PROPERTIES OF COMPOSITE MATERIALS FOR MODELING HIGH TEMPERATURE RESPONSE

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ABSTRACT

Methods are provided for obtaining composite material high temperature thermal properties, decomposition properties, and changes in material morphology during heating. This includes review of experimental techniques that have been used to develop properties as well as analysis that needs to be performed on data to develop some of these properties. Approaches for validating determined properties are also discussed. Experiments in an Environment Scanning Electron Microscope (ESEM) all real-time observation of material morphology, which can be used to support constitutive model development as well as formulating materials with reduced flammability.

Keywords: Thermal conductivity, specific heat capacity, heat of decomposition, Arrhenius kinetics, permeability, porosity, material morphology, ESEM

INTRODUCTION

Accurately predicting the thermal response of composite materials exposed to fires requires modeling the heat and mass transfer in the material during the exposure. Heat transfer through charring, degrading materials has been studied by several investigators in various levels of detail [1-10]. In many of these cases, the heat transfer was modeled as one-dimensional heat transfer through a degrading material with a heat flux exposure on one side as shown in Figure 1. Decomposition was typically modeled using an Arrhenius kinetics based model with various methods employed for predicting flow of gases within the material to the exposed surface.

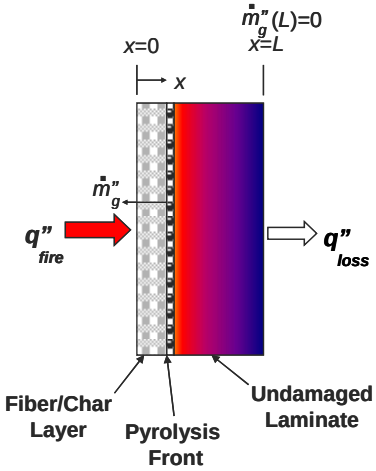


Figure 1. Decomposition of a composite material exposed to fire conditions on one side.

In order to perform this modeling, a substantial amount of material properties are required in the model. This includes thermal properties (thermal conductivity, specific heat capacity) at a range of temperatures for each material state (i.e., virgin, char/reinforcement), decomposition kinetics, heat of decomposition, pyrolysis gas composition, and permeability and porosity at a range of temperatures. Predicting the heat transfer through a decomposing material requires thermal properties for each material state over the range of expected temperatures (up to 1100^{o}C).

Techniques are presented in this paper for obtaining material properties for high temperature modelling. Some of these techniques are based on standard ASTM methods, while others are inverse methods. In all cases, some type of validation testing was performed to demonstrate that the properties obtained were correct and could be used in predictive calculations. Methods are also discussed for observing morphology of materials as they heated in support of developing constitutive models for changes in permeability and porosity of these materials as they decompose.

DECOMPOSITION MODEL

The decomposition model currently being used in the research is based on the heat and mass transfer model was based on model in Ref. [6]. This is a one-dimensional model for degrading materials with unidirectional pyrolysis gas flow through a porous char/reinforcement toward the heated surface, as depicted in Figure 1. The model is presented here to show where different parameters are needed in the modeling and to support determination of parameters based on analysis of data.

The decomposition model includes both the conservation of energy and conservation of mass. The convective-diffusion energy equation is solved for a charring or reinforced material undergoing thermal decomposition

$$mC\frac{\partial T}{\partial t}+\left(h+\Delta h_d-h_g\right)\frac{\partial m}{\partial t}+\dot{m}_g C_g\frac{\partial T}{\partial x}\delta x=\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)V \tag{1}$$

The conservation of mass within the material which relates the mass loss rate of the solid material to the formation of pyrolysis gases and flow of these gases within the material is

$$-\frac{\partial m}{\partial t}=\frac{\partial \dot{m}_g}{\partial x}\delta x+\frac{\partial m_g}{\partial t} \tag{2}$$

