Modelling of Non-Isothermal Crystallization of Polypropylene/Glass Fiber Composites

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ABSTRACT

This paper shows a simple model of the non-isothermal crystallization of polypropylene and its composites. The relationship between the maximum crystallization temperature and the cooling rate follows a logarithmic function. The tangent of the curve of the transformation is affected by α. The relation between α and the cooling rate also involves a logarithmic function. The simple model can be applied directly to estimate the trend of the transformation when the polymers are produced by cooling. The behaviour of T_{CMAX} can redress the trends of the transformation.

1. INTRODUCTION

On the subject of isothermal crystallization, many papers have studied the Avrami theory /1/ that the time of the phase transition is in proportion to the Avrami number, and the theory has been verified /2-5/.

In the 1930s and 1940s, Evans /6/ and many physical chemists developed the phase transition of non-isothermal crystallization from statistical theories, but the phenomenon of non-isothermal crystallization has not been explained because of the large number of parameters. Non-isothermal crystallization, as opposed to isothermal crystallization, considers the time-dependent external parameters, such as temperature, stress, pressure and molecular orientation /7,8/. Generally the theory of non-isothermal crystallization is the sum of the phase transition of all kinds of nuclei, and the nucleation rate and the nuclei growth rate are subordinated to a function of time, i.e., the cooling rate. In the 1970s, Ozawa /9/ tried to apply non-isothermal crystallization to isothermal crystallization, but the theory is unable to explain the phenomenon because of the Avrami number varying with temperature /10,11/. The non-isothermal crystallization is very important in polymer processing, because the crystallization temperature and crystallinity, depending on cooling rate, have an important effect on the final polymer properties.

We have tried to prepare a simple model to explain total crystallization with varying cooling rate. The trends of maximum crystallization temperature were examined, and we have also tried to prove the relationship between the change of maximum crystallization temperature and the rate of phase transition. With the information of the relation between maximum crystallization temperature and the rate of phase transition, and the cooling rate, we can utilize the model directly for producing polymer products.

2. EXPERIMENTAL

Polypropylene

FINA Chemicals have supplied the homo-polypropylene, code 10060G. The melt flow was 35 (230°C/2.16 kg, g/10).

Glass fibers

Code 2219 E-glass fibers were supplied by VETROTEX International. The surface of the fibers was treated with silano-organic compounds for application of polypropylene matrix of composites. To prepare no-sizing fibers, the fibers were put in a furnace for 30 min at 600°C.

Fabrication of the composites

A hydraulic press was used. first, two films were made at 210°C and 100 bars. The 2 - 5 mm long glass fibers were carefully scattered between two films. After placing the materials in the stainless steel mold, having a good skin and being 1 mm thick, the press was heated and pressed under the same conditions as those used for the fabrication of films.

Fiber volume fractions

After completion of D.S.C., the samples were put in a furnace and kept 30 min at 600°C. they were then weighed on a balance. Table 1 presents the codes of the samples and the fiber volumes.

Differential scanning calorimeter

A Perkin Elmer DSC-7 was used to measure the crystallization temperature as a function of the cooling rate to study the non-isothermal crystallization. The weights of the samples were between 10 mg and 15 mg. All samples, in order to eliminate the effect of thermal history, were heated to 210°C and left for 5 minutes. The cooling rates were 5, 10, 20, 30 and 40°C/min. When the temperature reached 60°C, the sample was re-heated to 210°C.

Table 1

Codes of samples

Code	Full Name	Sizing Conditions	Wt% of Fibers
PP	Polypropylene	No	0
NSC	Non-sizing Composite	No	10.7
SC	Sizing Composite	Yes	2.4

3. DISCUSSION

The molten polymer crystallizes in accordance with lowering of the temperature. The heat flow (exotherm) varies with the increase in the cooling rate. The crystallization reaction is exothermic, and the maximum peak of the exotherm can be called the maximum crystallization temperature ($T_{C.MAX}$).

