FORMULA DETERMINATION FOR THE SOLIDIFICATION OF SPENT RESIN

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ABSTRACT

A quasi steady apparatus was applied to measure the thermal conductivity of solid. The temperature distributions in the solids, size ranging from 0.3 to 200L, were recorded during the course of curing. A theoretical equation of conduction in a cylindrical form with uniform energy generation was established for defining the thermal state of reaction. The heat of reaction calculated from theoretical equation on the basis of experimental values of maximum temperature and thermal conductivity agrees very well with the data reported. The relationships among heat of reaction, amount of curing agent, of retardant of loading of spent resin and water content were established.

INTRODUCTION

The curing reaction of unsaturated polyester generates a great deal of heat of reaction in a very short period of time, which makes the mass of product up to a high temperature, over 250°C usually, and then introduces cracks in cooling. In order to avoid this problem a design of thin size is taken, normally, by engineers for the sake of reducing the accumulation of heat and of keeping polymerized mass at a low level of temperature.

The conventional size of waste form for the management of radwaste in nuclear power station is a steel drum of 55-gallon of volume. In that condition, there is no way to eliminate problems of heat damage. When solidifying the spent resin, the high temperature is induced by the accumulation of heat of reaction, some unexpectable results would happen, such as decomposition of anionic resins and vaporizing the water contented that makes the mixed compound burst up (1,2,3,4). Then some facilities use the technology of refrigeration for the mixed compounds at a temperature down to -20°C when the polymerization reaction of thermosetting resin is extremely retarded and appeared to be stopped practically (4). The refrigeration process could avoid the solidification of the radwaste mixture from accident during mixing and keep its maintenance easy.

The authors had the idea of using no refrigeration apparatus if we could control the velocity of the reaction in case of using retardant and/or lowering the amount of catalyst. For the purpose of this goal, a system of basic study for the reactions of unsaturated polyester under various conditions including kinetics and thermodynamics were carried out by DSC technique (5). A theoretical equation of conduction in cylinder shape with uniform energy generation was established.

Incorporating the proceeding of calculation, the thermal conductivity of solid of various compositions, including moisture content and loading of spent resin, could be tested by an apparatus of quasi-steady state. On the other hand, the temperature distributions of solids which ranging their sizes from 0.3 to 200L were determined and the data of maximum temperature (θ_{max}) and of the time for the appearance of its θ_{max} (t_{max}) also could be found. From the results of experiments, these relationships could be checked with the theoretical equation to confirm their correctness.

EXPERIMENTAL PROCEDURE

The unsaturated polyester was supplied by Yong Shun Co., (2143BQ). The Catalyst was of 50% methyl ethyl ketone peroxide dissolved in dimethyl phthalate. Resorcin was used as retardant. Simulated spent resins were the mixture of two parts of anionic resin and one part of cationic one (Rhome Hass Amberlit IR410 and IR120) discharged from the conventional water stream treatment facility without radioactive properties.

A quasi steady state apparatus was designed for determining the thermal conduction coefficient of sample. The heat source and heat sink were in a shape of cylinder can made of copper with a wall thick of 5 mm. Its size was ϕ66mm$\times$120mm and a volume of 0.3L water contained in it. Test specimens were cut into a disc type of thickness from 0.5 to 5mm. At the beginning of the experiment, the heat

source was heated in a water bath up to about 90°C. Six sets of thermalcouple were connected to a recording system.

The solids sizes of 0.3L, 2L, 50L and 200L were conducted at the conditions of various loading of spent resin which contented different level of moisture and the ratio value of retardant to catalyst ranging 0 to 2.6%. The temperature distributions against the curing time in the solid were recorded.

RESULTS AND DISCUSSIONS

Calculation for the Testing of Thermal Conductivity

The solidified product of spent resin is a kind of composites which comprises a continuous phase of polymerized unsaturated polyester and a reinforcement of spent resins including anionic resin and cationic one. Furthermore, if we consider the state of spent resin, we would recognize that is also a kind of composites formed by polystyrene, water, air and the functional site.