The mass loss rate of the solid material due to thermal decomposition was predicted using the Arrhenius kinetic equation

$$\frac{dm}{dt}=-f\left(m\right)A\exp\left(-E/RT\right) \tag{3}$$

Using Darcy's Law for gas flow through a porous media, the mass flow rate of gas through the material is written as

$$\dot{m}_g=-\frac{\gamma m_g}{\mu\phi\delta x}\frac{dP}{dx} \tag{4}$$

The pressure of the gas is determined using the ideal gas equation of state with the volume being the void volume determined using the porosity,

$$P = -\frac{m_g RT}{M\phi V} \tag{5}$$

This set of equations is used to determine the temperature profile through the sample as well as the mass flow rate of gas through the sample. The model can include multiple materials with Dirchlet (constant temperature), Nuemann (heat flux), or Robin (heat flux, convection, and radiation) boundary conditions.

The model also supports temperature and state varying thermal properties. The material state is governed by a progress variable,

$$F = \left[\frac{m - m_d}{m_v - m_d} \right] \tag{6}$$

that tracks the fraction of material involved in the decomposition process. As a result, the value of F ranges from 1 to 0. The variable F was also used for calculating bulk thermal properties and scaling mass data from samples that have different initial and final density [4]. The specific heat capacity is defined as

$$C = FC_v + (1 - F)C_d \tag{7}$$

Similarly, the thermal conductivity was defined as

$$k = Fk_v + (1 - F)k_d \tag{8}$$

MATERIAL PROPERTIES AND MORPHOLOGY

Decomposition Kinetics

Decomposition kinetics were developed using the Netzsch *Thermokinetics* multivariate non-linear regression analysis software. This software is capable of determining kinetic parameters for mechanisms with a single step reactions to multiple step reactions with different reaction types. The software requires sample gravimetric data at several different heating rates (usually four). Using all of this data and the reaction mechanism, the software determines the kinetic parameters. Once the kinetic parameters have been determine, the reaction mechanism needs to be validated. This is typically done by comparing the gravimetric response of the sample during isothermal heating test with the kinetic model predictions for isothermal heating.

Data to determine the decomposition kinetics was developed using the Netzsch Simultaneous Thermal Analyzer (STA) 449 F1 Jupiter™ shown in Figure 2, which is a combination thermogravimetric analyzer (TGA) / differential scanning calorimeter (DSC). The STA measures mass loss as well as specific heat capacity during the same experiment. The instrument is capable of controlled heating and cooling at up to 50°C/min with isothermal segments at any point, and will reach temperatures up to 1500°C. Platinum sample crucibles were used in order to maximize the temperature sensitivity of the S-type sample platform thermocouples.

During the experiments reported in this paper, the instrument was raised to a temperature of 40°C at 5°C/min and held at constant temperature for 20 minutes to equilibrate prior to beginning the heating segment. During the heating segment, samples were raised to final temperatures of 610-620°C at heating rates of 5, 10, 20, and 40°C/min. Prior to each run of the instrument, the sample chamber was taken to 92-95% vacuum, and then refilled with pure nitrogen (inert). The flow of nitrogen was then maintained at a rate of 50

mL/min for the duration of the experiment. In order to maximize the quality of the data that the instrument collected, a baseline run was conducted before each sample run. The baseline run allowed for the output curves from the instrument to show only the effect of the degrading sample, thereby removing any instrument error resulting from the temperature ramp.

(a) Overall view of STA.

(b) Sample holder inside STA.

Figure 2. Netzsch Simultaneous Thermal Analyzer (STA) 449 F1 Jupiter^{TM}, a combined thermogravimetric analyzer (TGA) / differential scanning calorimeter (DSC).

Figure 3 contains a plot of decomposition data (the symbols) from the STA for E-glass / 411-350 vinyl ester. Using this data and a single step nth-order reaction type, kinetic parameters were developed for this material. The predicted decomposition rates with this model are shown in Figure 3 as the lines in the plot. It is important to use all of the heating rate data in the *Thermokinetics* software to determine the kinetic parameters to ensure the offset between heating rates is properly predicted.

