## HEATED POLYMER

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The conduction problem is presented and solved for a hollow two-layer cylinder having the first layer made of a polymer; the internal boundary moves and there is repeated heating from within. Allowance is made for the heat of reaction in the first layer.

We consider repeated heating from within for a hollow two-layer cylinder whose first layer is of polymer and whose second layer is highly conducting (steel, copper, etc.). Convection and radiation are responsible for the heat transfer between the polymer and the hot gas on the inside, and also between the second layer and the medium on the outside. The polymer on heating undergoes changes that absorb heat, release gaseous decomposition products, and alter the thermophysical parameters of the material. When the inside surface of the polymer reaches the failure temperature $\mathrm{T}_{\mathrm{f}}$, it starts to move with a speed $\mathrm{v}(\tau)$. The cylinder cools internally and externally when the heating stops (Fig.1). The processes all repeat during the next heating cycle in accordance with the altered thermophysical characteristics and the temperature distribution.

The following is the heat-balance equation for an elementary volume of the first layer:

$$
\begin{equation*}
q_{r} \alpha r \Delta z \Delta \tau=q_{r+\Delta r} \alpha(r+\Delta r) \Delta z \Delta \tau+c \gamma \alpha r \Delta r \Delta z \Delta T-H \Delta \gamma \alpha r \Delta r \Delta z-c_{1} \Delta T \Delta \tau \sum_{r_{k}=r}^{R} \frac{\Delta \gamma\left(\tau, r_{k}\right)}{\Delta \tau} \alpha r_{k} \Delta r \Delta z \tag{1}
\end{equation*}
$$

Here the left side is the heat passing through an elementary section at $r$ in time $\Delta \tau$, while the first term on the right is the heat passed by an elementary section at $r+\Delta r$ in time $\Delta \tau$ and the second term is the amount of heat absorbed by the intervening layer in time $\Delta \tau$, which raises the temperature by $\Delta \mathrm{T}$, while the third term is the heat absorbed by phase and chemical changes in that volume and the fourth term is the heat needed to raise the temperature by $\Delta T$ in time $\Delta \tau$ for the gases formed in the section $r$ to $R$.

The following assumptions are made: a) the gas escapes from the material almost instantaneously; b) the gas takes up the temperaiure of the material while passing through the pores; c) the gas does not react with the residue.

Then (1) becomes

$$
\begin{equation*}
\left(c \gamma-H \frac{\partial \gamma}{\partial T}\right) \frac{\partial T}{\partial \tau}=\lambda \frac{\partial^{2} T}{\partial r^{2}}+\frac{\partial \lambda}{\partial T}\left(\frac{\partial T}{\partial r}\right)^{2}+\frac{1}{r} \frac{\partial T}{\partial r}\left(\lambda-c_{g} \int_{r}^{R} r \frac{\partial \gamma}{\partial T} \frac{\partial T}{\partial \tau} d r\right) \tag{2}
\end{equation*}
$$

Here $\lambda, \mathrm{c}$, and $\gamma$ are dependent on T and on the previous history of the material, while $\mathrm{c}_{\mathrm{g}}$ is the specific heat of the gas formed.

TABLE 1. Heat of Decomposition as a Function of Temperature

| $T,{ }^{\circ} \mathrm{K}$ | 293 | 373 | 473 | 573 | 673 | 773 | 873 | 2073 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $H$ | 0 | 0,84 | 2,5 | 4,2 | 4,2 | 2,5 | 0,84 | 0 |

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Fig. 1. Section through cylinder.
Fig.2. Temperature-distribution curves for the polymer, heated for seven periods of 30 sec at 30 sec intervals.

