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Thermal degradation kinetics of resole phenol-formaldehyde resin/multi-walled carbon nanotube/cellulose nanocomposite

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ABSTRACT

This study investigated thermal degradation kinetics of multi-walled carbon nanotubes (MWCNTs) reinforced resole phenol-formaldehyde (PF) resin/cellulose nanocomposite, using thermogravimetry (TG) analysis as a function of the content or surface treatment of MWCNTs with or without a surfactant. FT-IR spectroscopy showed that the oxidation provided hydroxyl or carboxyl groups with MWCNT's surface while the silanization resulted in the silane attachment to MWCNT's surface. Conventional TG (CTG) thermograms demonstrated six thermal degradation steps, corresponding to various components of the nanocomposite, and also showed that the use of surfactant hastened thermal decomposition of the nanocomposite. The activation energy (E) obtained by the Kissinger method slightly increased as the MWCNT content increased while that of the cellulose degradation was independent on the MWCNT content. Both the oxidation and silanization treatments of MWCNTs' surface resulted in an increase of the E values compared to that of the control sample. The activation energy (E_α) based on the isoconversional method increased up to $\alpha = 0.5$, and then was rapidly elevated to fluctuations. The activation energy (E_m) based on the temperature modulated TG (MTG) analysis was within the range of the E value calculated by the Kissinger method for the thermal degradation of cellulose, a main component of the nanocomposite. These results show that MTG method provides similar activation energy to that of CTG method for thermal degradation of the nanocomposite, and indicate that MTG method be efficiently used to obtain activation energy without many scans from multiple heating rates.

1. Introduction

Two types of carbon nanotubes (CNTs), i.e., single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) are available in these days since the discovery of CNTs in 1991 [1]. SWNTs consist of a single sheet of graphene rolled seamlessly to form a cylinder with diameter of order of 1 nm and length of up to centimeters [2]. By contrast, MWCNTs consist of an array of such cylinders formed concentrically and separated by 0.35 nm, similar to the basal plane separation in graphite [1]. MWCNTs can have diameters from 2 to 100 nm and lengths of tens of microns. Owing to unique properties such as excellent strength, modulus, electrical and thermal conductivities along with a low density, CNTs resulted in a tremendous attraction for research on polymer-based nanocomposite [3,4]. For example, tensile properties of SWCNTs were measured inside an electron microscopy, and reported tensile moduli between 0.32 and 1.47 TPa and strengths between 10 and 52 GPa [5]. Tensile modulus and strength using bundles of MWCNTs prepared by chemical vapor deposition (CVD) was reported as 0.45 TPa and ∼4 GPa [6]. Yu et al. [5] also employed the same method, and obtained modulus values of 0.27–0.95 TPa and tensile strengths in the range 11–63 GPa. However, there is a variation in these properties of CNTs upon fabrication methods such as laser ablation [7] and CVD [8,9], or, decomposition of CO [10].

Polymer-based nanocomposite is commonly defined as the combination of a polymer matrix and additives that have at least one dimension in the nanometer range. In order to exploit excellent mechanical properties of CNTs, varieties of polymer matrices were used to provide with reinforcements as reported in a review [11]. A quite number of works have been done on CNTs reinforced nanocomposite based on thermoset polymers even though it was much less than those on thermoplastic polymers [11]. Since the first report [12], epoxy resins have been widely studied as a potential matrix for CNTs-based nanocomposite due to their wide range of industrial uses [13–16].

Among thermosetting polymers, phenol-formaldehyde (PF) resin is one of the most common formaldehyde-based resins which provide outstanding performance in adhesion, high temperature resistance, flame resistance and electric insulation. Thus, PF resins have been used to improve mechanical properties, moisture

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resistance, or fire resistance in many applications. For example, PF resin is impregnated into cellulose paper to fabricate decorative or protective laminates on the surface of wood-based composite products. These laminate papers are hot-pressed onto the surface of composite wood products to provide a hard surface finish. Excellent mechanical properties of MWCNTs are expected to provide a very effective reinforcement with PF resin that is impregnated into cellulose paper.

A very limited work has been done on PF resin as a matrix for CNTs reinforcement because CNTs are extremely difficult to disperse in a polymer matrix due to its agglomeration caused by Van der Waals force [17]. For example, Yin et al. [18] used CNTs to reinforce novolac PF resin in powder form for the preparation of PF resin/graphite composites, and found that the surface modification of CNTs by introducing hydroxyl groups improved bending strength and conductivity of the composites. Liu and Ye [19] also modified MWCNTs by introduction of carboxyl group, benzene ring, or boric acid, and found an enhanced thermal stability of MWCNTs/PF resin nanocomposite. The improved thermal stability was ascribed to a better interfacial interaction between MWCNTs and PF resin matrix.