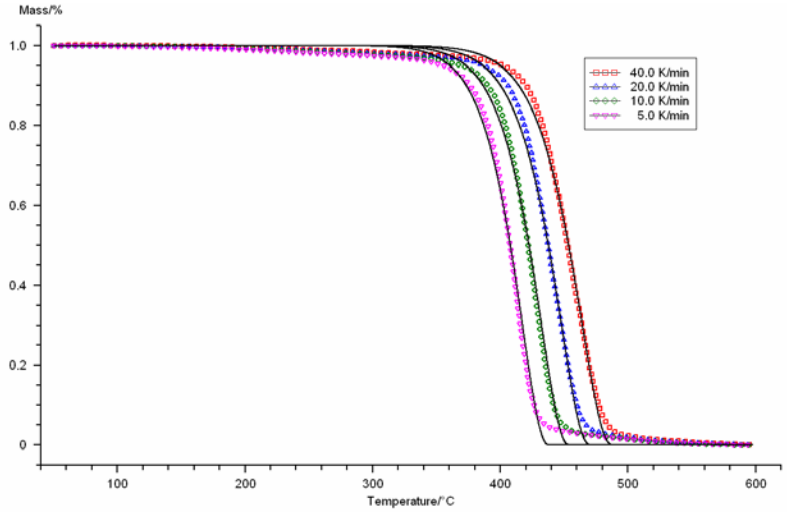
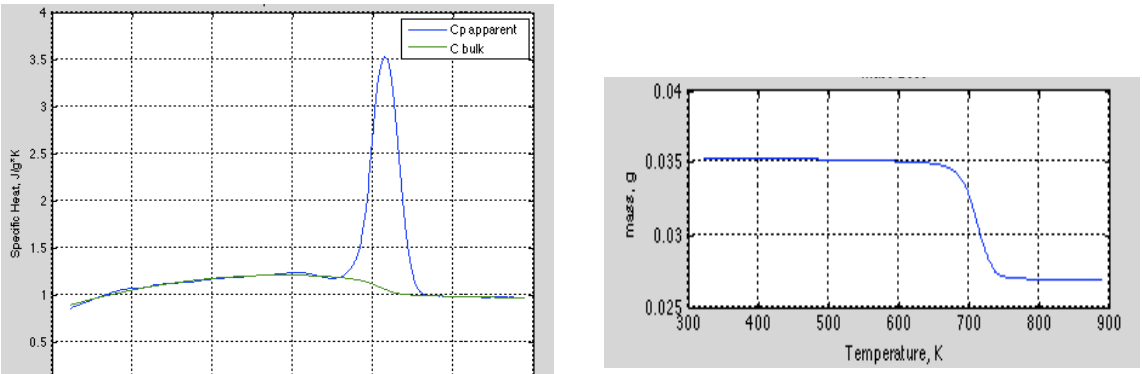


Figure 3. Gravimetric data (symbols) for E-glass 411-350 vinyl ester along with predict decomposition using nth-order reaction with A=1.398x10^{10} (1/s), E=176.28 kJ/mol, n=0.5958.

Specific Heat Capacity and Heat of Decomposition

Experiments in the STA were also used to determine the apparent specific heat capacity of the material as a function of temperature. The apparent specific heat capacity of the material is both the sensible and latent parts of the energy required to heat the sample. The apparent specific heat capacity measurement is a more difficult measurement than the gravimetric measurement. Results were also found to be sensitive to mass when the sample size did not cover most of the bottom of the crucible. Therefore, samples were prepared so that they fit tightly in the crucible. For accurate results, the methodology in ASTM E1269 needs to be followed and platinum crucibles were used. In accordance with this method, a baseline test was performed followed by a calibration test with a sapphire reference sample in the crucible.

Following the calibration tests, the STA was used to measure the apparent specific heat capacity of E-glass 411-350 vinyl ester with respect to the instantaneous mass. The apparent specific heat capacity from the STA are provided in Figure 4. Figure 4b contains the gravimetric response of the sample with temperature. At temperatures where the majority of mass loss was measured, there was a significant increase in the apparent specific heat capacity. This indicates more energy was required to heat the sample due to the decomposition process being endothermic. The sensible specific heat capacity, labelled as C bulk in Figure 4a, was determined using Equation 7 and polynomial fits for specific heat for the virgin and char material. Polynomial fits were developed using the data before and after decomposition.