Behaviours of $T_{C.MAX}$

Table 2 presents the experimental results of $T_{C.MAX}$. We can see that the points of maximum crystallization temperature move to lower temperatures with increasing cooling rate ($\phi(t)$). In the case of composites, they have a lower value of $T_{C.MAX}$ than that of the matrix. When the cooling rate is 5 and 10°C/min, NSC samples have higher $T_{C.MAX}$ than SC samples, but, with respect to increasing cooling rate, the difference can be negligible. The plot of $\ln\phi(t)$ versus $T_{C.MAX}$ is presented in Fig. 1. The equation of the straight line fitting, as shown in Fig. 1, is presented as follows:

$$T_{C.MAX} = A + B \cdot \ln\{\phi(t)\} \tag{1}$$

The values of the constants A and B are shown in Table 3.

Table 2

Values of $T_{C.MAX}$

Code (°C)	5 (°C/ min)	10 (°C/ min)	20 (°C/ min)	30 (°C/ min	40 (°C/ min)
PP	120.2	116.1	111.2	108.4	106.3
NSC	121.3	116.1	110.7	107.9	105.3
SC	119.8	115.4	110.9	107.0	105.9

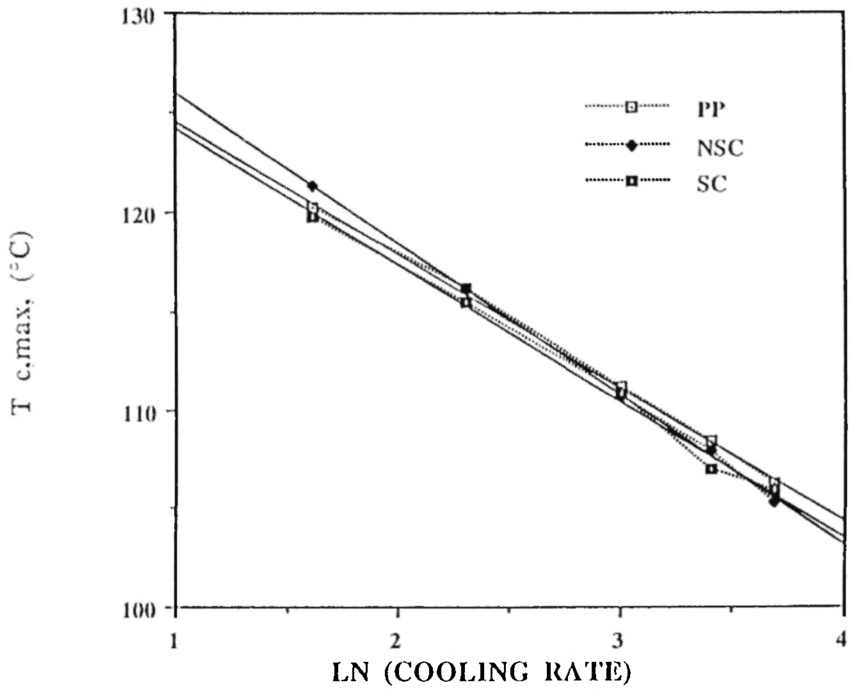


Fig. 1: Relation between T_{CMAX} and the cooling rate.

Table 3
Constants A and B

Code	A(°C)	B	r
PP	131.26	-6.722	0.999
NSC	133.63	-7.632	0.999
SC	131.04	-6.873	0.997

Table 4
Values of ALPHAS

Code (°C)	5 (°C/ min)	10 (°C/ min)	20 (°C/ min)	30 (°C/ min	40 (°C/ min)
PP	-0.881	-0.718	-0.542	-0.451	-0.381
NSC	-0.811	-0.676	-0.514	-0.395	-0.365
SC	-0.825	-0.674	-0.536	-0.423	-0.352

Transformation behaviour

The transformation ($X(T)$) versus the variation of temperature can present an S-type curve. But a plot of $\ln\{X(T)/(1-X(T))\}$ versus the variation of temperature shows a straight line. Fig. 2 presents this phenomenon which is the relation between $\ln\{X(T)/(1-X(T))\}$ and the variation of temperature; and Table 4 presents the values of the slopes. We can express the slope as the coefficient (α: ALPHA), because it is the rate of heat flow per unit of temperature. We can also find that the values of α increase with increasing cooling rate. The relation between α and $\ln\phi(t)$ appears as the same phenomenon of T_{CMAX} and $\ln\phi(t)$. Fig. 3 presents the relation. The equation of the straight line fitting, as shown in Fig. 3, is given as follows:

