

PYROLYSIS MODELING OF POLYMER COMPOSITES FOR FIRE SIMULATIONS

A. Matala^{a*}, S. Hostikka^{b,a}

^aVTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Finland

^bAalto University School of Engineering, Department of Civil and Structural Engineering, P.O.Box 12100, 00076 Aalto, Finland

[*anna.matala@vtt.fi](mailto:anna.matala@vtt.fi)

Keywords: pyrolysis modelling, fire simulation, CFD

Abstract

The fire safety of polymer composites can be evaluated by coupled simulations of the gas-phase fire phenomena (CFD) and solid pyrolysis. In this paper, the process of parameter estimation is presented for the pyrolysis modelling of polymeric material. The process and the methods are demonstrated using a carbon fibre-epoxy composite. Small and bench scale experimental results are used as a basis of the modelling.

1. Introduction

Fibre-reinforced polymer composites are used in many applications because they are strong, stiff and light. Their fire behavior, however, is not always optimal. This is a problem especially in the transportation sector, e.g., with airplanes and ships, where there is large number of people involved and the evacuation possibilities are limited. Typical polymer resins start degrading around 250-500°C [1] and the released gases may burn in the presence of oxygen. The flames accelerate the thermal degradation further, and the remaining structure is not strong anymore. Furthermore, the carbon fibres are known to degrade at high temperatures and especially in the presence of oxygen, leading to a complete degradation of the composite structure [2] [3].

In EU Commission project, FIRE-RESIST, different mechanisms of composites' flame retardancy have been studied and developed. Models have been developed for the heat transfer and thermal degradation processes in order to improve the current means of fire simulation and to be able to predict the flame spread also in circumstances significantly different from the standard testing. If these modelling methods could be tested and validated, they could also be used in the product development of new composite materials saving the time and money that are now spent in sample manufacturing. In this work, the pyrolysis modelling is done using Fire Dynamics simulator that couples the solid phase pyrolysis model with CFD calculation [4] [5]. In addition, simple versions of the pyrolysis models are

prepared for a finite-element model (FEM) of the structure in order to predict the thermal degradation of mechanical properties in loaded situations.

Polymers decompose thermally in elevated temperatures releasing different gases, some of which may be combustible. In the presence of air, these gases may ignite, leading to flaming combustion. The modelling of the fire spread in composite material begins from the solid phase pyrolysis. In the pyrolysis model, the decomposition rate depends on the temperature of the material, and the three reaction and component specific parameters. These parameters cannot be measured directly, and need to be estimated from small scale experimental results. The calculated heat transfer depends on other parameters, called thermal parameters. They can be either directly measured or estimated from cone calorimeter results. Modelling the pyrolysis within composites is challenging because they consist on several components, and their structure and geometry may be strongly asymmetric [6].

In this paper, the process of parameter estimation is presented for the pyrolysis modelling of polymeric material. The process and the methods are demonstrated using a carbon fibre-epoxy composite. Small and bench scale experimental results are used as a basis of the modelling. In addition to the traditional Thermogravimetric analysis, also a new method called Microscale combustion calorimetry is used for obtaining the heat of complete combustion of the sample. All the model parameters are measured or estimated from the experimental results by using genetic algorithm. The challenges of the modelling of the composites are also further discussed, and different decisions of the modeller are assessed.

2. Methods

This paper concentrates on modelling for CFD calculations. In another ECCM16 paper (Gutkin et al.), the FEM modelling has been discussed in more detail. The material model for CFD may be more complicated, including several decomposition reactions. In FEM, the pyrolysis must be modelled using single-step reaction.

All the material models in this paper were implemented using the Fire Dynamics Simulator, version 6 [4] [5]. The modelling process is shown in Figure 1. It consists of four main phases: Sample preparation, experimental work, modelling and parameter estimation, and model validation.

The Step 1, sample preparation, is to familiarize oneself with the sample material, and prepare it for testing. Studying background information on the target material helps to plan the experiments and determine reaction path later in the modelling phase.

