# Kinetic Rate Equation Combining Ultraviolet-Induced Curing and Thermal Curing. I. Bismaleimide System

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## ABSTRACT:
A novel and general kinetic rate equation combining ultraviolet-induced (UV-induced) curing and thermal curing was successfully derived from the conventional thermal-kinetic rate equation. This proposed novel kinetic rate equation can be applicable to the curing system either simultaneously or individually by UV-induced and thermal cure methods. This general kinetic rate equation is composed of the reaction order \( n \), activation energy \( E_a \), curing temperature \( T \), energy barrier of photoinitiation \( E_Q \), intensity of UV radiation \( Q \), concentration of photoinitiator [I], and a few other parameters. The proposed equation was supported by experimental data based on the curing systems of 4,4\(^\text{-}\)-bismaleimidodiphenylmethane (BMI) and 2,2-bis(4-(4 maleimido phenoxy) phenyl propane (BMIP). The BMI and BMIP systems were isothermally cured at various temperatures, or simultaneously cured with varying intensity of UV radiation (wavelength 365 nm). Conversion levels for the various cured samples were subsequently measured with a FTIR spectrometer. The reaction order \( n = 1.2 \), activation energy \( E_a = 40,800 \) J/mol, and \( E_Q = 7.5 \) mW/cm\(^2\) were obtained for curing BMI system. The reaction order \( n = 1.3 \), activation energy \( E_a = 53,000 \) J/mol, and \( E_Q = 9.1 \) mW/cm\(^2\) were obtained for curing BMIP system. The values of \( n \) and \( E_a \) in the same curing system (BMI or BMIP) are irrespective of the curing method (either simultaneously or individually by UV-induced and thermal cure methods). The salient results of this study show that UV radiation only enhances the initiation rate and UV radiation do not influence the activation energy \( E_a \). The experimental results are reasonably well represented by these semi-empirical expressions.


Key words: kinetics; curing of polymers; bismaleimide; UV cure

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## INTRODUCTION

Bismaleimide resins are some of the most important thermosetting polymers because of their outstanding dielectric and mechanical properties at elevated temperatures.¹ Some examples of their application include the multilayer-printed circuit boards for large-scale computers, encapsulation resins and passivation layers for IC dies, advanced carbon fiber composites for the aerospace industry, and structural adhesives.²

The cure kinetics of ultraviolet-induced (UV-induced) curing or thermal curing have been individually and substantially investigated for various thermosetting polymers and recent inorganic/or- ganic hybrids such as epoxy hybrid³ and acrylate hybrid.⁴,⁵ UV-induced curing of polymer coatings has until recently been dominated by photoinitiated radical polymerization processes, partly because of their curing efficiency. UV-induced curing of thermosetting systems involving maleimides have been investigated with regard to the resulting structures,⁶,⁷ kinetics and mechanism,⁷–¹⁰ bulk and surface properties¹¹ reactivity,⁸,⁹ effect of the UV dosage,¹⁰ effect of the photoinitiators, and curing temperature.¹² None of these studies, however, have proposed a generally valid kinetic rate equation, with the sole exception of the Decker’s study,⁹ in which a kinetic rate equation was introduced for a special system. Decker investigated the influence of the light intensity on the cure kinetic of a DVE-3/Q-bond system, where DVE-3 refers to divinyl ether of triethylene glycol, and Q-bond is a liquid bismaleimide with a 36-carbon-atom cycloaliphatic branched structure from Quantum Materials; Decker proposed the following kinetic rate equation:

\[
R_p = kQ^{0.6}[M]
\]
where $R_p$ refers to the rate of polymerization of the maleimide monomer, $Q$ is the light intensity, and $[M]$ is the concentration of the maleimide monomer.

