

# Study of Catalytic Infrared Curing Powder Coating Technology: Experiments and Modelling

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Tongzhao Wang 26 January 2025

#### Abstract

Catalytic combustion can effectively and cleanly convert the chemical energy of fossil fuels into infrared radiation energy. However, there is little research on the use of this technology to cure powder coatings. In order to carry out the application and theoretical study of this technology, a catalytic infrared heating equipment based on a Pt/Al<sub>2</sub>O<sub>3</sub> noble metal catalyst was designed, constructed, and tested. Experimental and modeling studies were carried out in this study using Polyester/TGIC and GMA/DDDA powder coating systems, respectively.

Based on a literature review and analysis, a feasibility and heat transfer process study was first carried out using Polyester/TGIC powder coatings. The optimal curing parameters for the catalytic infrared curing process for powder coatings were determined via experiments at 220 °C for 3 min and 230 °C for 2 min. As the curing temperature increased and the curing time increased, the mechanical properties of the coating were found to improve. However, the gloss of the coating was reduced and the color darkened. A one-dimensional heat transfer model was developed to investigate the heat transfer process for powder coatings. This study introduced an internal heat source for the first time, and the heat transfer process for polyester-based powder coatings with different substrate thicknesses was numerically simulated. The numerical simulations demonstrated that the efficiency of the heat transfer between the catalytic infrared gas supply and the coating surface was 0.4. When the substrate thickness was 1 mm, the coating was most rapidly cured at 230 °C. When the substrate thickness was  $\geq 2$  mm, the most rapid curing occurred at 220 °C.

Next, the curing process study was conducted using GMA/DDDA System powder coatings. Fourier-transformed infrared (FT-IR) spectroscopy is employed to record the concentration of epoxide groups with respect to time under different temperature conditions, with the reaction conducted under IR radiation. The resulting data were then fitted by the Levenberg–Marquardt algorithm using MATLAB software to obtain the kinetic parameters, namely the rate constant (*k*), catalytic constants (n and m), reaction activation energy ( $E_a$ ), and the pre-exponential factor (*A*) of the curing reaction. Additionally, this study proposed a new concept: the "photo-thermal synergistic effect" of infrared curing and its evaluation criteria using a dimensionless quantity, i.e., photo-thermal synergistic index ( PTSI). Incredibly, this index integrates the impact of IR curing technology on two aspects: the curing process and the properties of the cured product.

Overall, this work contributes to advancing the understanding and application of catalytic infrared curing, offering a theoretical and experimental basis for industrial-scale implementation.

**Keyword:** catalytic infrared; powder coating curing; heat transfer model; kinetic model; photo-thermal effect.

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May there be peace in the world and freedom for all.

### **List of Publications and Patents**

#### **Publications**

 Wang, T.; Xia, L.; Ni, M.; Pan, S.; Luo, C. Fundamentals of Infrared Heating and Their Application in Thermosetting Polymer Curing: A Revi ew. Coatings 2024, 14, 875. https://doi.org/10.3390/coatings14070875. (Cha pter 1 and Chapter 2, First author)

 Wang, T.; Lun, I.Y.F.; Xia, L.; Wang, Y.; Pan, S. Kinetic Study of Infrared Heat Curing of Thermosetting Polymers. Coatings 2024, 14, 1560. https://doi.org/10.3390/coatings14121560. (Chapter 3, Chapter 6 and Chapter 7, First author).

3. Wang, T.; Lun, I.Y.F. Catalytic Infrared Curing of Thermosetting Compounds: Current Status and Future Prospects As A Systematic Review of Current Studies. (Chapter 8, under review, First author).

4. Yuan, Y.; Pan, S.; Wang, T\*.; Xia, L.; Liu, Y.; Wang, X.; Li, L.; Wa ng, T. Experimental and Numerical Investigations on Curing a Polyester-B ased Powder Coating by Catalytic Infrared Radiation. Appl. Sci. 2023, 13, 2187. <u>https://doi.org/10.3390/app13042187</u>. (Chapter 3, Chapter 4 and

#### Chapter 5, Corresponding author).

5. Chang, L.; Chong, W.T.; Wang, X.; Pei, F.; Zhang, X.; Wang, T.; Wang, C.; Pan, S. Recent Progress in Research on PM2.5 in Subways. Envir on. Sci.: Processes Impacts 2021, 23, 642–663, doi:10.1039/D1EM00002K. (Participating author).

### Patents

Pan, S.; Jia, Z.; Wang, T., Li, L. A drying system and drying method for large workpieces (一种大型工件用烘干系统及烘干方法). ZL202110402749.9. Innovation patent, Granted.( Chapter 3, Catalytic infrared curing oven)

Abstract	I
Acknowledgements	III
List of Publications and Patents	IV
Contents	VI
List of Figures	X
List of Tables	XIII
Nomenclature	XV
Chapter 1: Introduction	1
1.1 Background and overview	1
1.2 Motivation for the project	6
1.3 Aims and objectives	7
1.4 Thesis outline and content	7
Chapter 2: Literature review	10
2.1 Heat Transfer Process	13
2.1.1 Classification and Selection of IR Heaters	13
2.1.2. Monitoring Devices	17
2.1.3. Thermal Transfer Model	21
2.1.4. Numerical Simulation Methods	27
2.2. Curing Process	30
2.2.1. Monitoring Techniques and Models	30
2.2.1.1 Spectrum Analysis	32
2.2.1.2 Electrical Property Analysis	
2.2.1.3. Thermal Property Analysis	34
2.2.1.4. Optical Fiber Measurement Analysis	

# Contents

2.2.1.5. Ultrasonic Analysis	.37
2.2.1.6. Mechanical Property Analysis	.38
2.2.2. Curing Theory	.40
2.2.2.1. Flory–Stockmeyer Theory	.40
2.2.2.2. Non-Equilibrium Thermodynamic Fluctuation Theory	41
2.2.2.3. Avrami Theory	42
2.2.2.4. DSC Kinetic Model	43
2.2.3. Non-Thermal Effect and Properties of Cured Products	.45
2.2.3.1. Non-Thermal Effect	.46
2.2.3.2. Properties of Cured Products	.47
2.3. Discussion	. 48
2.4. Summary	51
Chapter 3: Research Methodology	. 54
3.1. Equipment Setup	. 54
3.2. Polyester/TGIC System Curing Experiment	. 58
<ul><li>3.2. Polyester/TGIC System Curing Experiment</li><li>3.2.1. Materials</li></ul>	. 58 . 58
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> </ul>	. 58 . 58 . 59
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> </ul>	. 58 . 58 . 59 . 59
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> <li>3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test</li> </ul>	. 58 . 58 . 59 . 59 . 59
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> <li>3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test</li> <li>3.2.2.3. Fourier-Transform Infrared Spectroscopy of the Powder Coatings</li> </ul>	. 58 . 58 . 59 . 59 . 59
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> <li>3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test</li> <li>3.2.2.3. Fourier-Transform Infrared Spectroscopy of the Powder Coatings</li> <li>3.2.2.4. Curing Methods and Test Conditions</li> </ul>	. 58 . 58 . 59 . 59 . 59 . 59 . 60
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> <li>3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test</li> <li>3.2.2.3. Fourier-Transform Infrared Spectroscopy of the Powder Coatings</li> <li>3.2.2.4. Curing Methods and Test Conditions</li> <li>3.2.3 Heat transfer process study</li> </ul>	. 58 . 58 . 59 . 59 . 59 . 59 . 60 . 62
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> <li>3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test</li> <li>3.2.2.3. Fourier-Transform Infrared Spectroscopy of the Powder Coatings</li> <li>3.2.2.4. Curing Methods and Test Conditions</li> <li>3.2.3 Heat transfer process study</li> <li>3.2.3.1. Geometric Model</li> </ul>	. 58 . 58 . 59 . 59 . 59 . 60 . 62 . 63
<ul> <li>3.2. Polyester/TGIC System Curing Experiment</li> <li>3.2.1. Materials</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2 Feasibility Study</li> <li>3.2.2.1 Experimental Setup</li> <li>3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test</li> <li>3.2.2.3. Fourier-Transform Infrared Spectroscopy of the Powder Coatings</li> <li>3.2.2.4. Curing Methods and Test Conditions</li> <li>3.2.3 Heat transfer process study</li> <li>3.2.3.1. Geometric Model</li> <li>3.2.3.2. Numerical Method</li> </ul>	. 58 . 58 . 59 . 59 . 59 . 60 . 62 . 63 . 63

3.3.1. Materials
3.3.2. The IR Curing Process
3.3.2.1. Experimental Setup
3.3.2.2 Determination of Degree of Cure
<b>3.4. Summary</b>
Chapter 4: Feasibility study71
<b>4.1. Introduction</b>
<b>4.2. Heating Performance Test</b>
4.2.1. Characteristics of the Catalytic Infrared Radiation Panel
4.2.2. FT-IR Analysis
<b>4.3. Heating Performance Test</b>
<b>4.4 Curing Tests</b>
4.4.1. Adhesion Test
4.4.2. Gloss Test
4.4.3. Hardness Test
4.4.4. Impact Resistance
4.4.5. Color Test
<b>4.5. Summary</b>
Chapter 5: Heat Transfer Process Study
<b>5.1. Introduction</b>
5.2. Heat Transfer Model
5.3. Model Validation
5.4. Application of the Model
<b>5.5. Summary</b>
Chapter 6: Curing Process Study96

6.1. Introduction	96
6.2. Curing Kinetics	97
6.2.1. The Samples' Degree of Cure	97
6.2.2. The Curing Process Kinetic Parameters	100
6.3. Summary	105
Chapter 7: Photo-Thermal Synergistic Effect	106
7.1. Introduction	106
7.2. Conceptualization	106
7.3. photo-thermal synergistic index	108
<ul><li>7.3. photo-thermal synergistic index</li><li>7.4. Summary</li></ul>	<b>108</b> 113
<ul><li>7.3. photo-thermal synergistic index</li><li>7.4. Summary</li><li>Chapter 8: Conclusion</li></ul>	<b>108</b> 113 115
<ul> <li>7.3. photo-thermal synergistic index</li> <li>7.4. Summary</li> <li>Chapter 8: Conclusion</li> <li>8.1 Summary of the study</li> </ul>	<b>108</b> 113 115 115
<ul> <li>7.3. photo-thermal synergistic index</li> <li>7.4. Summary</li> <li>Chapter 8: Conclusion</li> <li>8.1 Summary of the study</li> <li>8.2 Discussion</li> </ul>	<b>108</b> 113 115 115 117
<ul> <li>7.3. photo-thermal synergistic index</li> <li>7.4. Summary</li> <li>Chapter 8: Conclusion</li> <li>8.1 Summary of the study</li> <li>8.2 Discussion</li> <li>8.3 Contributions to Knowledge</li> </ul>	<b>108</b> 113 115 115 117 120
<ul> <li>7.3. photo-thermal synergistic index</li> <li>7.4. Summary</li> <li>Chapter 8: Conclusion</li> <li>8.1 Summary of the study</li> <li>8.2 Discussion</li> <li>8.3 Contributions to Knowledge</li> <li>8.4 Future Research Directions</li> </ul>	<b>108</b> 113 115 115 117 120 121

# **List of Figures**

Figure 2- 1. Number of publications per year (Source: WOS; Date: 17 March
2024)11
Figure 2- 2 Clustering time analysis (2004–2024) of WOS searches of journals
in the polymers curing field through citespace 6.3. R211
Figure 2-3. Schematic showing a newly designed thin-film heat flux sensor: (a)
cross section and (b) top view
Figure 2- 4. Geometric modeling of surface heat transfer
Figure 2-5. Geometric modeling of volumetric heat transfer25
Figure 2- 6. Non-isothermal DSC spectra of the hybrid and pure polyester
coatings obtained under a scanning rate of 10 °C·min-1 [37]35
Figure 2-7. FOS output during isothermal scans at 50, 60, and 70 °C [71] 37
Figure 2- 8. Storage modulusand loss tangent versus time by DMTA [75]39
Figure 3-1. The Overview structure of the studies presented in this thesis54
Figure 3- 2. (a) Catalytic infrared curing oven. (b) Schematic diagram of
infrared curing furnace with catalytic combustion
Figure 3- 3. Catalytic infrared radiation panel
Figure 3- 4. (a) Fiber-supported noble metal catalyst. (b) Methane conversion
versus temperature with the Cat-1 and Cat-2 catalysts
Figure 3- 5. Test equipment and processes: (a) adhesion test, (b) gloss test, (c)
hardness test, (d) film impact resistance test, and (e) color test
Figure 3- 6. Geometric model63
Figure 3-7. Coating temperature versus time with different grid sizes
Figure 3-8. Coating temperature versus time with different time steps

Figure 3- 9. PerkinElmer Spectrum Two FT-IR Spectrometer
Figure 3- 10. Schematic illustration of the curing reaction between GMA acrylic
resin and dodecanedioic acid69
Figure 4- 1. (a) Relationship between the surface temperature of the radiant
panel and the gas intake. (b) The catalytic infrared radiation intensity of the
radiant panel
Figure 4- 2. The infrared spectra of the polyester-based/TGIC powder coating:
(a) variation with wavenumber and (b) variation with wavelength74
Figure 4- 3. Variation in coating temperature and substrate bottom surface
temperature with time76
Figure 4- 4. Coating adhesion test results77
Figure 4- 5. Changes in the coating gloss with curing temperature after different
curing times
Figure 4- 6. Changes in the coating gloss with curing time with different curing
temperatures
Figure 4- 7. Coated pencil hardness test results for the coatings
Figure 4- 8. Impact resistance test results for the coatings
Figure 4- 9. The effects of temperature on the coatings' CIE laboratory color
model values
Figure 5-1. Heat transfer diagram for coating and substrate system
Figure 5-2. Comparison of measured and simulated coating temperatures 90
Figure 5- 3. Comparison of experimental and simulated temperatures during the
curing process

Figure 5- 4. (a) Temperature distribution of coating and substrate at a curing
temperature of 220 °C. (b) Temperature distribution of coating and substrate at a
curing temperature of 230 °C
Figure 5-5. Predicted coating temperatures with varying substrate thickness. 94
Figure 5- 6. Heating times required for the coating temperature to reach 220 $^{\circ}$ C
and 230 °C with different substrate thicknesses94
Figure 6-1. FTIR absorption spectrum of the uncured powder coating
Figure 6- 2. FTIR absorption spectra of GMA/DDDA samples IR-cured for
different time intervals at (a) 150 °C, (b) 160 °C, and (c) 170 °C99
Figure 6-3. Kinetic model fitting of the cure rate vs. time data obtained for the
samples IR-cured at (a) 150 °C, (b) 160 °C, and (c) 170 °C 102
Figure 6- 4. Arrhenius plot for IR curing process of GMA/DDDA103
Figure 6- 5. Comparison of experimental and model-predicted kinetic behavior
of the curing reaction at 165 °C104
Figure 7-1. Heat transfer modes of the IR curing process108
Figure 7- 2. Evaluation of IR curing technology based on the photo-thermal
synergistic index (PTSI) 111
Figure 8-1 The Overview structure of this studies

# List of Tables

Table 2- 1. Literature summary
Table 2- 2. Classification of IR heaters and literature summary17
Table 2- 3. Comparison of different monitoring devices.    17
Table 2- 4. Thermal transfer model classification.    26
Table 2- 5. Comparison of different numerical simulation methods and available
studies
Table 2- 6. Comparison of different monitoring techniques and models
Table 2- 7. Comparison of different curing theories.    45
Table 2- 8. Comparison of absorption models.    46
Table 2- 9. Comparison of three different curing technologies.    50
Figure 3-1. The Overview structure of the studies presented in this thesis54
Figure 3- 2. (a) Catalytic infrared curing oven. (b) Schematic diagram of
infrared curing furnace with catalytic combustion56
Figure 3- 3. Catalytic infrared radiation panel
Figure 3- 4. (a) Fiber-supported noble metal catalyst. (b) Methane conversion
versus temperature with the Cat-1 and Cat-2 catalysts
Figure 3- 5. Test equipment and processes: (a) adhesion test, (b) gloss test, (c)
hardness test, (d) film impact resistance test, and (e) color test
Figure 3- 6. Geometric model
Figure 3-7. Coating temperature versus time with different grid sizes
Figure 3-8. Coating temperature versus time with different time steps
Figure 3- 9. PerkinElmer Spectrum Two FT-IR Spectrometer
Figure 3- 10. Schematic illustration of the curing reaction between GMA acrylic
resin and dodecanedioic acid

Table 4- 1. Classification chart for paint adhesion tests.    77
Table 4- 2. Comparison of curing parameters with those obtained from the
literature
Table 5- 1. Relative errors for measured and simulated coating temperatures
$(\eta tot = 0.4).$
Table 6- 1. Thermosetting polymers curing reaction kinetic models and the
corresponding parameters
Table 6- 2. Degree of cure for GMA/DDDA powder coatings at different curing
temperatures after varying reaction intervals
Table 6- 3. Numerical values of the kinetic model parameters obtained at
different temperatures
Table 8- 1 Comparison of infrared heat transfer models    117
Table 8- 2 Comparison of curing theory and monitoring techniques

# Nomenclature

### Abbreviations

IR	Infrared
UV	Ultraviolet
NIR	Near-infrared radiation
SIR	Short-wavelength IR
MIR	Medium-wavelength IR
NIR-A	Near-infrared absorber
CFD	Computational fluid dynamics
Tg	Glass transition temperature
SMC	Sheet molding compound
RTM	Resin Transfer Molding
VOCs	Volatile organic compounds
PMF	Positive matrix factorization
TGIC	Triglycidyl isocyanurate
DGEBA	Digycidylether of Bis-phenol-A
RTDs	Resistance temperature detectors
FE	Finite element
DSC	Dynamic differential scanning calorimetry
ZM	Zone Method
MCM	Monte Carlo method
DOM	Discrete ordinates method

DTM	Discrete transfer method
FVM	Finite volume method
DTA	Differential thermal analysis
DEA	Dielectric Analysis
TMA	Thermo-mechanical analysis
DMTA	Dynamic Mechanical Thermal Analysis
ТА	Thermal analysis
FOS	Fiber optic sensor
LPG	Liquefied petroleum gas
OSP	Organo-modified silica particle
EP	Epoxy powde
GMA	Glycidyl methacrylate
DDDA	Dodecanedioic acid
FT-IR	Fourier-transformed infrared
PTSI.	Photo-thermal synergistic index

# Symbols

$C_p$	Heat capacity
е	Thickness
Ε	Spectral irradiance
h	Convective exchange coefficient
R	Universal gas constant
S	Metallic substrate
Т	Temperature
x	Conversion degree
а	Absorption coefficient
αλ	Spectral absorption coefficient
$\lambda c$	Thermal conductivity
λ	Wavelength
ρλ	Spectral reflectance
σ	Stefan–Boltzmann constant
$Q_0$	Incident radiative flux
$Q_2$ , $Q_4$	Energy absorbed by the paint film
$Q_3$	Energy transmitted by the paint and reflected by the substrate
$Q_5$	Energy absorbed by the metallic substrate,
$Q_{emitted}$	Energy lost by radiative emission from the two faces of a system
A(t)	Absorption peak areas of the group to be analysed
A(0)	Absorption peak areas of the group to be analysed at the beginning of the reaction
$\mathcal{E}^{*}$	Complex dielectric coefficient
ε <sup>'</sup>	Dielectric coefficient that indicates the storage capacity of the resin

- $\varepsilon''$  Dielectric loss or loss factor that indicates the energy dissipation part of the resin
- $\Delta H_R$  Reaction heat of the entire curing process
- $\Delta H_t$  Reaction heat of the curing reaction at time t
- $E_m^0$  Initial cured modulus of the resin system
- $E_m^{\infty}$  Fully cured modulus of the resin system
- $E_m(t)$  Modulus at time t
- $E'_t$  Shear energy storage modulus at time t
- $E'_0$  Shear energy storage modulus at the beginning of curing
- $E_{\infty}$  Shear energy storage modulus at end of curing
- $\Delta \tan \delta_t$  Area below the loss peak at time t
- $\Delta \tan \delta_{\infty}$  Area below the loss peak at the end of curing
- $\alpha$  Curing degree at the gelation point
- r Ratio of the A and B functional groups at the beginning of the reaction
- $\rho$  Functionalisation unit concentration
- $G_0$  Minimum torque on the experimental curing curve
- $G_{\infty}$  Maximum torque on the experimental curing curve
- au Relaxation time
- $G_{\infty}$  Final elastic modulus
- G(t) Elastic modulus at time t
- $t_g$  Gelation time, which is indicated on the isothermal curing curve.
- *A* Pre-exponential factor
- $E_a$  Reaction activation energy
- t Times
- T Temperature

- *R* Universal gas constant
- $k_0$  Elastic modulus at time t
- $k_1$  Reaction constants
- $k_2$  Reaction constants
- $k_3$  Reaction constants
- *m*, *n* Order of reaction
- *PTSI* Photo-thermal synergistic index
- $\Delta t_{IR}$  Time periods to reach the highest degree by the IR curing technique
- $\Delta t_{REF}$  Time periods to reach the highest degree by the reference curing technique
- $\alpha_{IR}$  The highest degrees of cure achieved by the IR curing technique
- $\alpha_{REF}$  The highest degrees of cure achieved by the reference curing techniques
- $A_P$  Powder coating area, m<sup>2</sup>
- $A_R$  Radiation panel area, m<sup>2</sup>
- $C_g$  Conversion factor
- $C_{p_p}$  Specific heat capacity of the paint, J/kg·°C
- $C_{p_s}$  Specific heat capacity of the substrate, J/kg·°C
- $e_p$  The thickness of the paint, mm
- *e*<sub>s</sub> The thickness of the substrate, mm
- $E_R$  Radiation force of the radiation panel, W/m<sup>2</sup>
- $h_p$  Convective heat transfer coefficient for the coating, W/m·°C
- $h_s$  Convective heat transfer coefficient for the substrate, W/m·°C
- *l* Distance between the radiant panel and the coating, m
- $\overline{Q}_{abs}$  Infrared radiation absorbed by the powder coating, W/m<sup>2</sup>
- $\overline{Q}_{convevtion}$  Convection heat flux between the system and air, W/m<sup>2</sup>

- $\overline{Q}_{emitted}$  Radiation heat flux between the system and environment, W/m<sup>2</sup>
- $\overline{Q}_{reaction}$  Heat released by the exothermic chemical reaction, W/m<sup>2</sup>
- $Q_{abs}$  Heat absorbed by the powder coating, W
- $Q_{chem}$  The chemical energy of gas, W
- $Q_P$  Internal heat source, W/m<sup>3</sup>
- $Q_R$  Radiation panel radiation energy, W
- $T_{\infty}$  Air temperature, °C
- $T_{s,} T_{p}$  The temperatures of the upper and lower surfaces, °C
- *w* Solid angle, sr
- *ε* Emissivity
- $\eta$  Efficiency
- $\rho$  Volume mass, kg·m<sup>-3</sup>

## **Chapter 1: Introduction**

#### 1.1 Background and overview

With the increasing prominence of environmental and energy issues, countries and their governments have begun to increase their environmental protection efforts, and many countries have introduced many environmental regulations, especially regulatory restrictions on the emission of volatile organic compounds (VOCs)[1] [2]. The use of organic coatings is one of the many sources of VOCs emissions. For example, Changjie Cai [3] et al. found that the use of paint solvents accounted for 15% of the main sources of VOCs in Shanghai according to the positive matrix factorization (PMF) model. Reducing the use of organic solvents can effectively reduce the emission of VOCs, so organic solvent-free powder coatings, waterborne coatings, and other green coatings have become the main research and development direction of the industrial coatings industry. Therefore, green coatings such as organic solvent-free powder coatings have become the main research and development direction of the industrial coatings industry. Powder coatings have developed rapidly in recent years due to their low production costs and relatively simple production processes. They are now recognized for their high production efficiency, environmental friendliness, and excellent coating film performance.