That causes a very complicated nature of thermal conductivity for a solid. There is no way to calculate the conductivity of a solid by equation at present, but can be determined by experiment on the basis of bulk. Using a quasi-steady state apparatus incorporate the equation derived from the heat-transfer rate through the wall as determined by the Fourier law as shown in Eq. (1), the thermal conductivity could be evaluated consequently.

$$q = -KA \times \frac{d\theta}{d\theta} = KA \times \frac{\theta 1 - \theta 2}{L}$$ (Eq. 1)

where A and L are area and thickness of specimen: $\theta 1$, $\theta 2$ are temperatures of heat sink before and after test and K is the thermal conductivity.

The heat quantity q was evaluated from the total gain of heat on the heat sink end during the period of test.

The effect of water content of spent resin on the thermal conductivity for solidified products was shown as a function as shown in Fig. 1, in which the black dot on the coordinate expresses the value for the solid of dry pure unsaturated polyester. The thermal conductivity of water is about six times greater than that of resin, that shows the linear relationship as the amount of water and the ratio of loading of spent increased.

Temperature Distribution Testing

The solidification of radwastes in a steel drum can be considered as a cylindrical form and the transient temperature in its shape is one-dimensional flow so that the equation of heat conductance is $\theta = \theta(r,t)$, where θ, r an t are temperature in solid of at distance of r from center line and time t respectively (6). If the curing reaction to be kept at constant, the temperature is steady and a function of the radial coordinate only. The solid in air at ambient temper-

ature θ_∞ and the convective heat-transfer coefficient between the solid and air is $\bar{h}_c$. In this condition the ambient air temperature is known rather than on the surface temperature of the solid. The appropriate boundary condition is, therefore, one of which the heat conducted to the exterior surface of the solid is equal to the heat convected into the air. The center line must be insulated because of the fact that it is a line of symmetry. When the two boundary conditions are used to solve the general ordinary differential conduction equation, the temperature distribution in the solid becomes Eq. (2).

$$\frac{\theta(r) - \theta_\infty}{\theta_\infty} = \frac{Hr_o}{2\bar{h}_c\theta_\infty}(1 + \frac{\bar{h}_c r_o}{2k} - \frac{\bar{h}_c r^2}{2r_o k})$$ (Eq. 2)

The maximum temperature at the center of solid is therefore:

$$\theta_{(o)} = \theta_{max} = \theta_\infty + \frac{Hr_o}{2\bar{h}_c}(1 + \frac{\bar{h}_c r_o}{2k})$$ (Eq. 3)

where r_o is radius of solid, $\theta_{(o)}$ is temperature at center line, H is heat generated per unit weight of solid and K is the conductivity coefficient.

In using Eq. (3), there are still two unknown terms $\theta_{(o)}$ and H remained. They depend mostly on the size of solid and on the amount of curing agent. How the curing agent affects the maximum temperature of solid at center? A series of solidification tests under the conditions on the bases of volume of 0.3L, of constant curing agent (1 wt% of matrix) and of the amount retardant varying from 0 to 3 wt% were carried out. The following equations were obtained:

$$\theta_{max} = 207 - 76.6R$$ (Eq. 4)

$$t_{max} = 10^{1.57R + 1.45}$$ (Eq. 5)

Where θ_{max} is the maximum temperature at the center. R is the weight percent ratio of retardant to curing agent, and t_{max} is the time in minute for the θ_{max} to reach. According to Eq. (4) the θ_{max} becomes zero when the value of R equals to 2.6. That means reaction did not happen. In fact, however, even we could not find any temperature difference in an experiment at the conditions of R = 3 and of after 17 days. Then there are two points could be drawn intuitively: First, curing reaction did not happen, and the second, the heat generated was escaped which did not examine by thermalcouple. The first consideration is incorrect because of after a long period of time the compound became a rigid solid. No doubt that must had been caused by curing reaction. So that the heat escaping from the surface of solid is very possible.

In Eq. (5) the amount of retardant at any desired time of reaction could be determined and it is also the key which means to control the time when the heat to be removed from

the surface of solid. It also implies that we can eliminate the failure of solidification for spent resin which contains water by the mastering the value of θ_{max} properly.

