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Effect of polyhedral oligomeric silsesquioxane nanoparticles on thermal decomposition of cyanate ester resin

Y. Lin, M. Song

Department of Materials, Loughborough University, Loughborough LE11 3TU, UK

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ABSTRACT

A series of cyanate ester resin (CY)/polyhedral oligomeric silsesquioxane (POSS) nanocomposites were prepared successfully. Morphology and thermal stability of the CY and its nanocomposites with POSS were studied by means of scanning electron microscopy (SEM) and Thermogravimetric Analysis (TGA). With the addition of POSS, the thermal stability of CY is dramatically improved. Under air atmosphere, the full decomposition temperature increased by 146 °C, with incorporation of only 1 wt% POSS. The heat generated by the thermal degradation of the CY/POSS nanocomposites is around 4 times less than that of the neat CY. Under nitrogen atmosphere, the char yield of the CY increased up to 15 wt% with addition of the POSS. Besides, the heat required for the degradation of the CY/POSS nanocomposites was much higher than that of the neat CY. These results reveal that the incorporation of the POSS resulted in change of the degradation mechanism of CY. The breakdown of POSS/CY network retarded the breakdown of the triazine rings of CY hence the thermal stability of POSS/CY nanocomposites were improved comparing to that of pristine CY. Furthermore, the formation of char retarded the degradation of benzene rings as well.

1. Introduction

With technological development and increasing demand for materials with enhanced properties, cyanate ester resins (CYs) have been brought to popular attention, due to their superior properties compared with the conventional thermosetting materials [1]. For instance, the glass transition temperature of CYs is located between 250 °C and 290 °C, which fills a temperature regime intermediate between that of epoxy resins and hazardous polyimide or BMI resins [2]. The high glass transition temperature results in their outstanding dimensional stability and thermal stability, even at temperature as high as 350 °C. Furthermore, unlike polyimide, cyanate ester resins are easy to process in a manner similar to epoxy [3]. The moisture absorption (0.6%–2.5%) and moisture absorption rate of CYs are also lower than those of epoxy, polyimide, and BMI resins. Besides, excellent mechanical properties, good radiation resistance, high flame resistance, low dielectric constant, low dissipation factor and low outgassing make CYs currently in widespread use for high temperature applications, structural aerospace composites, microwave transparent composites, encapsulants, adhesives, and electronic insulating applications [4–6]. However, although the CYs own outstanding dimensional stability and thermal stability, they still cannot meet the requirements at the crucial temperature above 400 °C, for applications in advanced military and aerospace engineering. Thus, reinforcement of the CYs for high performance applications becomes necessary. In last decade, hybrid organic polymer/inorganic nanocomposites have attracted plenty of research interest for various applications, such as in mechanical, thermal and electronic fields [7–11]. It is believed that inorganic nanoparticle/CY nanocomposites can be one of solutions to improve their thermal stability, in order to meet the ever-increasing demand for high-performance polymeric materials.

POSS reagents, which own nanosized ladder, cage, or partial cage structures, are interesting silicon based compounds with the formula (RSiO1.5)n. The R can be hydrogen, or a range of polar structures and functional groups. The size of POSS is between 1 and 3 nm in diameter, which is recognised as one of the smallest particles of silica. Due to their hybrid (inorganic-organic) nature, the POSS reagents become compatible with polymers, biological systems or any organic surfaces. Thus, incorporation of POSS reagents into organic polymers offers a unique opportunity to prepare nanocomposites with truly molecular dispersions of the inorganic fillers [2,12]. POSS reagents have outstanding thermal stability and attractive oxidative resistance even at temperatures that higher than 500 °C. Furthermore, the insulating property and gas permeability of the POSS are also good [13]. The enhancement of physical properties of polymeric materials by incorporation of POSS has been shown in a wide range of thermoplastics [14–17], as well as

* Corresponding author.
E-mail address: m.song@lboro.ac.uk (M. Song).
thermosetting materials [18–21]. Modification of CYS with POSS has been attempted by several groups. Liang et al. [22] incorporated octaaminophenyl-POSS and cyanopropylcyclopentyl-POSS into a CY to prepare the CY/POSS nanocomposites. It was found that both types of POSS additives can improve the high-temperature mechanical properties of the CY. The storage modulus values of the octaaminophenyl-POSS/CY nanocomposites improved. Zhang et al. [23] prepared a series of CY/expoxy-functionalized POSS (Ep-POSS) nanocomposite by casting and curing. The Ep-POSS/CY nanocomposite showed enhancement in impact strength and flexural strength due to formation of tough whirls and fiber-like pull-outs during fracture, which are induced by addition of Ep-POSS. Furthermore, the thermal decomposition temperature of 10 wt% Ep-POSS/CY nanocomposite is 44 °C higher than that of pristine CY. Jothibasu et al. [24] prepared POSS/CY nanocomposites through an in situ method by thermal curing with application of diaminodiphenylmethane as a coupling agent. The thermal and morphological properties of the CY incorporated with different concentration of the POSS, were studied. The 5 wt% POSS/cyanate ester nanocomposite displayed the highest glass transition temperature among those studied. Furthermore, the thermal stability of nanocomposites increased with the increasing concentration of the POSS.