In this study, we attempted to fabricate MWCNTs reinforced resole PF resin/cellulose nanocomposite as a potential candidate for surface laminates on wood-based composite panels. Therefore, this study focused on thermal stability of the nanocomposite in order to assess their feasibility as surface laminates for wood-based composite products. A brief summary of relevant thermal decomposition kinetics follows.

2. Thermal degradation kinetic analysis

2.1. CTG data

The single-step kinetic equation for polymer degradation is usually expressed as [20,21]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α represents the extent of conversion (α = 0–1), t is time, $k(T)$ is the rate constant, and $f(\alpha)$ is the reaction model, which describes the dependence of the reaction rate on the extent of reaction. The extent of conversion, α, is experimentally determined by the below equation using TGA data.

$$\alpha = \frac{m_0 - m(T)}{m_0 - m_\infty} \tag{2}$$

Where m_0 is the initial mass, m_∞ is final mass, and $m(T)$ is a mass at a temperature. In most cases the temperature dependence of $k(T)$ can be satisfactorily described by the Arrhenius equation, whose substitution into Eq. (3) yields:

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

where E is the activation energy and A is the pre-exponential factor. Various methods can be applied to find the kinetic parameters, particularly the E when kinetics follows a single equation expressed as the Eq. (1).

For non-isothermal conditions, the Eq. (3) is converted into the Eq. (4) when the temperature is raised at a constant heating rate, β:

$$\beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{4}$$

Assuming β = constant, and rearranging in terms of two variables gives:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)dT \tag{5}$$

Integration of Eq. (5) involves solving the temperature integral in the following Eq. (6):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_\alpha}\exp\left(\frac{-E}{RT}\right)dT = \frac{AE}{\beta R}p(x) \tag{6}$$

where $x = E/RT$. Since the $p(x)$ function, the temperature integral, has no exact analytical solution, it can be solved using either approximations or numerical integration [21]. One of the simplest approximations by Doyle [22] is given as Eq. (7):

$$p(x) = 0.0048e^{-1.0516x} \tag{7}$$

From Eqs. (6) and (5), it follows

$$\ln(\beta) = -5.331 - 1.0516\left(\frac{E}{RT}\right) + \ln\left(\frac{AE}{Rg(\alpha)}\right) \tag{8}$$

The E can be calculated from a plot of log β versus $1/T$. Since the multi-heating rate method uses the relationship between the peak temperature (T_p) of the DTG peak and its corresponding heating rate.

Another method by Kissinger [23] is based on the fact that at the T_p of a DTG peak, the maximum conversion rate is equal to zero:

$$\left[\frac{d}{dt}\left(\frac{d\alpha}{dt}\right)\right]_{T=T_p} = 0 \tag{9}$$

According to Kissinger, appropriate approximations lead to the simple Eq. (10) derived from Eq. (9):

$$\ln\left(\frac{\beta}{T_{p2}}\right) = -\frac{E}{RT_p} + \ln\left(\frac{AR}{E}\right) \tag{10}$$

which is the equation of a straight line between $\ln(\beta/T_{p2})$ and $-1/T_p$. The E can be calculated from the slope and the pre-exponential factor from the intercept. Thus, the Kissinger method provides a single value of activation energy for the whole reaction process.

The isoconversional kinetic analysis or so-called “model-free kinetics” method requires performance of a series of experiments at different temperature programs and yield the values of effective activation energy (E_α) as a function of conversion (α).

Coat and Redfern [24] suggested the following approximations for the $p(x)$ function:

$$p(x) = x^{-2}e^{-x}\left(1 - \frac{2}{x}\right) \tag{11}$$

In general, the part of $(1 - 2/x)$ of the Eq. (7) is neglected and an oversimplified approximation leads to Eq. (12), which is used [25].

$$p(x) = x^{-2}e^{-x} \tag{12}$$

Submitting Eq. (12) into Eq. (6) and taking logarithm results in an isoconversional equation:

$$\ln\left(\frac{\beta_i}{T^2_{\alpha,i}}\right) = -\ln\frac{A_\alpha R}{E_\alpha g(\alpha)} - \frac{E_\alpha}{RT_{\alpha,i}} \tag{13}$$

The subscript i denotes different heating rates. The Eq. (13) provides a straight line between $\ln(\beta/T^2_{\alpha,i})$ and $1/T_{\alpha,i}$. The E_α can be calculated from the slope and the pre-exponential factor from the intercept. The above isoconversional method was proposed by Vyazovkin and Sbirrazzuoli [26], which was used in this study.