In discussing the size of solid concerning to the parameters of Eq. (3), to select a composites of 50 v/v of 5% moisture content (the k value then be defined from Fig. 1, being $k = 4.2 \times 10^{-4}$ cal/cm.deg.sec), the values of 2L, 50L and 200L (their radius were $r_0 = 5.6$ cm, 19 cm and 28.5 cm respectively), and to calculate the heat of generation as a function of $\Delta\theta = \theta_{max} - \theta_\infty$ and of $\bar{h}_c$., their relationships are shown as Fig. 2 ($r_0 = 5.6$cm), Fig. 3 ($r_0 = 19$cm) and Fig. 4 ($r_0 = 28.5$ cm). It is that as the radius of solid increases the effect of overall convection coefficient $\bar{h}_c$. to be infinitive. At this point in the development of the principles of conduction, we should recognize the occurrence of several dimensionless groups $\dfrac{Hr_0}{\bar{h}_c\theta_\infty}$ and $\dfrac{\bar{h}_c r_0}{k}$. The first term is actually a dimensionless generation and the product of the two terms is the dimensionless generation too. The second dimensionless group is the Biot number, which appears in problems involving the combined conduction/convection mode of heat transfer. The Biot number is the ratio of conductive resistance in the solid to convective resistance in the fluid. When the Biot number approaches zero, the solid is practically isothermal and the temperature varies most in the fluid. As the Biot number approaches infinity, the opposite is true. The resistance in the solid is much larger than that in the fluid, the fluid is nearly isothermal, and the temperature differences occur predominantly in the solid. That is a small size solid the heat removing from the surface is quick and the value of $\bar{h}_c$'s effect remarkably. It is also why the data obtained from the testing of small size specimen can not be applied to a scale up solid directly. The effective ranges of $\bar{h}_c$ are about 100×10^{-4}cal/cm^2.deg.sec, 15×10^{-4}cal/cm^2.deg.sec, and 10×10^{-4}cal/cm^2.deg.sec. for solids of $r_0 = 5.6$, 19 and 28.5 cm respectively. The overall heat transfer coefficients when heat flow to gas, generally, are $\bar{h}_c = 1.2$ to 3.6×10^{-4}cal/cm^2.deg.sec. for convention and $\bar{h}_c = 2.3$ to 23×10^{-4}cal/cm^2.deg.sec. for a following gas (6). At $\theta_{max} = 114°C$, $\theta_\infty = 24°C$, $r_0 = 28.5$ cm and $k = 4.2 \times 10^{-4}$cal/cm.deg.sec, for example, when heat transfers from solid to gas at free convection ($\bar{h}_c = 1.2$ to 3.6×10^{-4}cal/cm^2.deg.sec) the calculated H is 0.9 to 1.4×10^{-4}cal/cm^3.sec. At the same conditions but in a state of flowing gas stream ($\bar{h}_c = 2.3 \times 10^{-4}$cal/cm^2 deg.sec to 23×10^{-4}cal/cm^2 deg.sec.) the corresponding value of H is from 1.2×10^{-4}cal/cm^3.sec to 1.77×10^{-4}cal/cm^3.sec.. The $\bar{h}_c$ value even increases 20 times but the H value is only a double more. The role of adjusting the value of the $\bar{h}_c$ to be a limited factor is identified again.

The major factor effect on the reaction rate are the amount of curing agent and retardant described before, and a proper compounding those the reaction can be controlled.
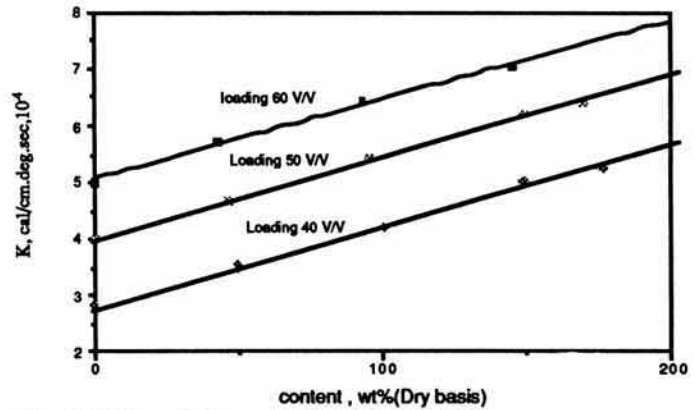

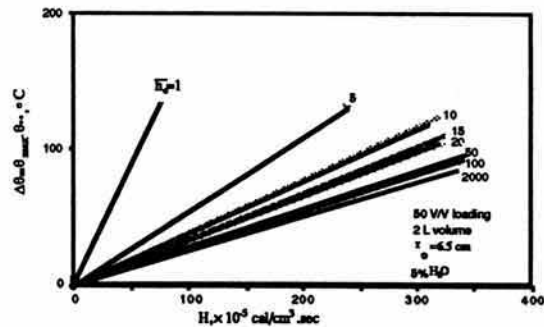Fig. 1. Effect of Water Content on the Thermal Conductivity.

