulations indicate that cross-linked polymers tend to undergo further cross-linking when burned eventually forming high molecular weight, thermally stable chars. This prediction has been confirmed in Cone Calorimeter flammability measurements made on both radiation and chemically cross-linked polymers.

The scope of this research has now been expanded to include the study of materials used in aircraft cabin interiors. Cone Calorimeter measurements were made to assess the effects of electron beam irradiation and heat treatments on the flammability of the honeycomb composites used in the sidewalls, ceilings and stowage bins of

commercial aircraft. The purpose of this paper is to communicate preliminary results and to set forth a plan for future research.

BACKGROUND

Description of the Computer Model

Molecular dynamics modeling is a useful tool for exploring mechanisms of thermal degradation in polymers [1-3]. The model developed at BFRL consist of 7 chains arranged in accordance with the experimentally determined crystal structure of polyethylene (PE). Each chain is made up of 50 carbon and 100 hydrogen atoms (Figure 1). Hamilton's equations of motion

$$\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}, \qquad \frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt} \qquad (i=1,2,\ldots,3N), \tag{1}$$

are solved for the coordinates (q_i) and momentum (p_i) of the N atoms which constitute the model polymers. The Hamiltonian has the form

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{N-1} V_s(r_{i,i+1}) + \sum_{i=1}^{N_C-2} V_b(\theta_{i,i+1,i+2}) + \sum_{i=1}^{N_C-3} V_t(\phi_{i,i+1,i+2,i+3}) + \sum_{i=1}^{N_C-3} \sum_{j=i+3}^{N_C} V_{nb}(r_{i,j}) + \sum_{i=1}^{N_C} \sum_{j=1}^{N_s} V_{ext}(r_{i,j}), \tag{2}$$

where N_C denotes the number of carbon and N_H the number of hydrogen atoms. The first term on the right hand side of Eq.(2) represents the kinetic energy of the $N = N_C + N_H$ atoms. The next terms are the potential energies for bond stretching (V_s) and bending (V_b) and a torsional potential (V_t) which restricts internal rotation around the C-C bonds. These are followed by non-bonded potential energy (V_{nb}) interactions between the atoms in the dynamic polymer chains, as well as their interactions with an additional N_s atoms which constitute the bulk material or an external surface (V_{ext}). The explicit forms for these potential energy functions have been reported elsewhere [3].

The thermal degradation of polymers involves a complex sequence of chemical reactions. Two reactions which are thought to play a major role are hydrogen transfer and depolymerization. An example of intramolecular hydrogen transfer is depicted in the following scheme:

$$R\text{-}CH_2\text{---}CH_2\text{-}\overset{\overset{H}{|}}{C}H\text{-}R \rightarrow R\text{-}CH_3 + CH_2\text{=}CH\text{-}R. \tag{3}$$

The resulting fragments can react again and again in recursive fashion producing a broad spectrum of volatile

