Modelling and experimental validation of thermoset resin curing during pultrusion

A N Vedernikov, A A Safonov and I S Akhatov
Skolkovo Institute of Science and Technology, Center for Design, Manufacturing and Materials, Moscow, Russia

Aleksandr.Vedernikov@skoltech.ru

Abstract. Mathematical modelling of the pultrusion manufacturing process involves many parameters of the resin mixture. In this article thermo-chemical behavior of resin used for pultrusion of glass fiber/epoxy-vinyl L-shaped profiles was characterized. Profiles were manufactured at pulling speeds of 200, 400, and 600 mm min⁻¹. Dependency of resin specific heat from temperature was determined by differential scanning calorimetry (DSC); the influence of temperature on resin's thermal conductivity was found; parameters of resin cure kinetics were described. Subsequently, the gained parameters were used for numerical simulation of the pultrusion thermo-chemical problem in ABAQUS software. The temperature and cure degree evolutions obtained from the experiments run at different pulling speeds, and those from the numerical model were shown to be correlated.

1. Introduction
Recently fiber reinforced polymers (FRPs) have been widely adopted as structural elements in the civil engineering and construction sector due to their better mechanical properties compared to those of traditional materials (steel, timber, concrete) [1-4]. As the most efficient manufacturing technique of composite materials, pultrusion allows the production of constant cross-section profiles with virtually unlimited length and least engineers’ involvement [5,6]. Advantages of pultruded profiles are apparent: high strength-to-weight ratio [7-9] improved corrosion resistance [10-12] and durability [13-15], ease of transportation, installation, and maintenance [16].

The thermoset pultrusion process starts from pulling fiber reinforcement (unidirectional rovings, mats, woven fabric) through the bath, filled with the resin matrix [17,18]. Next, impregnated material is pulled to the preformer for the elimination of excessive resin [19]. Then preformed reinforcement is guided to the heated die for the initiation of resin polymerization process [20]. Cured composite is subsequently directed to the cutting saw by the system of puller units [21]. Nevertheless, the performance of the final pultruded product is very sensitive to processing parameters [22,23] and the choice of raw materials [24-26]. Aiming quality improvement of produced profiles by minimizing residual stresses [27], occurrence of cracks [28] and manufacturing induced shape distortions, mathematical modelling of the pultrusion process is a widely applied tool [29,30]. It allows to avoid time-consuming and expensive trial-error experiments [31,32]. Since the pultrusion manufacturing process incorporates thermo-chemical and mechanical problems, plenty of input parameters of composite raw elements are needed to achieve mathematical modelling reliable results [33,34].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd
The objective of the current article is to experimentally determine temperature-dependent parameters of resin mixture: specific heat and thermal conductivity. These parameters are subsequently coupled with resin kinetics and utilized to solve the pultrusion thermo-chemical problem in ABAQUS software. The computation procedure results are then compared to those detected during the pultrusion experiment performed at three different pulling speeds (200, 400, and 600 mm·min\(^{-1}\)).

2. Materials and methods

2.1. Pultrusion process setup and experimental determination of resin parameters

Resin mixture and pultruded profiles manufactured with Pultrex Px500-6T (Pultrex, UK) pultrusion machine were produced at the Laboratory of Composite Materials and Structures of the Center for Design, Manufacturing and Materials (Skolkovo Institute of Science and Technology, Moscow, Russia). The matrix used for this study was epoxy vinyl-based Atlac 430 (DSM Composite Resins AG, Switzerland). To improve the quality of the resin mixture the following components were added: Trigonox C (Akzo Nobel Polymer Chemicals B.V., The Netherlands), Perkadox 16 (Akzo Nobel Polymer Chemicals B.V., The Netherlands), BYK-A555 (BYK Additives & Instruments, Germany), and Zinc Stearate (Baerlocher GmbH, Germany). Mentioned additives played the following roles: Trigonox C – initiator for (co)polymerization of ethylene, styrene, acrylonitrile, acrylates, and methacrylates; Perkadox 16 – initiator for suspension polymerization of acrylates and methacrylates; BYK-A555 – deaerator; Zinc Stearate – friction reduction. The amount of each component used in the resin mixture is indicated in table 1.