The initial condition is $\mathrm{T}(\mathrm{O}, \mathrm{r})=\mathrm{T}(\mathrm{r})$.
The boundary conditions are as follows for the internal boundary $\Gamma(\tau)$ of the material and the external boundary at $\mathrm{r}=\mathrm{R}$ :

$$
\begin{gather*}
\lambda \frac{\partial T}{\partial r}=\alpha_{\mathrm{g}}\left(T-T_{\mathrm{g}}\right)+\varepsilon_{\mathrm{g}} \sigma\left[T^{4}-T_{\mathrm{g}}^{4}\right]  \tag{3}\\
\lambda \frac{\partial T}{\partial r}=\lambda_{1} \frac{\partial T_{1}}{\partial r} ;  \tag{4}\\
T(R ; \tau)=T_{1}(R ; \tau) .
\end{gather*}
$$

Condition (3) neglects reactions between the gas and the residue.
The following are the initial and boundary conditions for the second layer:

$$
\begin{gather*}
c_{1} \gamma_{1} \frac{\partial T_{1}}{\partial \tau}=\lambda_{1} \frac{\partial^{2} T_{1}}{\partial r^{2}}+\frac{\partial \lambda_{1}}{\partial T_{1}}\left(\frac{\partial T_{1}}{\partial r}\right)^{2}+\frac{\lambda_{1}}{r} \frac{\partial T_{1}}{\partial r},  \tag{5}\\
T_{1}(0 ; r)=T_{1}(r),  \tag{6}\\
T_{1}(R ; \tau)=T(R ; \tau),  \tag{7}\\
\lambda_{1} \frac{\partial T_{1}}{\partial r}=\lambda \frac{\partial T}{\partial r} \text { for } r=R,  \tag{8}\\
\lambda_{1} \frac{\partial T_{1}}{\partial r}=\alpha_{\mathrm{c}}\left(T_{\mathrm{c}}-T_{1}\right)+\varepsilon \sigma\left(T_{\mathrm{c}}^{4}-T_{1}^{4}\right) \text { for } r=R_{1}
\end{gather*}
$$

Calculations show that the temperature difference across the second layer is only a few degrees for a temperature of several hundred degrees when a thick polymer layer is in contact with a thin highly conducting second layer. We therefore neglect equations (5)-(8) and replace the effect of the second layer on the first by a thermal-capacity term in the boundary condition (4), which becomes

$$
\begin{gather*}
\lambda \frac{\partial \dot{\partial} T}{\partial r}=\alpha_{\mathrm{c}}\left(T_{\mathrm{c}}-T\right)+\varepsilon \sigma\left(T_{\mathrm{c}}^{4}-T^{4}\right)-c_{1} \gamma_{1} \delta_{1} \frac{\partial T}{\partial \tau} \text { for } r=R,  \tag{9}\\
\delta_{1}=R_{1}-R .
\end{gather*}
$$

The equation for the boundary $\Gamma(\tau)$ is

$$
\begin{equation*}
\Gamma(\tau)=r_{0}+\int_{0}^{\tau} v(\tau) d \tau, \tag{10}
\end{equation*}
$$

where $\mathrm{v}(\tau)$ is determined by experiment for $T \geq T_{f} ; \mathrm{v}(\tau)=0$ for $T<T_{f}$, where $T_{f}$ is the surface temperature at which flow occurs on account of mechanical disruption of the char by the gas flow.

To (2) we apply

$$
\begin{equation*}
r=\Gamma(\tau)+x[R-\Gamma(\tau)], \quad 0 \leqslant x \leqslant 1 \tag{11}
\end{equation*}
$$

to refer this to an equation for a fixed boundary, which gives

$$
\begin{gather*}
\frac{\lambda}{[R-\Gamma(\tau)]^{2}} \frac{\partial^{2} T}{\partial x^{2}}+\frac{\partial \lambda}{\partial T} \frac{1}{[R-\Gamma(\tau)]^{2}}\left(\frac{\partial T}{\partial x}\right)^{2}+\frac{1}{\{\Gamma(\tau)+x[R-\Gamma(\tau)]\}[R-\Gamma(\tau)]} \frac{\partial T}{\partial x} \\
\times\left\{\lambda-c_{1} \int_{x}^{1}[\Gamma(\tau)+x(R-\Gamma(\tau))] \frac{\partial \gamma}{\partial T}\left[\frac{\partial T}{\partial \tau}-\frac{v(1-x)}{R-\Gamma(\tau)} \frac{\partial T}{\partial x}\right][R-\Gamma(\tau)] d x\right\}=\left(c \gamma-H \frac{\partial \gamma}{\partial T}\right)\left[\frac{\partial T}{\partial \tau}-\frac{v(1-x)}{R-\Gamma(\tau)} \frac{\partial T}{\partial x}\right] . \tag{12}
\end{gather*}
$$

Then $\partial T / \partial r$ is replaced in the boundary conditions by

$$
\frac{1}{R-\Gamma(\tau)} \frac{\partial T}{\partial x}
$$

Equation (12) with the boundary conditions has been solved by the grid method [1] with an M-20 computer.