Thermosetting powder coatings sprayed on the surface of the substrate require high temperatures to make the powder molecules melt and perform cross-linking reactions to form a coating film, which plays a special role in protection, decoration and other effects. Although traditional curing

techniques are well established, they are often associated with challenges related to energy consumption and processing time [4]. Specifically, if the powder coating is heated by hot air circulation, a higher hot air temperature is required, and the hot air in the oven is heated by the combustion of fossil fuels. Increasing the temperature of the hot air consumes more fuel, resulting in increased energy consumption for coating, and the traditional combustion of fossil fuels produces a large amount of pollutant gases. In addition, when using hot air to heat the surface coating of workpieces, especially thicker workpieces such as large-scale construction machinery, due to its large heat capacity, the coating warms up more slowly, and is increasingly unable to meet the needs of the actual production. Most of the existing studies have carried out reasonable optimization of oven by means of numerical simulation, so as to reduce energy consumption. Satit et al. [5] used computational fluid dynamics (CFD) modeling and simulation methods to conduct a large-scale study of temperature distribution and flow patterns in a convective paint oven. The validated CFD model is used to investigate the temperature distribution and the flow pattern for two proposed options: eliminating stored heat and rearranging airflow. Yi et al. [6] developed a CFD model to investigate the thermal-transfer efficiency of the existing hot -air convection ovens in a continuous production lines. The increase of the line speed was investigated by varying the temperature, velocity of airflow, and modifications of nozzles. Through simple modifications the line speed can be increased, allowing the reduction of cycle time. Therefore, the search for efficient, clean and environmentally friendly new heating methods has become a hot topic in the field of coating and curing research.

In the production process, people gradually found that infrared (IR) heating technology can solve these problems. Compared with other heating methods, the way of thermal radiation directly heating objects, not only to avoid the loss of heat heating the surrounding objects and can shorten the heating time, improve productivity, so infrared heating technology has gradually been applied to the field of coating curing. Compared to the traditional heat convection curing technology, IR technology offers the advantages of high energy density, low thermal inertia, and high adaptability in the curing field, providing an effective solution for fast and low-energy curing of thermosetting polymers [7]. For instance, Dilmurat et al. [8] assessed the curing mechanism, current application status, and primary advantages and disadvantages of various curing processes for advanced polymer composites. C. F. JASSO et al. [9]used four different curing methods: traditional convection oven, long wave infrared (IR) radiation oven, medium wavelength infrared radiation oven, and open curing conditions without oven heating at room temperature to cross-link the general unsaturated polyester resin. The results show that the medium-wavelength IR oven as a curing condition provides the highest conversion, glass transition temperature (Tg) and mechanical properties of the best choice. Subasri et al.[10] prepared decorative hydrophobic coatings, and the coating is cured using near infrared curing technology. The densified coatings were characterized for their thickness, roughness, contact angles and adhesion. The results show that the properties of the near-infrared radiation cured pigmented coatings were found to be comparable with those of the conventionally cured coatings. Compared to conventional curing, the coating can be cured quickly using near-infrared

radiation (NIR), thus minimizing processing time. Barletta et al. [11] conducted an experimental study to analyze the degree of chemical conversion of the pigmented basecoat, the overall coating morphology and its thermal, mechanical and tribological properties based on infrared radiation time and power. The result shows that the intermediate range of curing time and IR power investigated leads to properly cured basecoats and subsequently to better morphological, mechanical and tribological behavior of the whole coating system. Kumar et al. [12] investigated infrared radiation (IR) post curing process for glass fiber reinforced polymer composite laminates as an alternative to conventional thermal cure. The result shows that IR curing results in volumetric heating and the entire composite laminate will be uniformly heated resulting in uniform curing of all the layers and hence the stresses are reduced. More uniform crosslinking takes place and hence there is no uncured resin patches with in the laminate. In addition, IR utilizes only 25% of total time as compared to conventional curing method. IR curing process has drastically reduced the curing time. Among these methods, IR curing technology has emerged as highly valuable technique. The application of IR radiation has demonstrated a potential in improving the curing process of thermosetting polymers via deep penetration into the material and controlled heating within the polymer matrix. Infrared heating technology including electric infrared and gas infrared [8]. Electric infrared uses electric energy as the input energy, electric heating wire, resistance wire or special material heating wire as the heating body, radiating infrared radiation of different wavelengths, such as quartz lamps, the temperature of the heating body ranges from 400 to 2000 °C. Due to the problems of high power

consumption, high cost of lamp consumables, high cost, and the need for regular maintenance, electric infrared heating technology in the field of large-scale painting has not been widely used.

Catalytic infrared radiation is energy in the form of electromagnetic waves, which are generated from the reaction of natural gas with oxygen under the action of a catalyst. Gas-catalyzed infrared technology makes up for the shortcomings of electric infrared and hot air circulation heating methods, and gives full play to the advantages of high efficiency and environmental protection of the infrared heating method. The application of catalytic infrared technology for powder coating curing has the following potential advantages [13] [14] [15]:

1. Catalytic infrared heating equipment predominantly produces mid-wave and long-wave infrared radiation. This matches the spectral absorption characteristics of powder coatings, accelerating the curing process;

2. Catalytic infrared technology directly converts gas into infrared radiation under the action of a catalyst, resulting in higher energy conversion efficiency. The conversion rate for methane, the main component of natural gas, can reach more than 98%;

3. Catalytic combustion releases infrared radiation energy, enabling the efficient and complete combustion of gas at low temperatures. Low-temperature (<600 °C) combustion reduces the generation of polluting gases, such as CO and NO<sub>x</sub>. Lower pollutant emissions can be obtained ( 5 ppm compared to 150–200 ppm with conventional combustion) [13]. It is assumed that only CO<sub>2</sub> and H<sub>2</sub>O are produced.

Therefore, employing catalytic infrared technology for the curing of powder coatings has important research significance and good potential for application in engineering. However, to the best of our knowledge, the properties and primary experimental data for catalytic infrared curing of powder coatings have not yet been reported, and the theoretical and practical research on the technology for coating curing and drying is not deep enough, and there is a lack of basic experimental data.

#### **1.2 Motivation for the project**

Although theoretically speaking, the catalytic infrared heating technology with its unique advantages in curing powder coatings should be very promising, the technology has not been widely applied in the actual engineering and academic research fields. In particular, several gaps in both experimental and theoretical research need to be addressed:

- 1. Lack of experimental studies on the feasibility of catalytic infrared curing of powder coatings, especially the matching of curing equipment and powder, curing effect, curing conditions, etc. have to be studied;
- 2. No model has yet been reported for the prediction of the temperature changes in coatings during catalytic infrared curing process;
- There have been no kinetic studies of the curing behavior involving the volumetric absorption of IR radiant energy, resulting in a limited ability to predict curing behavior;
- 4. A lack of an assessment methodology for IR curing technology makes it challenging to provide reliable guidance on the feasibility for practical engineering applications.

#### **1.3 Aims and objectives**

This thesis is dedicated to filling the four research gaps mentioned above both experimentally and theoretically, and is expected to serve as a guide for the production of powder coatings and the design of catalytic infrared systems. The objectives of this thesis are:

1. To construct a catalytic infrared curing system for carrying out powder coating curing experiments to test the mechanical and optical properties of the cured layers, and to determine the optimum curing conditions;

2. To develop and validate a heat transfer model for catalytic infrared curing technology, which will be used to predict the system's temperature changes during the curing process;

3. To carry out a kinetic study of catalytic infrared curing technology, establish and validate a kinetic model for curing and determine model parameters;

4. To establish qualitative evaluation criteria for catalytic infrared curing efficiency, which can be used to guide the formulation of powder coatings or the optimisation of curing equipment in practical engineering.

#### 1.4 Thesis outline and content

**Chapter 2** Literature Review- This chapter presents a detailed review of the current research on infrared curing technology, focusing on two key aspects: the heat transfer process and the curing process. By highlighting existing gaps and challenges in the field, this chapter lays the theoretical foundation for the experimental and modeling studies conducted in subsequent chapters. Additionally, it reflects on the author's perspective regarding future

7

research directions in IR-based curing technologies, underscoring the potential for continued innovation in this domain.

**Chapter 3** methodology- This chapter details the experimental design, including the development of a catalytic infrared heating system and the preparation of polymer samples. It elaborates on the analytical techniques used, such as FT-IR, to monitor curing progress and heat transfer dynamics. Data analysis approaches are also presented to ensure robust and reproducible findings.

**Chapter 4** Feasibility study- The aim of this chapter is to carry out a feasibility study of catalytic infrared curing technology, to study the spectral matching of curing equipment and coatings, to test the effect of applying catalytic infrared curing technology on the quality of coatings under different heating conditions, and to assess the mechanical or optical properties of the cured coatings under different conditions in terms of adhesion, gloss, hardness, impact resistance and colour.

**Chapter 5** Heat Transfer Process Study- This chapter focuses on modeling and analyzing heat transfer mechanisms during curing. A one-dimensional heat transfer model is developed to investigate the heat transfer process for powder coatings. This study introduces an internal heat source for the first time, and the heat transfer process for polyester-based powder coatings with different substrate thicknesses is numerically simulated.

**Chapter 6** Curing Process Study- In this chapter, Fourier-transformed infrared (FT-IR) spectroscopy is employed to record the concentration of epoxide groups with respect to time under different temperature conditions, with the reaction conducted under IR radiation. The resulting data are then

fitted by the Levenberg–Marquardt algorithm using MATLAB software to obtain the kinetic parameters, namely the rate constant (k), catalytic constants (n, m), reaction activation energy ( $E_a$ ), and the pre-exponential factor (A) of the curing reaction.

**Chapter 7** Photo-Thermal Synergistic Effect- This chapter proposes a new concept: the "photo-thermal synergistic effect" of infrared curing and its evaluation criteria using a dimensionless quantity. Incredibly, this index integrates the impact of IR curing technology on two aspects: the curing process and the properties of the cured product, and provides a reference for the application of this technology in practical engineering.

**Chapter 8** Conclusion- he final chapter summarizes the findings and contributions of the dissertation. In this chapter, according to the technical line of research, three aspects, i.e., heat transfer process, curing process, and theoretical research are compared and discussed with other scholars' research. It highlights the practical implications of the research and provides recommendations for integrating catalytic infrared curing into industrial operations. The chapter also discusses the limitations of the current study and outlines future research directions, emphasizing the potential for further innovations in this field.

### **Chapter 2: Literature review**

Since the number of studies related to catalytic infrared curing technology is very small, this chapter broadens the scope to infrared curing of thermoset polymers. To provide a comprehensive summary and comparative analysis of the heat transfer and curing processes involving IR curing, articles from the WOS database concerning other curing techniques were searched and screened using "thermosetting polymers", "curing process", and "heat transfer" as the topic index terms. In total, 298 articles were obtained after screening. A comparison of the number of articles published per year is presented in Figure 2- 1. It can be found that this direction has always maintained a relatively stable research progress and has become more popular since 2016. In order to identify current research hotspots, this study presents a clustering time analysis through citespace 6.3. R2, as shown in Figure 2-2. Based on the analysis of the node types to select keywords, the literature was divided into 10 clusters according to research topics, and #0 nanocomposites cluster includes the most literature studies. The lines in Figure 2-2 represent the citation relationships. Each node represents a keyword and the time it first appeared, the size of the circle represents the citation intensity of the literature, and the circle represents the time it was cited. Notably, clustering focuses more on the materials characteristic such as nano materials and polymers and less on studies involving IR curing.



Figure 2- 1. Number of publications per year (Source: WOS; Date: 17 March 2024).



Figure 2- 2 Clustering time analysis (2004–2024) of WOS searches of journals in the polymers curing field through citespace 6.3. R2.

In addition, research on curing thermoset composites by infrared irradiation is focused and directional. The search was conducted using "thermoset", "curing process", and "infrared" as index terms, and the core collection was utilized for subject searching. Moreover, the wildcard "\*"was used to account for occasional plural usage of subject terms. The retrieved articles were screened by keywords, and 30 articles matched the topics of interest; these have been summarized in Table 1. Table 2- 1 and Figure 2- 2 show that there are relatively few articles dealing with the IR curing technology in the relevant research field, both in terms of number and proportion. This is largely attributable to the complexity of the IR heat transfer and curing mechanisms, coupled with the fact that the current research on this technology tends to focus on particular aspects and lacks systematic generalization and analysis. Therefore, it cannot provide sufficient basic support for further research and promotion of this technology. This chapter focuses on the two fundamental processes of heat transfer and curing in the research field on thermoset curing. It provides a comprehensive summary and analysis of recent advancements in utilizing IR radiation for curing thermosetting polymers from the perspectives of equipment, models, and theoretical aspects. Furthermore, the review describes the constraints and shortcomings in the study on IR curing technology, and provides direction and technical support for the present study, i.e., catalytic infrared curing of powder coatings.

Tab	le 2-	1.	Literature	summary
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Material	Substrate	Schedule	IR Source	Reference
DGEBA-type epoxy system	Zinc steel plates		Near-IR (NIR) panel heaters	[16]
Powder coating	•		Gaseous IR heaters	[17]
Unidirectional fiber composites			IR heaters	[18]
AS4/3501-6 epoxy resin prepreg	AISI 304 stainless steel		IR heaters	[19]
Glass fiber-reinforced unsaturated polyester-styrene system		85 °C/3 h	Long-wavelength IR radiation, medium-wavelength IR radiation	[9]
Polyester + TGIC powder coating/polyester-based powder coating	Steel standard test panels	255 °C/105 s	IR radiation (SIR, MIR, NIR)	[20]
Polyester-based system powder/epoxy-polyester-based system	steel panels	255 °C/105 s	IR radiation (SIR, MIR, NIR)	[21]
Polyester epoxy hybrid powder primer	SMC (sheet molding compound) panels and sheet metal panels		IR heaters	[22]

Thermosetting	Steel standard	255 °C/105 s	IR lamps (MWIR,	[23]
powders/polyester-based system	test panels	255 0/1058	SWIR, NIR)	[23]
Glass fiber-reinforced DGEBA-type			IR heaters	[12]
epoxy system			ID 1 4	[24]
Epoxy resin (K1M-0)		20 05 °C/150 min	IK neaters	[24]
BADGE type epoxy resin/4-4'-aminophenylmethylaniline		and 28–150 °C/146 min	IR heater (3–8 μm wavelength, 2 kW capacity)	[25]
Epoxy polyester/polyurethane powders	Metal sheets	1.5 kW/30 s or 2 kW/20–30 s	IR radiation setting the power of IR lamps within the range of 1.0–2.0 kW	[11]
Decorative hydrophobic coatings		250 °C/30 min	NIR radiation	[10]
Polyestermelamine paints/highly absorbent pigments	Steel galvanized with zinc		Convective ovens, NIR heaters	[26]
Carbon fiber-reinforced epoxy matrix			IR heaters	[27]
Gold nanoparticles integrated into a maleate polyester			NIR	[28]
Solvent-blended acrylic resin (polymer matrix)/melamine as hardener	Steel sheet		NIR heating module with 12 tungsten-halogen lamps/2990 K and 4.3 kW	[29]
Composites made of epoxide thermoset resin			IR heaters	[7]
Polymer–composite rods reinforced with fibers			Ceramic IR heaters	[30]
Thermoset-automated fiber placement			LED-based heating unit	[31]
Poly-epoxide adhesive/epoxy pre-polymer		50 °C/40 min	IR heaters	[32]
One-component thermoset coatings		175 °C/15 min	NIR heaters	[33]
Catalyzed cyanate ester resin	Aluminum sheet	260 °C	Medium wavelength heaters (3–7 µm)	[34]
Fiber-reinforced polymer composites		28–85 °C/10–60 min	IR heaters	[35]
Polyepoxy adhesive/epoxy prepolymer			IR heaters	[36]
Solvent-borne epoxy primers			Gas catalytic IR heaters	[37]
DGEBA type epoxy resin	stainless steel	70 min	3–8 μm wavelength of 2 kW capacit	[12]
DGEBA type epoxy resin	stainless steel	70 min	3–8 μm wavelength of 2 kW capacit	[38]

#### 2.1 Heat Transfer Process

#### 2.1.1 Classification and Selection of IR Heaters

IR heating methods are based on the conversion of electromagnetic energy to heat energy without heating the air in between, via the molecular resonance. Polymers contain various couplings such as couplings of vibration modes of CH, CH<sub>2</sub>, CH<sub>3</sub>, and CC, which vibrate at specific frequencies. Most of the vibration frequencies of these molecules correspond to short-wavelength IR (SIR) and medium-wavelength IR (MIR) regions above 1.5  $\mu$ m. Under resonance energy irradiation, the vibrations intensify and produce thermal energy [8]. Based on the energy source, IR heaters can be divided into three basic types, namely, gas-fired, gas catalytic, and electric heaters. Each type has its own unique characteristics and applications; thus, they should be selected and designed based on the practical needs [40].

Gas-Fired IR Heaters: Fueled by natural gas or propane, gas-fired IR heaters can produce significant amounts of heat. The IR radiation from the burning flames is dominated by medium and long wavelengths [8]. Owing to their reliance on radiation rather than convection, gas-fired IR heaters aid in the economic and efficient heating of large workpieces, especially in open or semi-open environments. Such heaters are popular for commercial and industrial heating needs and are often used in conjunction with convection ovens to achieve faster heating. Although their initial cost is higher, they offer several advantages such as independence from electricity, cost-effective operation, energy saving, and greater reliability and durability compared to electric IR emitters. Gas-fired IR heaters provide uniform heating with high thermal efficiency and rapid control; nevertheless, they require well-ventilated spaces to minimize the risk of carbon monoxide poisoning. Although they may not be suitable for extremely high heating demands, they can efficiently produce moderate heat over an extended duration [41]. Gas-fired IR emitters include direct flame IR radiators, ceramic burners, metal fiber burners, and high-intensity porous burners.
Gas Catalytic IR Heaters: Gas catalytic IR heaters function through the catalytic combustion of gas. The gas, which is often propane or natural gas, is passed over a catalyst, usually prepared with platinum or palladium, initiating a chemical reaction that produces heat without a visible flame [42]. This method involves a highly efficient heating process, emitting MIR radiation and far infrared (FIR) radiation (3-7 µm). Compared to traditional gas-fired or electric heaters, the heat produced is generally gentler and more evenly distributed. In oven design, gas catalytic IR heaters are commonly used in scenarios requiring consistent, low-intensity heat over extended periods. In general, diffusion catalytic combustion occurs at around 400 °C [Yuan et al., Qin et al.], while the temperature for the pilot-premixed catalytic combustion reaches above 500 °C. The absence of a flame during combustion allows the radiant surface to be placed closer to the object, which leads to increased efficiency. This combustion device generates low or near-zero emission concentrations of organic volatiles, such as NO<sub>x</sub>, in the flue gas, resulting in minimal pollution. Furthermore, the surface temperature of gas catalytic IR heaters is uniform, and their surface can be customized.