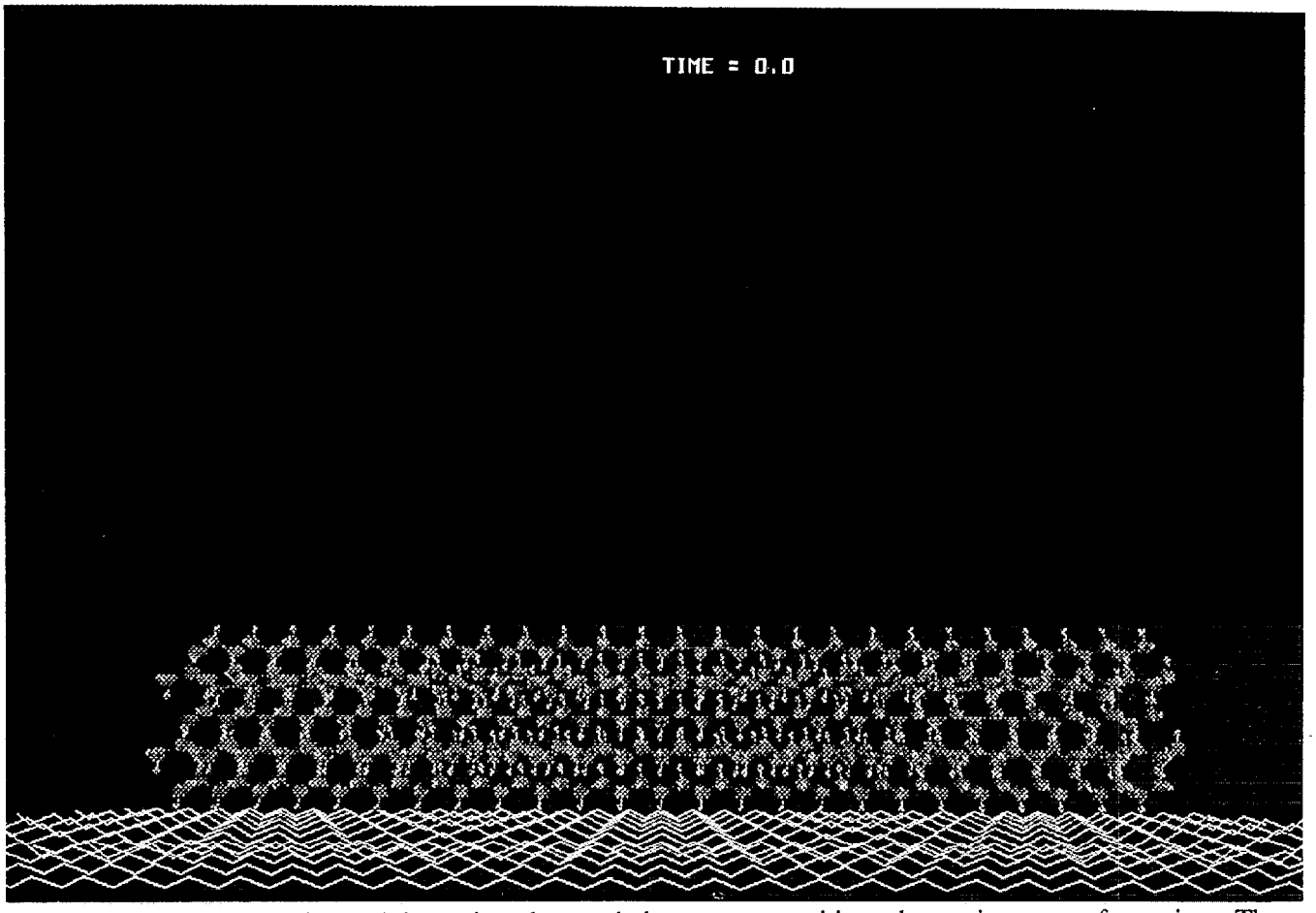


Figure 1. At time t=0, the 7 dynamic polymer chains are arranged in a planar zig-zag conformation. The static surface is indicated by white lines.

hydrocarbons which are readily combusted. In the depolymerization reaction,

$$R\text{-}CH_2\text{---}CH_2\text{-}CH_2\bullet \rightarrow R\text{-}CH_2\bullet + CH_2{=}CH_2, \tag{4}$$

the monomer splits off from a free radical fragment generated by the random scission of a C-C bond. These reaction channels, as well as the additional possibility of intermolecular hydrogen transfer between free radical fragments, are accounted for in the computer program. Both hydrogen transfer and depolymerization are modeled as concerted processes so that bond making occurs simultaneously with bond breaking.

We also allow for a number of other reaction channels which, although inactive in the thermal degradation of PE, are thought to be critical to the formation of char. Included in this list are the chain stripping, cyclization and intermolecular cross-linking reactions illustrated in Eqs.(5)-(7).

$$R-\underset{\underset{H}{|}}{CH}-\underset{\underset{H}{|}}{CH}-CH_2-R \rightarrow R-CH=CH-CH_2-R + H-H \tag{5}$$

$$R-\underset{\underset{H}{|}}{CH}-(CH_2)_4-\underset{\underset{H}{|}}{CH}-R \rightarrow R-\underset{\underset{\underset{CH_2}{|}}{CH_2}}{CH} - \underset{\underset{\underset{CH_2}{|}}{CH_2}}{CH}-R + 2H\bullet \tag{6}$$

$$\begin{array}{l} R-\underset{\underset{H}{|}}{CH}-CH_2-CH_2-R \\ \\ \quad H \\ \quad | \\ RCH-CH_2-CH_2-R \end{array} \rightarrow \begin{array}{l} R-CH-CH_2-CH_2-R \\ \quad | \\ R-CH-CH_2-CH_2-R \end{array} + H-H \tag{7}$$

The degradation process terminates when reactive fragments combine to form stable products. The mechanism incorporated in our computer model is the radical recombination reaction illustrated in Eq.(8).

$$R-CH_2\bullet + \bullet CH_2-R \rightarrow R-CH_2-CH_2-R \tag{8}$$

Computer Simulations

The chains were in a planar zig-zag conformation at the onset of the simulations (Figure 1). Thermal motion was initiated by giving each atom a three dimensional velocity chosen at random from a uniform distribution. Once the atoms in the model polymers were set in motion, they quickly adopted a Maxwell-Boltzmann velocity distribution [2]. The equations of motion were integrated using the differential equation solver ODE [5]. This routine is based on a predictor-corrector algorithm and uses a variable step-size. All forces were evaluated analytically. Simulations were carried out for 5 to 10 picoseconds at temperatures ranging from about 500 K, which is typical of the pyrolysis of PE, up to about 2000 K. These calculations required about 1 hour of CPU time on NIST's Cray Y-MP[1] computer. Trajectories were downloaded to a Silicon Graphics Crimson/GTX workstation where they were viewed

[1] Certain commercial equipment and materials are identified in this paper in order to adequately specify procedures. Such identification does not imply recommendation or endorsement, nor does it imply that they are the best available for the purpose.

in the form of movies.