Fig. 2. Effect of Heat Generation on the Solid's Maximum Temperature Calculated by Theoretical Equation.
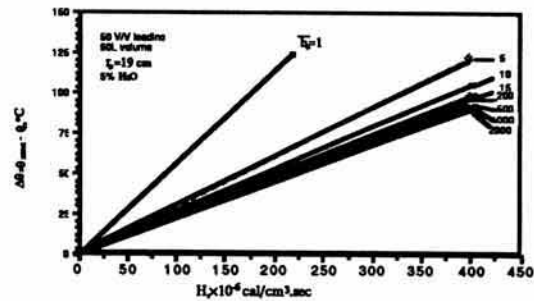

Fig. 3. Effect of Heat Generation on the Solid's Maximum Temperature Calculated by Theoretical Equation.

On the basis of experimental results, some ideal conditions were determined as follows: loading of spent resin on true volume basis is 50 v/v, the water content of spent resin is about 5 wt% on dry basis, curing agent is 0.5 wt% of unsaturated polyester, and the retardant is 0.1 to 0.4 wt% of unsaturated polyester.

To facilitate obtaining a procedure for full scale operation of solidification, all the data including θ_{max} and t_{max}

393

were determined on the above conditions with a size of 2L ($r_o = 6.5$ cm) and then each corresponding H value was calculated by Eq. (3). Relationships between θ_{max}, t_{max}, H and wt% of curing agent minus wt% of retardant (wt%P.O.-wt%R.T.O.), and between θ_{max}, t_{max}, H and loading of wt% spent resin are shown in Fig. 5 and Fig. 6 respectively. They are very important data for the determination of composi-
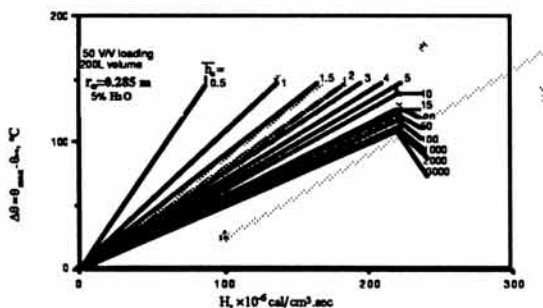

Fig. 4. Effect of heat generation on the solid's maximum temperature calculated by theoretical equation.
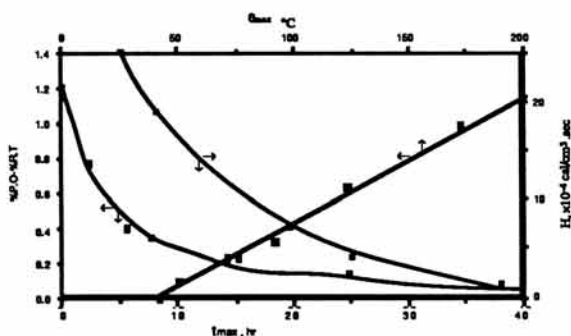

Fig. 5. The Relationships of θ_{max}, H, t_{max} and the amount of curing agent and retardant, data on the basis of 2L volume, 50 v/v loading of spent resin, and curing agent 0.5%.

tion when a full scale solid will be done. The process for the design of solidification operation must follow the following steps: (1) $\bar{h}_c$ value is selected which is determined by the environmental condition, $\bar{h}_c = 0.9 \times 10^{-4}$ cal/cm².deg.sec to 1.4×10^{-4} cal/cm².deg.sec for a free air convection, (2), selecting the value of $\Delta\theta = \theta_{max} - \theta_\infty$ on the basis of ambient temperature and the desired value θ_{max}, (3) using the values of $\Delta\theta$ and of H from equation (4), (4) from Fig. 5 the value of (wt%P.O.-wt%R.T) is obtained, and (5) all the compositions of a 200L solid will be determined finally.