The Step 2 is the experimental work. For modelling, the most important experiments are Thermogravimetric analysis (TGA) and cone calorimeter tests. If possible, the components should be tested both separately and in composite form. TGA should be performed both in nitrogen and air in order to see the difference of the oxidative environment, and at several heating rates (2-30 K/min). The cone calorimeter experiments should be performed at several heat fluxes (25-75 kW/m²) as well.

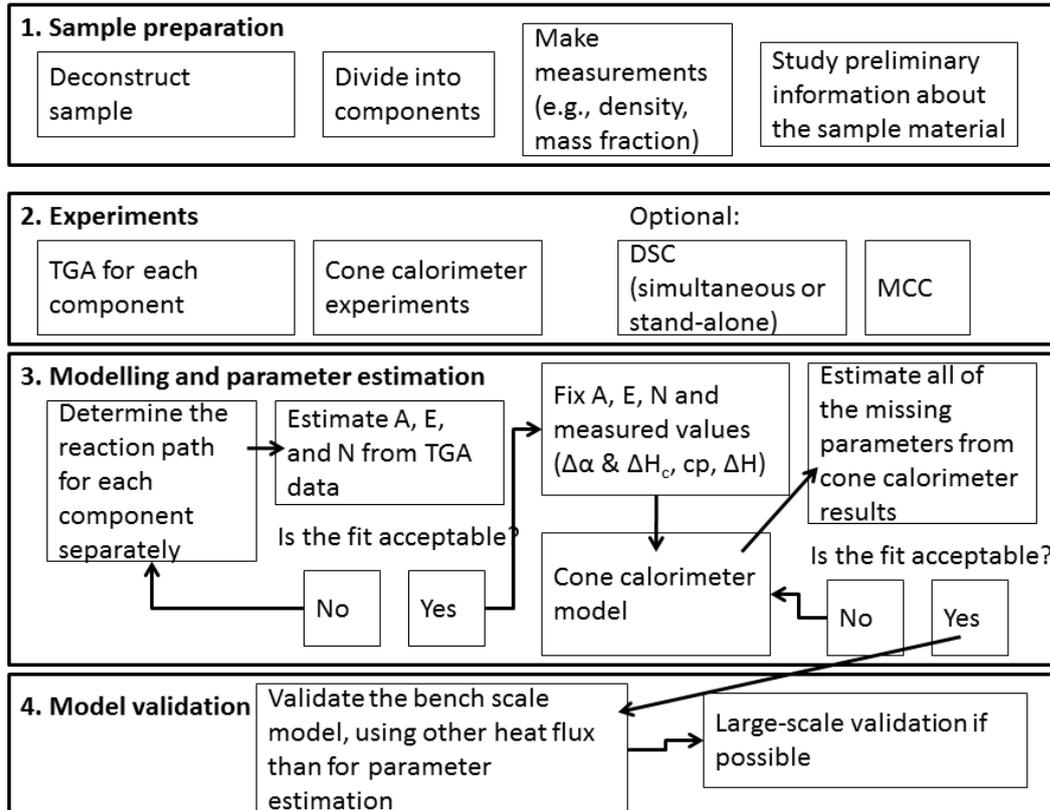


Figure 1. Material modelling process and parameter estimation.

Step 3, modelling and parameter estimation, is the most challenging and important part of the process. It starts from the specification determination of the reaction path, including decisions about reaction types, number of reactions, material composition (or the reacting components) and the residue materials. Literature information helps at this point, but it also seems that the larger scale results are not very sensitive to the choice of the reaction path [6] [7]. The kinetic parameters (pre-exponential factor (A), activation energy (E) and reaction order (N)) are typically estimated from TGA results. Their values depend strongly on the chosen reaction path, and once they are estimated, they cannot be generally used with any other reaction path. When the kinetic parameters have been successfully estimated, they are fixed, along with all other measured parameters (e.g., density, specific heat capacity). Then the cone calorimeter model is made, including decisions of the layer structure and other parameters. When the cone calorimeter model has been created, all the missing parameters are estimated by fitting the

model predictions of the heat and mass loss rates to the corresponding cone calorimeter results. If the resulting parameters repeat the cone calorimeter results accurately, the material model is completed.