It is believed [2,12,22,25,26] that the addition of functionalized POSS could affect the network formation, mechanical and thermal performance of CYS significantly. However, the influences of POSS on the thermal properties of CYS have never been studied systematically and fundamentally. For instance, is there any difference in thermal performance of CYS and its nanocomposites with POSS under air and nitrogen atmosphere? Does the degradation mechanism of CYS change with the incorporation of POSS? At what stage does the addition of POSS show the most significant influence? In order to develop high performance CY/POSS nanocomposites for crucial military and aerospace applications, the effect of POSS on the thermal performance of CYS needs to be clearly understood. Thus, in this paper, the influences of POSS on thermal performance of a CY under air and nitrogen condition were carefully studied. The degradation activation energies of the CY and its nanocomposite with POSS were calculated, in order to reveal the fundamental theory behind.

2. Experimental

2.1. Materials

Cyanate ester resin (CY, trade name: PT-30), was purchased from LONZA LTD. The CY has a low viscosity (80 c.p.s.) at its processing temperature (120 °C), and has < 0.5% volatiles and generates no gaseous by-products during cure. TriSilanolPhenyl POSS (C42H38O12Si7 MW = 931.34 g/mol) was purchased from Hybrid Plastics Inc. Fig. 1 shows a schematic of the respective molecular structures.

2.2. Preparation of CY/POSS mixtures and cure of CY/POSS nanocomposites

The CY resin was firstly held at 100 °C for 30 min with magnetic stirring to remove moisture. Afterwards, the resin was heated to 120 °C, and calculated amounts of the TriSilanolPhenyl POSS were added into the low viscosity resin to yield the CY/POSS mixtures with various POSS concentration. These mixtures were mixed by stirring at 120 °C for 80 min. After mixing, all the POSS/CY resins as prepared were sealed in glass bottles and stored at –20 °C for further use.

In order to cure the CY/POSS nanocomposites, the CY/POSS mixtures were firstly pre-cured at 100 °C in vacuum oven for 30 min to remove all the moisture. Afterwards, the CY/POSS resins were cured at 230 °C for 1 h, and followed by post-curing at 290 °C for another 1 h.

2.3. Characterisation

To observe dispersion of the POSS in the CY matrix, scanning electron microscopy (SEM) images of the fracture surface of the CY/ POSS nanocomposites were taken by field emission gun scanning electron microscopy (SEM) (LEO 1530VP instrument). The samples were fractured at room temperature. The samples with fractured surface on the top were placed on specimen holder using double-sided carbon conductive tape. Gold coating was applied afterwards for better conductivity. Thermogravimetric Analysis (TGA) was performed on a DSC-TGA 2950 instrument (TA instruments). The samples were heated from room temperature to 1000 °C at a heating rate of 10 °C/min (5 and 15 °C/min for the measurement of activation energy). The rate of gas (air or N2) was 60 ml/min.

3. Results and discussion

Fig. 2 shows the SEM images of the CY and its nanocomposites incorporated with the POSS with various concentrations. It can be shown clearly that dispersion of the POSS in the CY is homogeneous. For the CY/POSS nanocomposite with low concentrations, such as 1 wt%, there is no aggregation of the POSS found. For the CY/POSS nanocomposites with high concentrations (5 wt% and 10 wt%), a few particles with diameter of around 700 nm were observed. These results indicate that the aggregation of the POSS molecules occurred with high concentration of the POSS incorporation.