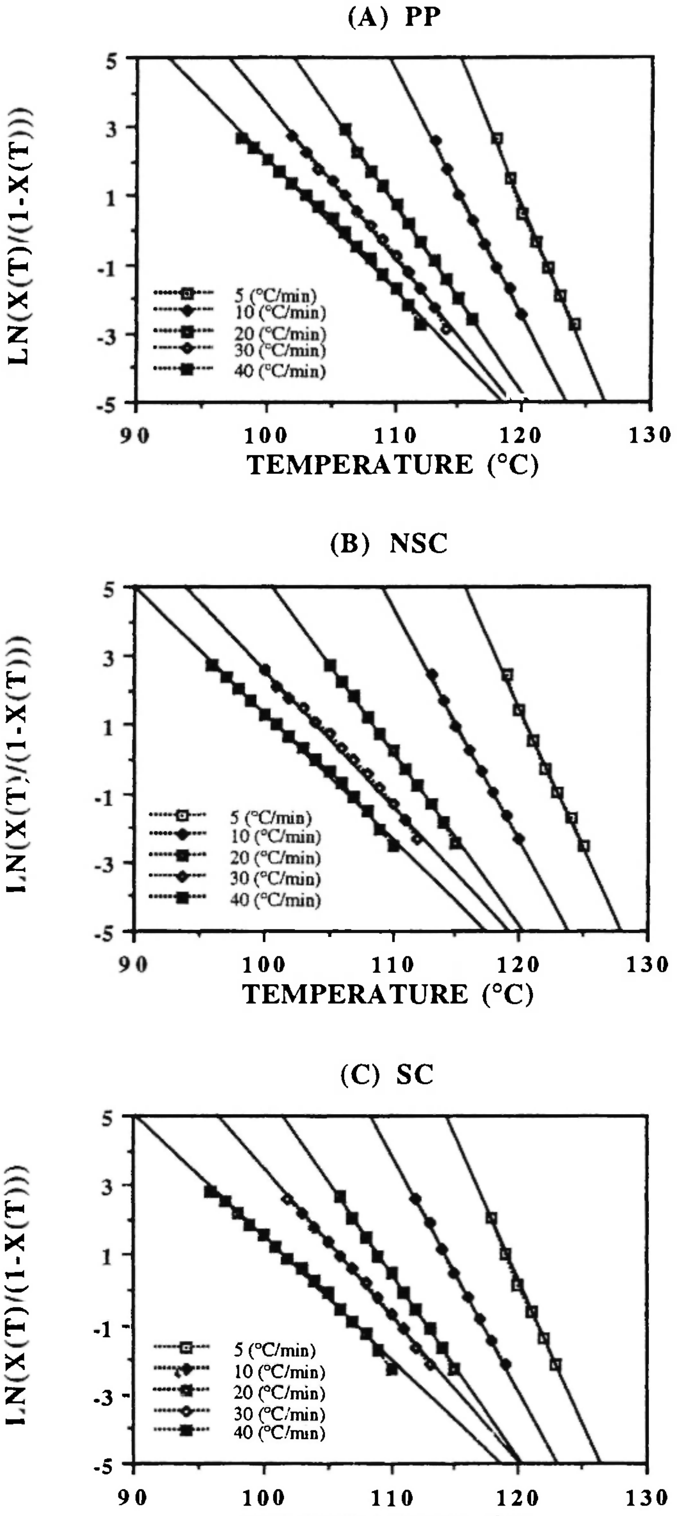
$$\alpha = C + D \cdot \ln\{\phi(t)\} \qquad (2)$$

The constants C and D are shown in Table 5.

4. MODELLING

The following modelling can be proposed for the transformation:

$$\ln\frac{X(T)}{1-X(T)} = \alpha \cdot T + \beta \qquad (3)$$



(A) PP

(B) NSC

(C) SC

Fig. 2: Behaviour of $X(T)$ with the variation of temperature (A) PP, (B) NSC and (C) SC.

