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ENERGY DEPOSITION IN EPOXY SAMPLES BY ABSORPTION OF
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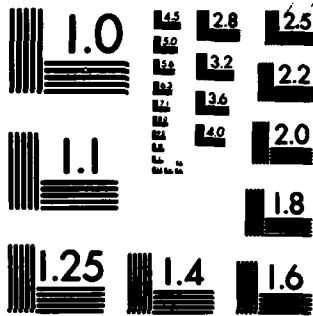
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McDonnell Douglas Research Laboratories
Saint Louis, Missouri 63166

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2 July 1981

Subject: ENERGY DEPOSITION IN EPOXY SAMPLES BY ABSORPTION OF 1.315 μ m RADIATION

To: L. J. Cohen, E. A. Fitzgerald

CC: D. P. Ames, J. C. Leader

From: J. D. Kelley

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1. The purpose of this memo is to describe a model for absorption of 1.315 μ m radiation in epoxy composites. The model allows estimation of the percentage of the energy in a radiation pulse which can be absorbed by an epoxy sample before pyrolytic degradation at the surface blocks further absorption. The fundamental premise is that the effects of energy deposition on a 1-100 μ s time scale can be treated within the framework of a thermalization model. By this I mean that intra- and intermolecular relaxation processes are taken to be fast enough so that the energy which is absorbed is randomized in times less than a microsecond so that a temperature profile in the material can be defined. Further, it is assumed that those processes which lead to "blackening" of the surface are representable by a single rate constant with an Arrhenius temperature dependence; i.e., $k = A \exp(-\Delta H/RT)$. Thus, this model does not consider nonequilibrium processes such as multiphoton absorption, plasma formation at the surface, etc. In this sense, the model will provide an upper limit to the bulk deposition of energy from a laser pulse.

2. The model is developed in a general form, but for the purposes of numerical calculation the following specifications are assumed: pulse energy, 2 kJ/cm²; pulse duration, 1-100 μ s; pulse shape, square wave. The following values are used for the relevant physical properties of the epoxy composite (taken from the Handbook of Chemistry and Physics, CRC Press, 59th Edition): thermal conductivity (k), 4×10^{-4} cal s⁻¹ cm⁻¹ °C; specific heat (c), 0.4 cal g⁻¹ °C⁻¹; density (ρ), 1.1 g cm⁻³.

3. From data obtained at MDRL, the intensity profile in the sample is taken to be

$$I = I_0 \exp[-(7 \text{ cm}^{-1})x]. \quad (1)$$

We proceed by calculating the temperature profile neglecting thermal conductivity effects. It is shown below that thermal conduction is negligible in this system for the pulse durations considered. Let $I_0 = I_0(t)$; the amount of energy deposited in a sample layer of 1 cm² cross sectional area between x and x + dx in time t is

$$E_x dx = \int_0^t [I(x,t') - I(x + dx,t')] dt' \quad (2)$$

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and from Eq. (1)

$$E_x dx = \left[\int_0^t I_0(t') dt' \right] 7 \exp(-7x) dx. \quad (3)$$

For simplicity we take $I_0(t)$ to be a square pulse from $t = 0$ to $t = t^*$ such that

$$\int_0^{t^*} I_0(t) dt = 2 \times 10^3 \text{ J/cm}^2$$

or

$$I_0(t) = 2 \times 10^3 (t^{*-1}) \text{ W/cm}^2.$$

Then from Eq. (3)

$$E_x(t) dx = 14 \times 10^3 (t/t^*) \exp(-7x) dx. \quad (4)$$

Since the volume of the 1 cm^2 layer of thickness dx is $dx(\text{cm}^3)$, the mass is $1.2 dx(\text{g})$. The temperature increase ΔT is given by

$$\Delta T(x,t) = \frac{14 \times 10^3 (t/t^*) \exp(-7x) \text{ J cm}^{-3}}{(0.4 \text{ cal g}^{-1} \text{ K}^{-1})(4.2 \text{ J/cal})(1.1 \text{ g cm}^{-3})}$$