The progression depicted in Figures 2 and 3 is representative of what happens in simulated thermal degradations of PE and other linear polymers. The chains fragment into fuel for gas phase combustion before a significant number of inter-molecular cross-links (highlighted in white) can form. In contrast, an incipient char was produced when a significant number of hydrogens (exceeding 20% of the total) was removed from the model polymers at the onset of the simulations. This gives cross-linking reactions a head start so that they can compete with fragmentation (Figures 4 and 5). The strength of the cross-links which form between polymer chains increases with the magnitude of the surface interaction (V_{ext}). Presumably, this is because the chains are brought closer together as a result of their mutual attraction to the surface. This observation suggests that a filler, particularly one that has a strong affinity for the polymer, will facilitate the formation of heat resistant chars.

RESULTS AND DISCUSSION

Polyethylene

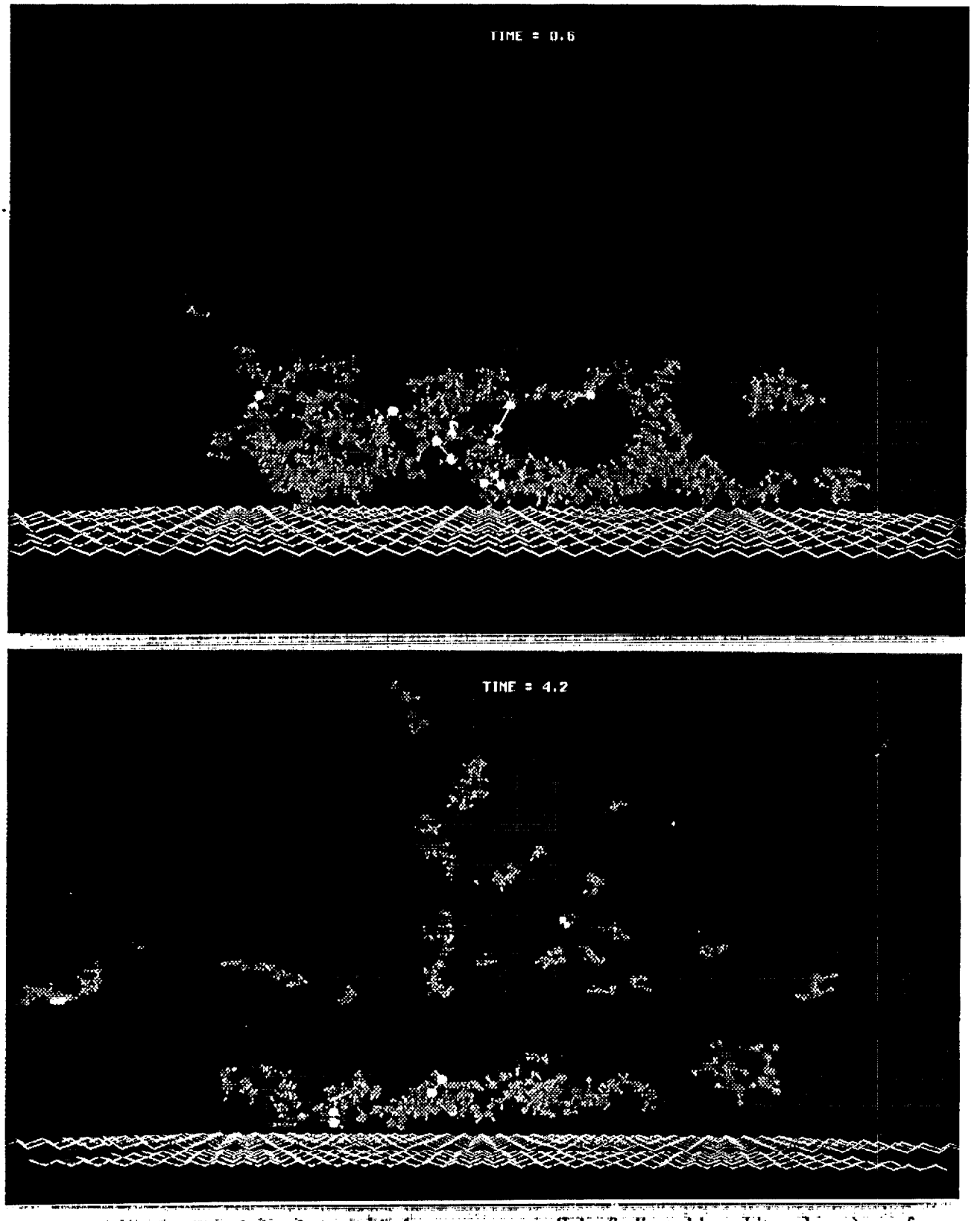
Under normal circumstances, linear PE does not char when it is burned. This was confirmed in experiments using the NIST Cone Calorimeter [6]. The cross-linked polymers, which were prepared by γ and (1 Mev) electron beam irradiations of linear PE, however, did leave measurable amounts of char. Indeed, glowing combustion, as indicated by the formation of red-hot embers, was observed when the cross-linked polymers were burned. The effectiveness of electron beam irradiation on delaying the time to ignition of PE is depicted in Figure 6. The performance of the irradiated samples during these experiments was particularly striking. The more highly cross-linked layer on the top formed a thin char which retained the gases generated by the decomposition of the polymer in the interior of the sample. Eventually, the gases broke through and the sample ignited leaving behind a thin skin of carbonaceous material when the flame self-extinguished. This behavior suggests that it may be possible to achieve a significant reduction in flammability by grafting a fire resistant shell to the surface of the plastic.

