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Ultraviolet light transmission and curing kinetics

I. Saenz-Dominguez, I. Tena, M. Sarrionandia, J. Torre, J. Aurrekoetxea



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CRediT author statement

Iván Sáenz Domínguez: Methodology, Formal analysis, Investigation, Writing - Original Draft preparation, Visualization.

Iosu Tena: Conceptualization, Data Curation, Writing-Reviewing and Editing.

Mariasun Sarrionandia: Validation, Writing-Reviewing and Editing.

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AN ANALYTICAL MODEL OF THROUGH-THICKNESS PHOTOPOLYMERISATION OF COMPOSITES: ULTRAVIOLET LIGHT TRANSMISSION AND CURING KINETICS

I. Saenz-Dominguez ^{a*}, I. Tena ^b, M. Sarrionandia ^b, J. Torre ^a, J. Aurrekoetxea ^b

^a *Irurena Group., Ctra. de Tolosa s/n, 20730 Azpeitia, Spain.*

^b *Mechanical and Industrial Production Department, Mondragon Unibertsitatea, Loramendi 4, 20500 Mondragón, Spain.*

*Corresponding author: i.saenz@irurenagroup.com

Abstract

In this paper, a kinetic model able to predict the evolution of the through-thickness degree of cure of ultraviolet (UV) cured composites has been developed and validated. The kinetic model, which is based on the autocatalytic model, depends on the temperature of the composite and the absorbed intensity by the photoinitiators. This intensity is calculated by an optical model divided into discrete values of wavelength. As a result, the kinetic model considers the main factors of UV curing: the resin, reinforcement and thickness of the composite; the incident UV light spectrum; the absorbance range of photoinitiators and its consumption during the photopolymerisation. The main values of the model can be obtained by spectrometry and measuring the electric resistance of the composite during the whole UV curing process.

Keywords: A. Polymer-matrix composites (PMCs); B. Cure behaviour; B. Optical properties; C. Analytical modelling

Nomenclature

A_{0_λ}	initial absorbance of the photoinitiator system at a specific wavelength	T	temperature ($^{\circ}\text{C}$)
A_{B_λ}	absorbance due to the resin and the reinforcement at a specific wavelength	t	exposure time (s)
A_λ	absorbance at a specific wavelength	z	depth from the exposed surface (mm)
c	concentration of the photoinitiator system	z_{\max}	total thickness of the composite (mm)
I_0	incident intensity (W/m^2)	α	curing degree
I_{0_λ}	incident intensity at a specific wavelength (W/m^2)	β	constant exponent of k
I_{B_λ}	transmitted intensity through the cured composite at a specific wavelength (W/m^2)	ε_{c_λ}	molar extinction coefficient of the photoinitiator system at a fixed concentration and wavelength (mm^{-1})
I_T	transmitted intensity (W/m^2)	ε_λ	molar extinction coefficient of the photoinitiator system at a specific wavelength ($\text{M}^{-1} \text{mm}^{-1}$)
I_{T_λ}	transmitted intensity at a specific wavelength (W/m^2)	λ	wavelength (nm)
I_P	absorbed intensity by the photoinitiator system (W/m^2)	ζ	constant of k_0 (s^{-1})
k	rate constant (s^{-1})	θ	photoinitiator consumption variable (s^{-1})
k_0	temperature dependent kinetics constant	μ	constant of k_0 (mm^{-1})
k_λ	attenuation coefficient at a specific wavelength (mm^{-1})	ψ	constant of θ (mm^{-1})
m	autocatalytic exponent	ω	variable of θ (s^{-1})
n	reaction order	ω_0	constant of ω ($\text{m}^2/\text{W s}$)

1. Introduction

Ultraviolet (UV) curing process has been proved to be a promising method to cure composites by several authors [1–4]. The low cost of equipment and the low energy consumption of this technology [1] have made UV curing one of the most popular alternative fast-curing methods to the conventional thermal curing approach. In fact, some potential composite manufacturing processes are currently combined with this technology, such as braiding [5], infusion [6], automated fibre placement [7], pultrusion [3,8,9] or additive manufacturing [10,11]. The free radical polymerisation is the most common chemical process in UV curing and it can be divided into three stages: initiation, propagation and ending [1,12,13]. In the initiation stage, the photoinitiator starts the curing reaction through the transformation of the energy of the UV light into chemical energy to produce free radicals [14]. In the propagation stage, these free radicals are bonded with monomers until a chain termination is occurred in the ending stage by bimolecular reaction between radicals (coupling), or by transfer of an atom from one chain to another (disproportionation) [1,13]. Thus, only the initiation stage is sensitive to the UV light, whereas propagation and ending are thermally driven [12]. Actually, during the UV curing process, the three stages are given simultaneously as the light crosses the thickness of the composite from the exposed to the non-exposed surface. This means that when some photoinitiators have not been activated yet, the propagation and ending stages have already started in the parts closer to the exposed surface.

