

INVESTIGATION OF PYROLYSIS CHARACTERISTICS OF SILICONE-PHENOLIC MATRIX NANOCOMPOSITES THROUGH KINETIC ANALYSIS AND REAXFF MD SIMULATIONS

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ABSTRACT

The pyrolysis characteristics of the polymeric nanocomposites are dominantly governed by the pyrolyzable components to accommodate a specific thermodynamic environment. The pyrolysis behaviour of the pyrolyzable system including silicone and phenolic aerogels (SiOC/PR) of siliconemodified phenolic aerogel matrix nanocomposites was investigated by TG and TG-FTIR, which shows that a mass ratio of PR to SiOC of 3:1 exhibits better thermal stability. The distributed activation energy model (DAEM) was employed to investigate the decomposition kinetics, and the results show that the five-pseudo-components DAEM effectively represents the decomposition conversion signature of SiOC/PR. Methanol, the major volatile product affecting the thermal decomposition of the SiOC/PR system, was analysed at an atomic scale by ReaxFF molecular dynamics (MD) simulations for its reaction pathways. The MD results show that there are two main pathways for the production of methanol, which are extraction reactions of methyl intermediates and hydroxymethyl intermediates, respectively. The Si-O-Si backbone of SiOC can bridge the PR fragments at elevated temperatures, which impacts the yield of condensed residues. Based on TG experimental data, the dependence of weight loss on temperature for SiOC/PR systems with different mixture ratios was predicted by artificial neural networks (ANN). The ANN with a 20*3*1 topology exhibits promising prediction performance. Our work aims to provide practical guidance for engineers to optimize process procedures with a better knowledge of the features of chemical systems.

1 INTRODUCTION

Polymeric composites are a vast and versatile class of ablative thermal protection materials, which is typically employed to protect vehicles from extreme heating during re-entry flight [1]. Polymer matrixes like phenolic resins absorb heat and release gaseous products during high-temperature thermal decomposition, which block heat transfer and leave the residue char [1, 2]. The char phase with high emissivity can radiate heat efficiently and act as a thermal insulator [3]. A variety of formulation types such as honeycomb cells and silicones are utilized as filler components in polymeric composites to improve heat/oxidation resistance [4, 5]. For instance, the lightweight silicone-modified phenolic aerogel matrix (SiOC/PR) nanocomposites provide superior oxidation resistance by silicone component decomposition at elevated temperatures forming inorganic silica, which covers the surface of reinforced fibres and the charred matrix to prevent in-depth diffusion of oxygen [6-8]. However, the addition of the pyrolyzable silicone results in a more complicated pyrolysis behaviour of the composites, and the evolution of the pyrolysis gas and the decomposition mechanism are poorly understood.

The typical experimental technique to analyse thermal decomposition is thermogravimetric analysis (TGA), which allows analysing the kinetics of solid-state reactions in the dependence of weight loss on temperature/time [9]. Some coupled thermal analysis techniques like thermogravimetric-Fourier transform infrared spectroscopy (TG-FTIR) analysis are also performed for the quantitative or qualitative analysis of pyrolysis gaseous products [10-12]. Based on TG data from multiple heating procedures, apparent activation energy *E*, pre-exponential factor *A*, and mechanism function $f(\alpha)$ can be obtained by kinetic methods. The isoconversional method is suitable for solving *E* with unknown $f(\alpha)$, and the linear model fitting method is capable to find $f(\alpha)$, yet both methods are used to characterise the

single-step decomposition process and perform poorly for multi-step decomposition behaviour. As a comparison, the distributed activation energy model (DAEM) separates the multi-step decomposition process into a series of independent reactions, each governed by a mathematical distribution function [13, 14]. Therefore, DAEM is widely used to study the pyrolysis kinetics of polymers with multiple decomposition stages [15-17].

In contrast to experimental chemistry, computational chemistry such as molecular dynamics (MD) simulation techniques can reveal the physics or chemistry of bulk materials at the atomic scale [18, 19]. MD simulations are performed using the molecular force field, which describes the interactions between atoms via energy terms like covalent, van der Waals, and electrostatic interactions [20]. Molecular force fields can be divided into nonreactive and reactive force fields, relying on whether covalent bonds can be created and broken. ReaxFF, a reactive force field developed by van Duin et al., utilises a bond-order formalism to describe interactomic interactions and is widely used in the study of decomposition reactions [21-24].