**Electric IR Heaters:** Electric IR heaters utilize electricity to heat an element, such as a ceramic or metal, quartz tube, or carbon element, which then emits IR radiation., and these heaters can operate at different temperatures and have quick response times, often heating up and cooling rapidly [43]. Although their operating costs may be higher than those of gas-fired heaters, they are more advantageous in applications requiring precise temperature control and rapid thermal cycling; thus, they are commonly used in small- to medium-sized IR ovens. Electric IR emitters consist of a metal

filament placed inside a sealed enclosure, which is either filled with inert gas or evacuated. Radiant energy is generated by passing an electric current through a high-resistance wire, causing the element and the surrounding material to become incandescent [44]. Electric IR emitters can operate at temperatures up to 2600 K, corresponding to near-infrared (NIR) radiation of 0.7 to 1.5 µm. The wavelength spectra of these electric IR emitters and emissive powers are controlled via the power input to the system. Various electric IR radiant emitters with different specifications, e.g., reflector-type incandescent lamps, quartz tubes, metallic tubes, ceramic tubes, and non-metallic rods, are available for specific purposes. Incandescent lamps are classified as short-wave emitters, while quartz tubes and resistance elements are classified as medium- and long-wave emitters, respectively. Unlike natural gas-, diesel-, and propane-fueled emitters, electric IR heaters generate zero emissions [40].

The choice of an IR heater depends on various factors, such as specific heating requirements of the application, cost considerations, and available infrastructure. When designing an IR heating system, matching the emission spectra of the emitter with the absorption spectra of the material to be heated is crucial for the overall efficiency of the system. Moreover, the physical properties of the medium in the working chamber, the geometrical parameters describing the relative positions of the IR emitter and the irradiated object, and the spectral emissivity distribution of the IR emitter are factors that significantly affect the system's performance. Table 2- 2 presents a comparison of the key performance parameters for gas-fired, gas catalytic, and electric IR heaters and includes literature references on the use of IR curing technology. It

can be observed that electric IR heaters are the most commonly used in such studies.

	Gas-Fired IR Heaters	Gas Catalytic IR Heaters	Electric IR Heaters
Wavelength range (µm)	2-4.5	3–7	0.7-1.5
Temperature rating (°C)	800-1200	350-500	500-1000
Thermal efficiency (%)	80%-85%	85%-90%	70%-80%
Response time	Medium	Slow	Fast
Working lifespan (Years)	10–15	15–20	5-10
Advantages	High heat output, efficient large-area heating	Uniform heat distribution, energy-efficient	Fast response time, precise temperature control
Limitations	Low precision, high operating temperature	Slow response time, low temperature range	High operating cost, short lifespan
Literature	Deans et al., 1999 [2]	Stojanovii et al., 2024 [37]	[21] [45] [23] [20] [34] [18] [24] [46] [47] [12] [32] [48]

## Table 2-2. Classification of IR heaters and literature summary.

## 2.1.2. Monitoring Devices

The curing process is significantly affected by temperature and time, thus necessitating the use of robust, sensitive, and accurate monitoring equipment. Table 2- 3 presents a comparative analysis of various temperature-monitoring devices as well as references to the relevant literature in the field of IR curing.

Material Properties	Typical Instrument	Limitations	Reference
Thermal property	Thermocouple Pyrometer temperature	Low accuracy and restricted temperature range	[23] [21] [45] [20] [34] [27] [32] [48]
-	IR camera	Accuracy affected by the ambient temperature, distance, and geometry	[27]

Table 2-3. Comparison of different monitoring devices.

Electric	RTD	Fragile and	
property	KID	somewhat destructive	-
Hoot flux	Thermopile	High calibration complexity and high	[23]
	calorimetric	sensitivity to thermal regulation	[21]

Thermal Imaging: Thermal imaging is a technique that utilizes IR cameras to capture thermal radiation emitted by the surface of an object and convert it into a visible image that depicts the temperature distribution. Thermal imaging offers a non-contact and non-invasive means of monitoring the temperature changes and the curing degree of thermosetting polymers during IR curing. Furthermore, thermal imaging can reveal spatial and temporal variations in the temperature field, which can affect the curing kinetics and mechanical properties of the final product. Thermal imaging has been extensively used to investigate the effects of various parameters, e.g., IR power, curing time, sample thickness, and IR wavelength, on the IR curing process of thermosetting polymers [49]. However, thermal imaging brings forward certain limitations, such as low spatial resolution, high cost, and sensitivity to environmental factors, including ambient temperature, humidity, and airflow [50].

**Resistance Temperature Detectors:** Resistance temperature detectors (RTDs) are sensors that measure temperature based on the change in electrical resistance of a metal wire or a thin film. RTDs can offer high accuracy, stability, and repeatability, but they also have certain disadvantages, such as slow response time, self-heating effect, and interference from external electromagnetic fields. RTDs are usually embedded in the polymer matrix or attached to the specimen surface, which may affect the heat transfer and curing processes. Although RTDs can measure the local temperature of a polymer, they cannot provide global temperature distributions or heat flux

information. RTDs have been utilized to measure the temperature of thermosetting polymers during IR curing. The results of RTDs have been compared to those obtained by other methods, such as thermal imaging and thermocouples [50]. However, the use of RTDs is challenging in terms of calibration, installation, and durability, particularly for high-temperature and high-pressure applications.

Thermocouples: Thermocouples are sensors that measure temperature based on voltage generated at the junction of two different metals. They usually consist of two dissimilar metal wires connected at a welded junction. Their function is based on the Seebeck effect experienced by conductors with temperature gradients along their length [51]. In the context of polymer curing processes, the generation of thermoelectric voltage in thermocouples is predicated upon the temperature gradient between the sensing junction and the open ends. These sensors are capable of measuring a broad spectrum of temperatures and are valued for their rapid response times and simplistic design. However, they exhibit several limitations such as low sensitivity, inherent non-linearity, and susceptibility to calibration discrepancies. When integrated into a polymer matrix or affixed onto the surface of a specimen, thermocouples may introduce localized thermal perturbations and lead to heat dissipation issues. Although effective for recording localized temperature variations within a polymer, thermocouples do not provide comprehensive data on overall temperature distribution or heat flux across the material. This limitation is significant in applications requiring detailed thermal mapping during polymer curing. Thermocouples have been used to measure the temperature of thermosetting polymers during IR curing [7]. However,

thermocouples bring forward certain disadvantages in terms of accuracy, stability, and reliability, particularly for low-temperature and low-voltage applications.

Heat Flux Sensors: Heat flux sensors are devices that measure the rate of heat transfer per unit area across a surface. They utilize measurement techniques with different principles, such as thermopile, calorimetric, or Gardon gauge, to perform these measurements. Heat flux sensors can provide direct and quantitative information regarding the heat transfer and curing kinetics of thermosetting polymers under IR radiation. They are usually placed on the side opposite the IR source, which may reduce the interference and disturbance to the curing process [52]. Moreover, heat flux sensors can measure the heat flux distribution and the heat balance of the system, which can help to optimize the IR curing parameters and improve energy efficiency. They have been used to measure the heat flux of thermosetting polymers during IR curing as well as to correlate the heat flux with the conversion degree and mechanical properties. However, heat flux sensors have certain drawbacks in terms of sensitivity, linearity, and durability, especially for high-heat-flux and high-temperature applications [53]. Figure 2-3 illustrates a novel thin-film heat flux sensor, which was developed by Xu et al. to measure heat flux in two directions [54].



Figure 2- 3. Schematic showing a newly designed thin-film heat flux sensor: (a) cross section and (b) top view [54].

#### 2.1.3. Thermal Transfer Model

Modeling of heat transfer is essential to perform studies concerning heat transfer processes. However, before this can be achieved, it must be clarified whether IR heat transfer should be regarded as a surface-to-surface heat transfer phenomenon or a more complex bulk heat transfer phenomenon [55]. Chern et al. [18] considered optical depth as the determining parameter and reported that if the optical thickness was greater than 5, the radiation could be regarded as a surface phenomenon, and thus treated as a part of the boundary conditions of the energy equation. This is the case, for instance, for most carbon fiber-reinforced composites, but not for glass/epoxy composites. This section is grouped based on surface and volume transport, and both types of models are presented and analyzed with examples.

Surface Radiation Transport: Energy Balance and Boundary Conditions: Bombard et al. developed a mathematical model that incorporated an understanding of the fundamental mechanisms governing thermal transfers. The model was employed to predict film temperature changes and the extent of reaction when the powder coating was exposed to radiative flux. The thermal model is based on Fourier's law of heat conduction. Figure 2- 4 illustrates the boundary conditions imposed on the upper surface of the powder film and the lower surface of the metallic substrate [23].



Figure 2-4. Geometric modeling of surface heat transfer [23].

The thermal equilibrium is determined by considering the temperature variation across the thickness of the powder-coated metal sample and the curing degree conversion, which ranges from 0 at the beginning to 1 upon completion. For the powder domain, the following equations apply [23]:

$$\nabla \left(\lambda_{c,p} \nabla T_p\right) = \rho_p C P_p \frac{\partial T_p}{\partial t} + Q_{reaction}$$
(2.1)

$$\nabla \left( \lambda_{c,s} \nabla T_s \right) = \rho_s C P_s \frac{\partial T_s}{\partial t}$$
(2.2)

$$Q_{reaction} = \rho_p e_p \Delta H_0 \frac{dx}{dt}$$
(2.3)

The kinetic model that is used to describe the polymerization of the two powder-coated systems is an autocatalytic model given by Sestak–Berggren:

$$\frac{dx}{dt} = k_0 exp \left(-\frac{E}{RT}\right) k^m (1-x)^n \tag{2.4}$$

The boundary conditions are

$$-\lambda_{c,p}\frac{\partial T_p}{\partial Z} = \alpha_{p,T_p}\phi_i - \sigma\varepsilon_S(T_S^4 - T_\infty^4) - h_s(T_s - T_\infty)$$
(2.5)  
at  $Z = 0$ 

$$-\lambda_{c,p}\frac{\partial T_p}{\partial Z} = -\lambda_{c,S}\frac{\partial T_S}{\partial Z} \text{ and } T_P = T_S$$
(2.6)  
at  $Z = e_p$ 

$$-\lambda_{c,S} \frac{\partial T_S}{\partial Z} = \sigma \varepsilon_S (T_S^4 - T_\infty^4) + h_s (T_s - T_\infty)$$
(2.7)  
at  $Z = Z_{\text{interface}} = e_p + e_s$ 

The initial conditions are:

$$T_P(Z,0) = T_1 \quad \forall 0 \le Z \le Z_{interface}$$
(2.8)

$$T_s(\mathcal{Z}, 0) = T_2 \quad \forall \mathcal{Z}_{interface} \leq \mathcal{Z} \leq e_p + e_s \tag{2.9}$$

$$\mathcal{X}(Z,0) = 0^+ \quad \forall 0 \leq Z \leq Z_{interface}$$
 (2.10)

To study the temperature and curing degree as a function of time during the curing process in the three dimensions, Igor Zhilyaev et al. [34] developed a mathematical model to predetermine the IR heater parameters required to cure composite components with complex shapes. Mathematical modeling and optimization were performed by using the finite element (FE) software COMSOL Multiphysics. The governing equations are presented in detail later in this chapter. The developed model can be described with the following general points [34]:

- The model simulates the absorption of the IR energy by the upper surface of the composite via surface-to-surface radiation equations;
- 2. The IR energy absorbed by the upper surface of the composite is integrated into the heat transfer equations as a heat flux boundary condition;
- 3. Heat transfer within the part occurs through conduction to the bottom of the composite;
- 4. The curing degree is calculated based on the heating rate;
- 5. The exothermic heat of the resin is introduced to the heat equations as the heat source.

The developed model incorporates advanced simulations to accurately represent the IR energy absorption by the upper surface of the composite. For this purpose, it utilizes surface-to-surface radiation equations and integrates the absorbed IR energy as a heat flux boundary condition into the heat transfer equations. Furthermore, conduction within the part is considered for the heat transfer to the bottom of the composite, and the curing degree is calculated based on the heating rate. Moreover, the model introduces the exothermal heat of the resin as a critical component in its comprehensive heat equations [34]:

$$\rho_{c}c_{p}\frac{\partial T}{\partial t} = \nabla k\nabla T + (1 - \nu_{f})\rho_{m}H_{total}\frac{\partial \alpha}{\partial t}$$
(2.11)

Since only a quarter of the original geometry is considered, the symmetry boundary condition is applied to boundaries formed during the geometry division:

$$-n \cdot (\Delta k) = 0 \tag{2.12}$$

A heat flux boundary condition is used on the bottom boundary of the aluminum plate to simulate the heat exchange between the oven and the ambient space:

$$-n \cdot (k\nabla T) = h_b(T_{ext} - T) \tag{2.13}$$

Since the air domain is not considered, the free convection boundary condition is applied on the upper surface of the composite, mount, and aluminum plate bodies:

$$-n \cdot (k\nabla T) = h_t (T_{amb} - T) \tag{2.14}$$

The parameters of the curing kinetic equation for the resin were determined experimentally by isothermal and dynamic differential scanning calorimetry (DSC) trials:

$$\frac{d\alpha}{dt} = \left[A_1 exp\left(-\frac{E_1}{RT}\right)(1-\alpha)^{n_1} + A_2 exp\left(-\frac{E_2}{RT}\right)\alpha^m\right](1-\alpha)^{n_2} \quad (2.15)$$

Volume Radiation Transport: Energy Balance and Boundary Conditions: The most significant difference between the volumetric absorption heat transfer model and the surface absorption heat transfer model lies in the setting of the boundary conditions. In particular, the radiant heat flow does not transfer heat to the interior of the object and the substrate in the form of heat conduction in the differential equations for heat transfer [51].

Véchot et al. [20] assumed that when the film thickness was small enough and the metal substrate was a fairly good conductor of heat, then the temperature could be assumed to be constant in all the substrate + paint systems. This assumption was experimentally verified by measuring the temperature with two thermocouples (type K, 3% accuracy): one fixed underneath the metal plate and the other attached on the cured paint.



Figure 2-5. Geometric modeling of volumetric heat transfer [56].

Subsequently, they used the following mathematical expression to solve the thermal balance [20]:

 $\frac{dT}{dt} (Cp_p \rho_p e_p + Cp_{sup} \rho_{sup} e_{sup}) = Q_{abs} - Q_{reaction} - Q_{emitted} - Q_{convection} (2.16)$ Assuming that the substrate absorbs all the energy, the thermal equilibrium can be established as follows:

$$Q_{abs} = Q_0 (1 - \rho_P^*) - Q_0 \tau_P^2 (1 - \alpha_{sup}) = Q_0 - Q_1 - Q_3$$
  
=  $Q_2 + Q_4 + Q_5$  (2.17)

where  $Q_0$  is the incident radiative flux,  $Q_2$  and  $Q_4$  are the energy absorbed by the paint film,  $Q_5$  is energy absorbed by the metallic substrate, and  $Q_3$  denotes energy transmitted by the paint and reflected by the substrate; this term (order two) was considered negligible for this paint. Furthermore,  $Q_{emitted}$  represents the energy lost by radiative emission from the two faces of the system and is defined as follows:

$$Q_{emitted} = \sigma \varepsilon_{sup} \left( T^4 - T_1^4 \right) + \sigma \varepsilon_p \left( T^4 - T_2^4 \right)$$
(2.18)

Q<sub>reaction</sub> represents the heat released by the exothermic chemical reaction.

$$Q_{reaction} = \rho_p e_p \frac{dx}{dt} \Delta H_0 \tag{2.19}$$

 $Q_{\text{convection}}$  represents the thermal losses due to natural convection from the upper and lower surfaces of the system.

$$Q_{convection} = h_{ai}(T - T_1) + h_{as}(T - T_2)$$
 (2.20)

The numerical simulations of the heat balance were performed using the Matlab software, and the results revealed that despite its simplicity, the thermal model was able to satisfactorily predict the experimental heating rate.

Over the last three decades, several researchers have devoted significant research efforts to develop heat transfer models for the IR curing process. These heat transfer models are classified and compared in Table 2- 4. In correlation with the contents of Table 2-1, there are no studies on heat transfer model for catalytic infrared curing technology.

Table 2-4. Thermal transfer model classification.

	Heat Transfer Method		Geometric Model				
Mode	Radia tion	Radiation and Convection	3D/2D Model	1D Model	Controller	Software	Reference
Surface					PID	Matlab	[21]

absorption		$\checkmark$		 MPC		[23]
-				 PID & MPC		[45]
	$\checkmark$		$\checkmark$	PID	COMSOL	[34]
						[18]
		$\checkmark$			COMSOL	[24]
		$\checkmark$			COMSOL	[46]
	$\checkmark$			SQP	Matlab & COMSOL	[47]
	$\checkmark$		$\checkmark$		COMSOL	[27]
	$\checkmark$					[17]
			$\checkmark$		FLUENT	[48]
					Matlab	[20]
volumetric absorption		$\checkmark$				[18]
	$\checkmark$					[32]
		$\checkmark$				[38]
		$\checkmark$				[12]

### 2.1.4. Numerical Simulation Methods

IR radiative transfer problems encountered in various engineering fields are usually very complex. This is attributed to factors such as nonlinearity of the governing equations, transparent or opaque radiation interfaces in complex geometrical systems, and radiation characteristics that vary with wavelength and direction. In this section, six commonly used numerical simulation methods for radiative heat transfer are introduced, and their applicability is compared and evaluated based on six different requirements [57].

**Zone Method:** The zone method treats each zone (a discrete volume in the computational domain) as a separate radiating surface. The radiation exchange between different zones is computed based on view factors, which quantify the geometric relationship between zones. This method is suitable for problems that involve complex geometries, where the view factor calculations are manageable [58].

Monte Carlo Method: The Monte Carlo method (MCM) is based on probabilistic principles and involves tracking numerous photon 'packets' or 'particles' within the computational domain. At each interaction point (due to scattering or absorption), a random process determines the new direction of the photon 'packet' and the energy it carries forward. Monte Carlo method (MCM) is one of the sampling-based approaches which can handle the issue of high dimensionality in the probabilistic Uncertainty quantification (UQ) framework. MCM has many advantages, such as non-intrusive, robust, flexible, and simple for implementation [54]. However, due to the cumbersome computational work of large amount of ray tracings, the computational speed of this method is very slow which is not suitable to conducting coupled analysis with other process in thermal fluid problems [55].

**Ray-Tracing Method:** The ray-tracing method (RTM) is a widely used numerical simulation approach in the field of radiative heat transfer. RTM involves tracing the path of energy-carrying rays as they move through a medium and interact with surfaces, enabling the calculation of radiant heat transfer within complex systems. By considering the emission, absorption, and scattering phenomena encountered by the rays, this method provides a comprehensive analysis of radiative energy transfer. RTM provides a systematic approach to model and predict thermal radiation behavior, facilitating the design and optimization of high-performance thermal systems [59].

**Discrete Ordinates Method:** The discrete ordinates method (DOM) is used to solve the radiative transfer problem. The solution of the radiative transfer equation (RTE) requires discretization of both angular and spatial domains. The idea of DOM is to represent the angular space by a discretized set of directions, and only radiative intensity at these discrete directions is solved. Each direction is associated with a quadrature weight. Both the

28

directions and the weight are chosen carefully to ensure accuracy of angular integration, which is important for discretizing the in-scattering term and calculating the radiative heat flux. After the angular discretization is finished, the original integral-differential form of RTE becomes a set of coupled partial differential equations, which can then be discretized and solved by traditional techniques for solving partial differential equations [57].

**Discrete Transfer Method:** The discrete transfer method (DTM) is one of the widely used methods in radiative transfer. It has been extensively used to solve pure radiation and combined radiation, conduction and/or convection mode problems [58]. In this method, the energy emitted is divided into the hemisphere along finite number of rays, the radiation leaving the surface element in a certain range of solid angles can be approximated by the single ray [59].In recent times, DTM has attracted the attention of various researchers as the method offers an advantage in terms of its applicability for complex geometries as compared to DOM. Coelho [60]has compared the accuracy of results obtained using DTM and DOM for radiative heat transfer in non-grey gases. It was reported that for such applications, the DTM predicts more accurate results and fares better in comparison with DOM. In addition, Nirgudkar et al. [61]proposed a simplified method for solving transient forms of RTE in two-dimensional participating media using DTM.

**Finite Volume Method:** The finite volume method (FVM) is a method for obtaining numerical solutions to differential equations, such as the radiative transfer equation. In FVM, the computational domain is divided into a finite number of small "control volumes" and the governing equations are integrated over each control volume. The net flux of radiation across the

29

control volume boundaries is used to update the radiation energy density within each control volume. FVM is particularly good at conserving energy, a key requirement for precise radiative transfer simulations [60].

There are benefits and drawbacks to each of the aforementioned strategies. The adaptability of the geometry, compatibility with flow, burns, chemical reactions, and other heat transfer modes, adaptability to anisotropic scattering and inhomogeneous media, feasibility of multiscale analyses and simulations (microscopic, macroscopic), mesoscopic, and ease of handling semi-transparent interfaces and probing directions, and efficient and accurate calculations are all necessary for a successful simulation method. To yet, there isn't a flawless computational technique that can meet all of the aforementioned criteria at once. Based on the aforesaid description, the advantages and disadvantages of several numerical simulation methods for radiation heat transfer are listed in Table 2- 5; the "Ref." column includes relevant studies on the subject of IR curing.

