Recent progress in kinetics of thermal degradation mechanisms in polymer composites

Abstract

This mini-review encompasses the most recent developments in the field of condensed phase kinetics with special emphasis on prediction of thermal degradation mechanisms in polymer composites. In this context, it initially reviews, in a brief way, the pre-existing reaction model determination approaches along with their advantages and disadvantages. Then, the advanced kinetic approach to reaction mechanisms, which takes into consideration the dependence of activation energy of system on degree of reaction progress, is detailed. Some of the important applications of the advanced kinetic approach on complicated thermal degradation mechanisms in epoxy and (particularly in) urea-formaldehyde cellulose (UFC) composites filled with metal particles are also discussed. The soundness of the advanced kinetic approach in predicting the thermal degradation mechanisms of polymer composites and its future applications are also taken into consideration.

Keywords: polymer composites, thermal degradation kinetics, mechanism; kinetic approach, matrices, thermo electrical, precursors, optimization, commercialization, thermal stability, scanning calorimetry, thermogravimetric, non-isothermal analysis

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Abbreviations: UFC, urea formaldehyde cellulose; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; GLIM, generalized linear integral is conversional method; OFW, ozawa-flynn-wall; KAS, kissinger-akahira-sunose; UDF, user defined fitting function; LMA, levenberg-marquardt algorithm; GO, graphene oxide; CNTs, carbon nanotubes;

Introduction

Composite materials are the materials which consist of two or more components with significantly different physical and/or chemical properties, those when combined together, produce a material with the characteristics different from the precursors. The individual components remain distinguishable within the finished structure, forming however an interface which is usually responsible to impart particular properties to the composites. A composite material comprises a matrix and at least one of the reinforcements. The choice of matrices and reinforcements vary, depending upon the applications of finished product. In the case of polymer composites, the matrix used is always a polymer. Polymer composites are fabricated commercially aiming to be employed in diverse applications.[1] They may either be insulating or conducting, though both of them are equally useful. Insulating composites are applicable as thermal greases, thermal interface materials, and electric cable insulations, while conductive composites are exploited in thermo electrical and thermo mechanical applications, and organic electronics.[1,2–6] However, in order to continue satisfying the global demands (particularly of energy), there are certain issues which need to be addressed regarding the polymer composites.[7] One important issue is the process control for their efficiency optimization and thus eventual commercialization. Answering this task requires thorough investigation of the polymer composites; not only their structures, but also and especially the mechanisms of temperature dependent processes taking place in them demand consideration.

Kinetic analysis of thermally activated condensed phase processes is capable of determining their activation parameters in order to analyze the transition states, and finally the process mechanisms. Kinetic parameters are physically meaningful in controlling the process under consideration, and predicting thermal stability/life of

materials outside the experimental range.[8] Nevertheless, thermally activated condensed phase processes are known for their complexities, and even apparently simple processes might consist of various steps. In this frame of reference, firstly, this mini-review discusses briefly the pre-existing mechanistic approaches based on condensed phase kinetics along with their advantages and disadvantages. In the next phase, the most recent and advanced kinetic approaches to manipulate particularly the intricate mechanisms of in polymer composites are detailed. Some of the important applications of the advanced kinetic approaches on complex thermal degradation mechanism in epoxy/ metal composites and complicated multi-step mechanisms in urea-formaldehyde cellulose (UFC) composites filled with metal particles are also discussed. An account of the prospective studies based on advanced kinetic approaches will also be given and discussed.

Kinetic analysis of thermal degradation processes in polymeric materials

In polymeric and organic materials, although the differential scanning calorimetry (DSC) may provide certain valuable information about the materials, though the assessment of their thermal degradation processes and particularly their kinetics are preferably carried out by thermogravimetric analysis (TGA).[9] The unit-less parameter degree of reaction advancement or degree of conversion (α) of a thermally stimulated condensed phase process can be defined as following by employing thermogravimetric analysis

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \qquad (1)$$

Where, 'm_0' is the initial mass of reactant, 'm_t' is its mass at certain temperature (non-isothermal analysis) or time (isothermal analysis) during the reaction and 'm_∞' is its mass at the end of reaction. In condensed phase processes, the reaction rate $d\alpha/dt$ being the function of 'α' can be represented as;

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (2)$$

Equation (2) is the basic kinetic equation of condensed phase processes. In the case of thermally stimulated processes, the value of rate constant 'k' is often substituted in Equation (2) by Arrhenius equation which then takes the following form;

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \tag{3}$$

Where, 'A' is the pre-exponential factor, E_α is the energy of activation, $f(\alpha)$ is the function of degree of conversion, called reaction model, and R is gas constant. Physically, 'A' describes the collision frequency of the particles involved in the formation of activated complex, E_α is the activation energy barrier(s) of reaction, and $f(\alpha)$ is an expression for the mechanism of reaction.[8] Some well known condensed phase reaction models are given in Table 1 and Figure 1.