A kinetic rate equation in an UV-induced curing system based on 2-hydroxyethyl methacrylate (HEMA)-terminated polyurethane (PU) was further proposed by Hsieh et al.\textsuperscript{13}:

$$\frac{d[C=C]}{dt} = k[C=C][I]^{0.5}[Q]^{0.5}[T]^{-1}$$

This equation contains the film thickness $[T]$, the initiator concentration $[I]$, the unreacted carbon-carbon double bond concentration $[C=C]$, and the light intensity $[Q]$.

The above two equations indicate that when UV light is not applied ($Q = 0$), polymerization apparently does not take place (i.e., the rate equation is equal to zero), even at an elevated temperatures. These forms of the rate equation are therefore not applicable to the curing systems which can be cured either by a UV-induced or thermal method, or by both. It is known that the curing system Hsieh et al.\textsuperscript{13} investigated can be cured either simultaneously or individually by UV-induced and thermal cure methods. However, the proposed equation is not applicable to the case of a sole thermal cure reaction. Consequently, a kinetic rate equation of general validity for all curing methods still needs to be determined.

In the cases of thermal cure, a general phenomenological model equation (autocatalytic kinetic equation) is currently in widespread use for the curing of the various thermosetting polymers, and is expressed as follows\textsuperscript{14,15}:

$$\frac{dx}{dt} = (k_1 + k_2x^n)(1 - x)^n$$

(1)

where $x$ is the percentage of conversion, $k_1(T)$ and $k_2(T)$ are reaction rate constants with two different activation energies and pre-exponential factors, and $n$ and $m$ are the reaction orders. The item $k_2x^n$ in eq. (1) results from the autocatalytic part of reaction; it is the weighting factor of the autocatalytic part of the reaction as compared with the regular reaction ($k_1$). An autocatalyzed reaction assumes that at least one of the reaction products is also involved in the propagating reaction. It is thus characterized by an accelerating isothermal conversion rate, with its maximum occurring well after the conversion initiation. This result is because the reactants can be converted via alternative paths. In some cases, the autocatalytic part of the reaction does not occur. Under these circumstances, eq. (1) can then be reduced to a simple form:

$$\frac{dx}{dt} = k_1(1 - x)^n$$

(2)

Presently, only limited information is available for accurate modeling of the bismaleimide curing mechanism. Several reaction paths, occurring simultaneously or in sequence, have been proposed for the curing process of bismaleimide-related resins.\textsuperscript{16} Bismaleimide can be cured via a sole thermal process\textsuperscript{17,18} or with a peroxide initiator.\textsuperscript{19} Because of the complicate reaction mechanisms involved, it is not easy to derive an accurate kinetic rate equation from them. Most researchers therefore treated the all reaction paths as a whole course (i.e., these reaction paths occur simultaneously), and utilized eq. (1) or (2) to analyze the kinetics of the thermal cure.\textsuperscript{19–21} Acevedo\textsuperscript{19} investigated the curing kinetics of a system containing $N$-phenylmaleimide with dicumylperoxide as a curing initiator in the temperature range of 393–433 K. Although there exists autocatalytic characterization in this curing system, he still used the first-order model without the autocatalytic part [eq. (2)] to fit his experimental data, and found that this model could better fit his experimental data up to 70% conversion. Goodwin\textsuperscript{20} explored the cure kinetics of 4,4'-bismaleimido-diphenylmethane (MDA-BMI) and a bisphenol A derivative in the temperature range of 453–473 K. He also tried to use the simple $n$-th order model [eq. (2)] to fit his experimental data; however, only a first-order model can fit the data obtained at 478 K to some extent. Boey\textsuperscript{21} investigated the curing kinetics of a system containing four main components (MDA-BMI, amine, epoxy, and diallylbisphenol A) at a temperature of 443, 463, and 483 K. He found that autocatalytic reactions did indeed take place in the studied system, and thus employed the autocatalytic model [eq. (1)] to fit the experimental data at first. However, eq. (1) does not fit the data over the entire range of the cure reaction process, and is particularly weak for higher curing temperatures. He therefore utilized eq. (2) with different values of $n$ to fit the experimental data obtained at different curing temperatures, and found that this equation better fit his data after 10% conversion. It should be pointed out that the curing systems described in Refs. 19–21 consist of at least two components, and thus undergo multiple cure reactions. Each reaction path proceeds at a different temperature range, which results in the poor fitness of eq. (1) or (2) for these systems.