The following are the working formulas for $T$ :

$$
\begin{align*}
& T_{i, j+1}=T_{i, j}+\frac{\Delta \tau}{\left[c\left(T_{i, j}\right) \gamma\left(T_{i, j}\right)-H\left(T_{i, j}\right) \frac{\partial \gamma\left(T_{i, j}\right)}{\partial T}\right]\left[R-\Gamma\left(\tau_{j}\right)\right]} \\
& \times\left\{\frac{\lambda\left(T_{i, j}\right)}{R-\Gamma\left(\tau_{j}\right)} \frac{T_{i+1, j}-2 T_{i, j}+T_{i-1, j}}{(\Delta x)^{2}}+\frac{\partial \lambda\left(T_{i, j}\right)}{\partial T} \frac{1}{R-\Gamma\left(\tau_{j}\right)}\right. \\
& \times\left(\frac{T_{i+1, j}-T_{i, j}}{\Delta x}\right)^{2}+\left[\frac{1}{\Gamma\left(\tau_{j}\right)+x_{i}\left[R-\Gamma\left(\tau_{j}\right)\right]}\right.  \tag{13}\\
& \quad \times\left(\lambda\left(T_{i, j}\right)-c_{i} \sum_{k=i}^{n}\left(\Gamma\left(\tau_{j}\right)+x_{k}\left(R-\Gamma\left(\tau_{j}\right)\right)\right) \frac{d \gamma\left(T_{h, j}\right)}{d T}\right. \\
& \left.\times\left(\frac{T_{k, j}-T_{k, j-1}}{\Delta \tau}\left(R-\Gamma\left(\tau_{j}\right)\right) v\left(1-x_{k}\right) \frac{T_{k+1, j}-T_{h, j}}{\Delta x}\right) \Delta x\right) \\
& \left.\left.+\left(c\left(T_{i, j}\right) \gamma\left(T_{i, j}\right)-H\left(T_{i, j}\right) \frac{d \gamma\left(T_{i, j}\right)}{d T}\right) v\left(1-x_{i}\right)\right] \frac{T_{i+1}-T_{i, j}}{\Delta x}\right\} \\
& \quad i=1,2, \ldots, n-1 ; j=0,1,2, \ldots, 0 \leqslant x \leqslant 1, \quad \tau>0
\end{align*}
$$



Fig. 3. Envelope temperature $\left({ }^{\circ} \mathrm{C}\right)$ for polymer material, a) 12 mm, b) 17 mm , thick. Curves 1), 2) continuous heating for $200 \mathrm{sec} ; 3), 6$ ) seven heatings of different lengths at 30 sec intervals; 4), 12) 42 sec intervals; 4), 7) heating for one period of 165 sec and six of five sec at 30 sec intervals; 10 , 13) 42 sec intervals; 5), 8) heating for $75,40,30,20,10$ and 10 sec , intervals $70,40,30,20,10,10 \mathrm{sec} ; 11), 14$ ) intervals $90,55,45,30,20,10 \mathrm{sec}$.

$$
\begin{align*}
& \text { At } \Gamma\left(\tau_{\mathrm{j}}\right)=\mathbf{r}_{0}+\int_{0}^{\tau_{i}} \mathrm{v}(\tau) \mathrm{d} \tau \\
& \qquad T_{0 j+1}=\frac{\frac{, \lambda\left(T_{0, j}\right)}{R-\Gamma\left(\tau_{j}\right)} \frac{T_{i, j+1}}{\Delta x}+\left[\varepsilon_{\mathrm{g}}\left(\tau_{j}, T_{0, j}\right) \sigma \frac{T_{\mathrm{g}}^{4}\left(\tau_{j}\right)-T_{0, j}^{4}}{T_{\mathrm{g}}\left(\tau_{j}\right)-T_{0, j}}+\alpha_{\mathrm{g}}\left(\tau_{j}\right)\right] T_{\mathrm{g}}\left(\tau_{j}\right)}{\frac{\lambda\left(T_{0, j}\right)}{R-\Gamma\left(\tau_{j}\right)} \frac{1}{\Delta x}+\left[\varepsilon_{\mathrm{g}}\left(\tau_{j}, T_{0, j}\right) \frac{T_{\mathrm{g}}^{4}\left(\tau_{j}\right)-T_{0, j}^{4}}{T_{\mathrm{g} \cdot}\left(\tau_{j}\right)-T_{0, j}}+\alpha_{\mathrm{g}}\left(\tau_{j}\right)\right]} \tag{14}
\end{align*}
$$