Table 1 $f(\alpha)$ and $h(\alpha)$ expressions of well known reaction models; maxima of $h(\alpha)$ function (α_{max}), where applicable

Reaction model	Notation	$f(\alpha)$	$h(\alpha)$	Maxima of $h(\alpha)$ (α_{max})
Reaction order	RO (n)	$(1-\alpha)^n$	$-n/(1-\alpha)$	......
Johnson Mehl Avrami General Equation	JMA (m>1)	$m(1-\alpha)\{-\ln(1-\alpha)\}^{1-1/m}$	$\left(\frac{\frac{1-1/m}{\ln(1/1-\alpha)}-1}{1-\alpha}\right)$	......
1D-Diffusion	D_1	$1/2\alpha$	$-1/\alpha$	......
2D-Diffusion	D_2	$-1/\ln(1-\alpha)$	$\ln(1-\alpha)^{1-\alpha}$	0.632
3D-Diffusion (Jander's Equation)	D_3	$\frac{3(1-\alpha)^{2/3}}{2\{1-(1-\alpha)^{1/3}\}}$	$-\frac{2}{3}\left[\frac{1}{1-\alpha}+\frac{1}{2(1-\alpha)^{2/3}\{1-(1-\alpha)^{1/3}\}}\right]$	0.522
3D-Diffusion (Ginstling Equation)	D_4	$\frac{3}{2\{(1-\alpha)^{1/3}-1\}}$	$-\frac{1}{3}\left[\frac{1}{\{(1-\alpha)^{-1/3}-1\}(1-\alpha)^{4/3}}\right]$	0.581
Šesták Berggren	SB (m, n)	$(\alpha)^m(1-\alpha)^n$	$\frac{m}{\alpha}-\frac{n}{1-\alpha}$	......
Power Law (Nucleation)	Pr	$(\alpha)^r$	$\frac{r}{\alpha}$	......
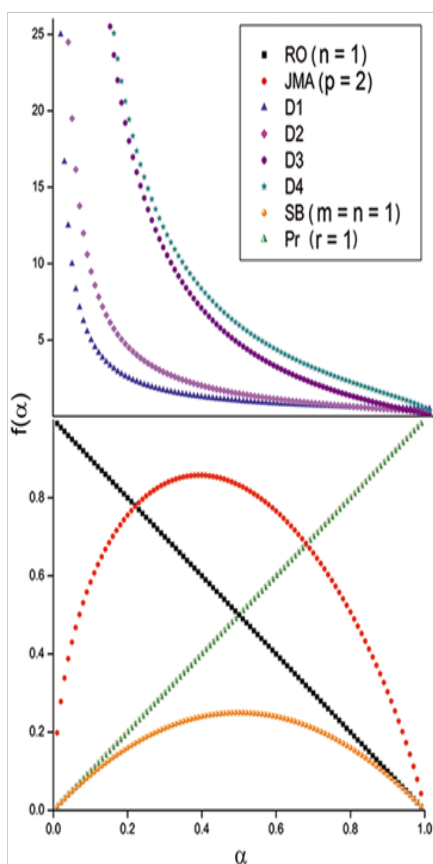
Figure 1 Graphical representation of different cases of well known condensed phase reaction models.

Determination of activation energy

Isoconversional methods are employed to examine the variation in activation energy with the degree of conversion, and therefore the nature and complexity of process. A condensed phase process is fairly approximated as single step if the variation in its activation energy with the degree of conversion is insubstantial, otherwise, the reaction is deemed as following a complex reaction pathway. Isoconversional methods can be isothermal/non-isothermal, differential/integral and linear/nonlinear.[8]

Taking logarithm of Equation (3) gives the following linear differential isoconversional method, known as the Friedman's method.[10]

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,\beta} = \frac{-E_\alpha}{RT_{\alpha,\beta}} + \ln Af(\alpha) \tag{4}$$

The E_α values can be determined by plotting $ln(d\alpha/dt)$ versus $1/T\alpha$ at constant values of α which demands numerical differentiation. The resulting E_α values might therefore be irregular.