Table 2- 5. Comparison of different numerical simulation methods and available studies.

Calculation	Complex	Anisotropic	Inhomogeneous	Semi-Transparent	Calculation	Ref
Method	Shapes	Scattering	Media	Interfaces	Accuracy	I.C.I.
ZM	-	-	+/-	-	Good	
MCM	+	+	+/-	++	Good	[17]
RTM		++	+/-	++	Very good	[46]
DTM	-		+/-	+/-	Good	
DOM	+	+	+	+/-	Moderate	
FVM	+	+	+	+	Good	

(++) Easy, (+) Feasible, (+/-) Moderate, (-) Difficult, (--) Very difficult.

### 2.2. Curing Process

### 2.2.1. Monitoring Techniques and Models

Numerous types of curing reactions can occur in thermosetting polymers. The curing process is intricate, involving the cross-linking of linear polymer chains or the polymerization of low polymers. here is general agreement that nearly all ultimate properties of thermoset systems are dependent on the state of crosslinking or curing situation when a resin reacts with a curing agent in such systems [63]. The properties of cured products depend highly on the structural composition of the material system and the curing reaction conditions [64]. Moreover, even products of the same brand but from different batches may exhibit different curing characteristics due to discrepancies in the material production process. Therefore, it is crucial to accurately monitor, evaluate, and study the curing process and its related parameters.

The complexity of the curing process and the actual curing system poses challenges in establishing an absolute measurement standard, leading to the absence of a unified standard measurement method at present. Typically, a measurable physical or chemical quantity related to the curing degree is selected as the basis for measurement. Careful observation of the changes and change rate of this value enables the determination of the curing degree and reaction rate, as well as essential process parameters such as the gelation time and complete curing event [65].

Different physical meanings are assigned to measurement methods according to the quantities that need to be measured. While some techniques work well in laboratories, others are more appropriate for online production line monitoring. Table 2- 6 summarizes the commonly used research methods for curing processes.

Table 2- 6. Comparison of different monitoring techniques and models.

<b>Method Classification</b>	<b>Representative Measurement Methods</b>	Measured Physical Quantity	Ref
	Chemical titration	Chemical group concentration	
Chemical reactions	IR, Raman, and other spectroscopic	Spectral signal intensity of chemical	
	methods	bonds	

Thermal properties	Differential thermal analysis (DSC, DTA)	Heat fusion changes during curing	[24] [46] [47] [23] [21] [45] [20] [47] [32] [48]
Electrical properties	Dielectric analysis (DEA)	Dielectric loss and ionic conductivity, and resistance	[34]
Mechanical properties	Dynamic spring method, dynamic thermo-mechanical analysis, dynamic torsion vibration method	Correlation of mechanical modulus and mechanical loss	
Fiber optic-based measurements	Fiber optic monitoring	Change in refractive index or absorption of signal waves	
Ultrasound measurements	Ultrasonic monitoring	Longitudinal ultrasonic velocity and attenuation	
Other methods	Viscosity method, hardness method, swelling method	Corresponding physical properties	

2.2.1.1 Spectrum Analysis

IR spectroscopy aids in direct determination of molecular structure information related to a measured system, which is mainly manifested by the position and intensity of absorption peaks [61]. The type of chemical bond (functional group) corresponding to an absorption peak can be assessed from the position of the absorption peak, as well as the effect of its chemical environment, e.g., solvation and adjacent groups. The intensity of the absorption peak reflects the concentration of corresponding groups within the material. By analyzing this information, the curing reaction mechanism during the curing reaction and the microstructure of the cured product can be inferred. Moreover, relevant curing kinetic parameters, such as gelation time, complete curing time, and curing rate, can be quantitatively calculated [62].

The concentration changes of the molecular groups involved in the curing reaction and the curing degree in the system can be calculated according to Equations (2.22) and (2.23), respectively [63].

$$C(t) = \frac{A(t)/A(t)_{standard}}{A(0)/A(0)_{standard}}$$
(2.21)

$$\alpha = 1 - C(t) = \frac{A(0)/A(0)_{standard} - A(Tt)/A(t)_{standard}}{A(0)/A(0)_{standard}}$$
(2.22)

where A(t) and A(t)standard are the absorption peak areas of the group to be analyzed and the internal standard group at time (t), respectively. Similarly, A(0) and A(0)standard are the absorption peak areas of the group to be analyzed and the internal standard group at the beginning of the reaction, respectively.

#### 2.2.1.2 Electrical Property Analysis

The electrical properties of thermosetting resins can sensitively reflect changes in the internal structure of the material and the state of molecular motion. DEA is the most widely used method for monitoring the curing process of thermosetting resins [64]. It involves the investigation of the changes in the dielectric properties of the resin during curing, enabling the monitoring of the liquid and solid states. DEA is flexible and suitable for real-time monitoring and process simulation on the production line and can be applied to various systems such as composite materials, adhesives, and coating sols. The basic principle of DEA involves the orientation response of polar groups and ions in an electric field, with the orientation degree being affected by factors such as temperature, frequency, polymerization, and viscosity. Changes to dielectric properties during curing are effected by factors including polymerization degree, temperature, and viscosity [65]. The phase change and amplitude attenuation of the inductive signal during dielectric testing can provide information regarding the resin viscosity, reaction rate, and curing degree.

The dielectric coefficient of a thermosetting resin can be expressed in complex form as [66]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{2.23}$$

$$\tan \delta = \varepsilon'' / \varepsilon' \tag{2.24}$$

where  $\varepsilon^*$  is the complex dielectric coefficient,  $\varepsilon'$  is the dielectric coefficient that indicates the storage capacity of the resin,  $\varepsilon''$  denotes the dielectric loss or loss factor that indicates the energy dissipation part of the resin, and tan  $\delta$  is the tangent of the loss angle.

### 2.2.1.3. Thermal Property Analysis

The thermodynamic parameters and physical properties of substances often exhibit correlations that are sensitive to temperature changes. Thermal analysis (TA), a method based on this principle, is widely employed in examining polymer structures and properties. The curing process of thermosetting resins is typically accompanied by noticeable thermal effects; therefore, it can be analyzed using TA methods. Commonly used TA techniques for resin curing analysis include enthalpy analysis and thermo-mechanical analysis (TMA), among others. Enthalpy analysis includes differential thermal analysis (DTA) and DSC [67]. In particular, the DSC method directly measures enthalpy data during the curing process, offering ease of operation, high resolution, and convenience for quantitative analysis; thus, it is more commonly used in resin curing research [73]. Currently, DSC is the most commonly used method for studying the IR curing kinetics of thermosetting resins (Table 6). According to Table 4, the DSC technology mainly focuses on the surface absorption mode. The use of DSC by Genty et al. [26] may be controversial considering the mechanism-based differences

exhibited by thermal and IR curing, particularly the different kinetic parameters of curing [30]. Mafi et al. [68] investigated the thermal behavior of hybrid epoxy/polyester and pure polyester powder coatings by DSC. The effect of curing temperature on the coating glass transition temperature (Tg) was also assessed via dynamic TMA (DTMA). The non-isothermal DSC spectra of the hybrid and pure polyester coatings obtained under a scanning rate of 10 °C ·min−1 are presented in Figure 2- 6.



Figure 2- 6. Non-isothermal DSC spectra of the hybrid and pure polyester coatings obtained under a scanning rate of 10 °C·min-1 [37]

It is generally assumed that the heat released during fusion is a result of the curing reaction. Therefore, the area under the exothermic curve is directly related to the curing degree ( $\alpha$ ), which can be calculated by determining the curing rate. This rate can be obtained as follows [69]:

$$\alpha = \frac{\Delta H_t}{\Delta H_R} \tag{2.25}$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_B} \frac{dH_t}{dt}$$
(2.26)

where  $\Delta H_R$  is the reaction heat of the entire curing process, which is constant for a particular resin curing system, and  $\Delta H_t$  denotes the reaction heat of the curing reaction at time t.

#### 2.2.1.4. Optical Fiber Measurement Analysis

Besides DSC, optical fiber measurement analysis can also be utilized to monitor and measure the temperature of the curing process [70]. Optical fiber sensors are advanced sensors that are based on optical measurement technology. They are characterized by high sensitivity and strong anti-electromagnetic interference. Simultaneously, optical fibers offer unique advantages such as small diameter, flexibility, high temperature resistance, and good compatibility with composite materials. Such sensors can be used to monitor the refractive index changes of the curing system or the absorption of the measured signal wave by the resin, thereby reflecting the curing process characteristics of the system. The advantages of fiber optic sensors include their small size, high sensitivity, and little effect on the mechanical properties of the material [71]. The need for implantation into the material, which can interfere with its curing reaction, high production costs, and lack of reusability are some of their disadvantages. Cusano et al. [71] designed and experimentally assessed an optoelectronic fiber optic sensor (FOS) capable of monitoring the polymerization reactions of thermoset polymer-matrix composites. As shown in Figure 2-7, the FOS output was recorded during isothermal scans at temperatures of 50, 60, and 70 °C.



Figure 2- 7. FOS output during isothermal scans at 50, 60, and 70 °C [71]. 2.2.1.5. Ultrasonic Analysis

The ultrasonic echo pulse technique is commonly used in ultrasonic thickness gauges to measure coating thickness on non-metallic matrix materials such as plastic and wood [78]. By analyzing the echo waveform digitally, the thickness of the coating can be accurately determined. Recent studies have reported the online monitoring of resin curing via ultrasonic methods. The propagation of high-frequency elastic waves in the ultrasonic state is associated with the dynamic mechanical deformation of the object being measured, reflecting changes in its internal structure and cohesive state [72]. The ultrasonic properties of resins are highly sensitive to the gelation and complete curing processes, providing valuable information regarding the changes in mechanical property. Ultrasonic measurement is essentially a dynamic mechanical analysis at high frequency, offering insights into the viscoelastic properties of the resin at different states of physical structure. Ultrasonic monitoring of resin curing offers several advantages such as non-destructive material assessment, high detection sensitivity, and simple operation [73]. Currently, ultrasound technology is primarily used for monitoring the resin curing process. The instantaneous curing of a resin can be determined by measuring its modulus Em, which is directly correlated with the cross-linking degree [74]:

$$\alpha(t) = \frac{E_m(t) - E_m^0}{E_m^\infty - E_m^0}$$
(2.27)

where  $E_m^0$  and  $E_m^\infty$  are the initial and fully cured moduli of the resin system, respectively, and  $E_m(t)$  denotes the modulus at time t.

## 2.2.1.6. Mechanical Property Analysis

The curing process of thermosetting resins involves the formation of cross-links between linear polymers or the polycondensation of functional monomers. The curing degree can be assessed by monitoring the consumption of functional groups [75]. Nevertheless, this measurement becomes less significant in the final stage of curing despite its effect on the mechanical properties of the resin. This final stage plays a critical role in determining the optimal properties of the cured resin. Consequently, relying solely on chemical methods to evaluate the resin curing behavior is inadequate. On the other hand, mechanical methods involve the measurement of relevant mechanical moduli such as the shear modulus, flexural modulus, and torsional modulus [76]. Tests are performed at different frequencies to determine the mechanical moduli and mechanical loss of the resin. Commonly used mechanical testing methods include the torsional pendulum method [84], twisted braid method [85], rheological method [86], DMTA [87], dynamic torsion vibration method [88], and others. Torsional braid analysis is derived from the torsional pendulum approach and is a free decay vibration method. DMTA measures and determines the dynamic mechanical properties of the specimen under cyclic alternating stress, and varying temperature, time, and

frequency parameters. Commercial DMTA can accommodate a wide range of deformation modes. Resin samples are typically treated as those in torsion braid analysis, where the samples are fixed to an inert material for analysis. During resin curing, the viscosity increases with increasing curing degree, particularly near the gelation point. This increase approaches infinity when the resin is fully cured, enabling the assessment of the resin curing process by measuring the viscosity changes. A plate rheometer can measure the complex shear modulus or the complex shear viscosity of the resin. Based on the need to control the mechanical properties of engineering materials, Ramis et al. [75] conducted a study on the curing process of a thermosetting powder coating. This coating was prepared using Carboxyl-terminated polyester and TGIC, and its curing was analyzed using DMTA, TMA, and DSC. Figure 2- 8 depicts the isothermal curing of the coating determined via DMTA.



Figure 2-8. Storage modulusand loss tangent versus time by DMTA [75].

Different measurement modes can be utilized to obtain the time, frequency, and temperature spectra of modulus and loss [77].

$$\alpha_m = \frac{E'_t - E'_0}{E'_{\infty} - E'_0}$$
(2.28)

$$\alpha_{\tan\delta} = \frac{\Delta \tan \delta_t}{\Delta \tan \delta_\infty} \tag{2.29}$$

where  $E'_t$ ,  $E'_0$ , and  $E'_{\infty}$  are the shear energy storage modulus at time t, at the beginning of curing, and at the end of curing, respectively, and  $\Delta \tan \delta_t$ and  $\Delta \tan \delta_{\infty}$  are the areas below the loss peak at time t and full curing, respectively.

## 2.2.2. Curing Theory

Numerous methods have been developed to characterize the curing reaction of thermosetting polymers. Consequently, various curing models have been established, which are mainly categorized as mechanism-based and phenomenological models. The mechanism-based models focus on analyzing the specific curing reaction mechanism, studying the kinetic relationships of the curing process, and theoretically considering all elementary reactions during the entire process. Conversely, phenomenological models do not consider individual elementary reactions but use a virtual apparent reaction to represent the entire curing process and study the main kinetic characteristics from a macroscopic perspective. Owing to the complexity of the curing process, particularly in its later stages where diffusion factors become dominant, it is challenging to identify each specific elementary chemical reaction. In such cases, a phenomenological model is a better option to describe the curing reaction.

### 2.2.2.1. Flory-Stockmeyer Theory

The Flory–Stockmayer theory describes the cross-linking and gelation processes of step-growth polymers. This theory was first proposed in 1941 by Paul Flory and was further developed in 1944 by Walter Stockmayer, who included crosslinks of any initial size distribution. Initially, Flory made the following three assumptions:

- 1. All functional groups on the branch unit have the same reactivity;
- 2. All reactions occur between functional groups A and B;
- 3. There are no intramolecular reactions.

Owing to these assumptions, a slightly higher conversion rate than that predicted by the Flory–Stockmayer theory is required to form a polymer gel. Gels are formed at slightly higher conversion rates due to steric hindrance, which prevents each functional group from having the same reactivity. Moreover, intramolecular reactions occur during this process [78].

The Flory–Stockmayer equation can be expressed as follows [79]:

$$\alpha = \frac{1}{[r + r\rho(f - 2)]^{\frac{1}{2}}}$$
(2.30)

where  $\alpha$ , r, and  $\rho$  denote the curing degree at the gelation point, the ratio of the A and B functional groups at the beginning of the reaction, and the functionalization unit concentration, respectively.

## 2.2.2.2. Non-Equilibrium Thermodynamic Fluctuation Theory

The curing process of thermosetting polymers, which transitions from a liquid to a solid state, is inherently a non-equilibrium process. This process is best understood through the non-equilibrium thermodynamic fluctuation theory, a branch of thermodynamics that addresses systems not in thermodynamic equilibrium [80]. In such systems, macroscopic quantities are used to extrapolate variables typically applied to systems in equilibrium, making this theory particularly useful for investigating these curing processes.

In the context of applications, Hsich utilized this theory to study the curing process of carbon black-filled natural rubber systems. The curing process of the rubber was monitored via a Monsanto rheometer. The measured quantity was the torque G(t) generated during the curing process, which is related to a certain modulus of the resin, e.g., the shear modulus. The magnitude of the torque reflects the curing degree. Based on the non-equilibrium thermodynamic fluctuation theory, the dynamic relationship of its curing process can be expressed as follows [81]:

$$\frac{G_{\infty} - G(t)}{G_{\infty} - G_0} = exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$
(2.31)

where  $G_0$  and  $G_{\infty}$  denote the minimum and maximum torque values on the experimental curing curve, respectively,  $\tau$  is the relaxation time, and  $\beta$  is the Kohlrausch exponent, which is inversely related to the width of relaxation time distribution.

#### 2.2.2.3. Avrami Theory

The Avrami theory, proposed by Kolomon Avrami, has been widely used to describe the phase transformation kinetics, including the curing of thermosetting polymers. This theory quantitatively relates the extent of the reaction to the transformation of the polymer structure over time [94]. By analyzing the nucleation and growth of polymer domains, the Avrami theory offers a systematic means to understand the curing process and predict the properties of the final thermoset materials.

The Avrami theory has been applied to interpret the kinetics of the curing of powder coatings, particularly polymer crystallization [95]. During the formation of an infinite network, several high-molecular-weight particles or molecular microgels due to cross-linking can be observed. Polymer crystallization that occurs during the curing of powder coatings is thought to be a physical form of crosslinking. Thus, the Avrami equation can be applied to predict the curing process of powder coatings. The relative curing degree at time t can be expressed by using the following equation [81]:

$$\alpha = \frac{G(t)}{G_{\infty}} \tag{2.32}$$

where  $G_{\infty}$  and G(t) denote the final elastic modulus and the elastic modulus at time t, respectively. Noteworthy, G can also denote other physical and mechanical quantities, e.g., the torque modulus.

After the gelation point, a modified Avrami equation can be used to explain the iso-thermal curing process [80]:

$$\alpha = 1 - \exp\left(-k\left(t - t_g\right)^n\right) \tag{2.33}$$

where  $t_g$  is the gelation time, which is indicated on the isothermal curing curve, and k represents the constant of the curing reaction rate after the gelation point. At lower curing temperatures (<90 °C), n = 3; as the reaction temperature increases, "n" gradually decreases.

## 2.2.2.4. DSC Kinetic Model

The DSC kinetic model provides a quantitative analysis of the curing kinetics of thermosetting polymers [96]. By employing TA techniques, this model can determine the reaction rate, activation energy, and curing degree during the curing process. The DSC kinetic model has proven to be valuable in characterizing the curing behavior of thermosetting polymers, enabling the precise control of both the curing conditions and the resultant material properties. The kinetic relationship is expressed by the following equation [82]:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2.34}$$

Autocatalytic reactions have certain characteristics. For example, they exhibit an induction period where the reaction rate is initially low, and only after a certain period, the reaction rate reaches its maximum value. The auto-catalytic model applied to the curing process of thermosetting resins was first proposed by Smith [83]:

$$\frac{d\alpha}{dt} = k\alpha^m (1-\alpha)^n \tag{2.35}$$

Kamal and Horie further improved it into the following composite form:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \tag{2.36}$$

where the terms  $d\alpha/dt$  represent the reaction rate,  $\alpha$  represents the curing degree, m and n are variables that determine the reaction order, and k, k<sub>1</sub>, and k<sub>2</sub> are apparent rate coefficients that correspond to the reaction rate intrinsic to the system and that catalyzed by protons generated during the curing process. These kinetic parameters can be determined by analyzing experimental data or mathematical fitting.

All the above-mentioned theoretical models start from a certain chemical or physical mechanism of the thermosetting material system, which is closely related to the curing process and thus aids in deducing its relevant kinetic relationship. The physical meanings of the obtained relationships differ, and so do their respective applications. Table 2- 7 summarizes common theoretical models that have been used to describe the curing process of thermosetting polymers.

Theory	Main Feature	Reference
Gelation theory	The critical conditions of gelation are derived theoretically; the chemical conversion at the gelation point depends only on the curing components in the system and is not related to the reaction temperature and experimental conditions.	[32]
DSC kinetic model	The reaction details in the curing process are ignored, and the entire curing process is considered a virtual macroscopic reaction. The kinetic characteristics of the virtual reaction (e.g., reaction order, activation energy, etc.) are investigated from a macroscopic perspective.	[23] [21] [45] [20] [34] [24] [46] [47] [27] [48]
Avrami theory	The solidification process is compared with the crystallization process of polymers. The micro-mechanism of the solidification process is analyzed using the crystallization kinetics equation.	
Non-equilibrium thermodynamic fluctuation theory	This theory connects the curing degree with the physical and mechanical properties of the resin and can predict their change during curing.	

Table 2-7. Comparison of different curing theories.

# 2.2.3. Non-Thermal Effect and Properties of Cured Products

Epoxy resins and unsaturated polyester resins, as well as vinyl resins, are the most used and widely applied varieties of general-purpose thermosetting resins. The materials used in the IR curing research (Table 2- 1) mainly concern these three categories. The absorption peaks of the IR spectra of the main reactive groups are concentrated in the MIR and FIR regions. This strong IR absorption property, which is different from the conventional 'thermal effect' and is called the "non-thermal" effect, facilitates the acceleration of the curing process and affects the mechanical properties of the curing product [32]. By analyzing the contents presented in Tables 2- 5 to 2- 7, it can be concluded that the current kinetic research on IR curing technology is mainly focused on the "thermal effect", while the research focusing on the 'non-thermal effect' is scarce (Table 2- 8). Moreover, research on the kinetic mechanisms and supporting monitoring tools are still lacking.

Absorption Model	<b>Monitoring Device</b>	Curing Theory	Reference
			[24]
			[46]
			[47]
			[27]
	DSC	DSC trinatia madal	[23]
Surface absorption	DSC	DSC kinetic model	[21]
			[45]
			[20]
			[47]
			[48]
	DEA	DSC kinetic model	[34]
	DSC	Gelation theory	[32]
volumetric absorption			[12]
			[38]

Table 2-8. Comparison of absorption models.