(a) DSC (b) TGA

Figure 4. STA results for E-glass 411-350 vinyl ester at 20°C/min.

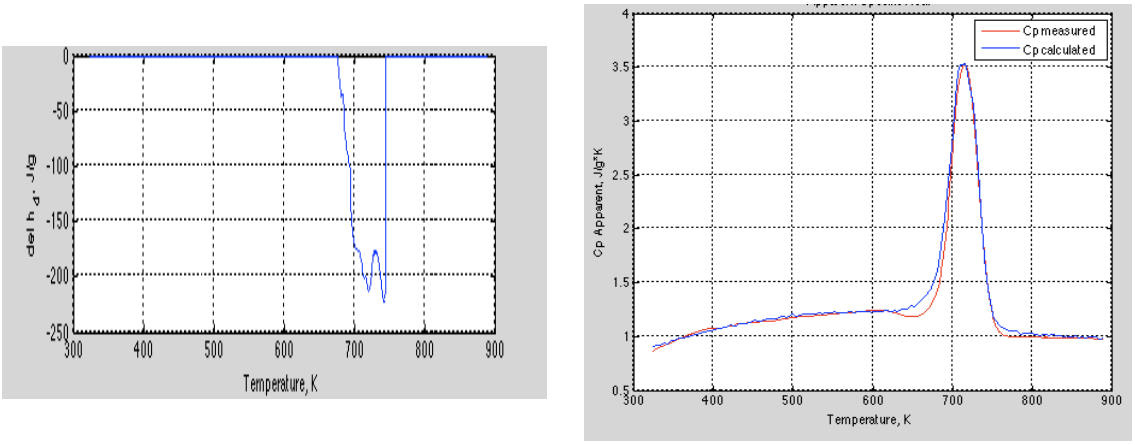
Modeling the decomposition of the material requires that the heat of decomposition of the material be determined. This can be determined using the apparent specific heat capacity data in Figure 4 and the energy equation for the sample in the test. The energy to heat up a sample in the STA must be equal to the energy input from the STA. Using Equation (1), the governing equation for this is

$$mC\frac{\partial T}{\partial t}+\left(h+\Delta h_d-h_g\right)\frac{\partial m}{\partial t}+\dot{m}_g C_g\frac{\partial T}{\partial x}\delta x-\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)V=G\dot{Q} \qquad (9)$$

Since the sample is small and the heating rates are slow, the temperature gradient across the sample is negligible which removes the spatial derivative terms in Equation (9). This reduces Equation (9) to a lumped capacitance type model with a term to account for material decomposition. Using the chain rule to reformulate the mass loss rate term, the energy equation for the DSC sample is written as

$$\left[mC + \left(h + \Delta h_d - h_g \right) \frac{dm}{dT} \right] \frac{dT}{dt} = G\dot{Q} \tag{10}$$

Pyrolysis gas composition determined from Ref. [13] for vinyl ester was used to determine the gas specific heat capacity and enthalpy. The sensible specific heat in Figure 4 was used to determine the material enthalpy, and the instantaneous mass in Figure 4 was used to determine the change in mass with change in temperature. Using the corrected heat flow from the STA, the heat of decomposition can be determined using Equation (10). Results of these calculations are provided in Figure 5. Note that a negative value for heat of decomposition indicates an endothermic reaction, which is expected for material decomposition. There is some variation in the heat of decomposition with temperature. A heat of decomposition of -201kJ/kg provides the best agreement between the model and the data, as shown in Figure 5b.