The artificial neural network (ANN) is extensively applied for estimating the nonlinear relationship between reaction conditions and pyrolysis characteristic quantities in thermal processes. Sun et al. developed a three-layer back propagation (BP) neural network to predict the sensitivity and yield of gas products using reaction temperature, sample size, and space velocity as inputs [25]. Chemical kinetic parameters were also predicted using ANN models by Sunphorka et al. [26, 27]. Bi et al. used heating rate, temperature, and mixture ratio as inputs to predict mass loss during pyrolysis process by ANN techniques [28, 29]. In summary, ANN is widely employed in pyrolysis studies and can provide a reference for selecting the relative content of pyrolyzable components for SiOC/PR nanocomposites.

The rest of the paper is organized as follows. Firstly, the decomposition stages were identified by macroscopic thermal analysis experiments and the primary gaseous products were qualitatively assessed. Subsequently, the kinetic parameters of each reaction stage were accurately determined by DAEM to gain insight into the kinetic behaviour. Then the evolution and reaction pathways of the critical gaseous products were analysed at an atomic scale by ReaxFF MD simulations to elucidate the pyrolysis behaviour and the effect of SiOC modifiers. Finally, the ANN technique was applied to predict the temperature dependence of weight loss for the SiOC/PR systems during pyrolysis process.

2 METHODOLOGIES

2.1 Materials preparation

Since fibres in the SiOC/PR nanocomposites hardly pyrolyze, only the pyrolyzable SiOC and PR components were considered. The material used in this study is premixed SiOC and PR powder, manufactured by Harbin Institute of Technology, China. Details on material preparation can be found in Ref. [7, 8]. Four different mass ratios of SiOC/PR systems were employed for experiments. For simplicity, the mass ratios of SiOC to PR of 1:2, 1:3, 1:4, and 1:5 are denoted as SiOC/PR-2, SiOC/PR-3, SiOC/PR-4, and SiOC/PR-5, respectively.

2.2 Experimental methods

2.2.1 TG experiments

The thermal decomposition of SiOC/PR systems was carried out by TG-DSC simultaneous thermal analyzer (NETZSCH STA449F3, Germany). The TG tests were performed on 6-10 mg of SiOC/PR powder in argon ambient with a flow rate of 70 mL/min (50 mL/min as purge gas and 20 mL/min as protective gas). The SiOC/PR powder was heated from ambient temperature to 1000 °C with a linear heating rate of 10 °C/min.

2.2.2 TG-FTIR experiments

The chemical substances of SiOC/PR powder during pyrolysis process were detected and identified by TG-FTIR (Nicolet iS50, USA). FTIR spectra with a wavenumber range from 4000 cm⁻¹ to 500 cm⁻¹ were observed with a resolution of 4 cm⁻¹. The SiOC/PR powder was treated from room temperature to 1000 °C with a linear heating rate of 10 °C/min in argon environment.

2.3 Kinetic model

The majority of kinetic methods used in thermal analysis consider the conversion rate to be a function of two variables (temperature T and conversion extent α) [13],

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha)$$
(1)

where t, k(T), and R are the time, Arrhenius rate constant, and gas constant, respectively.

The DAEM hypothesizes that the entire pyrolysis process consists of several parallel first-order reactions. Each pseudo-reaction has a separate activation energy distribution. The DAEM formula can be expressed as

$$\frac{d\alpha}{dT} = \int_0^\infty \frac{A}{\beta} \exp\left[-\frac{E}{RT} - \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT\right] f(E) dE$$
(2)

where β and f(E) are the heating rate and activation energy distribution function, respectively. The logistic distribution with a broader tail was used in this work because it performs better than the Gaussian distribution at the onset and end of each pseudo-stage for the complex decomposition processes of organic polymers [17]. In addition, the logistic distribution has only one parameter to be optimized compared to the Weibull distribution [30]. The logistic distribution function is

$$f(E) = \frac{\pi \exp\left[-\pi (E - E_0) / (\sqrt{3}\sigma)\right]}{\sqrt{3}\sigma \left\{1 + \exp\left[-\pi (E - E_0) / (\sqrt{3}\sigma)\right]\right\}^2},$$
(3)

where σ and E_0 are the standard deviation and mean activation energy for each pseudo-stage, respectively [17].

The discrete form was considered as a summation of each pseudo-component,

$$\frac{d\alpha}{dT} = \sum_{i=1}^{n} c_i \left(\frac{d\alpha}{dT}\right)_i,\tag{4}$$

where n is the number of pseudo-components. The c is the weighting coefficient for the pseudo-component and sum to unity.