| Component                                                      | Amount [kg] |
|----------------------------------------------------------------|-------------|
| Resin Atlac 430 (DSM Composite Resins AG, Switzerland)        | 25.07       |
| BYK-A555 (BYK Additives & Instruments, Germany)               | 0.09        |
| Trigonox C (Akzo Nobel Polymer Chemicals B.V., The Netherlands)| 0.38        |
| Perkadox 16 (Akzo Nobel Polymer Chemicals B.V., The Netherlands)| 0.13        |
| Zinc Stearate (Baerlocher GmbH, Germany)                      | 1.00        |

The length of the die was 600 mm. Four heating platens were used. L-shaped profiles were pultruded at three different pulling speeds: 200, 400, and 600 mm·min\(^{-1}\). Therefore, abbreviations of V-200, V-400, and V-600 are used in this paper. During the pultrusion process temperature evolution of the processing composite was recorded by wired thermocouples. They had a length of 7 m and were introduced within the profile before die entrance.

Independently from pultrusion process, the pure resin mixture was fully cured, and two samples were cut off to evaluate the temperature dependence of resin specific heat. Samples had a shape of cylinders with a radius of 4 mm and a thickness of 2 mm. For the purpose of this study Differential Scanning Calorimeter DSC 204 (NETZSCH-Gerätebau GmbH, Germany) was used. Experiments were carried out at the temperature range from 20°C to 100°C. Two samples were cut off to evaluate the temperature dependence of resin thermal conductivity. Samples had a shape of thin plates 10 × 10 mm and a thickness of 1 mm. For the purpose of this study Laser Flash Apparatus LFA 457 (NETZSCH-Gerätebau GmbH, Germany) was used. Experiments were carried out at the temperature range from 20°C to 100°C.

2.2. Heat-transfer model

The general 3D heat-transfer model describing the pultrusion process is presented in equation (1). Subscript “1” represents the pulling direction of pultrusion, while “2” and “3” are related to the
transversal direction. Index “c” determines the belonging of the property to the entire composite, while “r” and “f” are related to resin and fiber respectively.

\[
\rho_c C_{p,c} \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x_1} \right) = k_{x_1,c} \frac{\partial^2 T}{\partial x_1^2} + k_{x_2,c} \frac{\partial^2 T}{\partial x_2^2} + k_{x_3,c} \frac{\partial^2 T}{\partial x_3^2} + q
\]

\[
q = (1 - V_f) \rho_r H_{tot} \frac{da}{dt}
\]

Where \( \rho_c, \rho_r \) are densities of the composite and resin respectively; \( C_p \) represents specific heat; \( T \) is temperature; \( t \) is time; \( k_{x_1,c}, k_{x_2,c}, k_{x_3,c} \) are the thermal conductivities in the corresponding directions; \( v \) is pulling speed; \( q \) represents internal heat generation due to exothermic reaction of the resin; \( V_f \) represents fiber volume fraction; \( H_{tot} \) represents total heat released during curing; \( \frac{da}{dt} \) is rate of curing reaction.

Kinetic model of the \( n \)th order reaction with autocatalysis was used for the modelling of resin polymerization process [35]:

\[
\frac{da}{dt} = A e^{-\frac{E_a}{R_\text{g}}}(1 - \alpha)^n(1 + K_{\text{cat}}\alpha)
\]

Where \( \alpha \) represents instantaneous degree of cure; \( t \) is time; \( A \) represents a preexponential factor; \( E_a \) is activation energy; \( R_\text{g} \) is universal gas constant; \( n \) is the order of the reaction; \( K_{\text{cat}} \) is activation constant. Parameters of the model are presented in the table 2 in accordance to those described in [22].