## 2.2.3.1. Non-Thermal Effect

Kumar et al. [12] investigated the use of IR radiation curing as an alternative to conventional thermal curing. They concluded that IR curing could effectively reduce the process cycle time for polymer composites without compromising their strength. In another study, Kumar et al. [25] found that the IR technique achieves comparable properties with only 25% of the time required for conventional thermal curing, significantly reducing power consumption to between 33% and 41%. Genty et al. [32] referred to this rapid curing phenomenon as the 'non-thermal effect'. The 'non-thermal effect' concept in IR curing was introduced by Genty et al. [32], who highlighted the significant reduction in the gelation point time and glass transition time of IR curing at temperatures below 60 °C. This phenomenon, which is closely related to the IR heat flux, demonstrates evident selectivity for the molecular groups and the steps involved in the reactions. Moreover, during the entire curing process, the activation energy is lower than that under

thermal curing. The thermal and 'non-thermal' effects are not correlated but competitive. Generally speaking, the 'non-thermal effect' due to volumetric absorption could significantly reduce the curing time.

#### 2.2.3.2. Properties of Cured Products

Several studies have explored the efficacy of infrared (IR) and near-infrared (NIR) radiation for curing coatings and their impact on mechanical and chemical properties. Genty et al. [36] focused on IR curing, finding that while it did not affect adherence or moduli, it notably increased tensile and flexural strength in polymer composites. Choi et al. [29] highlighted challenges with NIR heating alone, emphasizing the importance of uniform temperature distribution to prevent defects like cracking and delamination during curing. Stojanović et al. [37] compared catalytic IR-cured primers with conventionally dried coatings, revealing enhanced cohesion and corrosion resistance in catalytic IR-cured primers, validated through DSC and FTIR analyses, indicating superior curing efficacy.

In particular, in the context of the topic of this study, this section also provides a review of studies related to the curing effect of powder coatings. ChuanXing Wang et al. [84] used a hot-air curing oven at 180 °C for 10 min to cure a two-layer powder coating. Furthermore, they investigated the effects of two curing strategies—co-curing and layer-by-layer curing—on the mechanical properties of the coating. The results showed that the coatings' adhesion, gloss, and hardness were higher with the layer-by-layer curing than those obtained with the co-curing mode. M. Puig et al. [85] cured polyester-based powder coatings with different organo-modified silica particle (OSP) concentrations (1, 2.5, 3.5, and 4.5 wt.%) using a hot air method at

180 °C for 15 min. Then, they tested the samples with different OSP concentrations for adhesion and impact resistance. The results showed that the samples with a 2.5% OSP concentration had improved adhesion and impact resistance. Jingwen Zhang et al. [86] used a hot-air curing oven to cure epoxy powder (EP) coatings with a graphene nanosheet (G) added at 210 °C for 10 min, and the adhesion and impact resistance of the cured composite (G/EP) coating and EP samples were tested. The results confirmed that the G/EP coating could significantly improve adhesion and impact resistance compared to the EP coating. [87] used ultraviolet light to cure coatings at different temperatures and found that the gloss of the coatings decreased more at higher temperatures. R. Knischka et al. [88] studied the color change in cured coatings with different near-infrared absorber (NIR-A) addition levels. They found that the coatings' a\* and b\* values decreased with increasing levels of NIR-A addition. Therefore, the mechanical properties and appearance of coatings are influenced by their components. The curing temperature and time are also very important for the coating curing quality.

### 2.3. Discussion

The heat transfer mechanism of IR radiation involves the conversion of the electromagnetic energy into heat energy through the resonance of electromagnetic waves with molecules. Polymers contain many couplings such as vibrational couplings of CH, CH<sub>2</sub>, CH<sub>3</sub>, and CC, and these molecules' vibrations correspond to IR regions above 1.5  $\mu$ m. The wavelength of IR radiation is concentrated between 0.7 and 7  $\mu$ m. The spectra of electric IR heaters can also be tailored according to the characteristics of the cured material. The volumetric absorption mode of IR radiation leads to a 'non-thermal effect', which reduces curing time and improves energy efficiency, leading to a reduction in overall costs. In particular, catalytic IR heaters, which are advantageous in the SIR and MIR regions, are rather attractive for heating polymers.

From the perspectives of heat transfer and curing process research, the numerical model can be better supported by experimental data, and it is especially good for matching complex 3D structures. However, the study of curing kinetics is still centered on the 'cured material' and lacks research on the kinetic model in line with the characteristics of IR curing technology. Correspondingly, the current monitoring techniques for heat transfer and curing processes tend to be more traditional, with a lack of applications such as radiant heat flux sensors and FTIR analysis, which are more suited to the characteristics of IR technology.

There has been controversy as to whether IR curing is a surface absorption phenomenon or a volumetric absorption phenomenon. It depends mainly on the physical properties of the material as well as on the spectral properties of the IR radiation. Combined analysis of the data presented in Tables 1 and 4 indicates that materials such as carbon fibers and glass/natural fibers usually absorb IR radiation at the surface. Moreover, attention should also be paid to the phenomenon of strong surface absorption consuming excessive electromagnetic energy, leading to a decrease in penetration depth.

In recent years, with the development of science and technology and the exploration of engineering practice, the curing technology of thermosetting polymers has also been developing. For instance, Dilmurat et al. [8] assessed the curing mechanism, current application status, and primary pros and cons of different curing processes for advanced polymer composites. Hay et al. [89] described the pros and cons of the main radiation curing routes compared to the thermal curing process. To analyze the IR curing technology more comprehensively, this section presents a systematic probe into the advantages and disadvantages of IR curing technology in four ways, using ultraviolet (UV) curing technology and traditional heat convection curing technology as reference objects, as presented in

Curing Method	Material	Penetration	Applicability	Cost	Ref
	No special	TT 11 CC / 11		Lower	[90]
Infrared	requirements for	physical properties, low	curing, good at		[91]
	applicability.	penetration into carbon	handling flexible	investment, running.maintena	[92]
	universality, and	fiber and glass/natural fiber polymer	workpieces, high	nce costs	[93]
	potential	noer polymer	controllatinty		[94]
	Need to add photoinitiators to polymers, can be used for curing energetic materials		Fast-curing, good at handling flexible workpieces, high controllability	High cost of photoinitiators and acrylic toxicity	[95]
		Can be hindered by fillers, very limited penetration in semi- and non-transparent polymers			[96]
Ultraviolet					[97]
					[98]
					[99]
					[100]
	No special		High controllability but limited by curing time	Lower investment, running,maintena nce costs	[101]
Convection	polymers, good	Faces the issue of 'surface'			[102]
	applicability,	heating' mechanism			[103]
	potential				[104]
	potential	potentia			[105]

Table 2-9. Comparison of three different curing technologies.

Comparative analysis reveals that compared with the traditional curing technology, IR curing technology offers advantages in the universality of curing materials, penetration, applicability, and economy, but in terms of curing speed, UV curing technology has a greater advantage.

Furthermore, UV-curable resins such as epoxides, vinyl ethers, and acrylates are also important monomers that offer effective media for energetic materials [106]. The integration of UV curable resin into energetic materials
has been a new direction in the field of explosive inks with high curing speed and high solid loading. Guo et al. prepared CL-20-based UV-curable explosive composites by UV-curable and direct ink writing techniques. The rate of curing, micro-scale structure, morphology, crystal type, impact sensitivity, and detonation ability of the specimen were characterized and analyzed. The results showed that the curing process of CL-20-based UV-cured explosive ink could be completed within 7 min after UV-curing for 3 min, revealing rapid curing speed [107]. The integration of UV-curing resins into energetic materials has shown good results, and the potential of applying IR curing to energetic materials can be explored in the future.

# 2.4. Summary

This chapter provides a comprehensive review of IR curing technology. The relevant literature on IR curing is summarized, analyzed, and compared, with specific emphasis on IR heaters, heat transfer models, numerical simulation methods, heat transfer and curing monitoring devices, and curing theory.

Based on the summary and analysis of IR heaters, three common types emerged: electric IR heaters, gas-fired IR heaters, and gas catalytic heaters. Among them, electric heaters are widely used; nonetheless, they have higher operating costs and shorter lifespans. The feasibility of gas catalytic IR technology in powder coating curing has been proven to be effective. In particular, combined with the "non-thermal effect", gas catalytic IR heaters offer broader application prospects in the field of low-temperature rapid curing. Based on the careful review on the heat transfer models, two main types of models emerged: surface and volumetric absorption models. Owing

to the complexity of heat transfer radiation and the limited research on relevant mechanisms, heat transfer models are often simplified into one-dimensional surface-to-surface heat transfer models when simple geometric shapes are involved. Moreover, there is limited research on volumetric absorption heat transfer models for complex geometric shapes. The most commonly used numerical simulation method is FVM, which is implemented by using commercial simulation software (COMSOL). DSC is commonly used for the parameter monitoring of surface absorption curing processes, while curing monitoring techniques for volumetric absorption modes have rarely been reported to date. The curing theory based on the DSC kinetics model is the most commonly used. Theoretically, IR volumetric absorption models should consider the decrease in the activation energy. Thus, the applicability of the DSC curing monitoring technique needs to be further investigated. Compared to conventional curing techniques, the IR technology, especially with respect to the volumetric absorption model, exhibits advantages in terms of curing time, mechanical properties, and corrosion resistance performance of the cured products. The improvement in these curing processes and the mechanical properties of the cured products are directly related to the decrease in the activation energy and the increase in the curing degree. However, the low penetration of IR radiation into some materials largely limits the application of this technology.

Based on the systematic analysis of the literature reviewed, several research directions are proposed for this study:

1. Catalytic IR curing technology deserves further research and new application directions, but its application in the curing field has not yet

52

been reported, and the feasibility of this technology is unknown, the subsequent research should focus on the radiation volumetric absorption characteristics of the technology;

- 2. It is also necessary to explore the curing process monitoring technology that matches the radiation volumetric absorption characteristics of infrared curing technology, and Fourier transform infrared detection technology is a feasible direction;
- 3. There is a lack of research on modeling and numerical simulation of heat transfer in catalytic infrared curing technology, especially for the heat volumetric absorption model;
- In subsequent studies, the curing kinetics model should continue to be developed to match the volumetric absorption characteristics of infrared curing technology;
- Quantification of the benefits of IR curing is still a complex task, and establishing a simple yet effective evaluation index would aid the research on IR curing technologies and engineering applications.

# **Chapter 3: Research Methodology**

This chapter describes the technological route, catalytic infrared curing equipment used for the study, as well as the devices and specific experimental setups for the 4-part study throughout the PhD research process, as shown in Figure 3- 1. Study 1 is the feasibility study, Study 2 is the heat transfer process study, and these two parts of the study are realized through experiments of curing Polyester/TGIC system powder coatings; Study 3 is the curing process study, and this part of the study is realized through experiments of curing GMA/DDDA system powder coatings. The same curing equipment was used for both experiments. Study 4 is a curing theory study.



Figure 3-1. The Overview structure of the studies presented in this thesis.

## **3.1. Equipment Setup**

A catalytic infrared equipment setup was constructed, including a catalytic infrared radiator system, a gas supply system, an electric control system, a temperature measurement system, and the main body of the equipment, as displayed in Figure 3- 2. The radiation plate  $(800 \times 400 \times 50 \text{ mm})$  used in the experiment is shown in Figure 3- 3, and its maximum power was 4 kW. Two catalytic infrared radiation panels were located on top of the equipment. The bottom platform was insulated and equipped with a base frame to prevent heat transfer between the coating sample and the platform. A control cabinet was used to adjust the distance between the radiation panels and the sample. During the curing process, the samples' temperatures and the air inside the equipment were measured using K-type thermocouples. We set one temperature measurement point centered at the top of the samples and one centered at the bottom. The temperature signals were transmitted to a computer. A portable infrared thermometer was used to measure the temperature at the panel's surface in real time. The gas used in this experiment was liquefied petroleum gas (LPG) from a tank. The details of the experimental instruments are shown in Table 3- 1.



(a)



(b)

Figure 3- 2. (a) Catalytic infrared curing oven. (b) Schematic diagram of infrared curing furnace with catalytic combustion.



Figure 3-3. Catalytic infrared radiation panel.

Table 3-1.	Details	of the	experimental	instruments.
			1	

Name	Picture	Model	Range	Precision	Error
K-Type thermocouple	Ø	WRNT-01	−200~500 °C	0.1	0.5%
Temperature logger		KCM-LCD16	−30~1300 °C	0.1	-
Infrared thermometer	All a construction of the	MS Plus	−32~530 °C	0.1	1%
Gloss meter		HG60	0~300 GU	0.1	0.2%

Universal colorimeter	NR10QC	L* 0–100 a*, b* –100–100	0.01	0.03%
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The catalyst used in this study was prepared using high-temperature calcination with fibrous alumina as the carrier and platinum and other trace metal components, as shown in Figure 3- 4a. The characteristics of this catalyst are summarized in Table 3- 2. The changes in the methane conversion rate with temperature under the action of the catalyst provided by Suzhou Catalytic Green Energy Co., Ltd. (Suzhou, China) are shown in Figure 3- 4b. Among the two alternative catalysts, Cat-1 catalyst has more efficient methane conversion capacity than Cat-2 catalyst, so Cat-1 catalyst was used in this study.



Figure 3- 4. (a) Fiber-supported noble metal catalyst. (b) Methane conversion versus temperature with the Cat-1 and Cat-2 catalysts.

Tuele 5 2.1 hjsteur properties of heer supported heere metur euturjst (eut 1)	Table 3- 2. P	hysical pro	operties of	fiber-supported	noble metal	catalyst (	(Cat-1)
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Index	Value	Unit
Dimensions	745  imes 395  imes 5	mm
Catalyst loading per area	350	g/m <sup>2</sup>
Average diameter	5	μm
Average particle size	18	nm
Specific surface area	150	$m^2/g$
Pore volume	0.14	cm <sup>3</sup> /g
Average pore size	5.25	nm
Elemental content	$Pt \le 1 \text{ wt.\%}, Al_2O_3 \ge 95 \text{ wt.\%}, SiO_2 \le 4 \text{ wt.\%}$	/
Ignition temperature	120 (LPG), 180 (natural gas)	°C
Service life	30,000	h

### 3.2. Polyester/TGIC System Curing Experiment

From the literature review in Chapter 2, it can be concluded that employing catalytic infrared technology for the curing of powder coatings has important research significance and good potential for application in engineering. However, there are no reports on the curing of powder coatings using catalytic infrared and there is a lack of research on modeling the temperature change of coatings.

Accordingly, this work aimed to study the influence of catalytic infrared treatment on coating quality under different heating conditions. The quality of the cured coatings under different conditions was evaluated in terms of adhesion, gloss, hardness, impact resistance, and color. The best curing parameters for a polyester-based powder coating were obtained, and a model was established for the prediction of the temperature changes in this powder coating with catalytic infrared heating. This work is expected to serve as a guide for the production of powder coatings and the design of catalytic infrared systems and may help improve the efficiency and energy savings of catalytic infrared heating systems.

## 3.2.1. Materials

The powder coating used in this study was a triglycidyl isocyanurate (TGIC) polyester system (provided by Jiangsu Aiyue Powder Coating Co. Ltd., Taicang, China), which is widely used in the metal coating industry. The characteristics of this powder coating are summarized in Table 3- 3. The substrates were test-grade galvanized steel panels, and the size of these plates was  $150 \times 70 \times 1$  mm. The powder coating was sprayed with a high-voltage

electrostatic spray gun, and the thickness of the paint film was controlled at 100  $\mu$ m.

Index	Parameter
	Polyester-based powder coating +
Composition	triglycidylisocyanurate crosslinker, acrylic acid,
Composition	barium sulfate, titanium dioxide, pigments, and
	various additives
Average particle size	34–38 μm
Color	White
Thermal conductivity (average)	0.1 W/m·°C
Glass transition temperature	53 °C
Curing conditions (hot-air oven)	200 °C for 10 min and 180 °C for 20 min
Storage stability	Below 25 °C; the storage time was 12 months

Table 3-3. Characteristics of the powder coating used in this study.

## 3.2.2 Feasibility Study

### 3.2.2.1 Experimental Setup

This work aimed to determine the radiant heating performance of a catalytic infrared radiation panel and investigate powder coating curing under various radiant heating conditions. The coating quality was examined using five tests. The measured data obtained from these experiments were used to verify the heat transfer model's reliability.

## 3.2.2.2. Catalytic Infrared Radiation Panel Characteristics Test

The radiant panel's performance affected the powder coating's curing quality. The radiant panel's surface temperature and surface radiation intensity were used to quantify its performance. In this study, the surface temperature of the radiant panel was tested with different gas flow rates and the surface radiation intensity was tested with different wavelengths.

3.2.2.3. Fourier-Transform Infrared Spectroscopy of the Powder Coatings

Fourier-transform infrared (FT-IR) spectroscopy (Thermo-Nicolet, Waltham, Massachusetts, USA) was employed to investigate the chemical structure of the powder coatings. The potassium bromide tablet method was used for testing, and the test range was set to 500~4000 cm<sup>-1</sup>.

# 3.2.2.4. Curing Methods and Test Conditions

A sample plate sprayed with a powder coating was placed on the internal platform underneath the radiant panel, and the coating temperature was increased to 180 °C, 190 °C, 200 °C, 210 °C, 220 °C, 230 °C, and 240 °C by controlling the gas flow into the radiation panel. The sample plate was held at these seven temperatures with 1 min intervals for 1 to 5 min, respectively. After heating, the sample plate was removed and cooled to ambient temperature.

The curing process potentially affects the mechanical properties of cured samples, such as the hardness, flexibility, impact resistance, appearance of the film surface, and chemical resistance [108]. Therefore, five mechanical properties of these cured samples were tested: adhesion, impact resistance, gloss, pencil hardness, and coating color. The test equipment and processes are shown in Figure 3- 5.

The test methods were as follows:

Adhesion: This test was conducted according to ASTM Test Method D3359, Method B using a multi-toothed blade (QFH-A, Dongguan Huanguo Precision Instrument Co., Ltd., Dongguan, China) suitable for standard adhesion tests. Specific method: Firstly, the cured coating template was fixed, and the multi-toothed cutter blade was set perpendicular to the template and drew a scratch. Then, the template was evenly covered with transparent tape

before it was removed to observe the scratching off, using the observer's judgment to determine the size of the adhesion area.

**Gloss:** This test was performed with a gloss meter measuring instrument (HG-60, Shenzhen Threenh Technology Co., Ltd.). Specific method: A calibrated gloss meter was placed on the coating so that no light entered, and the beam of the internal light source of the instrument was at an angle of 60° from the normal line of the tested coating surface. Then, the instrument was initiated and it read the gloss value of the coating. This test was conducted according to ASTM Test Method D523.

**Hardness:** The pencil thickness meter (Shanghai Gaozhi Precision Instrument Co., Ltd., Shanghai, China) was used to test the hardness of the cured films. This test was conducted according to ASTM Test Method D3363. Specific method: After curing, a pencil with the same hardness was used for three scratch tests to observe the damage to the template. The hardness of the hardest pencil that did not leave scratches larger than 3 mm on the coating was used as an indication of the hardness of the coating.

**Impact resistance:** In this test, a paint film impactor (QCJ-50/100, Tianjin Expo Weiye Hua Glass Instrument Co., Ltd., Tianjin, China) was used to test the hardness of the cured films. This test was conducted according to ISO 6272-2:2002. Specific method: The prepared coating was placed on the anvil at the lower part of the instrument. The hammer was lifted to 50 cm and allowed to fall freely, impacting the template. The damage to the coating surface was recorded.

**Color:** The colors of the coating surfaces were measured using a universal colorimeter (NR10QC, Shenzhen Threenh Technology Co., Ltd.,

Shenzhen, China). Specific method: A calibrated universal colorimeter was placed on the surface of the coating and activated to take readings.

Errors were mainly introduced in the operation for the testing of the mechanical properties (adhesion, hardness, and impact resistance) and due to the accuracy of the instruments for the gloss and color testing. Following the mechanical property tests performed with epoxy powder coatings in the study by Jingwen Zhang et al. [86], all tests were carried out three times to check the repeatability.



Figure 3- 5. Test equipment and processes: (a) adhesion test, (b) gloss test, (c) hardness test, (d) film impact resistance test, and (e) color test.

3.2.3 Heat transfer process study

#### 3.2.3.1. Geometric Model

The geometric model consisted of the powder coating and metal substrate, as shown in Figure 3- 6. The dimensions of the coating and substrate are shown in Table 3- 4, and the thermophysical properties of the coating and substrate are reported in Table 3- 5. The paint's thermophysical properties (specific heat capacity, density,  $\varepsilon$ ) were obtained from the literature [20]. Suzhou Catalytic Green Energy Co., Ltd. provided the thermophysical properties of the substrate.



Figure 3- 6. Geometric model.

Table 3-4. Dimensions of the coating and substrate.

Material	Length (mm)	Width (mm)	Thickness (mm)
Coating	150	70	0.1
Substrate	150	70	1

Table 3-5. Thermophysical properties of the coating and substrate.