The three main factors affecting the UV curing are the functional requirements of the composite, the UV source and the formulation of the photocurable matrix [1]. The first one determines the resin, the thickness and the reinforcement of the composite. In this way, the type of resin, the reinforcement architecture, the thickness of the composite and the fibre volume fraction determine the not time-dependent attenuation of the UV light [15]. The UV source determines the emitting spectrum and the intensity. The LED technology has been proved to be more efficient to cure composites than conventional arc lamps due to the higher penetration capacity [3]. In addition, UV LED sources allow using higher intensities which implies faster curing kinetics [4,9,16]. Regarding the formulation of the photocurable resin, several studies [1,3,4,9,12] proved that combining photoinitiators for depth and superficial curing is a successful approach for curing composites. This fact can be explained since the photoinitiators for depth curing allows a higher penetration of the UV light through the thickness of the composite due to the photobleaching effect, whereas photoinitiators for superficial curing avoid the inhibition of the reaction

with the oxygen [4]. In addition, the selected activation of the combination of photoinitiators should matches with the emission spectrum of the UV source, in order to absorb the most quantity of energy dose.

The common denominator of the three factors is the UV light intensity and its transmission through the thickness of the composite. UV light intensity has been widely considered in several mathematical models for the characterisation of holographic recording photopolymers [17–23]. In the same way, Martin *et al.* [24] presented a rate of cure model focused on the prediction of residual stresses and warpage of photocurable resins used in stereolithography (SLA). However, this kind of applications are based on thin unreinforced photopolymer layers and, as a result, the attenuation of the UV light intensity is not as critical as in thick composites. In fact, the attenuation of the UV light due to the cured composite increases as the thickness of the composite increase and is not time-dependent. The attenuation regarding the photoinitiator system varies in the time since the photoinitiators are consumed during the photopolymerisation [15]. This fact affects directly to the UV curing process through the thickness of thick composites, since the differences in intensity between the exposed and non-exposed surface can be high [1]. Thus, during photopolymerisation, there is a gradient of the degree of cure through the thickness of the composite. However, some of the current kinetic models for composite laminates [4,9,16,25,26] are restricted to a specific thickness and only analyse the non-exposed surface, considering that the degree of cure is homogeneous through the thickness. Other recent kinetic models [27–29] take into account the attenuation of the UV light through the thickness of the composite based on the Beer-Lambert law. However, these models do not combine the kinetic model with the evolution in time of the UV light, and consequently, they do not consider the real intensity for the photoinitiators decomposition. Finally, using the intensity as a single value and not as a spectrum is an incorrect assumption due to the presence of the photoinitiators, which absorb the UV intensity as a function of its absorbance spectrum.

Thus, the aim of the present paper is to combine an optical and kinetic model in order to obtain the predicted evolution of the degree of cure through the thickness of the composite during the photopolymerisation process. To that end, the optical model must be able to predict the absorbed intensity spectrum by the photoinitiator system during the UV curing process for any incident intensity, composite thickness and time.

2. Experimental procedure

2.1. Materials

In order to perform this study, a glass fibre/UV cured vinyl ester composite has been used. The reinforcement consists of 300 g/m² quasi-unidirectional E-glass tape. The reinforcement is described as quasi-unidirectional because it presents a small proportion (8% in volume) of fibres at 90° which maintain the cohesion of the unidirectional fibres. The resin is a UV curable vinyl ester supplied by Iruena Group (IRUVIOL GFR-17 LED). The selected photoinitiator system is a combination of Bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO) and 2-Dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (α aminoketone). The concentration of BAPO photoinitiator was 0.8 phr, whereas the concentration of α aminoketone was 0.6 phr. This UV curable vinyl ester formulation has been successfully applied for curing composites up to 2 mm [4]. All the specimens have been manufactured by hand-layup with 47% \pm 1% of fibre volume fraction, which was measured following the procedure described in ASTM D3171-09. In order to perform the optical and kinetic characterisation, four different thicknesses have been studied, 0.5 mm, 1 mm, 1.5 mm and 2 mm, which correspond to 2, 4, 6 and 8 layers of glass fibre respectively (maintaining the fibre volume fraction).

2.2. Optical characterisation

The optical characterisation has been carried out measuring the transmitted intensity (I_T) spectrum through the composite during the UV curing process at room temperature. The scheme of the optical analysis setup is shown in Figure 1a. The uncured specimens were placed between two quartz plates that were previously optically characterised in order to isolate their contribution to the measured UV spectrum. The thickness of the specimens was ensured by a calibrated thickness plate. The I_T spectrum has been measured in the centre of the non-exposed surface by a StellarNet Black-Comet spectrometer with a wavelength (λ) acquisition range of 190–850 nm.