Honeycomb Composite

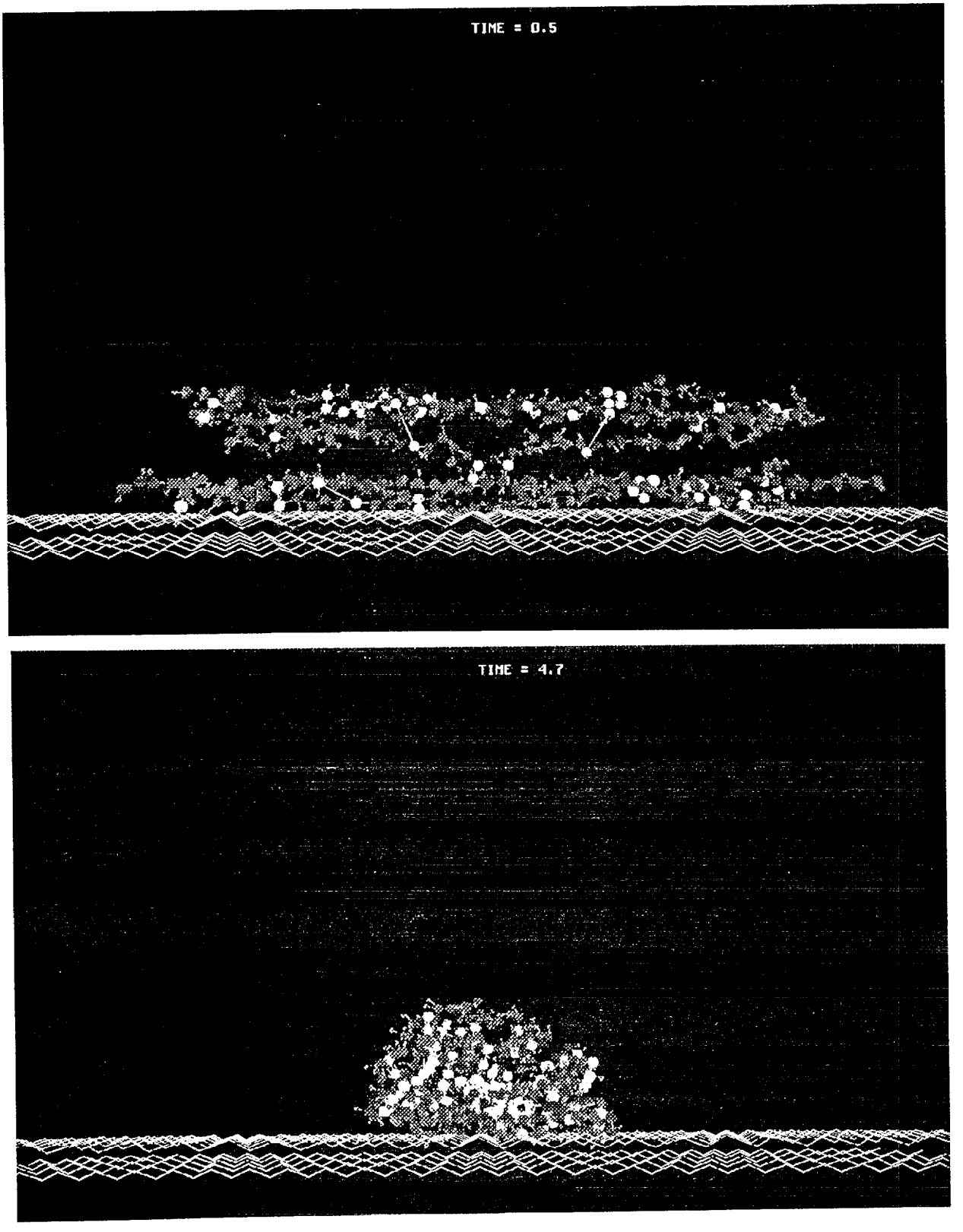
Honeycomb composite material was obtained from the FAA Technical Center. Samples were prepared by cutting the original panels into disks with an outer diameter of 7.5 cm. The rate of heat release (rhr) and ignition times were measured on the Cone Calorimeter for incident fluxes ranging from 30 to 60 kW/m^2. The critical flux of the honeycomb composite is 34.4 ($\pm$ 0.6) kW/m^2. This was determined from a series of measurements on independent samples which were subjected to increasing levels of incident flux.