In the literature, cure kinetics for various thermosetting polymers has been investigated individually either by ultraviolet-induced (UV-induced) curing or by thermal curing. There is not a kinetic rate equation, which can be applicable to the curing system simultaneously associating ultraviolet-induced (UV-induced) curing with thermal curing.
Accordingly, in this work we try to propose a novel and general kinetic rate equation which can be applicable to the curing system either simultaneously or individually by UV-induced and thermal cure methods. This kinetic rate equation should contain the UV light intensity \((Q, \text{ mW/cm}^2)\), the energy barrier for photoinitiation \((E_{Q_0}, \text{ mW/cm}^2)\), the temperature \((T)\), and the apparent activation energy \((E_a, \text{ J/mol})\). Meanwhile, this proposed kinetic rate equation is going to be further supported by the experimental data of the bismaleimide curing systems. In this work, neat bismaleimide monomers were used for simplicity. Cure reactions of neat bismaleimide proceed merely via a double-bond opening, rather than reacting with functional groups on another monomer. Neat bismaleimide monomers can be cured by either the UV-induced method or the thermal method, or by both. For reasons of efficiency, most neat bismaleimide monomers would be cured with UV radiation at an elevated temperature. To verify the applicability of the proposed kinetic rate equation, two different bismaleimide monomers, 4,4’-bismaleimidodiphenylmethane (BMI) and 2,2-bis(4-(4 maleimido phenoxy) phenyl propane (BMIP), were chosen. In BMI system, thermal curing occurs (466 K) immediately after being melted (413 K). But in BMIP system, there exists a long temperature range between melting temperature (363 K) and the thermal curing temperature (523 K). As the curing system of the BMIP monomer requires a higher curing temperature than the curing system of the BMI monomer, the photoinitiator presumably plays a more influential role in the UV-induced curing system of the BMIP monomer than in the BMI monomer system.

**DERIVATION OF A KINETIC RATE EQUATION COMBINING ULTRAVIOLET-INDUCED CURING AND THERMAL CURING**

The curing rate of neat bismaleimide at constant temperature is mainly determined by the amount of active sites (possibly free-radicals); this amount, in turn, is dependent on the initiation rate. The produced intermediate species are not capable of autocatalyzing the curing reaction. Accordingly, it may be reasonably assumed that the simple form of the kinetic rate equation [eq. (2)] can be applied to the neat bismaleimide curing system. Nevertheless, this fact needs to be evidenced by definite experimental results. In this work, we intend to expand eq. (2) into a new form of kinetic rate equation that contains both UV term and thermal term.

\[
\frac{dx}{dt} = k_1(1-x)^n
\]  

where \(k_1\) is the rate constant.

(a) The case of sole thermal cure without UV radiation.

\(k_1\) is a function of temperature only, and the Arrhenius relationship is expressed by:

\[
k_1 = f(T) = A \exp(-E_a/RT)
\]

where \(E_a\) is the activation energy, \(R\) is the gas constant, \(T\) is the absolute temperature, and \(A\) is the pre-exponential or frequency factor.

Taking the natural logarithm (to the base \(e\)) of both sides, we get

\[
\ln(k_1) = \ln A - E_a/RT
\]

A plot of \(\ln(k_1)\) versus \(1/T\) should produce a straight line; \(A\) can be obtained from the \(y\)-intercept, and \(E_a\) is determined from the slope. Alternatively, eq. (2) can be written as:

\[
\frac{dx}{dt} = A \exp(-E_a/RT)(1-x)^n
\]

(b) The case of thermal cure with UV radiation.