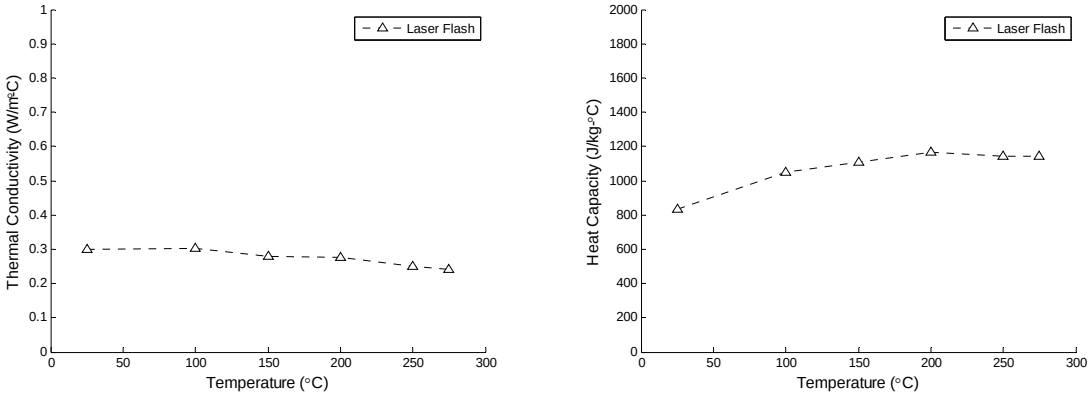


(a) (b)

Figure 5. (a) Calculated heat of decomposition and (b) measured and predicted apparent specific heat capacity using a heat of decomposition of -201 kJ/kg.

Thermal Conductivity

There are several ASTM standard test methods for determining the thermal conductivity of materials at elevated temperatures. Flash methods such as ASTM E1461 [11] are commonly used to determine the thermal diffusivity, thermal conductivity and specific heat capacity for solid materials. In this method, an impulse of heat is applied to a material and time required for the heat to travel through the material is measured. Using this, analysis is conducted to determine the thermal properties of the material. Results using a laser flash instrument to measure the thermal conductivity and specific heat capacity of through-plane (i.e., perpendicular to the woven fiber layer) E-glass vinyl ester are provided in Figure 6.



(a) Thermal conductivity (b) Specific heat capacity

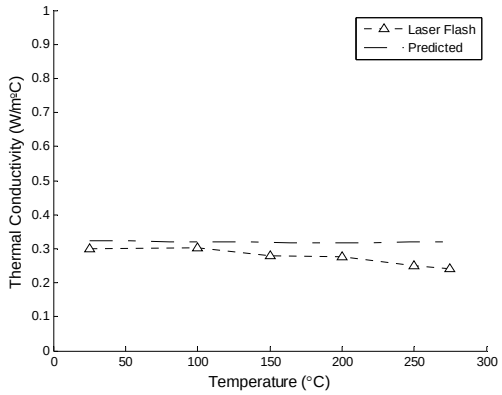
Figure 6. Thermal properties of E-glass vinyl ester from ASTM 1461 laser flash.

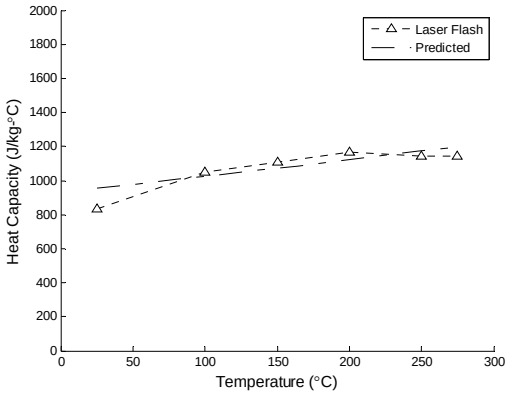
Inverse Techniques for Thermal Conductivity and Specific Heat Capacity

An alternative to performing these standard tests to measure thermal properties is to conduct inverse analysis on thermal response data of a sample exposed to known conditions. Inverse analysis involves varying the thermal properties within a heat and mass transfer model until the model is able to predict a set of experimental data. The correct thermal properties are obtained when the least squares difference between predicted and measured values is minimized. The advantage of doing this is that data can be developed using experimental equipment that the researcher commonly uses (e.g., cone calorimeter) with some instrumentation additions. This has been done for predicting the thermal conductivity and specific heat capacity of materials as a function of temperature [14,15]. In these studies, experiments were designed to limit the properties controlling the thermal response to allow for more accurate determination of properties.