In the pursuance of determining reliable activation energies of condensed phase processes, a generalized linear integral isoconversional method (GLIM) has been suggested by Arshad and Maaroufi with the following mathematical expression:[11,12]

$$E_\alpha = \frac{R}{a}\left[b\frac{d\ln T_\alpha}{d\left(\frac{1}{T_\alpha}\right)} - \frac{d\ln\beta}{d\frac{1}{T_\alpha}}\right] \tag{5}$$

In Equation (5), 'a' and 'b' are the constants which depend on temperature integral approximation.[13] For instance, (a, b)=(1.052, 0) for Ozawa-Flynn-Wall (OFW) method,[14] (a, b)=(1, 2) in the case of Kissinger-Akahira-Sunose (KAS) method,[15] and (a, b)=(1.0008, 1.92) in the case of Starink's method,[16] etc. Moreover, in Equation (5), *dlnβ/d(1/Tα)* and *dlnTα /d(1/Tα)* respectively are the slopes of straight lines drawn between *lnβ* and *1/Tα*, and *lnTα* and *1/Tα* at certain value of α. The activation energy of a condensed phase process at any value of 'α' can be directly determined by employing Equation (5), provided that the values of *dlnβ/d(1/Tα)* and *dlnTα /d(1/Tα)* at the respective value of 'α' are known.

Determination of reaction model

As discussed in the previous section, a reaction model can either be a simple or a complicated mathematical function of the degree of conversion constituting upon one or more parameters. It is capable of giving information regarding the nature and mechanism of a condensed phase process. The reaction model for condensed phase processes can be determined by either model fitting or model free methods, though model free methods are preferred.[8,11] In model free case, one of the useful methodologies was suggested by Malèk.[17] An average value of activation energy from isoconversional methods should already be known and then a pair of functions *y(α)* and can be utilized to determine the reaction model and its associated parameters as described in Equations (6) and (7) respectively:

$$y\left(\alpha\right) \approx \left(\frac{d\alpha}{dt}\right)\exp\left(x\right) \tag{6}$$

$$z\left(\alpha\right) \approx \pi\left(x\right)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \tag{7}$$

In Equations (6) and (7) $x=E/RT$ and $\pi(x)$ is a temperature integral function.[13] The maxima $(\alpha_M, \alpha_p^\infty)$ of *y(α)* and *z(α)* functions respectively and 'α_p' as the degree of conversion at maximum reaction rate guide to the most appropriate reaction models according to the proposed criterion.[17]

Another efficacious reaction model determination methodology is called the generalized master plots method.[18] Similar to the previous case, an average value of activation energy from isoconversional methods should be known and then the following equation is used to determine the suitable reaction models for the processes under consideration:

$$\frac{f\left(\alpha\right)}{f\left(0.5\right)} = \frac{\dfrac{d\alpha}{dt}}{\dfrac{d\alpha}{dt}_{0.5}}\frac{\exp\left(\dfrac{E}{RT}\right)}{\exp\left(\dfrac{E}{RT_{0.5}}\right)} \tag{8}$$

Where, $T_{0.5}$ is attributed to α=0.5. It should be taken into account that the above discussed give fairly reliable results if the change in activation energy of the reaction with degree of conversion is insignificant. If the activation energy of the system shows dependence on degree of conversion or temperature, those reaction model determination methodologies are not recommended.[8,11]

In order to kinetically interpret the complex condensed phase processes, Arshad and Maaroufi have put forward an advanced reaction model determination methodology taking into account the variable activation energy concept.[11] The main advantage of this methodology is that it may not only simulate single step but also multi-step processes, and it is effectively applicable in isothermal as well as non-isothermal kinetics. In their approach, they avail a modified Arrhenius equation which includes variable pre-exponential factor and activation energy as expressed in Equation (9):

$$\frac{d\alpha}{dt} = A_0\left(\frac{T}{T_0}\right)^n \exp\left(\frac{-E_\alpha}{RT}\right)f\left(\alpha\right) \tag{9}$$

Where, 'A_0' is the value of pre-exponential factor at initial temperature 'T_0' and 'n' is a numerical constant. Usually

$$n \in \left[0,1\right]$$

But it may possibly attain positive values other than mentioned in the interval and it can even be a negative number.