The residual sum of squares (*RSS*) and fitness parameter (*Fit*) were applied to evaluate the prediction performance of DAEM, which are expressed as Eq. (5) and Eq. (6),

$$RSS = \sum_{i=1}^{n_d} \left[\left(\frac{d\alpha}{dT} \right)_{\exp, i} - \left(\frac{d\alpha}{dT} \right)_{\operatorname{cal}, i} \right]^2,$$
(5)

$$Fit(\%) = 100 \times \frac{\sqrt{RSS / n_d}}{(d\alpha / dT)_{exp, max}}$$
(6)

where n_d and $(d\alpha/dT)_{exp, max}$ are the number of experimental data points and the maximum experimental conversion rate, respectively. Smaller *RSS* and *Fit* indicate a better quality of DAEM, meaning that the calculated kinetic parameters can effectively characterize the pyrolysis kinetics of the SiOC/PR systems.

2.4 Molecular dynamics simulations

2.4.1 Simulation modelling

The schematic diagram of the SiOC/PR nanocomposites at different length scales is shown in Figure 1a, with the macroscopic bulk composites, the microstructure with distributed SiOC network and homogeneous phenolic aerogel covered fibres, and the molecular model of SiOC/PR systems, respectively. Figure 1b shows the modelling process of the molecular model of SiOC/PR systems. The 200 methyltrimethoxysilane (MTMS) monomers and 50 dimethyldiethoxysilane (DMDES) monomers (stoichiometric ratio of MTMS:DMDES = 4:1) were randomly inserted into a cubic box with an initial density of 0.2 g/cm³. Each methoxy/ethoxy group was assumed to be hydrolyzed to a hydroxyl group, enabling crosslinking could be completed in a limited simulation time [31]. The crosslinking procedure is that the two closest Si-OH bonds release one H₂O through a condensation reaction and form one Si-O-Si bond, eventually forming a cross-linked network structure with Si-O-Si as the backbone. Details about crosslinking algorithm can be found in Ref. [32, 33].



Figure 1: The schematic diagram of the SiOC/PR nanocomposites, (a) macro-, micro-, and nano-scale SiOC/PR nanocomposites, (b) molecular model of the SiOC/PR system.

The phenol formaldehyde chains were employed to build the PR model [22, 23, 34]. Each strand has nine repeating units which are linked by a methylene bridge in the ortho-ortho sequence. SiOC/PR systems with different mixture ratios were achieved by varying the number of PR chains, as listed in Table 1. After the SiOC and PR models were assembled, the SiOC/PR systems were achieved the equilibrium configuration through geometric optimization and relaxation under NPT ensemble (constant

particle numbers, constant pressure, and constant temperature).

	SiC	DC		Number	
	Molecular formula	Relative molecular mass (g/mol)	Number of chains	Relative molecular mass (g/mol)	of atoms
SiOC/PR-2		16822	36	33948	6273
SiOC/PR-3	C ₂₉₄ H ₈₉₈ O ₃₄₆ Si ₂₄₅		54	50922	8533
SiOC/PR-4			71	66953	10658
SiOC/PR-5			90	84870	13033

Table 1: The modelling details of SiOC/PR systems with different mixture ratios.

2.4.2 Simulation details

The C/H/O/Si parameter set developed by Newsome et al. [35], a combined set appropriate for describing Si, SiO₂, SiC, and C/O/H systems, was utilized in this work. Isothermal simulations were performed from 2400 K to 3400 K at 200 K intervals, running for 500 ps per interval, to analyze the reaction mechanism. All simulation samplings were done under NVT ensemble (constant particle number, constant volume, and constant temperature), and the Berendsen thermostat was used for temperature control. Newton's equations of motion were time-integrated using the velocity-Verlet algorithm with a time step of 0.1 fs. Periodic boundary conditions were implemented in all directions. All MD simulations were carried out using the LAMMPS simulation software package [36].

2.5 Artificial neural network

The ANN was used to predict the temperature dependence of weight loss of SiOC/PR systems. The BP network was developed based on the Levenberg-Marquardt algorithm with low iteration consumption [37]. About 70% of the 1036 sets of TG experimental data were randomly employed for training the network, and 15% for testing and validating the network, respectively. The activation functions of the neurons in both the input and hidden layers are nonlinear hyperbolic tangent sigmoid functions (tansig), and the activation function for the output layer is the linear function (purelin). The root mean square error (RMSE), mean bias error (MBE), mean absolute error (MAE), and correlation coefficient (R^2) were calculated to evaluate the performance of the trained ANN [28, 29, 38].