Material	Thermal Conductivity W/m·°C	Specific Heat Capacity J/kg·°C	Density kg/m <sup>3</sup>	Е
Coating	0.1	1500	1590	0.91
Substrate	44.5	460	8237	0.92

3.2.3.2. Numerical Method

The finite element analysis software ANSYS Workbench 18.2 was used for the numerical simulation. The flow rate was set to 0.2 m<sup>3</sup>/h (with a corresponding internal heat source value of  $8.5 \times 10^7$  W/m<sup>3</sup>), and the thickness of the substrate was 1 mm. With a time step of 1 s, grid sizes of 21120, 28080, and 32480 were used for the simulation. The changes in the coating temperature with time for each group of grids are shown in Figure 3-7. The results of the 32480 grid simulation differed from those of the 21,120 grid simulation by a maximum of 3.31 °C. To ensure the accuracy of the numerical simulation, the 32480 grid size was used for subsequent simulations.

The changes in the coating temperature with three time steps (0.1 s, 1 s, and 10 s) are shown in Figure 3- 8. During the coating heating process, the simulated coating temperature was lower when the time step was 10 s. Considering the time and accuracy of the simulation, 1 s was selected as the time step for subsequent simulations.







Figure 3-8. Coating temperature versus time with different time steps.

3.3. GMA/DDDA System Curing Experiment

As stated in the summary of the literature review in Chapter 2, infrared (IR) curing is a relatively new technology that has received increasing academic attention in recent years. The volumetric absorption characteristic of IR energy compared to the surface absorption mode of conventional heating significantly impacts the temperature distribution and cure characteristics in thermosetting polymers. In response to these impacts and differences, some researchers have conducted studies to investigate IR volumetric absorption curing. For instance, Kumar et al. [12] found that IR curing required 25% of the time of conventional thermal curing to attain the same degree of cure and consumed significantly less energy. Meanwhile, Genty et al. [32] indicated that the selective absorption of IR radiation by specific molecular groups was responsible for non-thermal effects throughout the bulk of the sample that were closely related to the intensity of the radiation. The researchers regarded this phenomenon as responsible for the IR curing process's low activation energy requirement compared to that of conventional hot air curing. Furthermore, Yuan et al. [56] demonstrated that optimizing the process parameters increased the efficiency of IR curing by more than four times compared to conventional curing within the same time. Similarly, Knischka et al. [88] showed that the "non-thermal" effect produced by the volumetric absorption of IR radiation significantly reduced curing time for the same degree of cure.

In contrast to conventional thermal curing techniques, IR radiation curing allows for volumetric heat absorption, thereby influencing the curing behavior. This influence can be seen in two main areas: 1. Impact on the curing process: mainly reflected by changes in the cure rate due to a reduction in activation energy;

2. Impact on the properties of the cured product: mainly resulting from changes in the degree of cure, resulting in changes in the optical and mechanical properties of the cured product.

An analysis of the current research and applications of IR curing technology reveals two significant gaps [109]:

1. There have been no kinetic studies of the curing behavior involving the volumetric absorption of IR radiant energy, resulting in a limited ability to predict curing behavior;

2. A lack of an assessment methodology for IR curing technology makes it challenging to provide reliable guidance on the feasibility for practical engineering applications.

Thus, in order to explore the IR curing process more comprehensively, this study, as part of detailed ongoing research, focuses on the kinetic modeling and evaluation of the IR-induced volume heating response of the curing process in thermosetting polymers. For this purpose, glycidyl methacrylate (GMA)/dodecanedioic acid (DDDA) powder coatings were cured at different temperatures for variable time intervals using catalytic IR curing equipment. Meanwhile, Fourier infrared (FTIR) spectroscopy [61] [110] and MATLAB were, respectively, employed to determine the samples' degree of cure and fit the empirical data to the most appropriate kinetic model for evaluating the kinetic parameters of the curing process. Based on the results of this study, a new concept of 'photo-thermal synergistic effect' is introduced, which is discussed and explained in the following sections.

## 3.3.1. Materials

The thermosetting powder coating used in this study was a transparent GMA/DDDA system (provided by AkzoNobel Paints Co. Ltd., Suzhou, China), with its chemical composition detailed in Table 3- 6. Using a transparent coating was to avoid the unnecessary interference of pigmentation, which is known to affect the curing behavior of thermosetting materials significantly [21]. To prepare the samples for the proposed study, the as-obtained powder was spray-coated on test-grade galvanized steel substrates of  $150 \times 70 \times 1 \text{ mm}^3$  size (Figure 1) using a high-pressure electrostatic gun in such a way that the coating thickness was controlled within 100 microns for reliable IR volumetric absorption [56]. The manufacturer provides guidance on curing conditions for hot air curing technology: 170 degrees Celsius for 20 minutes; however, there is no guidance on the IR curing conditions of the powder.

Table 3- 6. Chemical composition of the GMA/DDDA powder coating system provided by the supplier.

Ingredients	Proportions
Acrylic resins	78%
3,9-bis(2,4-di-tert-butylphenoxy)-2,4,8,10-	0.2%
tetraoxa-3,9 diphosphaspiro [5.5]-undecane	0.270
2,3-epoxypropyl methacrylate	0.2%
Additive agent	1.6%
Curing agent (sebacic acid)	20%

# 3.3.2. The IR Curing Process

#### 3.3.2.1. Experimental Setup

The powder was cured at different temperatures by positioning the samples on the internal platform of the curing equipment and setting the coating temperature to 150  $^{\circ}$  C, 160  $^{\circ}$  C, and 170  $^{\circ}$  C, respectively, by

controlling the gas flow into the radiation plate. At each temperature, the curing process was carried out for different time intervals of 30 s, 60 s, 120 s, 240 s, 300 s, 360 s, 420 s, and 480 s for various samples, respectively. Following curing, each sample was cooled with liquid nitrogen and stored in vacuum-sealed packing for further analysis.

## 3.3.2.2 Determination of Degree of Cure

After curing, the degree of cure of the samples was determined by investigating the changes in the molecular structures of the materials. For this purpose, the characteristic molecular groups that participated in the curing reaction, that is, the epoxide and hydroxyl group, were analyzed using FTIR spectroscopy. For instance, approximately 1 mg of the cured sample was mixed with 150 mg of crystalline potassium bromide (KBr) and ground for 4 min before pressing it into shape under a pressure of 15 MPa. The resulting pellets were stored under dry conditions and sequentially scanned in the wave number range of 4000–400 cm–1 using the transmission mode of a Spectrum Two FTIR Spectrometer (PerkinElmer, Waltham, MA, USA) (Figure 3- 9).



Figure 3- 9. PerkinElmer Spectrum Two FT-IR Spectrometer. Since the curing reaction involves a ring-opening reaction of the epoxide

groups, as illustrated in Figure 3- 10, the concentration of the epoxide groups

must decrease with the extent of the reaction. Interestingly, the epoxide group strongly absorbs IR radiation; the intensity variation in its characteristic FTIR peak can provide information about its concentration changes in the samples. Therefore, Equations (3.1) and (3.2) were used to determine the concentration changes in the epoxide group and the degree of cure, respectively [63].

$$C(t) = \frac{A(t)/A(t)_{standard}}{A(0)/A(0)_{standard}}$$
(3.1)

$$\alpha = 1 - C(t) = \frac{A(0)/A(0)_{standard} - A(Tt)/A(t)_{standard}}{A(0)/A(0)_{standard}}$$
(3.2)

where A(t) and A(t)standard are the areas under the FTIR absorption peaks of the epoxide group in the sample and a standard, cured for time (t), respectively. Similarly, A(0) and A(0)standard are the areas under the same peaks of the sample and the standard at the beginning of the curing reaction, respectively.



Figure 3- 10. Schematic illustration of the curing reaction between GMA acrylic resin and dodecanedioic acid.

#### 3.4. Summary

This chapter details the research route and experimental design of this study, including the development of the catalytic infrared heating system and the preparation of the polymer samples. The curing results testing and analysis techniques used are detailed in two separate experiments. Data analysis methods are also presented to ensure robust and reproducible findings. Technical and theoretical support is provided for the next four areas of research.

# **Chapter 4: Feasibility study**

### 4.1. Introduction

for metal substrates, adequate protection is only possible if the coating remains bonded to the substrate for the design life of the metal structure and has excellent mechanical properties. The mechanical properties of the coating are usually tested in terms of adhesion, hardness, and impact resistance. In addition to ensuring the mechanical properties of the coating are appropriate, the aesthetic effect of the coating is significant. A natural and attractive appearance increases consumer satisfaction. Gloss and color tests are usually performed to evaluate the gloss and color difference in cured coatings.

In this chapter, the spectral match between the catalytic infrared radiation panel and the powder coating was tested, then the heating performance of the infrared device was tested, finally, the mechanical and optical properties of the cured film were tested. The best curing parameters for a polyester-based powder coating were obtained.

# 4.2. Heating Performance Test

## 4.2.1. Characteristics of the Catalytic Infrared Radiation Panel

The surface temperature of the radiant panel was mainly controlled by the intake gas volume, and the relationship between the surface temperature and gas flow is shown in Figure 4- 1a. The surface temperature of the radiant panel reached a maximum of 475 °C when the intake gas flow was 0.3 m<sup>3</sup>/h. When the gas flow was increased above 0.3 m<sup>3</sup>/h, the surface temperature decreased due to the excessive gas flow. At excessively high flow rates, the gas did not have enough time to react with and diffuse into the environment

around the surface of the radiant panel. Moreover, the oxygen on the surface of the radiant panel was swept away, resulting in insufficient oxygen and an incomplete gas reaction.

Infrared radiation (IR) can be divided into three categories according to the wavelength: near-infrared (NIR), mid-infrared (MIR), and far-infrared (FIR) radiation. A wavelength range of 0.75–2  $\mu$ m is generally defined as NIR, 2–4  $\mu$ m as MIR, and 4–1000  $\mu$ m as FIR [31]. The catalytic infrared radiation intensity curve obtained in this study is shown in Figure 4- 1b. The measured wavelengths were in the range of 2–25  $\mu$ m. Thus, this radiation was both MIR and FIR.



Figure 4- 1. (a) Relationship between the surface temperature of the radiant panel and the gas intake. (b) The catalytic infrared radiation intensity of the radiant panel.

## 4.2.2. FT-IR Analysis

Relevant studies[111] [112] [113] have emphasised that the depth of penetration of IR radiation is affected by a number of factors. However, given that the thickness of the coating layer in this study was 100  $\mu$ m, which is relatively thin compared to the penetration depths discussed in these studies, IR radiation can penetrate through the entire thickness of the coating layer. In the following section, spectral matching tests will be performed to determine that the present study can take advantage of the properties of infrared volumetric absorption.

FT-IR spectroscopy measures a sample's characteristic vibrational absorption bands to determine its chemical structure [61] The infrared spectra of the powder coatings are shown in Figure 4- 2. The absorption peaks of the functional groups were in the wavenumber range of 4000–500 cm<sup>-1</sup> (with a corresponding wavelength range of 2.5–20  $\mu$ m). The most intense absorption peaks were located in the wavenumber range of 2000–500 cm<sup>-1</sup> (with a corresponding wavelength range of 5–20  $\mu$ m). Therefore, the infrared radiation panel's infrared radiation range covered the absorption wavelengths of the powder coating's functional groups.

Moreover, most absorption peaks were located in the range of  $5-10 \mu m$ , matching the most intense infrared radiation wavelengths emitted by the radiation panel. Under the radiant panel, the functional groups of the coating absorbed infrared radiation energy and converted it into vibrational energy. At the same time, intermolecular energy transfer and whole-molecule resonance led to a crosslinking reaction and accelerated the curing of the powder coating.



Figure 4- 2. The infrared spectra of the polyester-based/TGIC powder coating: (a) variation with wavenumber and (b) variation with wavelength.

# 4.3. Heating Performance Test

During infrared radiation heating, the temperature difference between the top of the substrate (coating) and the bottom of the substrate is one factor determining the curing quality. If the temperature difference between the top and bottom is too great, there is a large temperature gradient inside the substrate, and the coating and the substrate may have poor adhesion.

As shown in Figure 4- 3, within 1 min of the beginning of heating, the top and bottom of the substrate had a significant slope and the temperature rose rapidly, indicating that the catalytic infrared radiation could heat the coating and the substrate rapidly. In addition, the maximum temperature difference between the top and bottom of the substrate did not exceed 7 °C during the curing process, which indicated that the temperatures of the substrate and the coating remained almost consistent during the curing process, which was conducive to the bonding of the coating and the substrate.





230 °C

Figure 4- 3. Variation in coating temperature and substrate bottom surface temperature with time.

# 4.4 Curing Tests

### 4.4.1. Adhesion Test

The adhesion results for the cured products after curing with catalytic infrared radiation are shown in Figure 4- 4. A rating higher than 4B is generally considered a qualified product [29], and the rating standards are shown in Table 4-1. With increasing curing temperature and curing time, the adhesion level of the coating increased. This was due to the enhanced degree of bonding between the coating and the substrate. When the curing temperature was 200 °C and the curing time was 5 min, an adhesion rating of 5B was obtained, meeting engineering requirements. With a curing temperature of 230 °C or 240 °C, a curing time of only 2 min was required to achieve an adhesion rating of 5B. Jong Won Choi et al. [29] used NIR radiation to cure a solvent-blended acrylic resin with an amine crosslinker coating, which did not meet the 4B standard. However, they combined an NIR curing system with a convective oven to obtain a coating that met this standard. The maximum allowable temperature for solvent-based coatings is generally low, and the high-power density of an infrared heater may induce thermal stress between the substrate and the coating, resulting in defects, such as local cracks and film deletion.

In contrast, powder coatings' maximum allowable temperature is generally high, and they do not have a solvent component. Therefore, powder coatings are more suitable for infrared curing. However, excessively high coating temperatures inevitably change other physical properties, such as color and gloss.

240°C	4B	5B	5B	5B	5B
230°C	4B	5B	5B	5B	5B
220°C	3B	4B	5B	5B	5B
210°C	1B	2B	3B	5B	5B
200°C	1B	1B	2B	3B	5B
190°C	0B	0B	1B	2B	2B
180°C	0B	0B	0B	0B	1B
	1min	2min	3min	4min	5min

Figure 4- 4. Coating adhesion test results.

Table 4-1. Classification chart for paint adhesion tests [14	4	1	•
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Grade	Area Removed	Cross-Cut Area of Six Parallel Lines
5B	None	
4B	Less than 5%	
3B	5–15%	
2B	15–35%	
1B	35-65%	
0B	Greater than 65%	

# 4.4.2. Gloss Test

Gloss is an optical property that indicates how the surface reflects light in a specular (mirror-like) direction [114]. The gloss of a colored powder system depends on the degree of dispersion and particle size distribution of the pigments, and gloss has little effect on the infrared absorptivity of coatings [115]. However, gloss affects the appearance of coatings. Therefore, the average gloss values for ten points on each sample were measured for analysis. The coating gloss decreased with increasing temperature for each curing time, as shown in Figure 4- 5. The coating gloss significantly declined at curing temperatures higher than 220 °C. As shown in Figure 4- 6, the curing time slightly affected the gloss at temperatures below 210 °C. The gloss values achieved at these low curing temperatures were within the gloss range required for the coatings (90  $\pm$  5). When the temperature exceeded 210 °C, the gloss sharply decreased with increasing curing time. When the curing time was 5 min and the curing temperature was 240 °C, the average gloss of the coatings decreased to below 85. This demonstrated the importance of controlling the temperature of the coating during curing.



Figure 4- 5. Changes in the coating gloss with curing temperature after different curing times.



Figure 4- 6. Changes in the coating gloss with curing time with different curing temperatures.

# 4.4.3. Hardness Test

Coating hardness increased with increasing curing time and temperature, as shown in Figure 4- 7. Most of the tested curing parameters resulted in coating hardness ratings that were better than H (meeting the minimum requirement for these coatings). It was determined during the testing that thinner coatings exhibited higher pencil hardness ratings than thicker coatings with the same curing parameters. This was related to the physical properties of the coatings and the substrates.

240°C	2H	3Н	4H	5H	5H
230°C	2H	3Н	4H	5H	5H
220°C	2H	2H	3H	4H	5H
210°C	2H	2H	3H	4H	4H
200°C	Н	2H	3H	3H	4H
190°C	HB	Н	2H	2H	3H
180°C	HB	HB	Н	2H	2H
	1min	2min	3min	4min	5min

Figure 4-7. Coated pencil hardness test results for the coatings.

## 4.4.4. Impact Resistance

Impact resistance, also known as impact strength, refers to the ability of a film on a substrate to rapidly deform under a heavy hammer impact without cracking or peeling away from the substrate. This test was performed to evaluate the flexibility of the coatings and their adhesion to the substrate. In this test, the impact height was 50 cm. As shown in Figure 4- 8, the impact test did not generate cracks when the coating was cured at 200 °C for 5 min. Thus, the shortest curing time required for the coating at 200 °C, and 240 °C, the shortest curing times were 4 min, 3 min, 2 min, and 2 min, respectively.

240°C	crackled	no crack	no crack	no crack	no crack
230°C	crackled	no crack	no crack	no crack	no crack
220°C	shed	crackled	no crack	no crack	no crack
210°C	shed	shed	crackled	no crack	no crack
200°C	shed	shed	crackled	crackled	no crack
190°C	shed	shed	shed	shed	crackled
180°C	shed	shed	shed	shed	shed
	1 min	2min	3min	4min	5min

Figure 4-8. Impact resistance test results for the coatings.

#### 4.4.5. Color Test

The laboratory color model developed by the International Commission on Illumination (CIE) can be used to describe human visual effects digitally. This lab color model consists of three elements: brightness (L\*) and the color channels a\* and b\*. The term L\* describes brightness and has potential values ranging from 0 (black) to 100 (white). The a\* coordinates represent the redness and greenness of a sample. The b\* coordinates represent the yellowness and blueness of a sample [35]. The coordinate ranges of a\* and b\* are approximately [-100, 100]. In this model, it was determined that the color of the tested coatings did not significantly change when varying the curing time at a fixed curing temperature. Therefore, the average values of L\*, a\*, and b\* measured at different temperatures were assumed to be representative test values for those temperatures. Figure 4- 9 shows that, as the temperature increased, the a\* value of the coating gradually decreased—that is, the "red" value decreased. The b\* and L\* values initially increased with increasing temperature. However, these values decreased when the curing temperature exceeded 230 °C. In particular, the value of L\* sharply decreased at excessively high curing temperatures. These results demonstrated that high temperatures had a strong effect on coating brightness.



Figure 4- 9. The effects of temperature on the coatings' CIE laboratory color model values.

The tests described in this section showed that the curing time decreased with increasing curing temperature because high temperatures increased the crosslinking of the powder molecules. The mechanical property and appearance requirements could be satisfied when a curing temperature of 200 °C was maintained for 5 min. This reduced the time by half compared to the hot-air curing conditions provided by the coating manufacturer (Table 3), which have to be maintained at 200 °C for 10 min. All of the test results met the requirements when the curing parameters were 220 °C for 3 min and

230 °C for 2 min. Considering energy consumption, efficiency, and coating quality, 220 °C for 3 min and 230 °C for 2 min were considered the best curing parameters. The optimal curing parameters were consistent with the values from the adhesion and impact tests, and the results of the hardness test at 210 °C and 1 min met the requirements. Gloss requirements were satisfied at 180 °C and 1 min. The results for the color tests met the requirements, except for a sharp drop in L\* values and a darkening of the coating at 240 °C. This was due to a sufficient temperature and time for the crosslinking reaction of the molecules inside the coating being used, ensuring better adhesion between the coating and substrate. The gloss and color were mainly related to the color filler in the coating composition, and the appearance of the coating deteriorated when the polyester resin, titanium dioxide, and other components in the coating aged and darkened after spending too much time in the high-temperature range. Consequently, a lower curing temperature was considered to be better for gloss and color.

To further evaluate whether the curing parameters obtained in this study were efficient, we compared the curing parameters required for powder coatings using catalytic infrared curing with those required by other curing methods described in the literature. As shown in Table 4- 2, the infrared heating method improves efficiency compared to the traditional hot-air heating method. The optimal curing parameters obtained in this study could reduce the time required by 80–90% compared to the hot-air curing parameters provided by the coating manufacturer.

The coating temperature was not maintained at a constant value when it was controlled; it fluctuated up and down. Moreover, there was an

82

unavoidable error in the thermocouple. In addition, there were operational and instrumental errors in the subsequent coating test. Therefore,  $220 \pm 5$  °C for 3 min and  $230 \pm 5$  °C for 2 min can be considered as the optimal curing parameters for the production process.

Table 4- 2. Comparison of curing parameters with those obtained from the literature.

Sr.	Coating Type	<b>Curing Method</b>	<b>Curing Parameter</b>	Ref.
1	Epoxy resin-modified PVC powder coating	Hot-air oven	180 °C for 10 min	[6]
2	Polyester-based powder coating	Hot-air oven	180 °C for 15 min	[7]
3	Epoxy powder coating	Hot-air oven	210 °C for 10 min	[8]
4	Polyester-based powder coating	Hot-air oven	150 °C for 15 min	[9]
5	Polyester/epoxy/acrylic resin powder coating	Hot-air oven	160 °C for 10 min	[36]
6	Solvent-blended acrylic resin with an amine crosslinker coating	NIR system	200 °C/5-15 min	[14]
7	Polyester-based powder coating	Catalytic infrared	220 °C for 3 min 230 °C for 2 min	This study

## 4.5. Summary

In this chapter, the radiative characteristics of the catalytic infrared equipment were tested, and the applicability of this curing system for curing powder coatings was investigated.