or

$$\Delta T(x,t) = (7.5 \times 10^3 \text{ K})(t/t^*) \exp(-7x). \quad (5)$$

If we consider the surface layer ($x = 0$)

$$\Delta T(x = 0, t) = (7.5 \times 10^3 t/t^*) \text{ K}. \quad (6)$$

Now we consider how much of the pulse can be deposited in the sample before thermal degradation blocks further bulk absorption. Clearly, the degradation will be most serious on the surface. Assume that we can define an Arrhenius rate constant $R(T)$ such that

$$R(T) = A \exp(-\Delta H/R_0 T)$$

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where $R_0 = 2$ cal/mole. Typical ΔH values for thermal degradation of organics are $\Delta H \sim 50$ kcal/mole so that the ratio of rate constants at T_1 and T_2 is ($T_2 > T_1$)

$$\begin{aligned} R(T_2)/R(T_1) &= \exp \frac{\Delta H}{R_0} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \\ &= \exp \left[25 \left(\frac{T_2 - T_1}{T_1 T_2} \right) \times 10^3 \right]. \end{aligned} \quad (7)$$

Further suppose that $R(500 \text{ K}) = 1 \text{ s}^{-1}$, i.e., it takes ~ 1 s for substantial degradation at 500 K (225°C). Then using Eq. (7) we see that at 700 K (425°C), $R(700 \text{ K}) \approx 1.6 \times 10^6 \text{ s}^{-1}$; in other words, substantial degradation occurs on a submicrosecond time scale for $T = 425^\circ\text{C}$. If ΔH were 25 kcal/mole rather than 50 kcal/mole, we could go up to $\sim 650^\circ\text{C}$ or so before damage on a microsecond scale occurs. We do not know ΔH or $R(500 \text{ K})$, but for almost any reasonable guess we would conclude that the ΔT upper limit would be 800°C or less. This means that $\Delta T(x = 0, t) \leq 800^\circ\text{C}$ or, from Eq. (6),

$$t/t^* = 0.11$$

which means that no more than 11% of the pulse energy can be deposited in the bulk sample even with a 1 μs pulse.

Finally, we go back and consider the effect of neglecting thermal conduction. The net rate of heat loss in a layer of thickness dx and area = 1 cm^2 due to conduction is

$$\frac{dq}{dt} = k \left. \frac{d^2 T}{dx^2} \right|_x dx. \quad (8)$$

For $x = 0$ (the surface layer) and $\Delta T = 800^\circ\text{C}$, we use Eq. (5) to obtain

$$\begin{aligned} \left. \frac{dq}{dt} \right|_{x=0} &= (4 \times 10^{-4})(49)(800) \text{ cal s}^{-1} \text{ cm}^{-3} \cdot dx \\ &= 15.7 (\text{cal s}^{-1} \text{ cm}^{-3}) dx \end{aligned}$$

but from Eq. (4), the energy deposition rate due to irradiation is

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$$\left. \frac{dE_x}{dt} dx \right|_{x=0} = \frac{14 \times 10^3}{t^*} dx \text{ J s}^{-1} \text{ cm}^{-3}$$

$$\approx \frac{3.3 \times 10^3}{t^*} dx \text{ cal s}^{-1} \text{ cm}^{-3}$$

since

$$t^* = 1-100 \mu\text{s}, \left. \frac{dq}{dt} \right|_{x=0}$$

is completely negligible compared to

$$\left. \frac{dE_x}{dt} dx \right|_{x=0}$$

and our model need not be corrected for thermal conduction on a 100 μs time scale (or even a 1 s time scale).

4. Conclusions:

- a. Even with the most optimistic assumptions, only $\sim 10\%$ of the energy in a 1-100 μs pulse containing 2 kJ/cm^2 can be deposited in the bulk of an epoxy sample.
- b. Thermal conductivity effects play a negligible role in this analysis.
- c. This "thermal equilibrium" model is a best-case for bulk absorption. Nonequilibrium effects at the surface due to the high irradiation intensities will, if anything, cause more severe attenuation of the radiation at the surface.

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