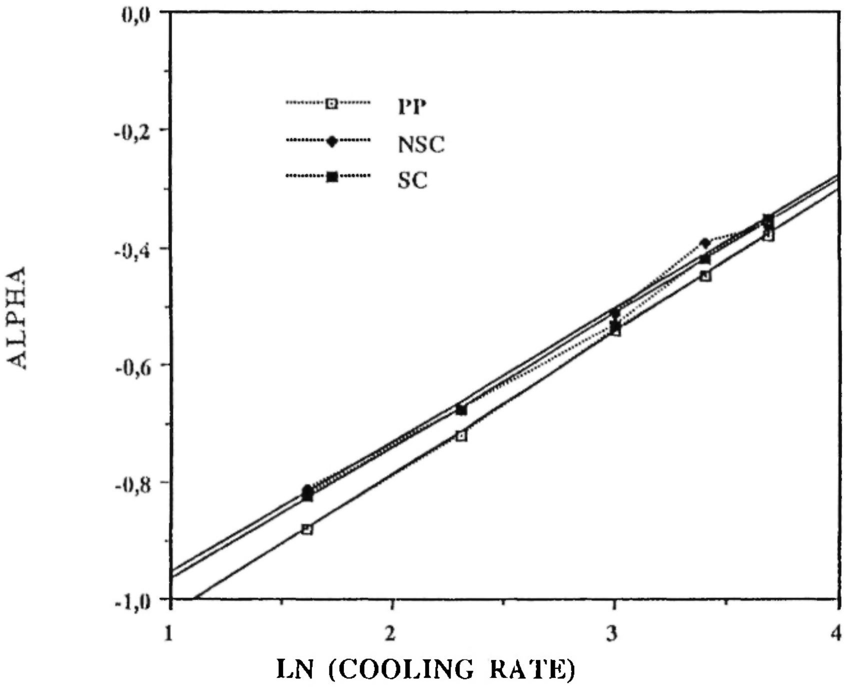


Fig. 3: Relation between ALPHA and the cooling rate.

Table 5
Constants C and D

Code	C	D	r
PP	-1.269	0.241	1.000
NSC	-1.178	0.223	0.996
SC	-1.194	0.226	0.998

Forming the exponential, we have:

$$\frac{X(T)}{1-X(T)} = \exp(\alpha \cdot T + \beta) \qquad (4)$$

Finally we can express the transformation as a function of the temperature:

$$X(T) = \frac{\exp(\alpha \cdot T + \beta)}{1+\exp(\alpha \cdot T + \beta)} \qquad (5)$$

The first order derivative form of Eq. (5) is:

$$X(T)' = \frac{\alpha \cdot \exp(\alpha \cdot T + \beta)}{\{1+\exp(\alpha \cdot T + \beta)\}^2} \qquad (6)$$

Eq. (6) presents the trend of the exothermic reaction, i.e., crystallization. And the second order derivative is:

$$X(T)'' = \frac{\alpha^2 \cdot \exp(\alpha \cdot T + \beta)\{1-\exp(\alpha \cdot T + \beta)\}}{\{1+\exp(\alpha \cdot T + \beta)\}^3} \qquad (7)$$

$T_{C.MAX}$ is the maximum peak of the exothermic curve, so the second order derivative can be zero, i.e, $X(T_{C.MAX})'' = 0$.

$$\alpha \cdot T_{C.MAX} + \beta = 0 \text{ and } \beta = -\alpha \cdot T_{C.MAX} \qquad (8)$$

Inserting Eq. (8) in Eq. (5), we obtain:

$$X(T_{C.MAX}) = \frac{1}{2} \qquad (9)$$

From Eq. (6) and Eq. (9), we get:

$$X(T_{C.MAX}) = \alpha \cdot X(T_{c.MAX}) \cdot \{1 - X(T_{c.MAX})\} = \frac{\alpha}{4} \qquad (10)$$