This study showed that catalytic infrared radiation can be used to cure polyester-based coatings efficiently, and that the coatings can meet engineering quality requirements. Mechanical property tests, including impact resistance test, hardness test and adhesion test, met standard requirements. However, experiments revealed that the optical index of the layers showed a certain degree of degradation as the curing temperature increased, which raised the need for low-temperature curing technology.

Using the catalytic infrared optimal curing parameters determined in this study, the yield can be increased by four to nine times with the same production time compared to the hot-air curing parameters provided by the coating manufacturer. Compared to the curing parameters provided in the literature [85] [116] for polyester-based coatings, the yield can be increased by 6.5 times with the same production time.

Overall, the studies in this chapter demonstrate the feasibility of catalytic infrared curing technology, which has a large potential for research and application in the field of powder coating curing.

# **Chapter 5: Heat Transfer Process Study**

### 5.1. Introduction

This chapter carries out a study of catalytic infrared heat transfer model. Radiative heat transfer occurred between the radiant panel and the coating surfaces. The coatings were very thin, and the thickness was low compared to the area of the coatings. Moreover, the radiative effect of the air on the coatings was weak. Therefore, the following assumptions and simplifications concerning the heat transfer process were made:

1. The film was isotropic and homogeneous, the coating temperature was uniform and consistent before curing, and the film thickness did not change during curing;

2. The density, thermal conductivity, specific heat capacity, and other physical properties of the coating and substrate were constant and did not change with temperature;

3. The thickness of the coating was set to  $e_p$ , and heat transfer only occurred in the Z direction;

4. Assuming that the heat transfer process was uniform, the heat transfer model in the substrate was simplified as one-dimensional heat transfer along the Z direction;

5. The radiative effect of air was not considered.

Due to the complexity of radiative heat transfer and the convenience of computational models for establishing stable heat transfer simulations, the model was simplified with the following assumptions:

1. Infrared rays have a specific penetration capability, and objects can be simultaneously heated within this penetration distance. Thus, the infrared heating rate of the coating was higher than that of hot-air heating. The thickness of the coating (100  $\mu$ m) was within this infrared penetration zone. Therefore, it was assumed that the temperature at every point in the coating simultaneously increased. Based on this analysis, the heat transfer process was simplified by equating the infrared radiation heating of the coating with the heating of the coating via an internal heat source;

2. The coating was very thin, so it was assumed that no attenuation of infrared radiation occurred along the thickness direction. Therefore, the intensity of the equivalent internal heat source within the coating was equal across all points in the coating.

## 5.2. Heat Transfer Model

Figure 5- 1 shows the relevant heat transfer equations for the powder coating and the metal substrate. Due to the low coating thickness, the metal substrate was relatively thin and had good thermal conductivity. The coating was measured multiple times with a thermocouple during the experimental test process. The heat balance of the powder coating and metal substrate system is shown below [20] [21]:

$$\frac{dT}{dt} \left( C_{p_p} e_{p+} C_{p_s} \rho_s e_s \right) = \overline{Q}_{abs-} \overline{Q}_{emitted-} \overline{Q}_{convevtion-} \overline{Q}_{reaction}$$
(5.3)

$$QabsA_P = \eta_{tot}Q_{chem} \tag{5.4}$$


Figure 5-1. Heat transfer diagram for coating and substrate system (adapted from L. Véchot et al. [20]).

The heat released by the curing chemical reaction was negligible compared to the other heat flux values. Thus, it was ignored in the calculation [20]. The heat balance equation for the powder coating and metal substrate system was simplified as Equation (5.5):

$$\frac{dT}{dt}(C_{p_p}\rho_P e_p + C_{p_s}\rho_s e_s) = \overline{Q}_{abs} - \sigma \left[\varepsilon_S(T_S^4 - T_{\infty}^4) + \varepsilon_p(T_p^4 - T_{\infty}^4)\right] - (5.5)$$
$$\left[h_s(T_s - T_{\infty}) + h_p(T_p - T_{\infty})\right]$$

The value of  $\eta_{tot}$  depends on the thermal efficiency of the radiation panel ( $\eta_R$ ), as well as the thermal efficiency of the heat transfer from the radiation panel to the powder coating ( $\eta_{ht}$ ) [17]. This relationship is shown in Equation (5.6). The radiation panel thermal efficiency was used to quantify the efficiency of the conversion of the chemical energy of the gas into radiation energy, as shown in Equation (5.7):

$$\eta_{tot} = \eta_R \eta_{ht} \tag{5.6}$$

$$\eta_R = \frac{Q_R}{Q_{chem}} \tag{5.7}$$

Where  $Q_{chem}$  is the chemical energy of the gas, according to the calorific value of the gas to carry out calculations, the calorific value of liquefied petroleum gas  $q_h$  is 22,000-29,000K cal/m<sup>3</sup>.

The radiation heat transfer efficiency was related to the heat energy  $Q_{abs}$ absorbed by the powder coating and the radiation energy  $Q_R$  of the radiation panel, in accordance with Equation (5.8):

$$\eta_{ht} = \frac{Q_{abs}}{Q_R} \tag{5.8}$$

The radiation panel area was much larger than the sample coating area, and the value of  $Q_{abs}$  was calculated according to Equation (5.9):

$$dQ_{abs} = \eta_{ht} \frac{E_R}{\pi} A_R dw \tag{5.9}$$

$$E_R = \frac{Q_R}{A_R} \tag{5.10}$$

$$dw = \frac{dA_p}{l^2} \tag{5.11}$$

Due to the characteristics of the infrared heating coating and the simplifications of this model,  $Q_{abs}$  was converted into an equivalent internal heat source  $Q_p$  using Equation (5.12):

$$Q_p = \frac{Q_{abs}}{V_p} = \frac{Q_{abs}}{A_P e_p} \tag{5.12}$$

Inserting Equations (5.6)–(5.11) into Equation (5.12) resulted in a linear relationship, as demonstrated by Equation (5.13):

$$Q_p = \frac{\eta_{tot}q_h}{\pi e_p l^2} q_V \tag{5.13}$$

$$Q_P = C_g q_V \tag{5.14}$$

Where  $q_v$  denotes the amount of gas flowing into the radiant plate, and  $C_g$  defined as the conversion factor to succinctly represent the relationship between the equivalent internal heat source and the gas flow.

### **Boundary Conditions:**

If  $C_g = \frac{\eta_{tot}q_h}{\pi e_p l^2}$ , then:

The boundary conditions of the model are set as follows: The coating and substrate temperatures were even and constant before the coatings were heated. An infrared thermometer was used to measure the initial temperature, which was 30 °C. The initial flow rate of the infrared radiant plate was 0.2 m<sup>3</sup>/h, and the corresponding internal heat source value was 8.5 W/m3. The ambient temperature was 80 °C (in the experimental testing, the actual temperature fluctuated around 80 °C by less than 5%). The values of  $h_p$  and  $h_s$  were 4.5 W/m<sup>2</sup> °C and 9 W/m<sup>2</sup> °C, respectively [21]. The surface around the coating and substrate was simulated as an insulated boundary (the coating and substrate only exchanged heat with the surrounding air and did not heat the surface).

#### 5.3. Model Validation

The total efficiency ( $\eta_{tot}$ ) of powder coating curing with a gas infrared heater is between 25% and 30% [17]. However, the total efficiency of powder coating curing with catalytic infrared heating equipment is unknown. Experimental data with a curing temperature of 240 ° C were used to determine the total efficiency value. The model was then validated using curing temperatures of 230 °C and 220 °C.

As shown in Figure 5- 2, the simulation results closely matched the experimental results when  $\eta_{tot}$  was 0.4. The relative errors are shown in Table 5- 1, and the maximum relative error was 7.6% at 1 min.



Figure 5-2. Comparison of measured and simulated coating temperatures.

Time (s)	40	50	60	70	80	90
Experimental data (°C)	143.2	159.3	176.2	185.1	196.9	207.1
Simulated data (°C)	132.85	148.73	162.73	175	185.68	194.93
Relative error (%)	7.23%	6.64%	7.64%	5.46%	5.70%	5.88%
Time (s)	100	110	120	130	140	150
Experimental data (°C)	211	218.1	221.4	225.7	228.5	232.5
Simulated data (°C)	202.91	209.75	215.61	220.61	224.85	228.46
Relative error (%)	3.83%	3.83%	2.62%	2.26%	1.60%	1.74%

Table 5- 1. Relative errors for measured and simulated coating temperatures ( $\eta$ tot = 0.4).

The model's accuracy was further verified using curing temperatures of 220 °C and 230 °C by changing the gas intake of the radiant panel. During the experimental process, the maximum gas flow rate of 0.20 m<sup>3</sup>/h was used for the coating in the initial heating stage to ensure that it was rapidly heated. The gas flow was reduced when the coating reached the curing temperature. When the coating was heated for 125 s, the gas flow was decreased to 0.16 m<sup>3</sup>/h. This maintained the curing temperature at 220 °C. When the coating was heated for 157 s, the gas flow was decreased to 0.18 m<sup>3</sup>/h. This maintained the curing temperature at 230 °C. After adjusting the gas flow meter, the gas flow required approximately 30 s to stabilize. Therefore, when the simulated curing temperature was 220 °C, the initial internal heat source value was 8.5 W/m<sup>3</sup>,

and at 156 s, the internal heat source value was adjusted to 6.8 W/m<sup>3</sup>. When the simulated curing temperature was 230 °C, the initial internal heat source value was 8.5 W/m<sup>3</sup>, and at 188 s, the internal heat source value was adjusted to 7.65 W/m<sup>3</sup>.

The simulation results are shown in Figure 5- 3. The simulated temperature values were lower than the measured temperature values during the entire heating process. This is because there was a delay in the reduction of the radiation intensity, after the gas flow to the radiation panel was reduced during the heating process. The maximum differences between the simulation and experimental data were 8.7% at 230 °C and 9.6% at 220 °C. Therefore, this model can accurately predict changes in coating temperatures in engineering applications.



Figure 5- 3. Comparison of experimental and simulated temperatures during the curing process.

## 5.4. Application of the Model

Temperature nephograms obtained at curing temperatures of 220 °C and 230 °C are shown in Figure 5- 4. The convective heat transfer coefficient of the coating surface was low, and the heat loss from this surface was also low. Therefore, in the initial phase of heating, the upper layer of the coating had a

higher temperature. The coating surface was heated for 155 s to achieve a curing temperature of 220 °C. This curing temperature was maintained for 3 min. Then, the coating surface was heated for 187 s to achieve a curing temperature of 230 °C. This curing temperature was maintained for 2 min. During this heating process, the temperature distribution of the coating became more uniform, with the highest temperature located in the middle of the coating. The internal temperature of the substrate was almost constant throughout the entire heating process.



(a)



Figure 5- 4. (a) Temperature distribution of coating and substrate at a curing temperature of 220 °C. (b) Temperature distribution of coating and substrate at a curing temperature of 230 °C.

To further analyze the heat transfer during the curing process and to provide a reference for production, numerical simulations were used to predict the coating temperature with different substrate thicknesses. The effects of metal substrate thicknesses ranging from 1 mm to 10 mm on the coating temperature were calculated using a gas inlet flow of 0.2 m<sup>3</sup>/h. As shown in Figure 5- 5, the rate at which the coatings were heated decreased with increasing substrate thickness. Figure 5- 6 shows the predicted times required for the coating temperature to reach 220 °C or 230 °C with different substrate thicknesses. When the substrate thickness was 1 mm, the coating required 2.58 min to reach 220 °C and 3.12 min to reach 230 °C. The minimum times required to cure the coatings with this catalytic infrared heating equipment were 5.58 min and 5.12 min for curing temperatures of 220 °C and 230 °C, respectively. Moreover, a shorter total curing time was required with a curing temperature of 230 °C, resulting in energy savings. Therefore, it is

recommended that a curing temperature of 230 °C should be used when the substrate thickness is 1 mm, and 220 °C should be used when the substrate thickness is  $\geq 2$  mm.



Figure 5- 5. Predicted coating temperatures with varying substrate thickness.



Figure 5- 6. Heating times required for the coating temperature to reach 220  $^{\circ}$  C and 230  $^{\circ}$ C with different substrate thicknesses.

### 5.5. Summary

In this chapter, a one-dimensional heat transfer model was established, then the model validation and numerical simulations were carried out using ANSYS software. The simulation model reported in this work can be used to predict the shortest time required to cure coatings with different substrate thicknesses. An internal heat source was introduced in the simulation model. This model could accurately predict the temperature change in the coating. The total efficiency  $\eta_{tot}$  was determined to be 0.4, which shows a high energy conversion efficiency. According to the numerical simulations, the optimal correspondence between the thickness of the substrate and the curing temperature has been obtained.when the substrate thickness was 1 mm, the optimal coating curing temperature was 230 °C. For substrate thicknesses  $\geq 2$  mm, a coating curing temperature of 220 °C was more efficient. This work is a significant reference for the design of production processes and catalytic infrared curing production lines.

# **Chapter 6: Curing Process Study**

## 6.1. Introduction

Following the framework of the thesis, this chapter carried out the study of the curing reaction kinetic model. As curing is a chemical process, its rate and mechanism can be explained via chemical reaction kinetic models. Equation (3) generally suggests that curing rate depends on the degree of cure and temperature [117].

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{6.1}$$

where  $\alpha$  is the degree of cure, t is the reaction time, d $\alpha$ /dt is the curing rate,  $f(\alpha)$  is a function that closely relates to the specific curing reaction, known as the reaction model function or mechanism function, and varies with the nature and condition of the substance being cured, and k(T) is the reaction constant, which can be described by the Arrhenius Equation (6.2) [117].

$$k(T) = A \exp\left[-E_a/(RT)\right] \tag{6.2}$$

where A and  $E_a$  are the pre-exponential factors and the reaction activation energy, respectively.

The most critical factor in solving the kinetic equation is to evaluate  $f(\alpha)$ . Only the most accurate mechanism function can solve the rate equation for the correct kinetic parameters. Table 6-1 presents the most commonly used thermosetting polymers' curing reaction models and the corresponding kinetic parameters [83]. Among these, the n-order reaction model is the simplest, while the Kamal model is the most complex, incorporating both n-order and auto-catalytic reaction mechanisms. In order to predict or optimize the curing process of thermosetting polymers, researchers usually select the suitable curing model by considering the physical properties of the substance being cured, the curing conditions, and other relevant factors.

Table 6- 1. Thermosetting polymers curing reaction kinetic models and the corresponding parameters.

Reaction Model	Curing Rate (da/dt) *	Kinetic Parameters *
n-order	$k_0(1-lpha)^n$	$k_0, n$
Auto-catalytic	$k_1 \alpha^m (1-\alpha)^n$	$k_1, n, m,$
Kamal	$(k_2 - k_3 \alpha^m)(1 - \alpha)^n$	$k_2, k_3, n, m$
* 1 . 1 1 . 0	1 1 1 0	

\* where  $\alpha$  is the degree of cure; m and n are the orders of reaction; and k0, k1 k2, and k3 denote the reaction rate constants.

## 6.2. Curing Kinetics

### 6.2.1. The Samples' Degree of Cure

As discussed in the experimental section in detail, the degree of cure for nine different time (30–480 s) intervals at each of the three curing temperatures, 150 °C, 160 °C, and 170 °C, was determined by IR spectroscopy. Figure 6- 1 illustrates the FTIR absorption spectrum of the uncured powder coating, from which it is evident that the epoxide groups in the samples generated a distinct absorption characteristic peak at 908 cm<sup>-1</sup>. In addition, the peaks at 2934 cm<sup>-1</sup>, 1726 cm<sup>-1</sup>, and 1143 cm<sup>-1</sup> corresponded to the methyl group's asymmetric telescopic vibration and the ester group's C=O and C-O-C vibrations, respectively.



Figure 6-1. FTIR absorption spectrum of the uncured powder coating.

To analyze changes in the reactive groups' concentration during the curing process, the FTIR spectra of the samples cured for different time durations at the same temperature were compared, as shown in Figure 6- 2. As evident from the figure, the intensity of the characteristic peak at 908 cm<sup>-1</sup>, corresponding to epoxide group vibration, significantly decreased with the reaction interval. Meanwhile, the intensity of the characteristic peak of the ester group's C=O near 1726 cm<sup>-1</sup> remained almost unchanged. Therefore, the epoxide and the ester group's C=O characteristic peak intensity were used as the sample and internal standard quantity, respectively, to calculate the degree of cure. Table6- 2 presents the results for the various time intervals at each temperature, indicating that even at the highest curing temperature of 170 °C, the degree of cure reached only up to 0.84 in 360 s. This value demonstrates incomplete sample curing that could be achieved by conventional curing under the same conditions, suggesting that the IR curing process was retarded.



Figure 6- 2. FTIR absorption spectra of GMA/DDDA samples IR-cured for different time intervals at (a) 150 °C, (b) 160 °C, and (c) 170 °C.

Table 6- 2. Degree of cure for GMA/DDDA powder coatings at different curing temperatures after varying reaction intervals.

Curing Temperature	Curing Time Interval (s)	<b>Degree of Polymer Cure</b>
	30	0.146
	60	0.199
	120	0.236

	180	0.262
150 °C	240	0.544
	300	0.634
	360	0.736
	420	0.776
	480	0.782
	30	0.1592
	60	0.2416
	120	0.3922
	180	0.5232
160 °C	240	0.6171
	300	0.7152
	360	0.7537
	420	0.7751
	480	0.8124
	30	0.2316
	60	0.3352
	120	0.5111
	180	0.6491
170 °C	240	0.7293
	300	0.7738
	360	0.8386
	420	0.8481
	480	0.8485

## 6.2.2. The Curing Process Kinetic Parameters

To determine the kinetic parameters, the empirical data in Table 3 were fitted to three kinetic models (Table 9- 3) via the Levenberg–Marquardt algorithm [20] using the MATLAB (R2024b) Optimization Toolbox. The optimal kinetic model and the corresponding kinetic parameters were then determined based on the values of the "Sum of Squared Errors" (SSE) and "Coefficient of Determination" ( $R^2$ ). Figure 6- 3 presents the fitted curves, while the corresponding kinetic parameters are provided in Table 6- 3.

Table 6- 3. Numerical values of the kinetic model parameters obtained at different temperatures.

Temperature [°C]	Model	$k_0 * [s^{-1}]$	$k_1 * [s^{-1}]$	$k_2 * [s^{-1}]$	$k_3 * [s^{-1}]$	n *	<i>m</i> *	SSE	<b>R</b> <sup>2</sup>
150	n-order	0.0026				0.8870		0.0523	0.8799
	Auto-catalytic	_	0.0065		_	1.7951	0.6776	0.0006	0.9985
	Kamal			0.0005	0.0116	1.7806	0.9987	0.0026	0.9940
160	n-order	0.0022	_			0.3253		0.0245	0.9474
	Auto-catalytic		0.0105			1.8461	0.6633	0.0007	0.9985
	Kamal			0.0033	0.0113	2.0822	0.9984	0.0031	0.9934
	n-order	0.2872	_		_	0.2872	_	0.0495	0.8846
170	Auto-catalytic		0.0176			1.9246	0.6884	0.0011	0.9975

Kamal — 0.0011 0.0100 1.4400 0.7715 0.0056 0.9870

\*  $\alpha$  represents the degree of cure; m and n are the orders of the reaction; and k0, k1, k2, and k3 denote the reaction rate constants.





Figure 6-3. Kinetic model fitting of the cure rate vs. time data obtained for the samples IR-cured at (a) 150  $^{\circ}$ C, (b) 160  $^{\circ}$ C, and (c) 170  $^{\circ}$ C.

It is evident from the results that the n-order model fits the experimental data the least accurately for all three curing temperatures. Meanwhile, both the Kamal and auto-catalytic models fit the experimental kinetic data of the low curing temperatures (150 °C and 160 °C) of the GMA/DDDA system. Nonetheless, the R<sup>2</sup> value of the auto-catalytic model is slightly larger than that of the Kamal model, in addition to its SSE value being closer to zero, indicating that for lower curing temperatures, the former model fits the experimental data better than the latter. Similarly, the auto-catalytic model also fits the high-temperature (170 °C) curing process's data more closely than the others. Thus, the auto-catalytic model best fits the kinetics of the curing process at all three temperatures.

Since the m and n values for the auto-catalytic model do not change significantly with the curing temperature, these can be averaged to 0.6764 and 1.8552, respectively, for the three temperatures. Furthermore, the activation energy of the process can be obtained by plotting the natural logs of the rate constants of the auto-catalytic model versus the reciprocal of the corresponding absolute curing temperatures according to the modified form of the Arrhenius Equation (6.3), as depicted in Figure 8.

$$ln k = ln A - E_a/(R T)$$
(6.3)

It is evident from figure 6- 4 that the plot showed a good linear relationship between ln *k* and 1/T, with its slope and y-intercept relating to the activation energy Ea and the pre-exponential factor A of the GMA/DDDA curing process. Therefore, using the MATLAB polyval function, the variables  $E_a$  and *A* were determined to be 77.611 kJ/mol and  $2.45 \times 10^7$  s<sup>-1</sup>, respectively, with great certainty, as evident from the SSE = 0.0006 and R<sup>2</sup> = 0.9988 values. Consequently, the GMA/DDDA curing process temperature-dependent reaction rate constant was evaluated as  $k = 2.45 \times 10^7 \exp(-77611/RT)$ .