The UV source using in this study is a Phoseon FireFlex UV LED, with an emitting window of 75 \times 50 mm². The maximum intensity is 8 W/cm² and the emission peak of this UV source is located at 395 nm. As it can be observed in Figure 1b, the absorbance range of both photoinitiators matches properly with the intensity spectrums. Three different incident intensities (I_0) on the upper part of the

composite have been used for optical analysis, 1758 W/m², 1182 W/m² and 530 W/m². It has to be mentioned that these intensity values have been selected in order to avoid the saturation of the spectrometer.

Insert Figure 1

2.3. Curing kinetics characterisation

The curing kinetics analysis has been carried out measuring the electric resistance and the temperature of the composite during the UV curing process at room temperature. The temperature evolution has been registered by thermocouples placed on the top, the middle and the bottom of the thickness of the composite. The electric resistance has been measured by a DC sensor (an Optimold system provided by Synthesites Innovative Technologies Ltd.). This technique is especially well adapted to the photocuring characterisation of composites with different thickness [4,9]. The DC sensor was in contact with the non-exposed surface, which is the last area to be cured. The procedure to calculate the evolution of the degree of cure from the resistivity data is explained elsewhere [4,9]. The same UV source than in optical analysis has been used and the selected I_0 are 5750 W/m², 4250 W/m² and 2910 W/m². These intensities have been selected in order to analyse intensities outside the range studied in the optical model. In addition, in order to analyse the effect of temperature on the curing kinetics of the resin, the Differential Scanning Calorimetry (Mettler Toledo DSC 1 equipment) equipped with an accessory for photo-calorimetry analysis (photo-DSC) has been used. Four isothermal temperatures have been analysed (25 °C, 50 °C, 75 °C, 100 °C) with the same intensity UV light (75 mW/cm²).

3. Modelling of the ultraviolet curing process

In this section, the optical behaviour of the composite during the UV curing process has been analysed, modelled and experimentally validated. The optical model predicts the behaviour of each wavelength in order to consider the effect of the consumption of the photoinitiator system during the UV curing process at any I_0 spectrum and thickness. With the sum of all wavelength, the evolution of the full spectrum of the I_T during the whole UV curing process can be obtained. Afterwards, the absorbed intensity by the photoinitiator system during the UV curing process can be obtained. Then, the kinetic model has been fed with the results of the optical model, and the evolution of the UV curing process has been also analysed, modelled and experimentally validated.

3.1. General assumptions

In order to develop the model, the composite has been divided into segments of 0.25 mm of thickness, which correspond to the single ply thickness. It has been supposed that the photoinitiator system is uniformly distributed through the thickness. The temperature through the thickness of the composite has been supposed constant. On the other hand, the composite is only irradiated on the top surface; therefore, the curing of the composite occurs from the exposed to the non-exposed surface. Consequently, the I_0 on this surface remains constant during the whole UV curing process. In contrast, in the rest of the layers, the intensity depends on time and depth due to attenuation of the UV light and the decomposition of the photoinitiators during the UV curing process [15].

3.2. Optical model

The optical behaviour of the composite during the UV curing process has been modelled based on the experimental data obtained from the optical characterisation. Figure 2a shows an example of the evolution of I_T spectrum during the UV curing process for specific I_0 and thickness. As I_T is related to the area under the spectrum, it can be described as the integral of the transmitted intensity through the composite in each wavelength (I_{T_λ}):

$$I_T = \int I_{T_\lambda} d\lambda \quad (1)$$

For a specific wavelength, the intersection points (Figure 2a) can be plotted with respect time, obtaining the evolution of I_{T_λ} (Figure 2b). In addition, the absorbance of a specific wavelength (A_λ) can be obtained (Figure 2b) applying the following equation [13]:

$$A_\lambda = \log \left(\frac{I_{0_\lambda}}{I_{T_\lambda}} \right) \quad (2)$$

where, I_{0_λ} is the incident intensity at a specific wavelength.

Once the experimental data has been obtained, the parameters of the optical model can be determined.