Finally, from Eqs. (1), (2), (5) and (8) we can take

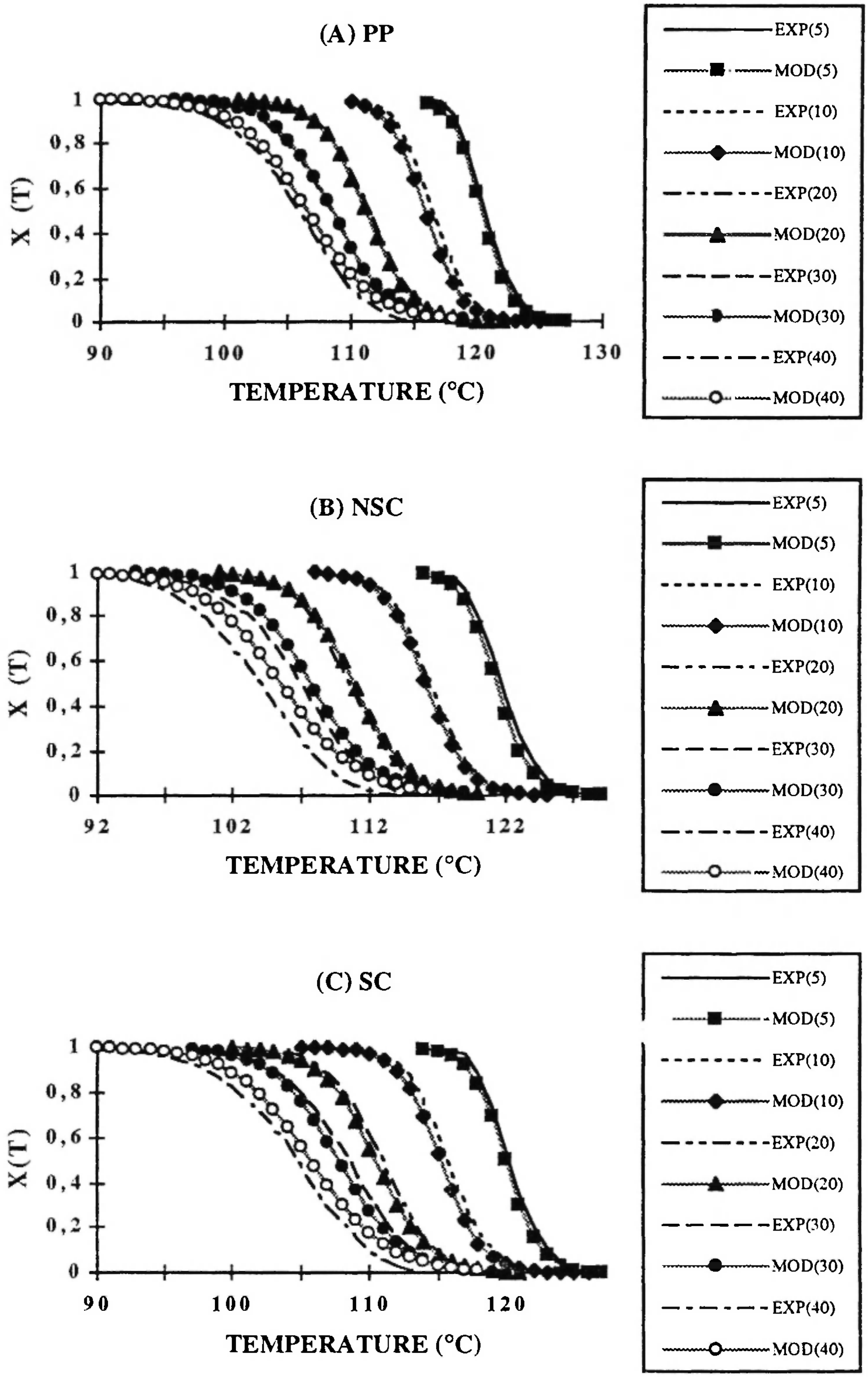
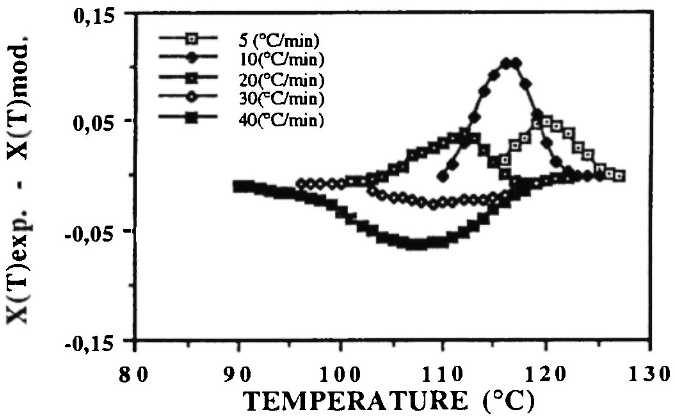
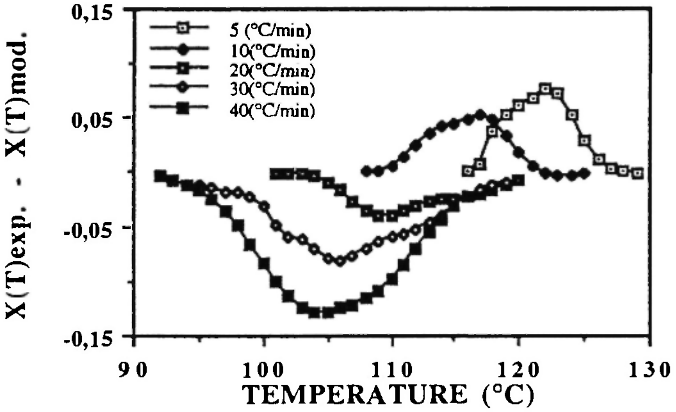