Figure 6-4. Arrhenius plot for IR curing process of GMA/DDDA.

In order to validate the model's applicability at random practical temperatures, the same coating material was cured at 165 °C (the powder coating is a low-temperature type, and excessive temperature conditions can have a significant impact on the curing results) using the same curing equipment, and the resulting experimental data were compared to the model-predicted kinetic curve of the reaction using MATLAB, as shown in Figure 6- 5. The subsequent data analysis yielded SSE and  $R^2$  values of

0.0008 and 0.9978, respectively, indicating the high accuracy and validity of the kinetic model.



Figure 6- 5. Comparison of experimental and model-predicted kinetic behavior of the curing reaction at 165 °C.

In this study, the dynamics of the GMA/DDDDA system were investigated using a catalytic infrared curing device and an FT-IR spectrometer. Two major types of errors, are expected in the experiment and measurements. To further improve the accuracy of the model fitting to the experimental data, experimental measurements are suggested to control the following sources of errors in future studies.

**Systematic errors:** The sources of systematic errors can include an inaccurate wave number calibration of the FTIR spectrometer or baseline drift, which results in a systematic shift in the absorption peaks and imprecise temperature control of the IR curing equipment, resulting in small (3%–5%) fluctuations in the coating temperature. In addition, inconsistencies in sample preparation, variations in the thickness of the film or the surface homogeneity, also change the IR absorption properties of the material predictably, leading to systematic errors in the results.

**Random errors:** For experiments, although standardized operating procedures are established, different operators/personnel may differently handle the equipment and samples, which can cause fluctuations in the measurement results. In the present study, the introduction of such errors is mainly probable while electro-spraying the powder, sampling the curing sample, and preparing samples for the IR analysis. In addition, instrumental changes also need to be considered; for example, during the FT-IR analysis, changes in the sample beam contact angle and light source intensity may lead to random fluctuations in the results.

### 6.3. Summary

In this study, the curing kinetics of the IR heating of a thermosetting polymer are investigated in detail. Briefly, Fourier infrared spectroscopy and MATLAB software (R2024b) were successfully used to collect and process curing kinetics data of GMA acrylic powder coatings. The experimental data were found to be consistent with the auto-catalytic reaction kinetic model, with the reaction activation energy  $E_a = 77.611$  kJ/mol, the pre-exponential A $= 2.45 \times 10^7$  s<sup>-1</sup>, and the curing parameters *m* and n = 0.6764 and 1.8552, respectively. Thus, the IR curing kinetics of the polymer system can be well described by the following kinetic equation:  $d\alpha/dt = 2.45 \times 10^7 \exp(-77611/RT)\alpha^{0.6467}(1 - \alpha)^{1.8552}$ . To the best of my knowledge, this study is the first to investigate the catalytic infrared curing kinetics and its parameters, which provides a feasible research method and technical reference for other scholars.

# **Chapter 7: Photo-Thermal Synergistic Effect**

## 7.1. Introduction

Powder coatings contain several types of chemical bonds, and these vibrate at specific frequencies, with strong absorptive interactions with infrared radiation at frequencies close to their own [19,20]. Thus, during infrared heating, electromagnetic energy is converted into thermal energy through molecular resonance, leading to a rise in the temperature of the coating and triggering the thermal effect. Meanwhile, infrared radiation directly influences the curing process. Genty et al. [36] referred to this curing characteristic specific to infrared technology as a "non-thermal" effect. They emphasized that this phenomenon is closely related to infrared heat flux, which is highly selective for the molecular groups and reaction steps involved in the curing process. In addition, throughout the curing process, the manifest activation energy is lower than that of thermal curing. Meanwhile, the thermal and 'non-thermal' effects are not correlated but rather competing. Thus, the introduction of the non-thermal effect has deepened the understanding of infrared curing technology at the mechanistic level; however, this research is limited to aspects that contribute to curing. In addition, from the industrial application point of view, there is still a need for a standard that can provide guidance for making scientific decisions when applying the technology. For example, coating manufacturers need a criterion to determine whether the coating formulation can be cured via infrared technology, while manufacturers with the will to apply infrared curing technology also need a criterion to assess the feasibility of using the technology.

## 7.2. Conceptualization

In this study, the kinetics investigation of the GMA IR curing process demonstrated that the curing rate and the degree of cure significantly differed from that of conventional hot air curing. For instance, according to the guidance notes for conventional curing of the polymer system, it must completely cure in 20 min at 170 °C. Nonetheless, the experimental data showed that by replacing the conventional heating method with IR heating for the same temperature, the thermosetting system stopped curing after 320 s of reaction and maintained a constant degree of cure at around 0.84 afterward. This finding suggests that the IR heating accelerated the curing rate of the polymer system; however, it decreased the degree of cure of the final product. In addition, Choi et al. [29] have indicated that a high power density of near-IR (NIR) radiation may generate significant thermal stresses between the substrate and the coating, which could lead to localized cracking and the delamination of polymeric films. Therefore, a comprehensive analysis of these findings indicates that IR curing technology can either facilitate or impede the overall curing performance of thermosets. IR curing technology is essentially a type of thermal curing technology [8]. As illustrated in Figure 7-1, IR curing technology combines the volumetric transfer/absorption of radiant energy in a specific wavelength range with other heat transfer modes, thereby inducing various changes in the curing process and the resulting product. On the one hand, functional groups involved in the curing reaction, such as epoxide rings, ester groups, or hydroxyls, are capable of directly absorbing IR photons at frequencies matching their bond vibrations. This photon-molecular resonance interaction may lead to enhanced vibrational excitation of the reaction bonds, a temporary decrease in the effective activation energy (Ea),

and an acceleration of the reaction kinetics. In addition, spectral matching between the wavelengths of infrared emission (typically mid- and far-infrared) and the vibrational modes of the coating material ensures that the radiation is efficiently absorbed throughout the depth of the coating, which facilitates a rapid and spatially uniform temperature rise, improving heat transfer and cure uniformity. This interaction creates a "photo-thermal synergistic" effect. Distinguished from the study by Genty et al. [32], the " photo-thermal synergistic" effect integrates both the thermal and "non-thermal" effects on the curing process, taking into account the phenomenon of impediments to curing by this technology.



Figure 7-1. Heat transfer modes of the IR curing process.

### 7.3. photo-thermal synergistic index

To predict the impacts of the photo-thermal synergistic effect of IR curing technology, a kinetic model is developed in the present study; however, there is still a need for a common criterion to simply assess the feasibility of the application of the IR curing technology in practical engineering. In the chapter *Literature review* of this thesis, the influence of IR curing technology on curing behavior is summarized, based on which this present model combines the photo and thermal effects of IR curing technology on the curing process and the properties of the cured products in terms of the curing time  $\Delta t$  and the degree of cure  $\Delta a$ , respectively. These two kinetic parameters are

mathematically linked to propose a dimensionless evaluation criterion, the photo-thermal synergistic index (PTSI), for assessing the feasibility of the IR technology, as follows:

$$PTSI = \Delta t' \times \Delta \alpha' \tag{7.1}$$

where

$$\Delta t' = \Delta t_{IR} / \Delta t_{REF} \tag{7.2}$$

$$\Delta \alpha' = \alpha_{IR} / \alpha_{REF} \tag{7.3}$$

$$\Delta t = t_{start} - t_{End} \tag{7.4}$$

and  $\Delta t_{\text{IR}}$  and  $\Delta t_{\text{REF}}$  are the time periods used to reach the highest degree of cure by applying the IR curing technique and a reference curing technique, respectively, whereas  $\alpha_{\text{IR}}$  and  $\alpha_{\text{REF}}$  are the corresponding highest degrees of cure achieved during these times. This evaluation criterion can be applied with three possible outcomes, as illustrated in Figure 11, and briefly explained as follows:

Case 1:

$$\Delta t' < PTSI < \alpha' \tag{7.5}$$

A PTSI value of less than  $\alpha$ ' but greater than  $\Delta t'$  (Equation (7.5)) suggests an accelerated curing process and an increased degree of cure, predicting a faster and higher properties cured product. Thus, under such conditions, the photo-thermal synergistic effect positively impacts the overall curing behavior. Under such conditions, coating formulations and/or equipment need not require any improvements and, therefore, the application of infrared curing technology is "recommended" with the advantages of energy and equipment conservation.

Case 2:

$$PTSI > \alpha' \tag{7.6}$$

A significantly large PTSI compared to  $\alpha'$  (Equation (7.6)) indicates an increased degree of cure and a slower curing process, predicting a cured product with a manufacturing time. Thus, while it forecasts a positive impact of the photo-thermal synergistic effect on the product's cure characteristics, an increase in curing time may lead to an increase in energy consumption. Therefore, IR curing for such systems could be considered for improving the product properties only.

Case 3:

$$PTSI < \Delta t' \tag{7.7}$$

A significantly small PTSI compared to  $\Delta t'$  (Equation (7.7)) indicates a negative influence of the IR curing technology on both the cure rate and the cure properties, predicting a slow curing process with poor product characteristics. Thus, under such conditions, IR technology is not recommended for curing due to the photo-thermal synergistic effect enhancing the manufacturing time while also compromising the product's quality. In engineering applications, this case forecasts an increase in the manufacturing cost and a need to modify the coating formulation or the curing equipment to meet the "Case 1" scenario mentioned earlier. Thus, this result means that the technology is "not recommended".



**Evaluation results** 

Figure 7-2. Evaluation of IR curing technology based on the photo-thermal synergistic index (PTSI).

As an example, for the GMA/DDDA system curing experiment, the standard curing condition for this coating is 20 minutes at 170 °C using hot air. However, in the experiment under the same temperature with the standard condition, the curing reaction stopped at 420 seconds and the final cure degree was 0.84. According to equations 7.1 to 7.4, it can be obtained:

$$\Delta t' = 0.35$$
$$\Delta \alpha' = 0.84$$
$$PTSI = 0.294$$

The calculations are consistent with the third case, therefore the system is not effective using IR curing and this curing technique is not recommended. The results of the impact resistance test on the cured layer also remained consistent with the calculations, as shown in Figure 7-3, where the layer was significantly detached after hammering.



Figure 7-3. Impact resistance test results of cured films.

In practical engineering, it is not important to explore the mechanism of the curing reaction while also inconvenient to measure the degree of cure of the product; the PTSI can be calculated using the product (mechanical, optical, or combination) properties. In order to further explain PTSI and enhance its applicability, this paper is based on the two aspects of engineering applications, i.e., the coating production [119] [120] and the applications, and takes the curing equipment [36] [29] [22] key parameters and the coating composition as the input, in conjunction with the previous review in section 2.2.3.2. *Properties of Cured Products*, then establishes the correlation among the three layers of parameters, and finally demonstrates the intrinsic correlation in the form of an artificial neural network, as shown in Figure 7- 3.



Figure 7-4. Artificial neural network for PTSI.

As shown in Figure 7- 4, engineers can obtain a large amount of data through the actual project to optimize and adjust the functional relationship between the parameters of each layer and then build a more engineering-guided PTSI, which can ultimately become a practical and reliable tool in engineering applications.

### 7.4. Summary

This chapter proposes a new concept: the 'photo-thermal synergistic effect' of infrared curing and its evaluation criteria using a dimensionless quantity( PTSI). Based on the main evaluation factors of the curing reaction, i.e., the two factors of curing degree and curing time. PTSI qualitatively evaluates the infrared curing behavior by establishing a comparative equation with the conventional thermal curing behavior, and the evaluation results are classified into three categories: "Recommend", "Not recommended", and "Can be considered", then the evaluative efficacy of the index was validated. In addition, the index uses an artificial intelligence neural network approach to synthesize the effects of infrared curing technology on both the curing process and the performance of the cured product, in order to facilitate the evaluation of the powder production and curing process in real engineering. Although still in its infancy, this evaluation criterion provides a straightforward and generalized dimensionless index for the applications of IR curing technology in practical engineering.

Overall, the studies in Chapter 6 and this chapter deepens our understanding of the IR curing reaction mechanism and provides a reference for the application of this technology in practical engineering.

# **Chapter 8: Conclusion**

## 8.1 Summary of the study

This dissertation presents a comprehensive study of catalytic infrared curing technology applied to thermosetting polymer systems, particularly applied to polyester/TGIC and GMA/DDDA systems. Through experimental investigations, numerical modeling, and theoretical development, the following key findings were achieved:

**Feasibility study.** Catalyzed infrared curing of powder coatings can be an effective alternative to heat curing because it can significantly shorten the processing cycle without compromising the mechanical properties of the material. Specifically for this study:

1. The maximum surface temperature of the radiation panel was 475 °C, and its infrared wavelength range was 2–25  $\mu$  m. The infrared absorption wavelengths of most of the functional groups of the polyester/TGIC powder coatings were in this region. Thus, the coatings were quickly cured with catalytic infrared radiation;

2. The optimal curing parameters for this catalytic infrared curing process were 230 °C for 2 min and 220 °C for 3 min. The mechanical properties of the coatings became stronger as the temperature and time increased. However, the gloss of the coatings appeared to decrease. When the temperature was too high, the color of the coatings became dark.

**Heat transfer process study.** A one-dimensional heat transfer model was developed and validated to predict thermal behavior during curing:

1. An internal heat source was introduced in the simulation model. This model could accurately predict the temperature change in the coating. The total efficiency  $\eta_{tot}$  was determined to be 0.4;

2. According to the numerical simulations, when the substrate thickness was 1 mm, the optimal coating curing temperature was 230 °C. For substrate thicknesses  $\geq$  2 mm, a coating curing temperature of 220 °C was more efficient.

**Curingr Process Study.** The experimental data were analyzed and curve fitted using Fourier transform infrared (FTIR) technique and MATLAB software to obtain conclusions: The experimental data were found to be consistent with the auto-catalytic reaction kinetic model, with the reaction activation energy  $E_a = 77.611$  kJ/mol, the pre-exponential  $A = 2.45 \times 10^7$  s<sup>-1</sup>, and the curing parameters *m* and n = 0.6764 and 1.8552, respectively. Thus, the IR curing kinetics of the polymer system can be well described by the following kinetic equation:  $d\alpha/dt = 2.45 \times 10^7 \text{ exp}(-77611/RT)\alpha^{0.6467}(1 - \alpha)^{1.8552}$ .

**Theoretical study.** The "photo-thermal synergistic effect" was conceptualized and quantified using the Photo-Thermal Synergistic Effect Index (PTSI), offering a novel framework for understanding and optimizing curing performance.

After simplifying the above findings again, the main results of this study are shown in Figure 8-1.



Figure 8-1 The Overview structure of this studies.

## 8.2 Discussion

The main purpose of this section is to compare this study with other scholars' research on infrared curing technology and to extract the main contributions and future directions of this technology. In this chapter, according to the technical route of the study, a comparative analysis is made in three aspects, i.e., heat transfer process study, curing process study, and theoretical study with other scholars' research.

Previous studies [109] have shown that the volume absorption model of infrared radiation may lead to changes in curing efficiency and the properties of product. This paper lists and compares studies related to this field involving infrared heat transfer research as shown in Table 8-1.

Model	Geometric Model	Calculation Method	Software	Ref.
Surface absorption	1D	FVM	Fortran 90 & IMSL Library	[21]
	1D	PDE	MPC@CB	[23]

Table 8-1 Comparison of infrared heat transfer models

	1D	PDE	MPC@CB-	[45]
	3D&2D	FE	COMSOL	[34]
	1D	-	-	[18]
	1D	FE	COMSOL	[24]
	1D	RTM	COMSOL	[46]
	3D&2D	FE	Matlab COMSOL	[47]
	3D&2D	FE	COMSOL	[27]
	1D	MCM	-	[17]
	3D&2D	FE	FLUENT	[48]
	1D	PDE	Matlab	[20]
volume absorption	1D	Internal heat source	ANSYS	[56]
1	1D	PDE		[18]

As can be seen from the above table, there are not many heat transfer modeling studies involving volume absorption of infrared radiation in the field of compound curing. In general, the numerical calculation of infrared heat transfer is more complex compared to heat conduction and heat convection, and the use of numerical methods and software simulations are the usual solutions. In this study, radiant energy is innovatively modeled and numerically calculated as an internal heat source, the concept of "total efficiency" is proposed, and numerical simulation and experimental validation are used to calculate and predict the heat transfer process [56], which greatly reduces the complexity of the radiant heat transfer calculations in the project, and provides a new technological approach for this type of research.

In this study, a curing kinetics study was carried out for volumetric absorption of infrared energy, and only Genty et al. [32] carried out the kinetic study of volumetric absorption model. However, the curing kinetics model is mainly divided into n-order model, auto-catalytic model and Kamal model, and the current scholars about the kinetics of the study are carried out around the cured material, as shown in Table 8-2, and they believe that the curing kinetics mechanism of the material is unchanged, without considering the effect of the change of the curing technology. In this study, the kinetic equations and parameters were obtained by using matlab for data fitting, and the first kinetic study was carried out for the volumetric absorption characteristics of infrared curing technology. In addition, this study enriches the infrared curing theory on the basis of the non-thermal effect proposed by Genty [32] and proposes the photo-thermal synergistic effect.

Absorption Model	Monitoring Device	<b>Curing Theory</b>	Modeling Methods	Ref
				[21]
				[23]
				[45]
				[24]
Surface D absorption	DSC	Kinetic model	Based on cured material	[46]
				[47]
				[27]
				[48]
				[20]
	DEA	Kinetic model	Based on cured material	[34]
volumetric absorption	FTIR	Kinetic model Photo-thermal synergistic effect	Based on curing technology	[121]
	DSC	Gelation theory Non-thermal effect	Based on material	[32]

Table 8-2 Comparison of curing theory and monitoring techniques

In particular, regarding the use of DSC, as shown in the table above, most scholars utilize DSC to calculate curing. It should be discussed that in the IR surface absorption mode, the internal heat transfer mode of the cured object is still dominated by heat conduction, so it is convenient and feasible to use DSC to calculate the degree of curing, but in the IR volumetric absorption mode, the IR heat transfer mode is changed and it is not possible to use DSC for in situ measurements. In addition, in a study [121], it was found that the volumetric absorption of IR energy brings about a change in the maximum degree of cure, so that the measurement of residual enthalpy of cured material using DSC would be subject to a large error. In this case, the use of Fourier Transform Infrared (FTIR) measurement becomes a more reliable option.

At present, in the field of coating, limited by higher curing temperature, there is no technological breakthrough in the curing of coatings with heat-sensitive substrates, e.g. MDF (medium density board) [120]. The introduction of catalytic infrared curing technology has allowed the use of non-metallic substrates. In this study, curing experiments were carried out using GMA/DDD low-temperature powder coatings, and from the results, it can be seen that the curing behavior of the powder coatings changed significantly, and although the curing rate was increased considerably, the maximum degree of cure was reduced. In general, the characteristics of the coating and the curing technology must match each other in order to realize the advantages of each [4]. For example, when using fast infrared curing technology, the leveling and cross-linking curing of the coating may take place at the same time, and it is necessary to expand the temperature difference between melting and curing, so as to allow the coating to be fully leveled and avoid 'hot spots' and other situations that hinder the curing process [8].

## 8.3 Contributions to Knowledge

This study helps to promote the understanding and application of catalytic infrared curing and contributes to the theory and practice in the following five main areas:

1. Provides a reliable and accessible experimental and theoretical framework for the study of catalytic infrared curing technology, and proposes a specific and feasible technical route; 2. The feasibility of a catalytic infrared curing powder coating system was experimentally verified, and the characteristics and curing effect( mechanical and optical properties) of catalytic infrared curing technology were also investigated;

3. The heat transfer model innovatively treated radiant energy as the internal heat source, proposed the concept of 'total efficiency', and determined by numerical simulation method, greatly reducing the complexity of the radiation heat transfer calculations in the project;

4. By focusing on the effect of infrared volumetric absorption on the curing process, a kinetic model suitable for infrared curing technology has been determined for the first time. In addition, FTIR is more effective in monitoring such curing behaviour than DSC;

5. The concept of photo-thermal synergistic effect was proposed for the first time in the field of curing, and the infrared curing effect is evaluated by the photo-thermal synergistic index( PTSI), which not only enriches the existing theory but also has a guiding role in the improvement of the production and curing process of powder coatings.

## **8.4 Future Research Directions**

The research results of this thesis provide technical routes, data and theoretical support for the further development of catalytic infrared technology, but at the same time there are certain limitations that can be improved in future research:

1. Carry out research on quantitative testing and analysis of the mechanical and optical properties of cured products, and establish a functional

121

relationship between curing properties and curing conditions, such as curing temperature, time, radiation flux, and radiation distance;

2. In order to monitor the curing behavior more accurately, in-situ detection techniques should be attempted, e.g., building a reaction cell for catalytic infrared curing and using an in-situ FTIR meter for online monitoring;

3. Further improve the "photo-thermal synergistic effect" evaluation system, to carry out the quantitative evaluation of the effect of the method of research, integrated powder coating properties and the characteristics of the infrared curing system continue to improve the artificial neural network for PTSI;

4. Research and develop powder coatings matching infrared curing technology, and carry out research on low-temperature rapid curing technology.

By addressing these areas, future research can further refine and expand the capabilities of catalytic infrared curing technology, ensuring its continued relevance and impact in industrial applications.
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