| \( A [s^{-1}] \) | \( E_a [kJ \cdot mol^{-1} \cdot K^{-1}] \) | \( n [-] \) | \( K_{\text{cat}} [-] \) |
|------------------|-------------------------------|---------|-----------------|
| \( 10^{9.34} \)  | 93.3                          | 1.91    | \( 10^{2.73} \) |

### 2.3. Finite element simulations

Mathematical modelling was performed at the FEM software ABAQUS. The following subroutines were used for the solution of the thermo-chemical problem: FILM (to define die temperatures and heat transfer coefficient as functions of position and time), USDFLD (to define cure degree of the composite as a field variable), HETVAL (to define a heat flux due to internal heat generation in the material during heat transfer analysis). The finite element model consisted of linear quadrilateral element (CPE4RT). The number of elements is over than 1000.

### 3. Results and discussions

The results of the temperature dependence of resin specific heat evaluation are presented in table 3. According to equation (4), the first-order polynomial was then used for the approximation of temperature dependent resin specific heat experimental results.

\[
C_p = 5.1T + 1080
\]

Where \( T \) represents the instantaneous temperature of the resin; \( C_p \) is instantaneous specific heat of the resin.

The correlation between resin thermal conductivity and temperature is found to be weak. Therefore, further resin thermal conductivity is considered independent from the temperature and adopted as the average value of experimental results equal to 0.177 \( W \cdot m^{-1} \cdot K^{-1} \).
Table 3. Temperature dependence of resin specific heat and thermal conductivity.

| Temperature [°C] | Measured value of specific heat | Measured value of thermal conductivity |
|------------------|---------------------------------|----------------------------------------|
|                  | $C_p1$ [J·kg$^{-1}$·K$^{-1}$]  | $C_p2$ [J·kg$^{-1}$·K$^{-1}$]          | $C_{average}$ [J·kg$^{-1}$·K$^{-1}$]  | $\lambda_1$ [W·m$^{-1}$·K$^{-1}$] | $\lambda_2$ [W·m$^{-1}$·K$^{-1}$] | $\lambda_{average}$ [W·m$^{-1}$·K$^{-1}$] |
| 20               | 1181                            | 1199                                   | 1190                              | 0.1730                          | 0.1761                          | 0.1746                              |
| 30               | 1227                            | 1241                                   | 1234                              | 0.1741                          | 0.1718                          | 0.1730                              |
| 40               | 1277                            | 1290                                   | 1284                              | 0.1773                          | 0.1704                          | 0.1739                              |
| 50               | 1333                            | 1339                                   | 1336                              | 0.1800                          | 0.1769                          | 0.1785                              |
| 60               | 1386                            | 1384                                   | 1385                              | 0.1802                          | 0.1787                          | 0.1795                              |
| 70               | 1430                            | 1421                                   | 1425                              | 0.1773                          | 0.1784                          | 0.1779                              |
| 80               | 1476                            | 1461                                   | 1468                              | 0.1793                          | 0.1765                          | 0.1779                              |
| 90               | 1538                            | 1518                                   | 1528                              | 0.1796                          | 0.1785                          | 0.1791                              |
| 100              | 1628                            | 1610                                   | 1619                              | 0.1823                          | 0.1817                          | 0.1820                              |

Figure 1 represents the evolution of composite temperature and cure degree as functions of coordinate measured in the pulling direction of pultrusion starting from the die entrance. Since the most significant part of the polymerization process happens within the die, only 600 mm length is considered. The solid line represents the results of mathematical modelling, while the dashed line is related to the experimentally obtained values. Good correlation between numerical and experimental results for all the pulling speeds is observed. Therefore, the thermo-chemical model of pultrusion presented above is considered to be experimentally verified.