Results are provided here for an E-glass vinyl ester composite sample. The inverse methodology was used to determine the through-plane (i.e., perpendicular to the woven fiber layer) thermal conductivity and specific heat capacity for the composite in the virgin state. Test data for the analysis was developed using constant heat flux tests on coupon size samples (0.1m square) and insulated on the unexposed surface. The sample temperature on the unexposed and unexposed faces was measured during the test and used for quantifying the thermal properties. Tests were conducted in an inert environment with the electric heater panel temperatures at 200 and 300^{o}C, which corresponds to heat fluxes of 4.1 and 8.6 kW/m^2 incident on the sample.

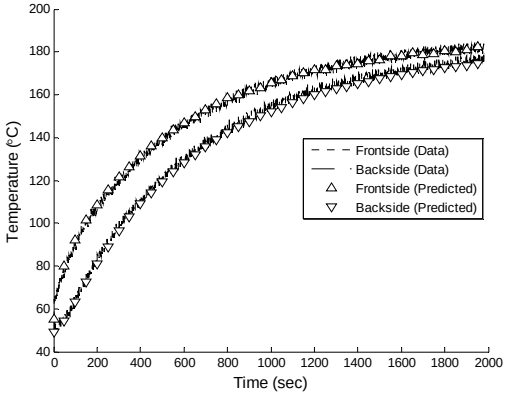
Results from the inverse analysis on the composite material using both tests as input in the inverse analysis simulation are provided in Figure 7. A quadratic function is used to describe the variation in the specific heat capacity and thermal conductivity with temperature. Also shown in these figures are the properties measured for E-glass vinyl ester using the ASTM 1461 laser flash technique. As seen in the figure, the inverse analysis results compare well with the laser flash data. Figure 8 contains a comparison of the measured temperatures with temperatures predicted using the properties in Figure 7 from the inverse analysis. The model was able to provide an excellent prediction of the data.

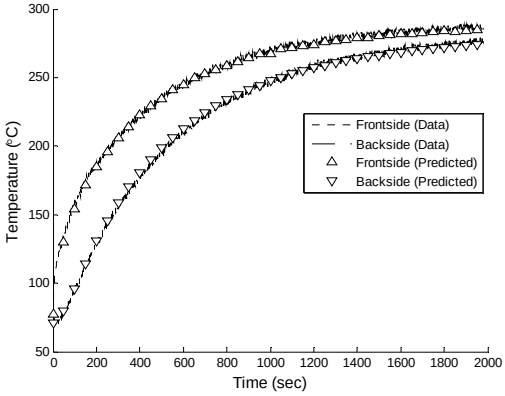




(a) Thermal conductivity (b) Specific heat capacity

Figure 7. Thermal properties of E-glass vinyl ester from inverse analysis.





(a) 200°C heater setpoint (b) 300°C heater setpoint

Figure 8. Thermal response predicted using properties from inverse analysis.

Material Morphology during Decomposition

Several methods are being used to observe and quantify the changes in the material morphology during decomposition. This is of interest because the morphology of the material will define the porosity and permeability of the material, which are required input for the decomposition model. In addition, char morphology is an important parameter in design of materials for reduced flammability and further understanding the morphology can help support this type of research.

Changes in material morphology at high temperatures are typically only evaluated through micrographs before and after the exposure, leaving the cause of the change in morphology unknown. Real-time material morphology changes have been observed using an Environmental Scanning Electron Microscope (ESEM) with an integrated heating stage. Experiments in the ESEM produce a digital video of the material response during controlled heating and cooling. The changes in material have been linked with changes in the gravimetric data for materials in the TGA. Results obtained from an ESEM experiment on a vinyl ester resin are provided in Figure 9. The images clearly show the formation and growth of pores during the decomposition process.