The measured rhr curves indicate that there are two stages involved in the burning process (Figure 7). Initially, these materials burn with a yellow luminous flame which is typical of the combustion of complex hydrocarbons. This appears as a distinct peak in the rhr centered at about 1.25 minutes. The luminosity, which is indicative of the presence of soot, disappears after about 20 seconds giving way to an unstable blue flame which characterizes the remainder of the burn (tail in the rhr curve extending beyond 1.5 minutes). The flame usually extinguishes on the order of a minute later even though the material continues to smolder. The blue flame is most likely due to fluorescence associated with the oxidation of CO emanating from the charred Nomex.

It is clear that any attempt to improve the fire resistance of this material must focus on reducing the rate of heat released during the first stage of the combustion process. In fact, we found that a dramatic reduction in the peak rhr ($\approx$ 50%) could be achieved by heat treating the samples. Figure 8 is the rhr curve for a sample which was heated overnight at a temperature of 250 °C. It was measured at the same incident flux (40 kW/m^2) as the rhr of the untreated composite displayed in Figure 7 (note change in the Y-axis scale). Although we have not yet



Figures 2 and 3. The chains fragment before strong cross-links (indicated by white spheres) can form.



Figures 4 and 5. An incipient char forms when hydrogens are removed at the onset of the simulations.