for $r=R$,

$$
\begin{equation*}
T_{n, j+1}=\frac{\frac{\lambda\left(T_{n, j}\right)}{R-\Gamma\left(\tau_{j}\right)} \frac{T_{n-1, j+1}}{\Delta x}+\left[\varepsilon_{0}\left(T_{n, j}\right) \sigma \frac{T_{0}^{4}-T_{n, j}^{4}}{T_{0}-T_{n, j}}+\alpha_{\mathrm{o}}\right] T_{0}+c_{\mathrm{M}} \gamma_{\mathrm{m}} \delta_{\mathrm{m}} \frac{T_{n, j}}{\Delta \tau}}{\frac{\lambda\left(T_{n, j}\right)}{R-\Gamma\left(\tau_{j}\right)} \frac{1}{\Delta x}+\left[\varepsilon_{0}\left(T_{n, j}\right) \sigma \frac{T_{\mathrm{c}}^{4}-T_{n, j}^{4}}{T_{0}-T_{n, j}}+\alpha_{0}\right]+\frac{c_{1} \gamma_{1} \delta_{1}}{\Delta \tau}} . \tag{15}
\end{equation*}
$$

The time step is chosen from

$$
\begin{equation*}
\Delta \tau<\frac{\left(\frac{R-r}{n}\right)^{2}}{2 \max \frac{\lambda(T)}{c(T) \gamma(T)}} \tag{16}
\end{equation*}
$$

Tables as follows [for $\lambda(T)$ ] supply $\lambda(T), \mathrm{c}(T)$, and $\gamma(T)$ : $\lambda(T)=\lambda_{1}(T)$ for $T_{0} \leq T \leq T_{k}$ if the temperature has not yet risen above $\mathrm{T}_{\mathrm{k}}$, and $\lambda(\mathrm{T})=\lambda_{2}(\mathrm{~T})\left(\mathrm{T}_{0} \leq \mathrm{T} \leq \mathrm{T}_{\mathrm{k}}\right)$ if the temperature at previous times has been above $T_{k}$, and $\lambda_{1}(T)=\lambda_{2}(T)$ for $T>T_{k}$, where $T_{k}$ is the temperature above which there is no considerable change in the density of the material.

It is envisaged that $\gamma$ follows an Arrhenius law:

$$
\begin{equation*}
\frac{\partial \gamma}{\partial \tau}=-\left[\gamma-\gamma_{h}(T)\right] k \exp \left(-\frac{E}{R T}\right) . \tag{17}
\end{equation*}
$$

Then (11) transforms to

$$
\begin{gathered}
\lambda(T) \frac{1}{R-\Gamma(\tau)} \frac{\partial^{2} T}{\partial x^{2}}+\frac{d \lambda(T)}{d T} \frac{1}{[R-\Gamma(\tau)]^{2}}\left(\frac{\partial T}{\partial x}\right)^{2} \\
+\frac{1}{\Gamma(\tau)+x[R-\Gamma(\tau)]} \lambda(T) \frac{1}{R-\Gamma(\tau)} \frac{\partial T}{\partial x}+c, k \frac{1}{\Gamma(\tau)+x[R-\Gamma(\tau)]} \\
\times \frac{1}{R-\Gamma(\tau)} \frac{\partial T}{\partial x} \int_{x}^{1}\left[\gamma(\tau)-\gamma_{k}(T)\right] \exp \left(-\frac{E}{R T}\right)\{\Gamma(\tau)+x[R-\Gamma(\tau)]\}[R-\Gamma(\tau)] d x \\
=c(T) \gamma(\tau)\left[\frac{\partial T}{\partial x}-\frac{v(1-x)}{R-\Gamma(\tau)} \frac{\partial T}{\partial x}\right]+H(T)\left[\gamma(\tau)-\gamma_{k}(T)\right] k \exp \left(-\frac{E}{R T}\right), \\
\\
\gamma(\tau)=\gamma_{0}-k \int_{0}^{\tau}\left[\gamma(\tau)-\gamma_{k}(T)\right] \exp \left(-\frac{E}{R T}\right) d \tau .
\end{gathered}
$$

Figure 2 shows the temperature distribution in the polymer on repeated heating. The second layer heats up considerably during the halts in the heating, because there are large temperature gradients at the boundary between the layers at the instant when the heating stops [2].