Fig. 3 shows TGA results of the CY under air and nitrogen atmosphere. The thermal degradation of the CY involved three reaction stages [27]. Under air, the first stage started from 415 °C, and the thermoxidative degradation of oxygen bond between the phenyl and triazine rings led to approximate 10% weight loss. The second weight loss of 15% happened between 449 °C and 601 °C, due to the breakdown of the triazine rings. After 601 °C, the third reaction which is benzene rings degradation resulted to approximately 75% weight loss. The decomposition process finished at 766 °C. Table 1 lists the key parameters of TGA analysis. The CY became more durable under nitrogen atmosphere than under air atmosphere. The first stage
degradation happened from 418 °C to 451 °C, with about 14% weight loss, followed by second stage degradation ending at about 701 °C. Even if the temperature increased to 1000 °C, the CY still did not completely degrade. Thus, the air atmosphere showed an accelerating effect on the degradation of the CY.

Fig. 4 shows the TGA results for the CY/POSS systems with various POSS concentration under both air and nitrogen atmosphere. Under air, although a slight impairment showed on thermal stability of the CY/POSS nanocomposites at the beginning, the addition of POSS improved the thermal stability of the CY significantly at above 600 °C. The full decomposition temperature increased from 776 °C to 916 °C, with the incorporation of only 1 wt% POSS. It is interesting that the thermal stability of the POSS/CY nanocomposites became worse with the increasing concentration of the POSS. This phenomenon may be relative to the aggregation of POSS at high concentrations. At high concentration above 5 wt%, the network formation of the POSS is not as good as that of 1 wt% due to aggregation (observed by SEM), which led to less improvement in the thermal stability. Furthermore, it is remarkable that the heat generated by the degradation of the CY/POSS nanocomposites was > 4 times less than that of the pure CY, as shown in Fig. 4 (B). The heat generated during degradation is due to break down of chemical bonds. Thus, this observation indicates that the addition of the POSS improved the thermal stability by retarding the breakdown of CY. Under nitrogen atmosphere, the char yield increased up to 15%
with addition of the POSS. Similar with the situation under air atmosphere, for the CY/POSS nanocomposites, the heat required for degradation under nitrogen atmosphere was much higher. Thus, the CY/POSS nanocomposites were more thermally stable comparing to the CY.

Studying thermal degradation kinetic of composites is vitally important for understanding the mechanisms of thermal decompositions of composites. Activation energy for decomposition of materials is crucial parameter for estimation the thermal stability and decomposition kinetic of materials. The activation energies of the CY and its nanocomposites versus the conversion during decomposition process under air atmosphere, were investigated here. The calculation of activation energy is based on an integral method, Flynn-Wall-Ozawa (F-W-O) method [28–31], which leads to \(-\frac{E_a}{R}\) from the slope of the line determined by plotting \(\log (\frac{d\theta}{dt})\) against \(1/T\) at any certain conversion.

For a single reaction, the conversion \(\alpha\) is defined as:

\[
\alpha_i = \frac{W_0 - W_i}{W_0 - W_f}
\]  

where, \(W_0\), \(W_i\), and \(W_f\) are initial weight before the reaction, weight at

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_{o1})</td>
<td>(T_{c1})</td>
<td>WL (%)</td>
</tr>
<tr>
<td>CY air</td>
<td>415</td>
<td>449</td>
<td>10</td>
</tr>
<tr>
<td>CY N(_2)</td>
<td>418</td>
<td>451</td>
<td>14</td>
</tr>
</tbody>
</table>

\(T_o\): onset temperature at which decomposition started.
\(T_c\): completion temperature at which decomposition finished.
WL: weight loss.

Fig. 3. Thermal analysis of pure CY with a heating rate of 10 °C/min under air atmosphere (60 ml/min) (A), and under nitrogen atmosphere (60 ml/min) (B).

Fig. 4. TGA results of CY/POSS systems. (A) Residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/POSS system, with a heating rate of 10 °C/min under air atmosphere (60 ml/min), (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/POSS system with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min).
time $t$ during the reaction, and final weight after the reaction, respectively.

If there are $n$ reactions during a typical decomposition process, the total conversion $\alpha$ is defined as:

$$a = \frac{\sum_i (W_0 - W_i)}{\sum_i (W_0 - W_{i+1})}$$

(2)

At the same conversion $a$, the $T$ is different for different heating rate. According to F-W-O equation, heating rate $\beta$ was transformed to $\log(\beta)$, and temperature $T$ was transformed to $1/T$. The $\log(\beta)$ was plotted against $1/T$, to get a linear trend line. The activation energy of conversion $a$, was calculated through the slope of the linear trend line, in which the slope equals to $-0.4567 \times \frac{E_a}{R}$.