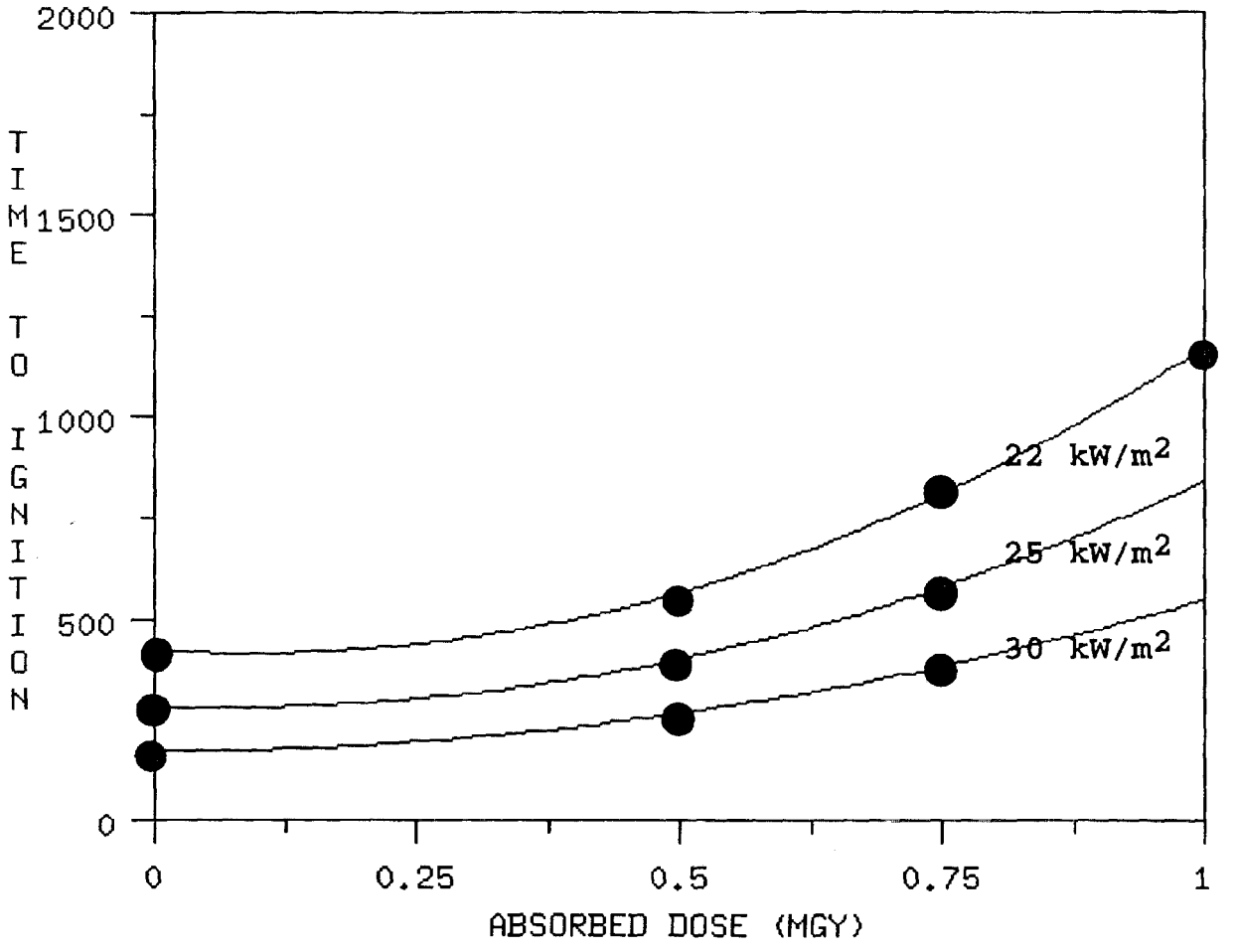
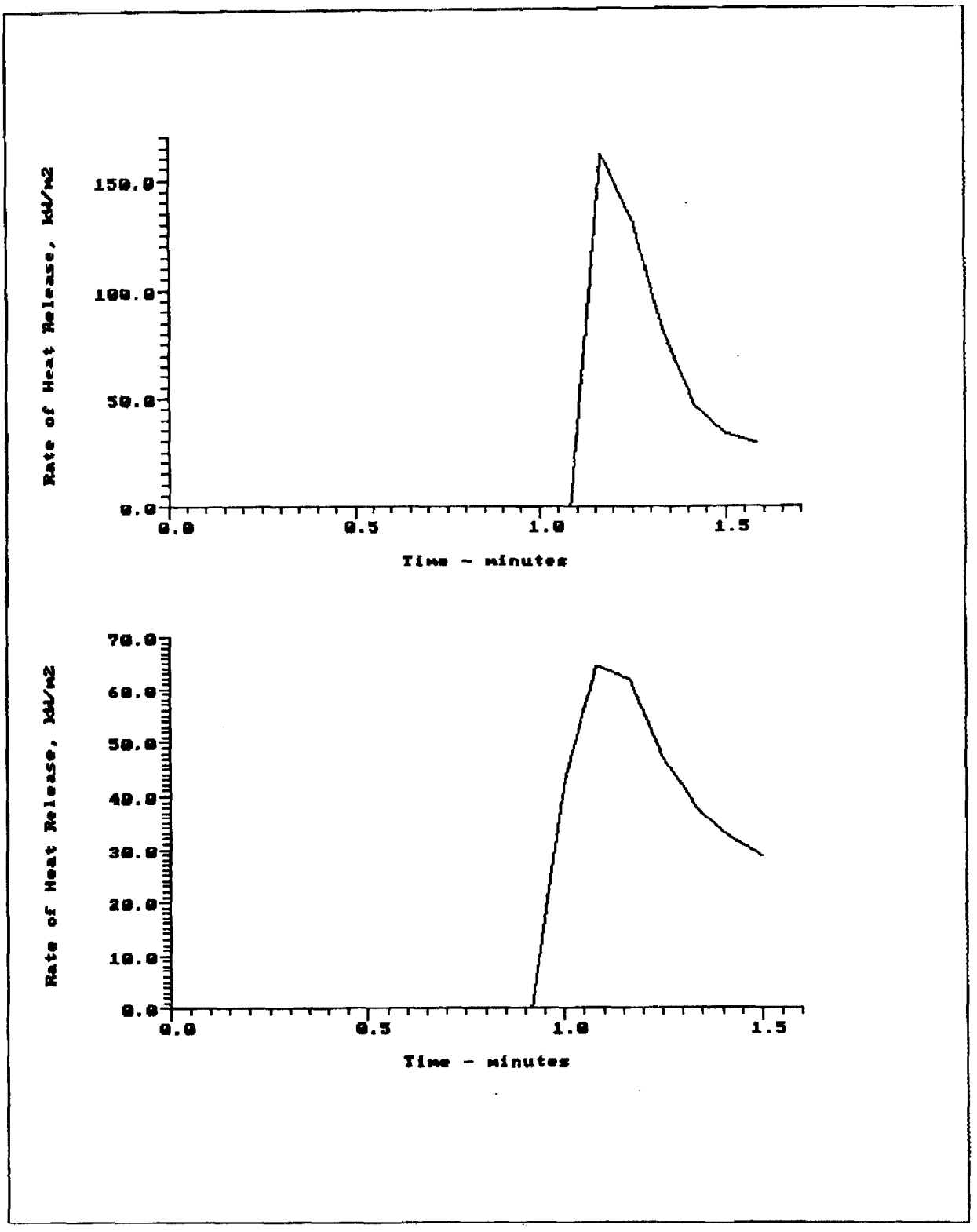