A practical solidification of solid of 200L volume was carried out with the conditions of 50 v/v loading (spent resin contented 5% moisture) 155.3 kg, unsaturated polyester 110 kg, curing agent 985 g, and retardant 825 g(0.4 wt%), and cast in a 200L steel drum in which 17 sets of thermalcouple
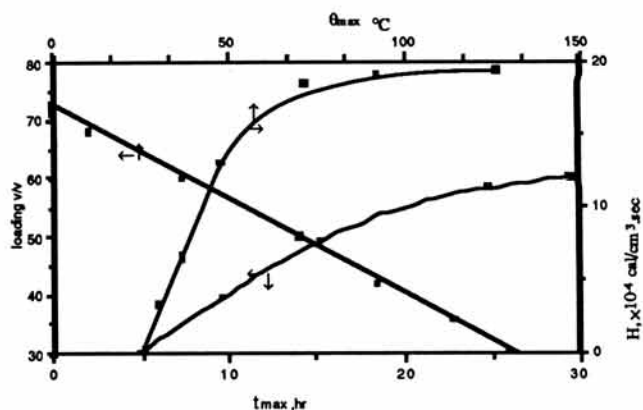

Fig.6. The Relationships of Spent, Resin Loading, θ_{max}, tmax and heat generation on the basis of 2L volume solid curing agent 0.5%, retardant 0.3% and value according loading.
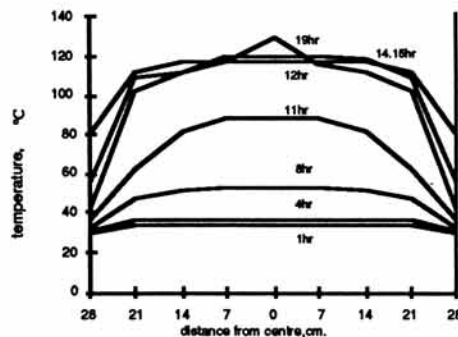

Fig. 7. The Profiles of Temperature Distribution as a Function of Time Escaped.

were arranged in the solid including center lines of vertical and of horizontal and inside of the drum wall. The profiles of temperature distribution as a function of time past is shown in Fig. 7.

The θ_{max} and t_{max} at each tested point of thermalcouple were noted at the side of each location as shown in Fig. 8.

A fact which against the expectation is the values of θ_{max} and t_{max} were not at center of the solid but locating at about one fourth of the center line under the surface. Two reasons may be considered. The first is that the solid stood on the cement floor contact with a thin rim of steel. most part of the bottom was separated by a distance of 1.5 cm layer of air which was enclosed by the steel drum and forming an effect of resistance of thermal conduction. The second is the characteristic upward direction of heat flow by which a rather high temperature than the ambient one was formed at the upper end of drum. The profiled of temperature distribution as a function of time is shown in Fig. 7. The

$$R = 0.4/0.545 = 0.74$$

$$\therefore \theta_{max} = 207 - 76.6 \times 0.74 = 148.7 \ ^\circ C$$

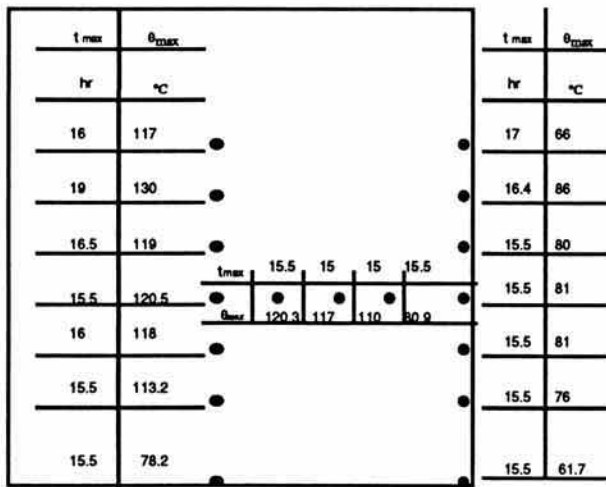| t_{max}	θ_{max}						t_{max}	θ_{max}
hr	°C						hr	°C
16	117						17	66
19	130						16.4	86
16.5	119						15.5	80
		t_{max} 15.5	15	15	15.5			
15.5	120.5	θ_{max} 120.3	117	110	80.9		15.5	81
16	118						15.5	81
15.5	113.2						15.5	76
15.5	78.2						15.5	61.7

Fig. 8. Distribution of t_{max} and θ_{max} in the cross section of 200L solid.

upward center line has the maximum temperature which coincided well with theoretical consideration.