On the basis of Equation (5), authors have derived a new function of the degree of conversion *h(α)* to predict the reaction mechanisms of complex solid state processes:[11]

In the case of complicated reactions under non-isothermal conditions,

$$h\left(\alpha\right) = \frac{\dfrac{d^2\alpha}{dt^2}}{\left(\dfrac{d\alpha}{dt}\right)^2} + \frac{\dfrac{dE}{d\alpha}}{RT} - \frac{\beta\left\{n+\dfrac{E_\alpha}{RT}\right\}}{T\left(\dfrac{d\alpha}{dt}\right)} \tag{10}$$

In order to determine the parameter '*n*' present in Equation (10), Equation (9) can be transformed into the following non-linear form:

$$y = a\left(x^b\right)\exp\left(-\frac{c}{x}\right) \tag{11}$$

While, $x=T$, $y=d\alpha/dt$; a=$\varphi(\alpha)$={$A_0/(T_0)^n$}$f(\alpha)$, b=n, c= $E\alpha/R$

As the reaction rate varies exponentially with temperature at constant values of 'α', the variation in reaction rate with temperature at constant values of 'α' can thus be fitted by an exponential type user defined fitting function (UDF) based on Equation (11) employing Levenberg-Marquardt algorithm (LMA) for 2D curves, which ultimately results in the generation of parameters a, b and c.[19]

It is worth pointing out that the accuracy of reaction model of a condensed phase process becomes sensitive to parameter 'n' when its activation energy acquires relatively lower value. However, when $E\alpha/RT$ factor in Equation (6) attains a value equal to or grater than 30,[20] the influence of parameter 'n' on the reaction model is generally insignificant, and Equation (6) takes the following form:

$$h\left(\alpha\right) = \frac{\dfrac{d^2\alpha}{dt^2}}{\left(\dfrac{d\alpha}{dt}\right)^2} + \frac{1}{RT}\left[\frac{dE}{d\alpha} - \frac{\beta E_\alpha}{T\left(\dfrac{d\alpha}{dt}\right)}\right] \tag{12}$$

Equation (12) takes the following form under non-isothermal conditions when the reaction follows single step kinetics:

$$h\left(\alpha\right) = \frac{1}{\frac{d\alpha}{dt}}\left[\frac{\frac{d^2\alpha}{dt^2}}{\frac{d\alpha}{dt}} - \frac{\beta E}{RT^2}\right] \qquad (13)$$

In the case of isothermal kinetics, putting $\beta = dT/dt = 0$ in Equations (10)/(12) and rearranging it, gives the following expression:

$$h\left(\alpha\right) = \frac{\frac{dE}{d\alpha}}{RT} + \frac{\frac{d^2\alpha}{dt^2}}{\left(\frac{d\alpha}{dt}\right)^2} \qquad (14)$$

Equation (14) takes the following form if the reaction consists of only one step:

$$h\left(\alpha\right) = \frac{\frac{d^2\alpha}{dt^2}}{\left(\frac{d\alpha}{dt}\right)^2} \qquad (15)$$

The right hand sides of Equations (10) and (12)-(15) can be obtained by experimental thermo-analytical data while their left hand sides can be simulated by the $h(\alpha)$ functions as shown in Figure 2.
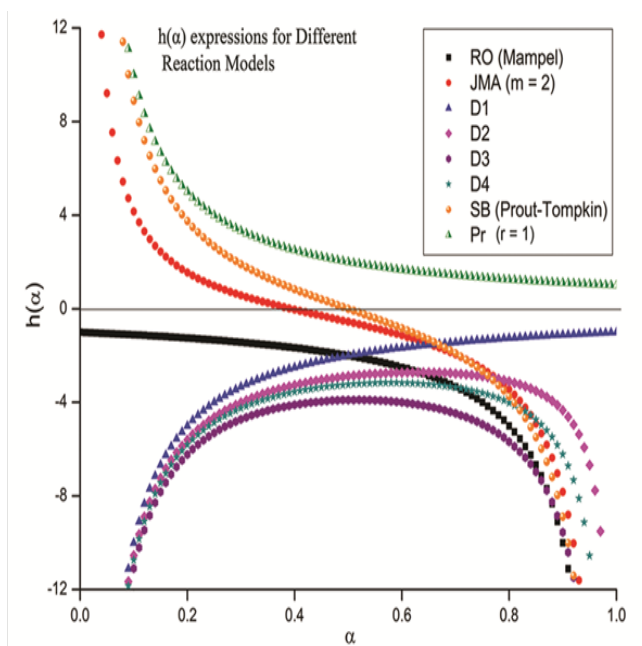
Figure 2 $h(\alpha)$ expressions of some well known reaction models in accordance with Figure 1.

A fair agreement between curves generated from thermo-analytical data and theoretical models can guide to the appropriate reaction models.

Although the $h(\alpha)$ functions as shown in Table 1 and graphically in Figure 2 can fairly lead to the most probable reaction models in the case of single-step processes, yet such situations are not very common in condensed phase processes. An accurate picture of reaction model over the whole range of degree of conversion for complicated multi-step reactions can however be visualized by the proposed approach.