When UV radiation is used in a thermal cure, UV radiation will induce the photoinitiator to generate much more free radicals (i.e., the initiation rate is higher), thereby increasing the curing rate. Thereafter, the curing rate will further increase with increasing curing temperature. The initiation rate of the thermal cure system will increase with the participation of UV radiation. The initiation rate resulted from UV light depends on the energy barrier of the photoinitiation \((E_{Q_0}, \text{ mW/cm}^2)\). The rate constant \(k_1\) is composed of thermal term and UV-induced term. The presence of UV radiation only increases the initiation rate, but does not influence the activation energy \((E_a)\) itself. Accordingly, the Arrhenius relationship can be rewritten as follows:

\[
k_1 = f(T, Q) = A(1 + \omega \exp(-E_{Q_0}/Q)) \exp(-E_a/RT)
\]

where \(Q\) refers to the light intensity (\(\text{mW/cm}^2\)), and \(\omega\) is the weighting factor of the UV-induced term of the reaction as compared to the thermal part of reaction. A general kinetic rate equation containing both UV term and thermal term can be expressed as:

\[
\frac{dx}{dt} = A(1 + \omega \exp(-E_{Q_0}/Q)) \exp(-E_a/RT)(1-x)^n
\]

This equation can be reduced to eq. (5) if UV light is not applied to the curing system or \(E_Q\) is very high (i.e., \(\omega \exp(-E_{Q_0}/Q) \ll 1\)). On the other hand, if the influence of the UV-induced term is greater...
than that of the thermal term (i.e., $\omega \exp(-E_Q/Q) \gg 1$), eq. (7) can be simplified into the following form:

$$\frac{dx}{dt} = A_1 \exp(-E_Q/Q) \exp(-E_a/RT)(1 - x)^n \quad (8)$$

The weighting factor $\omega$ in eq. (7) is related to the UV-induced term of the reaction and supposedly a function of the photoinitiator concentration [$I$], in the form of $\omega = \phi[I]^y$.

Introducing this relationship into eq. (7), we get

$$\frac{dx}{dt} = A(1 + \phi[I]^y \exp(-E_Q/Q)) \exp(-E_a/RT)(1 - x)^n \quad (9)$$

This is a general kinetic rate equation for a system with both UV radiation and thermal cure.

**ANALYSIS PROCEDURES**

(i) The rate constant $k_1$, reaction order $n$, activation energy $E_a$, and pre-exponential factor $A$ were first evaluated in a system without UV radiation.

In a first step, curing experiments were conducted at different temperatures without UV radiation. For a designed curing temperature, the data of conversion ($x$) versus the curing time ($t$) were measured, and subsequently a plot of $\ln(dx/dt)$ versus $\ln(1 - x)$ was drawn. Using eq. (10), we obtained the rate constant $k_1$ from the $y$-intercept, and the reaction order $n$ from the slope of the straight line.

$$\ln \left( \frac{dx}{dt} \right) = \ln k_1 + n \ln(1 - x) \quad (10)$$

Equation (10) was obtained by taking natural logarithm (to the base $e$) of both sides of eq. (2). Various $k_1$ values for the different curing temperatures ($T$) were thus collected. Then, using the eq. (4), we obtained the activation energy $E_a$ and the pre-exponential factor.

(ii) The energy barrier of photoinitiation ($E_Q$, mW/cm$^2$) and the weighting factor of UV-induced part of reaction ($\omega$) were subsequently evaluated in a system with both UV radiation and thermal cure.