Fig. 4: Comparison between modelling and experiments (A) PP, (B) NSC and (C) SC.

(A) PP



(B) NSC



(C) SC

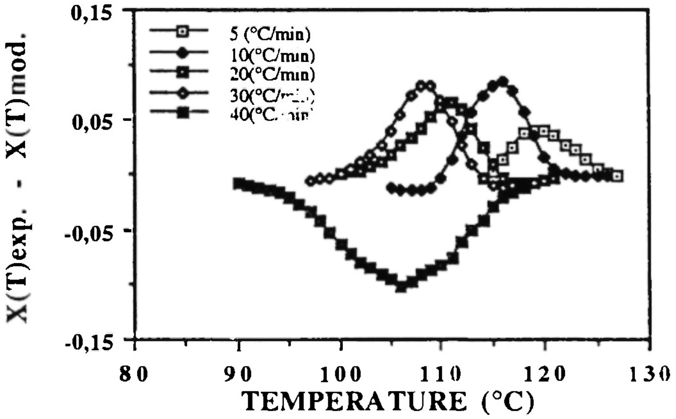


Fig. 5: Difference values of the transformation between modelling and experiments (A) PP, (B) NSC and (C) SC.

the modelling equation of the transformation:

$$X(T) = \frac{\exp \Delta T}{1 + \exp \Delta T} \tag{11}$$

where

$$\Delta T = \alpha \cdot \left(T - T_{C.MAX}\right),$$

$$\alpha = C + D \cdot \ln\{\phi(t)\} \text{ and}$$

$$T_{C.MAX} = A + B \cdot \ln\{\phi(t)\},$$

Results of modelling

Fig. 4 shows a comparison between the experiments and the modelling with Eq. (11). The tangents of the curves of the modelling are in good accord with those of the experiments. The tangents of the curves decrease with increasing cooling rate. The trend of the decrease depends on the α of Eq. (11). Fig. 5 presents the difference values between the experiment and the modelling. The difference values of the initial and the final region are 0.01, so the initial and final temperature of the transformation also agree with those of the modelling and the experiments. The maximum difference is 0.13 in the middle of the region. The trends of the transformation can be redressed by the behaviour of $T_{C.MAX}$.

5. CONCLUSIONS

In the case of semicrystalline thermoplastics, the mechanical properties can be affected by the total crystallinity. The Ozawa method cannot be adopted to explain the non-isothermal crystallization because the Avrami number changes with the variation of temperature. This phenomenon can be deduced from the change in the mechanism of crystallization.

Eq. (11) can be simply applied to produce the products of polypropylene and polypropylene composites for estimating the total crystallinity. This simple modelling has no Avrami number but a parameter, α. α is affected by the cooling rate. It is noteworthy that all samples have exactly the same values of α for varying cooling rates.

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