Model validation is the Step 4 of the process. Validation means the evaluation of the model's accuracy / uncertainty in the intended application. In this case, it means the capability to predict the thermal degradation of a solid in different circumstances. The validation also gives an idea in which situations the model can be trusted to predict fire spread correctly, and in which case the results should be used with caution.

More information about the used experimental methods and models is available in [6].

3. Results

The sample material in this example was a carbon fibre-reinforced epoxy composite. This 2 mm thick composite consisted of 32 w-% epoxy and 68 w-% carbon fibres. The modelling process presented in Figure 1 is here demonstrated step-by-step.

Sample preparation: Only complete composite was available, so the tests were not performed to the components (epoxy and carbon fibres) separately. This caused some difficulties in the modelling phase.

	SP	UNEW
ρ (kg/m ³)	1556	-
c_p (kJ/(K·kg))	21°C 0.96 50°C 1.03 81°C 1.14	-
α (mm ² /s)	21°C 0.54 50°C 0.56 81°C 0.52	30°C 0.38 40°C 0.39 60°C 0.35 80°C 0.34 124°C 0.11 152°C 0.09
λ (W/(K·m))	21°C 0.8 50°C 0.9 81°C 0.92	-

Table 1. Measured thermal properties of carbon fibre - epoxy composite by SP and UNEW.

Experiments: TGA results were available at three heating rates (10, 20 and 40 K/min) in nitrogen and standard cone calorimeter results at two heat fluxes (35 and 70 kW/m²). Density

(ρ), thermal diffusivity (α), specific heat capacity (c_p) and thermal conductivity (λ) were measured by SP and UNEW (Table 1).