The following calculation is another approach to obtain the thermal data for full size solid based on the theoretical equation and the experimental data with small size (2L) specimens. At the loading of 50 v/v, the compositions were MEK.P.O. 0.545 wt% and retardant (wt%P.O.) 0.4 wt% when its t_{max} was 25.5 hr and θ_{max} was 50.3°C.

wt% P.O. - wt% R.T. = 0.545 - 0.4 = 0.145

$\Delta\theta = \theta_{max} - \theta_\infty = 50.3 - 24 = 26.3$

Taking $\bar{h_c} = 1.4 \times 10^{-4}$ cal/cm^2.deg.sec., the relative value of heat of generation (H) for 200L solid could be obtained from Fig. 2. The still other method for the H value is applying Eq. (3) and the data of $\Delta\theta$, r_o,k and $\bar{h_c}$. By the datum of H = 9.5×10^{-5} cal/cm^3.sec, the values $\theta_{max} = 100°C$ and $t_{max} = 20$ hr are answered from Fig. 5 on the basis of the relationship of omax and the ratio of retardant to curing agent (R = wt%R.T.-wt%P.O). put the R value into Eq. (4) and calculated as follows:

$$\theta_{max} = 207 - 76.6R \qquad (Eq.\ 4)$$

The results of t_{max} obtained both by theoretical calculation and by experimental method agreed each other well. The θ_{max} value of experimental was 130°C which was greater than that of theoretical method by 30°C. This error was caused by the incomplete heat convention from the end of down side and upward flowing property of the heat convection described previously and they will be coincided in the condition of equal thermal dissipation from the surface. $\theta_{max} = 48.7°C$ obtained from experimental equation

had a positive error which is due to the amount of curing agent in the Eq. (4) being 1.0 rather than the value of 0.74 so that the former would react quickly than the latter and the cumulation of heat would be greater. Calculation, for instance, of heat of reaction for the matrix based on the θ_{max} experimented.

The θ_{max} at the center of 200L solid was 120°C and put the following data into Eq. (3) we get:

loading = 50 v/v
k = 4.2×10^{-4} cal/cm.deg.sec
$\theta_{max} = 120°C$
$\theta_\infty = 24°C$
$r_o = 28.5$ cm

$$\therefore H = (120-24) \times \frac{1.67 \times 10^{-6}}{0.81 + (1/15)} = 1.83 \times 10^{-4} \ cal/cm^3$$

·deg.sec.

The heat of reaction was generated during a period of time about double time of t_{max}. Because of at the loading of 50 v/v there was only 50 wt% of polyester in a unit volume, so that the value of H calculated from equation should time a factor of 2. For the calculation of total volume, the density of solid being 1.3 g/cm^3, the factor for 110 kg of polyester (=99.09 L) in a solid of 212.6 L was:

99.09 L/ 212.6L = 0.446

So the unit weight of pure polyester with 1 wt% of curing agent and without neither retardant nor spent resin, the heat of reaction determined by DSC is 200 J/g = 47.6 cal/g. There is some error (about 28%) between the values of experimental method and of theoretical one, and has about 20% difference from the data reported by Pusatcioglu et.al (7). The latter's error may be due to the difference in the component of polyester used.

CONCLUSION

1. The thermal conductivity of solidified spent resin increases with the increase of water content at the same loading.

2. All the thermal terms could be obtained by using theoretical equation on the basis of some known data which were obtained by experimental of samples of small size. The heat of reaction calculated by this method is quite well agree with those of literatures.

3. A full scale formulation can be expected by this method and a perfect process for the operation of solidification could be controlled.

4. The theoretical data agreed very well with those of experiment.

ACKNOWLEDGEMENT

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