Figure 6. Times to ignition for electron beam irradiated PE as a function of absorbed dose.

identified the offending component(s), we suspect that it is associated with the surface laminate. The observation that the flammable components are so easily removed suggests that it should be possible to affect an improvement in fire resistance by enhancing the bonding between the constituent layers. Our work with PE indicated that this might be accomplished by exposing the material to ionizing radiation. We have begun to explore this possibility by irradiating the honeycomb disks with 1 Mev electrons from a Van der Graaf accelerator. Unfortunately, this did not have a measurable effect on ignition times (Figure 9) or rhr (Figure 10). During the next phase of this project we will explore the efficacy of using ionizing radiation to graft a fire resistant shell to the surface of the composite.

CONCLUSIONS

Flammability measurements on the honeycomb composite panels used in the sidewalls, ceilings and stowage bins of commercial aircraft indicate that this material burns in two stages. Only the initial stage is associated with a significant release of heat. A dramatic reduction in the peak rhr was observed in flammability measurements of



Figures 7 and 8. Measured rhr at 40 kW/m^2 for honeycomb panels before and after heat treatments. The tail extending beyond 1.5 minutes indicates a second stage in the combustion of these materials.

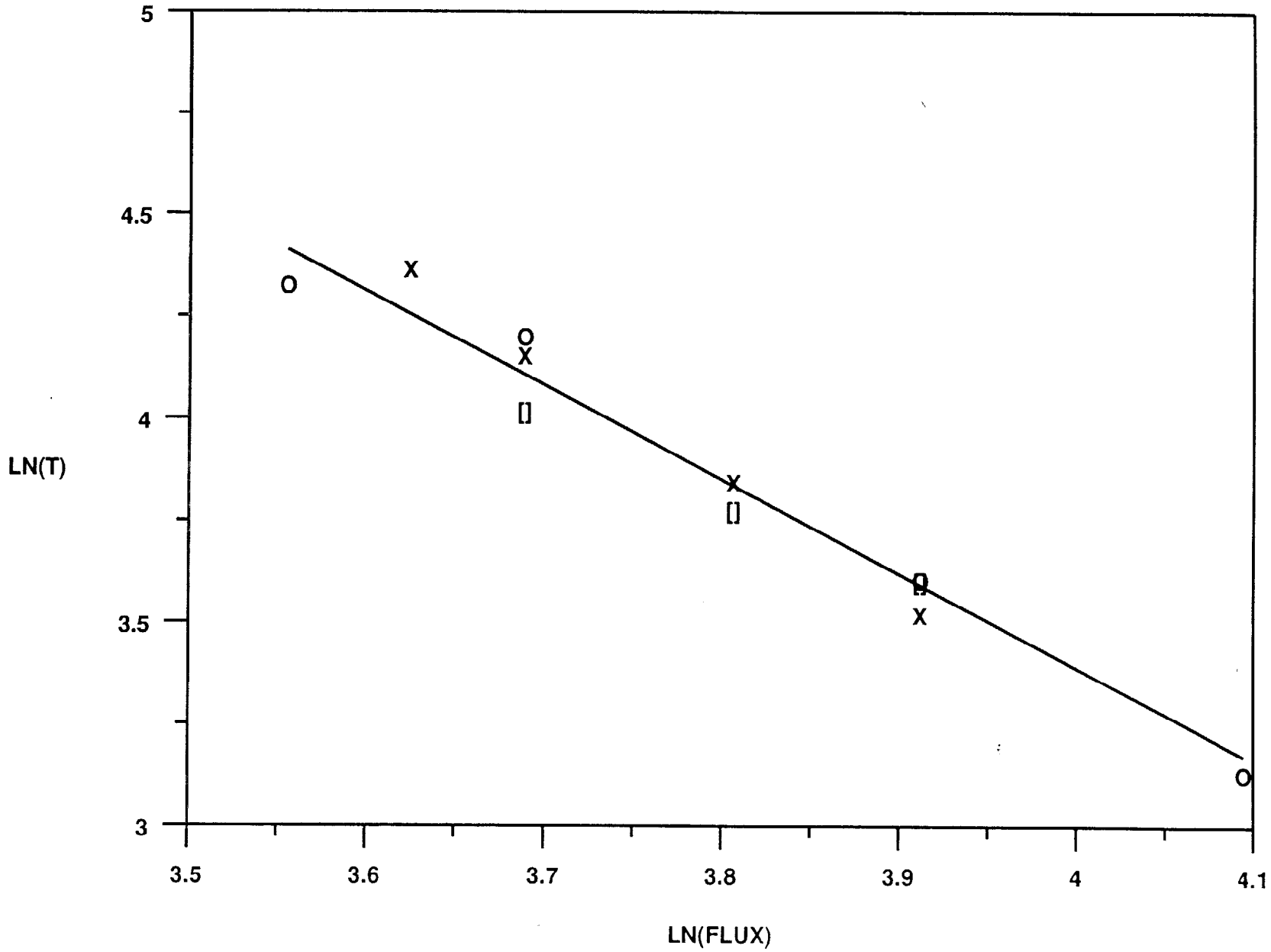


FIGURE 9. IGNITION TIMES CORRESPONDING TO DOSES OF 0 (O), 1.0 (X) AND 1.5 ([])