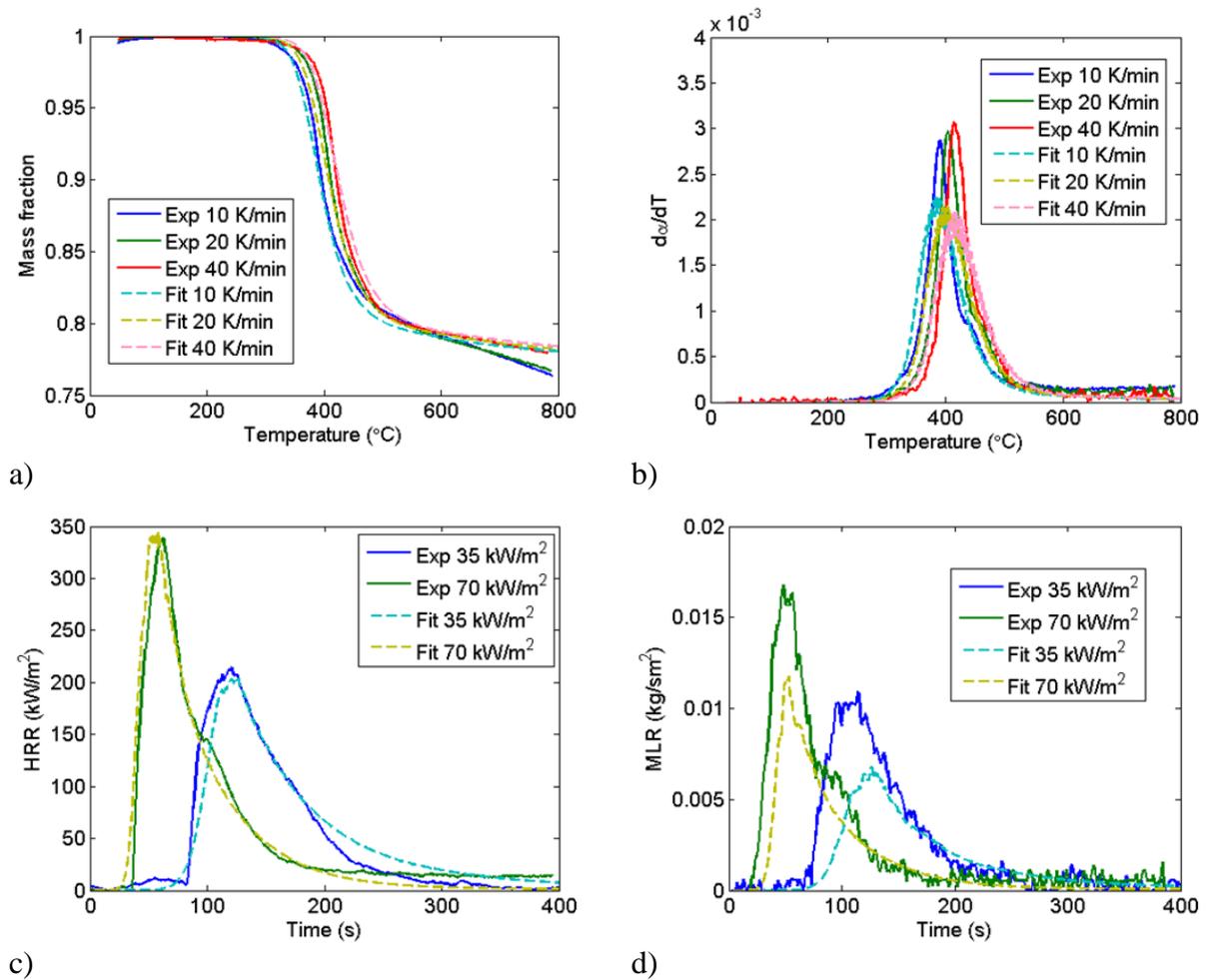


Figure 2. Comparison of experimental and calculated results for carbon-epoxy composite, model 1 (3 reaction steps). a) Mass fraction in TGA b) Mass loss rate in TGA c) Heat release rate in cone calorimeter d) Mass loss rate in cone calorimeter.

Pyrolysis modelling: Two models were developed for different applications; Model 1 with three reaction steps and temperature-dependent thermal values was developed for CFD calculations and Model 2 with only one reaction step and constant thermal values for FEM calculations. Measured values for composite density and thermal conductivity (for Model 1) were used; all the other parameters were estimated. The comparison between the experimental and fitted curves is seen for Model 1 in Figure 2 and for Model 2 in Figure 3. The parameter values are listed in Table 2 (kinetic) and Table 3 (thermal). Although the parameters of these two models are different, the overall fit is equally good at both cases. However, as the parameters are clearly model-dependent, they cannot be mixed or used with other models.