3 RESULTS AND DISCUSSION

3.1 Experimental analysis

The TG and DTG curves of SiOC/PR systems at a heating rate of 10 °C/min are shown in Figure 2. The TG tests were repeated three times for each mixture ratio. The DTG curves show that there are three main decomposition stages, with corresponding central temperatures of 270 °C, 515 °C, and 670 °C, respectively. The SiOC/PR-3 has the maximum average residual weight after complete decomposition (58.7 \pm 1.4%), and the lowest weight loss rate in the temperature range of 160-620 °C.



Figure 2: TG and DTG curves of SiOC/PR systems at a linear heating rate of 10 °C/min.

Figure 3 shows the chemigrams of methane, alcohols, and aromatic ring, which are produced by the decomposition of SiOC/PR systems. A small amount of methane was produced by SiOC/PR systems before 500 °C. As the decomposition temperature increases to 610 °C, the IR intensity of methane increases with increasing PR content, suggesting that this temperature range is largely related to the decomposition of PR, which corresponds to a higher mass loss rate in the DTG curves (Figure 2). The IR intensity of methane around 750 °C decreases with the increase of PR content, confirming the correlation between this temperature interval and SiOC degradation. In addition, SiOC/PR-3 has the maximum IR intensity for alcohols and aromatics, which could be related to its highest decomposition rate around 700 °C.



Figure 3: Chemigrams of (a) methane, (b) alcohols, and (c) aromatic ring of SiOC/PR systems during pyrolysis process. The IR absorption intensity in chemigrams was normalized by the initial weight of the powder sample.

3.2 Kinetic analysis

The DTG curves show that the SiOC/PR system exhibits multi-stage decomposition characteristics, for which classic isoconversional kinetic methods cannot accurately obtain the kinetic parameters of each stage. Therefore, A five-pseudo-components DAEM was tried to investigate the decomposition kinetics of SiOC/PR systems in detail. The nonlinear fitting results of the conversion rate curve of the

SiOC/PR-3 using the five-pseudo-components DAEM are shown in Figure 4, which indicates that the five-pseudo-components DAEM can describe the decomposition chemistry of SiOC/PR systems appropriately. The kinetic parameters of SiOC/PR systems are listed in Table 2.



Figure 4: The nonlinear fitting results of the SiOC/PR-3 system by five-pseudo-components DAEM.

System	Pseudo-	$\ln 4 (1/min)$	σ (kJ/mol)	E ₀ (kJ/mol)	С	RSS	Fit (%)
	component						
SiOC/PR-2	1	16.84	8.52	80	0.0588		
	2	25.30	21.32	129	0.1560		
	3	32.41	20.10	218	0.3469	1.75e-7	1.56
	4	48.22	28.91	380	0.2235		
	5	19.00	13.66	160	0.2148		
SiOC/PR-3	1	17.77	4.94	84	0.0759		
	2	33.34	21.70	168	0.1061		
	3	33.75	25.05	229	0.4326	2.86e-7	1.47
	4	44.00	17.89	351	0.2602		
	5	17.96	4.37	170	0.1252		
SiOC/PR-4	1	18.24	4.27	101	0.0572		
	2	35.24	11.54	162	0.1200		
	3	32.36	23.12	219	0.4997	1.89e-7	1.31
	4	44.99	20.05	360	0.2582		
	5	20.94	6.39	197	0.0649		
SiOC/PR-5	1	18.44	3.92	102	0.0492		
	2	35.02	12.48	161	0.1277		
	3	32.39	24.03	219	0.4947	1.04e-7	0.74
	4	45.05	20.89	360	0.2427		
	5	18.71	5.11	177	0.0857		

Table 2: Kinetic parameters of SiOC/PR systems at a heating rate of 10 °C/min calculated by fivepseudo-components DAEM.

3.3 ReaxFF MD simulations

Nearly 120 decomposition products were formed in the 500 ps isothermal simulation for SiOC/PR

systems. As shown in Figure 5, the primary products were identified as water, carbon monoxide, methane, C_2 hydrocarbons (ethylene and acetylene), and methanol. At the 3000 K isothermal temperature, the amounts of intermediates and products of the elementary reactions increase or decrease rapidly within the first 150 ps due to thermal non-equilibrium. The evolution of most products shows a gradual increase or decrease tendency as the mixture ratio of the SiOC/PR system changes. However, the methanol evolves differently, which is reflected in the fact that they are the most productive at a mixture ratio of 1:3 (Figure 5b). Two major reaction pathways for methanol were extracted from MD trajectories, as shown in Figure 6, one of which is the consumption of hydroxyl groups of phenolic fragments by methyl radicals resulting from the dissociation of SiOC side chains, and one of which is the extraction of hydrogen atoms by hydroxymethyl radicals.