F-W-O equation is shown as follows:

$$\log(\beta) = \log\left(\frac{AE_a}{Rg(a)}\right) - 2.315 - \frac{0.4567E_a}{RT}$$

(3)

where, $\beta$ is heating rate, $\beta = \frac{dT}{dt}$, $A$ is the pre-exponential factor (min$^{-1}$), $T$ is the absolute temperature (K), $R$ is the gas constant (8.314 J/K mol), and $E_a$ is the apparent activation energy.

Fig. 5 demonstrates the TGA results for the calculation of activation energies. The better thermal stability was shown at higher heating rate.

Fig. 6 shows the activation energy of the CY and the CY/POSS system. For the pure CY, the activation energy gradually increased in stage 1. However, it is quite interesting that in the stage 2, the activation energy increased significantly at the very beginning, and then decreased dramatically, became negative and reached its lowest value at conversion of 0.2, followed by a rapid increase again. The emergence of negative activation energy is relative to the reaction of nitrogenous chemicals, in this case, the degradation of triazine rings.

Arrhenius equation is shown as follows:

$$k = Ae^{-E_a/RT}$$

(4)

where $k$ is Arrhenius type reaction rate constant, $A$ is the pre-exponential factor, $T$ is the absolute temperature, $R$ is the gas constant, and $E_a$ is the apparent activation energy.

Generally, an increase in temperature ($T$) increases the reaction rate ($k$) for most of reactions. According to Arrhenius equation, this situation results to a positive activation energy. However, there are a very small number of exceptions for elementary reaction, which the reaction rate decreased with the increasing temperature, leading to negative activation energy, for example, oxidation of nitrogen monoxide. For a multistep mechanism reaction, it is also possible that the apparent activation energy is negative. The negative activation energy indicates that the reaction rate decreased with the raising temperature, which may imply high barrier for the reaction. According to the current result, it is inferred that the reaction of stage 2 became a multistep mechanism reaction, or a reversible reaction, rather than the simple breakdown of the triazine rings for pure CY.

For the POSS/CY nanocomposites, the addition of the POSS increased the activation energy throughout the decomposition process, which means formation of the higher reaction barrier. It is remarkable that the activation energy at stage 2 became positive, which indicates that the addition of the POSS changed the degradation mechanism of the CY at stage 2. According to our previous research on curing dynamic and network formation of the POSS/CY nanocomposites [32], The POSS reacted with the CY through formation of $\equiv O\equiv(\equiv C\equiv NH)\equiv O\equiv$ bond, to form a compact network during cure. Thus, relating this result to the thermal degradation results, it is believed that the breakdown of POSS/CY network dominated the degradation process at stage 2. The breakdown of POSS/CY network consumed huge amount of heat. Thus, this process created high barrier for the decomposition of the composite, and retarded the breakdown of the triazine rings.

Furthermore, the activation energy of the POSS/CY nanocomposite at the very beginning of stage 3 (at conversion of 0.3) is four times higher than that of the pure CY. This observation implies the formation

Fig. 5. TGA results of CY and its nanocomposites with different heating rates (A) CY, and (B) 5 wt% POSS/CY under air atmosphere (20 ml/min).

Fig. 6. Activation energy of CY and its nanocomposites with the 5 wt% POSS during decomposition versus conversion rate under air atmosphere.
of char, which retarded the degradation of the main body of the nanocomposites. The activation energy of the POSS/CY nanocomposite is higher than that of the pure CY by at least 30% throughout stage 3. The higher activation energy indicates more heat required for the degradation of the CY and its nanocomposites with the POSS. Thus, the thermal stability of the POSS/CY nanocomposites is significantly improved compared to that of pure CY in air.

4. Conclusions

The degradation of CY involved three reaction stages, which are thermoxidative degradation of oxygen bond between the phenyl and triazine rings, breakdown of the triazine rings, and benzene rings degradation. The air atmosphere showed an accelerating effect on the degradation of CY. With the addition of POSS, the thermal stability of the CY was dramatically improved. Under air atmosphere, the full decomposition temperature increased by 146 °C, with the incorporation of only 1 wt% POSS. The heat generated by the thermal degradation of the CY/POSS nanocomposites was more than four time less than that of the pure CY. Under nitrogen atmosphere, the char yield increased up to 15 wt% with the addition of POSS. The heat and degradation activation energy required for the degradation of the CY/POSS nanocomposites are much higher than that of pure CY. The result reveals that the incorporation of the POSS resulted in change of the degradation mechanism of CY. The breakdown of POSS/CY network dominated the degradation process at stage 2. This process created high barrier for the decomposition of the composite, and retarded the breakdown of the triazine rings. Furthermore, the formation of char retarded the degradation of benzene rings.

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