In this step, curing experiments were performed with various intensity of UV radiation at different specified temperatures. Using eq. (4), we obtained the various rate constants $k_1$ and reaction order $n$ values. Theoretically, the $n$ value obtained in this step (with UV radiation) should be identical to that in step (i) (without UV radiation). If we define $F(T)$ as $F(T) = A(-E_a/RT)$, then $F(T)$ should be a constant value for a specified curing temperature. Various $F(T)$ values for each specified curing temperature were thus calculated by using the $A$ and $E_a$ values obtained in step (i). eq. (6) can thus be rewritten as follows:

$$k_1 = F(T)(1 + \omega \exp(-E_Q/Q)) \quad (11)$$

Taking the natural logarithm (to the base $e$) of both sides of above equation and reorganizing the resulting relationship, we get

$$\ln(k_1/F(T) - 1) = \ln(\omega) + (-E_Q/Q) \quad (12)$$

A plot of $\ln(k_1/F(T) - 1)$ versus $1/Q$ was made, and we obtained the $\omega$ value from the $y$-intercept, and $E_Q$ from the slope of the straight line.

(iii) The value of $y$ and $\phi$ in the form of $\omega = \phi[I]^y$ was finally determined. Taking the natural logarithm of both sides of equation $\omega = \phi[I]^y$, we get

$$\ln \omega = \ln \phi + y \ln[I] \quad (13)$$

Various values of $\omega$ were collected by varying the photoinitiator concentration [$I$] in the curing systems. Then, a plot of $\ln \omega$ versus $\ln[I]$ was drawn. We obtained the $\phi$ value from the $y$-intercept, and the $y$ value from the slope of the straight line.

Finally, all the parameters ($n$, $E_Q$, $E_a$, $y$, $a$, and $A$) obtained by the previously stated procedures were substituted into eq. (9), and a generally valid kinetic rate equation containing both UV-induced term and thermal term was thus obtained.

**EXPERIMENTAL**

**Materials**

4,4’-bismaleimidodiphenylmethane (BMI) (Aldrich, USA) and diphényl(2,4,6-trimethyl benzoyl)phosphine oxide (TPO) (TCI, Japan) were used as purchased. TPO served as a photoinitiator. Another bismaleimide of 2,2-bis(4-(4 maleimido phenoxy)phenyl propane (BMIP) was synthesized and characterized in our laboratory.

The chemical structures of BMI and BMIP are shown below:
reaction even at the lower temperature of 413 K [Fig. 13(a)]. But, as compared with Figure 13(a), Figure 13(b) suggests that a higher curing temperature (473 K) obviously improves the curing efficiency (i.e., curing rate) at the comparable level of TPO concentration.

CONCLUSIONS

In the literature, cure kinetics of various thermosetting polymers was usually investigated by UV-induced curing or thermal curing individually. In this study, a novel and generally valid kinetic rate equation [eq. (9)] combining UV-induced curing and thermal curing was successfully derived and was supported by the experimental data. This general kinetic rate equation was derived based on a premise that the general kinetic rate constant $k_1$ is composed of thermal term and UV-induced term. The presence of UV radiation only increases the initiation rate, but does not influence the activation energy ($E_a$) itself. This general kinetic rate equation is composed of term for the reaction order $n$, activation energy $E_a$, curing temperature $T$, energy barrier of photoinitiation $E_Q$, intensity of UV radiation $Q$, concentration of photoinitiator $[I]$, and some other parameters.

Incidentally, the activation energy $E_a$, reaction order $n$, and pre-exponential factor $A$ are identical for a system with sole thermal curing (without UV radiation), and a system with both UV radiation and thermal curing. This salient result implies that the previously mentioned premise is right, i.e., UV radiation only enhances the initiation rate and has no influence on the activation energy ($E_a$). The initiation rate resulted from UV light depends on the energy barrier of the photoinitiation ($E_Q$).

Ultraviolet-induced and thermal curing of bismaleimide systems could be adequately modeled by the derived general kinetic rate equation [eq. (9)]; however, autocatalytic characteristics are not yet included. The derived general kinetic rate equation will be further investigated in the other curing systems, and autocatalytic characteristics may probably be included in the future.

References