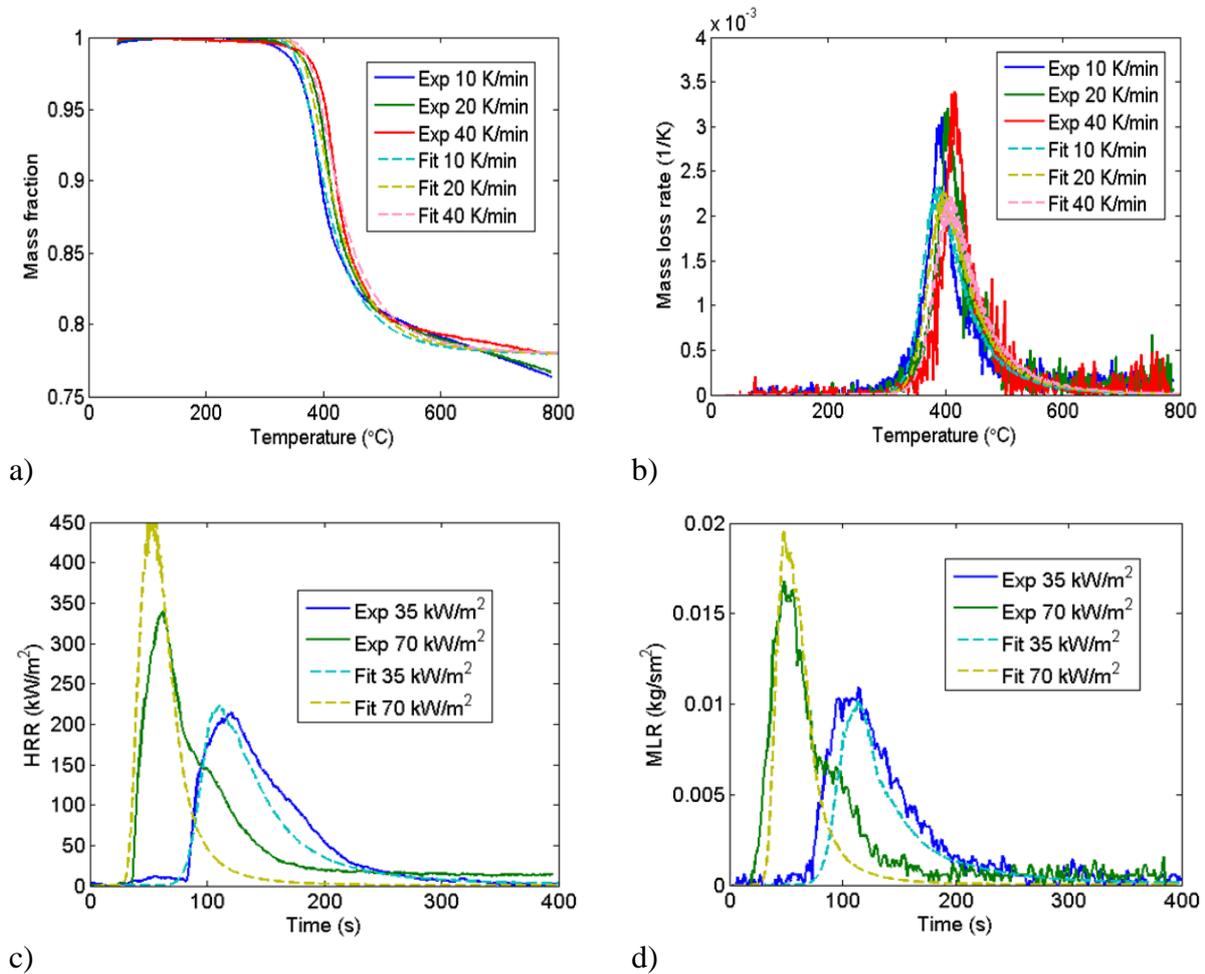


Figure 3. Comparison of experimental and calculated results for carbon-epoxy composite, model 2 (1 reaction step). a) Mass fraction in TGA b) Mass loss rate in TGA c) Heat release rate in cone calorimeter d) Mass loss rate in cone calorimeter.

There is no significant difference at cone calorimeter scale for simple and more complex pyrolysis model. The main benefit for the more complex reaction path is that it can more accurately capture the decomposition dynamics at significantly different heating rates, possibly leading to better predictions of the large scale flame spread. The pyrolysis model can also be used in product development, if the components (fibres and resin) are separated. This model does not take into account the degradation of fibres (only resin degrades in the model) or oxidation reaction. It does not seem to affect the accuracy of the results at the cone calorimeter scale, as the temperatures are not very high and the oxygen concentration near sample during flaming cone calorimeter test is low. However, this may have greater influence to flame spread in some other conditions, but cannot be confirmed due to lack of experimental results.

Model validation: The validation of the modelling concept and the composite material modelling is an on-going process, and will be completed during 2014. So far no large scale experimental results were available for this material. The cone calorimeter results are predicted reasonably well at two different heat fluxes instead of using only one.