By definition, $h(\alpha)$ function is expressed as following:

$$\frac{f'\left(\alpha\right)}{f\left(\alpha\right)} = h\left(\alpha\right) \qquad (16)$$

Integration of Equation (16) gives the following relation:

$$f\left(\alpha\right) = \exp\left(\int_{\alpha_0}^{1} h\left(\alpha\right) d\alpha\right) \qquad (17)$$

Where, α_0 is a value greater than zero, obtained by adding an infinitesimally small positive digit to zero.

Reaction models of complex condensed phase processes can be calculated by performing numerical integration of the curve obtained from Equations (10)/(12) in non-isothermal kinetics and/or Equation (14) in isothermal kinetics over (0, 1] and taking natural exponent of the resulting definite integral.

Discussion

The advanced kinetic approach described in the previous sections has been applied to predict the thermal degradation mechanisms in polymer composites filled with metal particles, which is a fascinating class of materials in regard particularly to their valuable worldwide applications. Application of the proposed kinetic approach on insulating and conducting epoxy/Sn composites reveals new and interesting mechanistic information about the thermal degradation processes of epoxy/Sn composites.[12] It has been pointed out that thermal degradation of epoxy resin fairly follows single-step reaction pathway. Tin does not alter the reaction mechanism of epoxy, though it accelerates the thermal degradation rate of epoxy by lowering the activation energy barrier of reaction. In addition, the increase in reaction rate of epoxy depends on tin contents in epoxy. It has also been demonstrated that the thermal degradation of epoxy/Sn composites can be satisfactorily modeled by Šestak-Berggren model suggesting autocatalytic mechanisms for the composites.

The innovative kinetic approach has also been applied to predict the thermal degradation mechanisms in urea-formaldehyde cellulose composites filled with metal particles (UFC/metal composites; while, metal=Al, Zn, Sn).[21–23] The isoconversional kinetic analysis of UFC/metal composites reveals that their thermal degradation might follow intricate reaction pathways. Since the activation energies of UFC/metal composites show substantial variations with the degree of reaction advancement, kinetic approaches capable of dealing with single-step processes become inapplicable in the case of UFC/metal composites. For that reason, advanced reaction determination methodology is employed on the thermoanalytical data of UFC/metal composites in order to probe their reaction mechanisms. Advanced reaction determination methodology not only confirms the findings of the isoconversional kinetic analysis but also provides interesting and important insights into the reactions mechanisms of UFC/metal composites. The obtained set of mechanistic information shows that the thermal degradation of UFC resin follows multi-step reaction mechanisms pursuing several parallel/consecutive reactions with predominantly nucleation/growth pathways. A detailed interpretation of the obtained kinetic parameters along with the dependence of reaction mechanism of UFC resin on the nature/contents of metal particles (especially zinc and aluminum) has also been given and discussed.[21–23]

It is worth noticing that the applications of the advanced kinetic approach are not merely limited to predicting the mechanisms of polymer composites filled with metal particles. An interesting and growing class of materials comprises composites of polymers filled with graphene/graphene oxide (GO) and/or carbon nanotubes (CNT's) in regard to their practical relevance. They are capable of finding applications in energy storage, sensors, fuel cells, radar-absorbing material, wind turbine blades, aerospace, automobiles, electronics devices, electromagnetic interface shielding, biomedical applications, etc.[24–29] Similar to polymer/metal composites, unraveling thermal degradation mechanisms of polymer/Graphene (or GO) and/or polymer/CNT's composites may help in process control and therefore efficiency optimization of these materials. Advanced kinetic approach, in this context, might be highly useful in predicting their thermal degradation mechanisms irrelevant of filler particle attributes (efficacious for both the micro as well as nanocomposites).

Conclusion

This mini-review has reported the most recent advances in kinetic approaches to predict the mechanisms of thermal degradation processes occurring in polymer composites. The merits and demerits of the pre-existing reaction model determination methodologies to cope with the condensed phase processes are discussed. An important flaw related to the pre-existing reaction model determination approaches is their non-capability of dealing with the complex multi-step processes. In turn, the recently suggested advanced kinetic approach is quite efficacious in predicting the thermal degradation mechanisms of condensed phase processes in general and in polymer composites in particular. Its main advantage is that it is may kinetically describe both simple and complex reactions taking place under isothermal/non-isothermal conditions in materials. Certain applications of the suggested kinetic approach on polymer composites of epoxy and urea-formaldehyde cellulose (UFC) filled with metal particles prove its soundness. Although initially tested for binary polymer composites, the advanced kinetic approach can be quite useful in the case of ternary polymer composites. Nevertheless, the mechanistic complexity in that case might considerably augment.

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Conflict of interest

The author declares no conflict of interest.

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