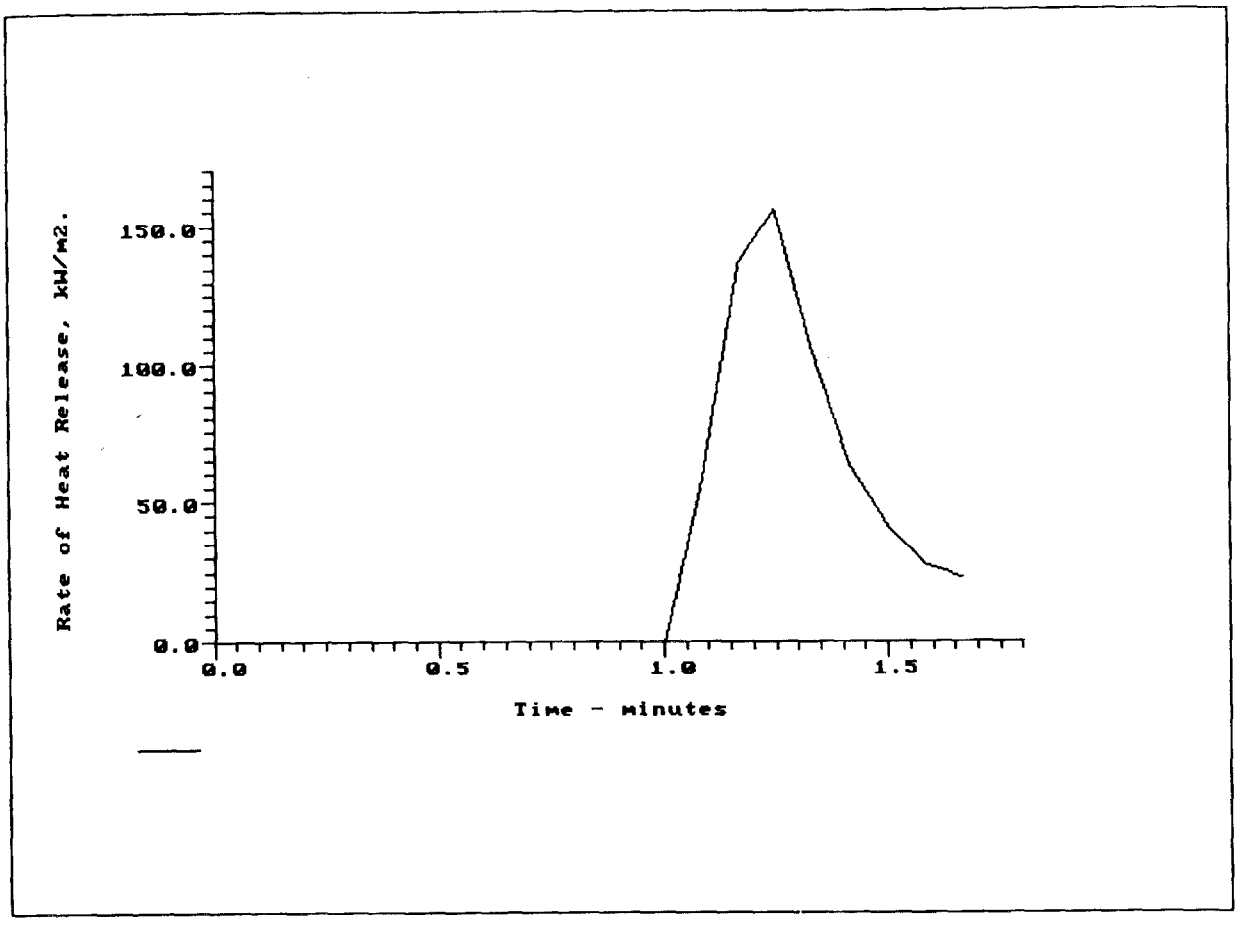


Figure 10. The rhr at 40 kW/m^2 for honeycomb panels which had absorbed a dose of 1.0 MGy.

material which had been heated overnight at 250 °C. This suggests that significant reductions in flammability may be achieved by improving the bonding between components. Future research will focus on the possibility of using radiative grafting to accomplish this objective.

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