Component	Mass fraction	ρ kg/m ³	A s ⁻¹	E kJ/kmol	N -	yF -	yI -	yR -	Residue -
Model 1									
Resin 1	0.32	1230	9.27E+10	1.56E+05	2.58	0.5	0	0.5	Resin 2
Resin 2	0	869	4.19E+18	1.61E+05	4.99	0.3	0	0.7	Resin 3
Resin 3	0	382	1.00E+08	1.09E+05	6.03	0.19	0	0.81	Char
Char	0	463	-	-	-	-	-	-	-
Fibres	0.62	1780	-	-	-	-	-	-	-
Model 2									
Resin 1	-	1556	4.10E+16	2.36E+05	4.34	0.22	0.00	0.78	char
char	-	1200	-	-	-	-	-	-	-

Table 2. Kinetic parameters for models 1 and 2 of carbon-epoxy composite.

Component	ϵ -	λ (21 °C) W/Km	λ (50 °C) W/Km	λ (81 °C) W/Km	c_p (21 °C) kJ/kgK	c_p (300 °C) kJ/kgK	ΔH kJ/kg	ΔH_c MJ/kg
Model 1								
Resin 1	1	0.8	0.9	0.92	2.58	3.13	819	36.1
Resin 2	1	0.06	-	-	2.65	-	1256	22.3
Resin 3	1	0.08	-	-	2.26	-	1803	12.2
Char	1	0.38	-	-	2.28	-	-	-
Fibres	1	0.01	-	-	1.69	-	-	-
Model 2								
Resin 1	1	0.49	-	-	2	-	280	25
char	0.78	0.15	-	-	3.3	-	-	-

Table 3. Thermal parameters of models 1 and 2 for carbon-epoxy composite.

4. Conclusions

The pyrolysis modelling process for polymer composite materials was presented and discussed. The process was demonstrated using carbon fibre-epoxy composite as an example. The results show that it is possible to model thermal decomposition of a composite material using TGA and cone calorimeter results for parameter estimation.

The accuracy of the results was not sensitive to the complexity of the model. The lack of fibre decomposition and polymer oxidation reactions did not seem to influence the accuracy of the cone calorimeter model. For a more general model, these factors should be taken into account since they may be significant for the flame spread under different conditions (very high temperatures and high oxygen concentration near sample). Separate reaction models should be used for the polymer and the fibres if the model was to be used in product development.

Acknowledgements

The work has been funded by European Commission project FIRE-RESIST (grant number 246037). SP (Sweden) and University of Newcastle (UK) are acknowledged for providing measured thermal properties for carbon-epoxy composite.

References

- [1] R.E. Lyon. Chapter 3, Plastics and Rubber. In Harper C.A., editor, Handbook of building materials for fire protection, pages 3.1-3.51, McGraw-Hill, New York, 2004.
- [2] N. Régnier and S. Fontaine. Determination of the thermal degradation kinetic parameters of carbon fibre reinforced epoxy using TG. Journal of Thermal Analysis and Calorimetry, Vol. 64: 789-799, 2001.
- [3] C. Branca, C. Di Blasi, A. Galgano, E. Milella. Thermochimica Acta, Vol. 517, 53-62, 2011.
- [4] McGrattan, K. et al. Fire Dynamics Simulator. User's Guide. NIST Special Publication 1019. 2014.
- [5] McGrattan, K. et. Al. Fire Dynamics Simulator Technical Reference Guide. Volume 1: Mathematical Model. NIST Special Publication 1018. 6th Edition. 2014.
- [6] Matala, A. Methods and applications of pyrolysis modelling for polymeric materials. VTT Science 44. Doctoral thesis, 2013.
- [7] Matala, A., Hostikka, S. Pyrolysis modelling of PVC cable materials. Fire safety science, Vol. 10, 917-930. 2011.