Figure 2 shows that $\partial^{2} \mathrm{~T} / \partial \mathrm{x}^{2}$ has an inflection in the region $573-673{ }^{\circ} \mathrm{K}$, which coincides with the peak in $\mathrm{H}(\mathrm{T})$, which means that the layer at $573-673^{\circ} \mathrm{K}$ acts as a barrier during transfer of heat from the polymer to the second layer. When that layer reaches $773-873^{\circ} \mathrm{K}$, the temperature of the shell starts to rise rapidly, which indicates that the polymer has charred completely.

Figure 3 shows the temperature as a function of time for the second layer under various conditions of heating.

The curves of Figs. 2 and 3 have been calculated for $\mathrm{r}_{0}=0.3 \mathrm{~m}, \mathrm{~T}_{\mathbf{f}}=2073^{\circ} \mathrm{K}$, initial temperature of material and medium $293^{\circ} \mathrm{K}, \alpha_{0}=5.8$, gas temperature within the cylinder $2273^{\circ} \mathrm{K}, \alpha_{i}=116$, and $\varepsilon_{i}=0.9$ during heating.


Fig.4. Thermal characteristics of material with temperature.

The other characteristics are dependent on $T$ : $\varepsilon_{i}$ (degree of blackness of the internal surface) varies from 0.8 to 0.5 $\left(293-2073^{\circ} \mathrm{K}\right), \varepsilon_{0}$ varies from 0.6 to $0.7\left(293-2073^{\circ} \mathrm{K}\right), c_{1}=460-$ $545\left(293-1173^{\circ} \mathrm{K}\right)$. Figure 4 shows how the thermophysical parameters vary with $T$, while Table 1 gives $H(T)$.

All the curves of Fig. 3 have been calculated for a total heating time of 200 sec with arbitrary cooling intervals. Figure 3 a is for polymer 12 mm thick, while Fig. 3 b is for 17 mm . Curves 1 and 2 show the temperature of the shell during continuous heating for 200 sec . The following conclusion can be drawn from curves 1,2 , and the rest: the shell temperature with arbitrary heating is $2-3$ times that for continuous heating for a fairly wide range of polymer thicknesses. We thus naturally have the concept of the conditions worst as regards shell temperature, i.e., heating and cooling times (with a fixed overall heating time) such as to give the highest temperature for the shell.

This latter condition was determined by a special search program.
The results of Fig. 3 show that the worst conditions occur when the first few heating cycles constitute a large fraction of the total heating time.

NOTATION
T is the temperature, ${ }^{\circ} \mathrm{K}$;
$\tau$ is the time, sec;
$r \quad$ is the radius, $m$;
$\lambda, \mathrm{c}, \gamma$ are the thermal parameters of material, $\mathrm{W} / \mathrm{m}{ }^{\circ} \mathrm{K}, \mathrm{J} / \mathrm{kg}{ }^{\circ} \mathrm{K}, \mathrm{N} / \mathrm{m}^{3}$;
$\mathrm{H} \quad$ is the heat of polymer decomposition, $\mathrm{J} / \mathrm{kg}$;
$\alpha_{i}, \alpha_{o}$ are the heat transfer coefficients, $\mathrm{W} / \mathrm{m}^{2}$;
$\delta_{1} \quad$ is the thickness of envlope, $m$;
$\varepsilon \quad$ is the effective emissivity;
$\mathrm{v} \quad$ is the velocity of inner boundary, $\mathrm{m} / \mathrm{sec}$;
$\alpha \quad$ is the angle;
$z \quad$ is the coordinate along cylinder generatrix.

## Subscripts

i refers to the gas inside the cylinder;

- refer to the gas outside the cylinder.


## LITERATURE CITED

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