Figure 5: Evolution of key decomposition species of SiOC/PR systems at 3000 K isothermal temperature, (a) essential decomposition products of SiOC/PR-3, (b) fitted methanol curves for SiOC/PR systems.



Figure 6: Snapshots of elementary reactions of methanol molecules in SiOC/PR systems during isothermal simulation. The methanol was produced via two key pathways, (a) one of which involves methyl intermediates, and (b) one of which involves hydroxymethyl intermediates.

Within the 500 ps isothermal simulation, the decomposition mechanism of SiOC/PR systems involves chain scission reactions in the parent SiOC chain followed by rearrangements, eventually reaching saturation in the size of the condensed phase. Apart from SiOC/PR-2, the condensed phases of SiOC/PR systems all reach saturation with a condensed phase percentage of 0.6 (the number of atoms

contained in the condensed phase divided by the total number of atoms contained in the chemical system), as shown in Figure 7a. This suggests that there is a threshold for the linkage of Si-O-Si skeleton with specific size to phenolic fragments, which is reached when the composition ratio of the SiOC/PR system in the bulk phase is approximately 1:3. At lower SiOC conditions (e.g., SiOC/PR-5), the abundant PR fragments in the chemical system can no longer be bonded to the Si-O-Si backbone, but generate more pyrolysis gases through free radical reactions. Conversely, the thermal stability of the SiOC/PR nanocomposites may be reduced when the PR content is lower (e.g., SiOC/PR-2). Figure 7b shows the number of chemical bonds contained in the final configuration of the SiOC/PR systems. The final configuration of SiOC/PR-3 has fewer Si-C bonds, while the yields of Si-Si and Si-H bonds are larger, suggesting that the cleavage of the SiOC side chain is more complete and more favourable for the formation of silica-rich residues [21]. Thus, the Si-O-Si backbone formed by the SiOC/PR nanocomposites during pyrolysis process acts as the heat shield and prevents the oxidation of the charred material by the boundary gases under high-temperature conditions [12, 39].



Figure 7: The evolution of condensed phase of SiOC/PR systems during isothermal simulations at 3000 K, (a) time evolution of condensed phase (normalized by the number of atoms in each SiOC/PR system), (b) population of bond types in the final configuration.

3.4 ANN prediction

The schematic diagram of the ANN topology consisting of one input layer, two hidden layers, and one output layer is shown in Figure 8a. The input layer includes three inputs, which are the mixture ratio, the heating rate, and the temperature. The mixture ratio was calculated according to the mass of SiOC divided by the total mass of the powder sample. The two hidden layers contain 20 neurons and 3 neurons, respectively. The output layer is the temperature dependence of the weight residue of SiOC/PR systems at a certain heating rate. The ANN with the topology of 20*3*1 (ANN-20-3) shows the best prediction performance with RMSE, MAE, MBE, and R² of 0.1586, 0.1205, 0.0004, and 0.9999, respectively. The comparison between TG experimental data and the ANN-20-3 prediction is shown in Figure 8b. The predicted results can reproduce the TG curves well, indicating that the ANN-20-3 can effectively predict the decomposition features of SiOC/PR systems.



Figure 8: ANN performance, (a) ANN topology of 20*3*1 with mixture ratio, heating rate, and temperature as inputs and TG data as output, (b) comparison results of TG tests and ANN-20-3 predictions.

4 CONCLUSIONS

The effect of pyrolyzable systems of the SiOC/PR nanocomposites on the pyrolysis characteristics was investigated by DAEM, ReaxFF MD simulations, and ANN predictions. The experimental results show that SiOC/PR-3 exhibits better thermal stability with a solid residue of 58.7±1.4% for complete pyrolysis and the lowest weight loss rate in the temperature range of 160-620 °C. The decomposition conversion behaviour of the SiOC/PR system was well represented by the five-pseudo-components DAEM. Two key reaction pathways for methanol were summarised by MD trajectory, which are via methyl and hydroxymethyl radicals as intermediates, respectively. Compared to the carbon-containing clusters formed by SiOC/PR systems with higher PR content (e.g., SiOC/PR-5), SiOC/PR-3 prefers to form the silica-rich phase, which exhibits better thermal stability due to the Si-O-Si backbone with high bond energy. The ANN model with a 20*3*1 topology effectively predicts the TG curves of SiOC/PR systems, using the mixture ratio of pyrolyzable components, heating rate, and temperature as inputs. We anticipate that this work will contribute to our understanding of the complex decomposition reactivity in silicone-modified phenolic aerogel matrix nanocomposites by providing elementary steps and reaction kinetics to guide component selection.

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