4. Conclusions
Both an experimental and a numerical study were performed to investigate thermo-chemical problem of pultrusion process in relation to the production of glass fiber/epoxy-vinyl L-shaped profiles. Tests on epoxy-vinyl based matrix were conducted to characterize the dependency of resin specific heat and thermal conductivity on temperature. Specific heat of the resin exhibited a linear temperature dependence, while thermal conductivity demonstrated weak correlation and was adopted as constant.
These results were then jointed to resin kinetic and used for the mathematical modelling of the thermochemical problem of pultrusion in ABAQUS software. Simulating the resin curing process, temperature and cure degree evolution profiles of composites were obtained for three pulling speeds: 200, 400, and 600 mm·min⁻¹. Modelling results demonstrated a good agreement with the results detected by thermocouples during the pultrusion experiment.

This paper is the first step of authors to experimentally characterize thermal and mechanical parameters of pultruded composites’ constituent parts needed for the further development of the linear viscoelastic mathematical model.

References

[1] Vedernikov A, Safonov A, Tucci F, Carlone P and Akhatov I 2020 Pultruded materials and structures: A review J. Compos. Mater. 54 4081–117
[2] Liu T, Feng P, Lu X, Yang J-Q and Wu Y 2020 Flexural behavior of novel hybrid multicell GFRP-concrete beam Compos. Struct. 250
[3] Shimba Carneiro Vieira P, de Souza F, Taissum Cardoso D C, Domingos Vieira J and de Andrade Silva F 2020 Influence of moderate/high temperatures on the residual flexural behavior of pultruded GFRP Compos. Part B Eng. 200
[4] Madenci E, Özkılcı Y O and Gemi L 2020 Experimental and theoretical investigation on flexure performance of pultruded GFRP composite beams with damage analyses Compos. Struct. 242
[5] Vedernikov A N, Safonov A A, Gusev S A, Carlone P, Tucci F and Akhatov I S 2020 Spring-in experimental evaluation of L-shaped pultruded profiles IOP Conf. Ser. Mater. Sci. Eng. 747 012013
[6] Fairuz A M, Sapuan S M, Zainudin E S and Jaafar C N A 2014 Polymer composite manufacturing using a pultrusion process: A review Am. J. Appl. Sci. 11 1798–810
[7] Zhu R, Li F, Shao F and Zhang D 2020 Static and dynamic behaviour of a hybrid PFRP-aluminium space truss girder: Experimental and numerical study Compos. Struct. 243
[8] Sutherland L S, Sá M F, Correia J R, Guedes Soares C, Gomes A and Silvestre N 2017 Impact response of pedestrian bridge multicellular pultruded GFRP deck panels Compos. Struct. 171
[9] Liu T, Liu X and Feng P 2020 A comprehensive review on mechanical properties of pultruded FRP composites subjected to long-term environmental effects Compos. Part B Eng. 191
[10] Xiong Z, Liu Y, Zuo Y and Xin H 2019 Experimental evaluation of shear behavior of pultruded GFRP perforated connectors embedded in concrete Compos. Struct. 222
[11] Madenci E, Onuralp Özkılcı Y and Gemi L 2020 Buckling and free vibration analyses of pultruded GFRP laminated composites: Experimental, numerical and analytical investigations Compos. Struct. 254
[12] Xin H, Mosallam A, Liu Y, Yang F and Zhang Y 2017 Hygrothermal aging effects on shear behavior of pultruded FRP composite web-flange junctions in bridge application Compos. Part B Eng. 110
[13] Li C, Yin X, Wang Y, Zhang L, Zhang Z, Liu Y and Xian G 2020 Mechanical property evolution and service life prediction of pultruded carbon/glass hybrid rod exposed in harsh oil-well condition Compos. Struct. 246
[14] Yang W-R, He X-J and Dai L 2017 Damage behaviour of concrete beams reinforced with GFRP bars Compos. Struct. 161
[15] Gooranorimi O, Suaris W, Dauer E and Nanni A 2017 Microstructural investigation of glass fiber reinforced polymer bars Compos. Part B Eng.
[16] Liu T, Vieira J D and Harries K A 2020 Predicting flange local buckling capacity of pultruded GFRP I-sections subject to flexure J. Compos. Constr. 24
[17] Bakis C E, Bank L C, Brown V L, Cosenza E, Davalos J F, Lesko J J, Machida A, Rizkalla S H and Triantafillou T C 2002 Fiber-reinforced polymer composites for construction - State-
the-art review J. Compos. Constr. 6