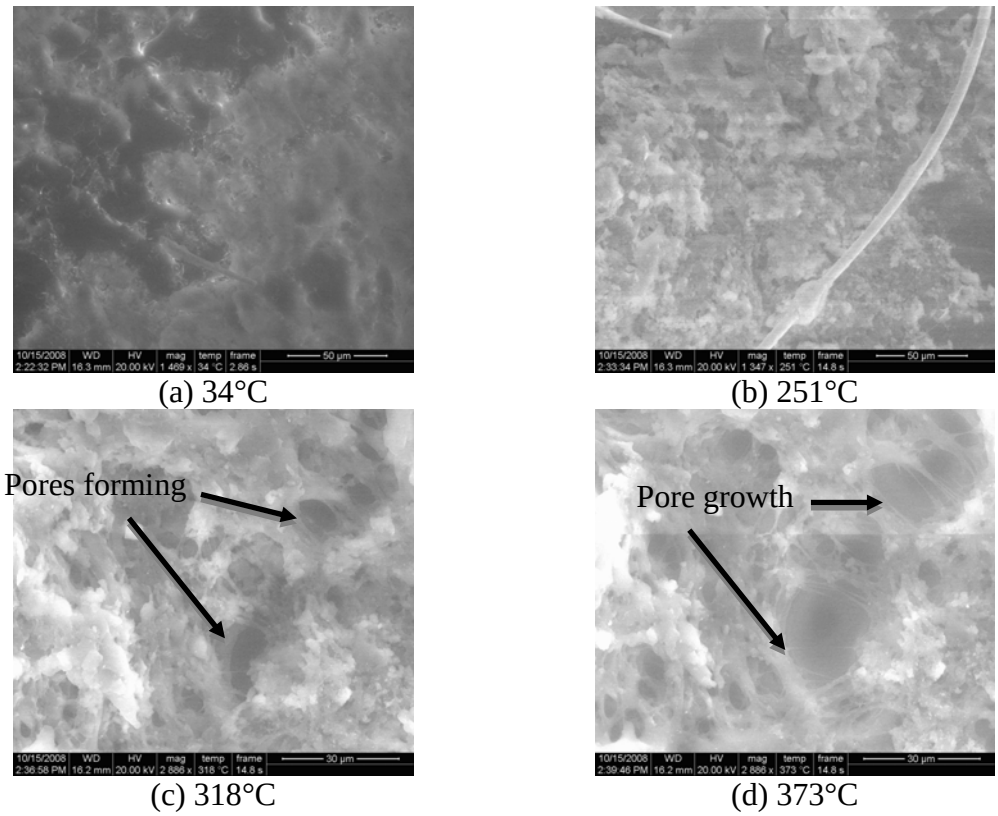


Figure 9. ESEM images of real-time vinyl ester resin decomposition.

SUMMARY

Methods were provided for obtaining composite material high temperature thermal properties, decomposition properties, and changes in material morphology during heating. This includes review of experimental techniques that have been used to develop properties as well as analysis that needs to be performed on data to develop these properties. These techniques can be used to develop quantitative properties for predictive calculations on material response at high temperatures. In addition, these methods can also be used to support material development for reduced flammability applications.

NOMENCLATURE

A pre-exponential factor, C specific heat capacity of sample, C_d specific heat capacity of decomposed sample, C_g pyrolysis gas specific heat capacity, C_v specific heat capacity of virgin sample, E activation energy, $f(m)$ reaction type, F decomposition progress variable, G correction factor for STA DSC measurement, h sample enthalpy, Δh_d heat of decomposition, h_g pyrolysis gas enthalpy, k thermal conductivity, k_d thermal conductivity of decomposed sample, k_v thermal conductivity of virgin sample, m mass of sample, m_d mass of decomposed sample, m_g mass of pyrolysis gas within sample, m_v mass of virgin sample, $\dot{m}_g$ pyrolysis gas flow rate, M molecular weight of pyrolysis gas, P pressure of pyrolysis gas within sample, $\dot{Q}$ heat flow in STA, R universal gas constant, t time, T sample temperature, V element volume, δx element length, ϕ porosity of sample, μ viscosity of pyrolysis gas, γ permeability of sample.

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