[18] Vedernikov A, Tucci F, Safonov A, Carlone P, Gusev S and Akhatov I 2020 Investigation on the shape distortions of pultruded profiles at different pulling speed Procedia Manuf. 47 1–5

[19] Starr T F 2000 Pultrusion for engineers

[20] Costa Dias R D C, Santos L D S, Ouzia H and Schledzewski R 2018 Improving degree of cure in pultrusion process by optimizing die-temperature Mater. Today Commun. 17 362–70

[21] Baran I 2015 Pultrusion: state-of-the-art process models (Shropshire: Smithers Rapra)

[22] Vedernikov A, Tucci F, Carlone P, Gusev S, Konev S, Firsov D, Akhatov I and Safonov A 2021 Effects of pulling speed on structural performance of L-shaped pultruded profiles Compos. Struct. 255

[23] Silva F J G, Ferreira F, Costa C, Ribeiro M C S and Meira Castro A C 2012 Comparative study about heating systems for pultrusion process Compos. Part B Eng. 43

[24] Sorina T G, Safonov A A and Khairetdinov A K 2010 Peculiarities of using carbon glass-reinforced plastic in pultrusion composite profiles for bridge engineering J. Mach. Manuf. Reliab. 39 47–51

[25] Paciornik S, Martinho F, de Mauricio M H and d’Almeida J R 2003 Analysis of the mechanical behavior and characterization of pultruded glass fiber–resin matrix composites Compos. Sci. Technol. 63 295–304

[26] Fairuz A M, Sapuan S M, Zainudin E S and Jaafar C N A 2016 Effect of filler loading on mechanical properties of pultruded kenaf fibre reinforced vinyl ester composites J. Mech. Eng. Sci. 10 1931–42

[27] Yuksel O, Baran I, Ersoy N and Akkerman R 2019 Investigation of transverse residual stresses in a thick pultruded composite using digital image correlation with hole drilling Compos. Struct. 223

[28] Safonov A, Gusev M, Saratov A, Konstantinov A, Sergeichev I, Konev S, Gusev S and Akhatov I 2020 Modeling of cracking during pultrusion of large-size profiles Compos. Struct. 235

[29] Baran I, Tutum C C, Nielsen M W and Hattel J H 2013 Process induced residual stresses and distortions in pultrusion Compos. Part B Eng. 51 148–61

[30] Safonov A A, Carlone P and Akhatov I 2018 Mathematical simulation of pultrusion processes: A review Compos. Struct. 184

[31] Ding A, Wang J and Li S 2020 Understanding process-induced spring-in of L-shaped composite parts using analytical solution Compos. Struct. 250

[32] Al-Dhaheri M, Khan K A, Umer R, van Liempt F and Cantwell W J 2020 Process induced deformations in composite sandwich panels using an in-homogeneous layup design Compos. Part A Appl. Sci. Manuf. 137

[33] Baran I, Akkerman R and Hattel J H 2014 Material characterization of a polyester resin system for the pultrusion process Compos. Part B Eng. 64 194–201

[34] de Cassia Costa Dias R, Costa M L, de Sousa Santos L and Schledzewski R 2020 Kinetic parameter estimation and simulation of pultrusion process of an epoxy-glass fiber system Thermochim. Acta 690

[35] Worzakowska M 2006 Kinetics of the curing reaction of unsaturated polyester resins catalyzed with new initiators and a promoter J. Appl. Polym. Sci. 102 1870–6