The predicted spectrum of I_T can be calculated solving I_{T_λ} from equation 2 as follows:

$$I_{T_\lambda} = 10^{(\log I_{0_\lambda} - A_\lambda)} \quad (3)$$

Thus, in order to predict the evolution of I_{T_λ} , the evolution of A_λ must be modelled. As it can be noticed in Figure 2a and 2b, when the photo-polymerisation starts (t_0), a low intensity is transmitted through the thickness of the composite. Moreover, the I_T spectrum does not present intensities in the wavelengths where both photoinitiators present higher absorbance (Figure 1b). Hence, it can be stated that the maximum absorbance is presented in this stage due to the photoinitiators has not been decomposed into free radicals yet, and they are absorbing the intensities at these wavelengths. As the UV curing process progresses (t_1 , t_2 and t_3), the amount of photoinitiator is consumed and therefore, the transmitted intensity increases [15] and its spectrum resembles that of the I_0 . At the final stages (t_4 and t_5), the transmitted intensity tends to an asymptote and the changes in the transmitted spectrum are slight and similar in shape to that of I_0 . This implies that the composite is completely through-cured [15]. Consequently, the value of the final absorbance observed in Figure 2b is due to the absorbance of the final material composite (cured resin and reinforcement).

Insert Figure 2

Based on the shape of the experimental curves of A_λ , equation 4 is proposed. In Figure 3 a schematic view of this equation can be observed. The intersection with the ordinate corresponds to the initial absorbance of the photoinitiator system and the absorbance due to the resin and the reinforcement ($A_{0_\lambda} + A_{B_\lambda}$), A_λ decreases with time exponentially and tends to the constant value A_{B_λ} .

$$A_\lambda = A_{0_\lambda} e^{-\theta t} + A_{B_\lambda} \quad (4)$$

where, A_{0_λ} is the initial absorbance of the photoinitiator system at a specific wavelength; θ is the photoinitiator consumption variable; t is the exposure time; and A_{B_λ} is the absorbance due to the resin and the reinforcement at a specific wavelength.

Insert Figure 3

3.2.1. Experimental parameters of the optical model

3.2.1.1. Absorbance due to the resin and the reinforcement (A_{B_λ})

The value of A_{B_λ} can be expressed by absorbance equation (equation 5), which is similar to the equation 2, but in this case, the absorbance depends on the I_{0_λ} and the transmitted intensity through the cured composite at a specific wavelength (I_{B_λ}):

$$A_{B_\lambda} = \log \left(\frac{I_{0_\lambda}}{I_{B_\lambda}} \right) \quad (5)$$

I_{B_λ} can be expressed by the Beer-Lambert law when the UV curing process has finished as follows:

$$I_{B_\lambda} = I_{0_\lambda} \cdot e^{(-k_\lambda \cdot z)} \quad (6)$$

where, k_λ is the attenuation coefficient of the sum of the resin and the reinforcement at a specific wavelength; and z is the depth from the exposed surface.

It is assumed that the absorbance of the resin in the liquid state is neglected since the gel time during the photo-polymerisation process is almost zero [1,3]. Figure 4a shows an example of the experimental values of I_{B_λ} for 395 nm with respect to thickness for the different I_{0_λ} . As it can be observed, the predicted curves fit accurately with the experimental data. Additionally, the attenuation coefficient k_λ for the same wavelength is independent of I_{0_λ} . The whole intensity spectrum has been analysed since each wavelength presents different values of k_λ (Figure 4b).

Insert Figure 4

3.2.1.2. Initial absorbance of the photoinitiator system (A_{0_λ}).

The absorbance of the photoinitiator system is usually described by its absorbance spectrum at a fixed concentration [12]. As the absorbance is linearly related to the concentration and the penetration through the thickness of the composite, the initial absorbance spectrum of the photoinitiator system can be expressed by [12,13]:

$$A_{0_\lambda} = \varepsilon_\lambda \cdot c \cdot z \quad (7)$$

where, ε_λ is the molar extinction coefficient of the photoinitiator system at a specific wavelength; and c is the concentration of the photoinitiator system.

Thus, if ε_λ at a fixed concentration (\mathcal{E}_{c_λ}) is experimentally obtained, A_{0_λ} for different thicknesses can be predicted following the next equation:

$$A_{0_\lambda} = \varepsilon_{c_\lambda} \cdot z \quad (8)$$

The values of \mathcal{E}_{c_λ} have been obtained from the predicted curves of A_{0_λ} . To that end, A_{0_λ} has to be fitted with the experimental curves of A_λ (Figure 3) and with the A_{B_λ} values previously obtained for the different thicknesses. Figure 5a shows an example of the experimental values and the predicted curve of A_{0_λ} for 395 nm and different thicknesses. The linear relation with thickness is related to the higher quantity of photoinitiators as the thickness increases. Analysing the experimental values of \mathcal{E}_{c_λ} (Figure 5b) it can be observed that the higher absorbance for all the thicknesses is presented in the left part of the UV intensity spectrum (380 nm to 395 nm), which matches with the absorbance spectrum of both photoinitiators provided by the supplier (Figure 1b).

Insert Figure 5

3.2.1.3. Photoinitiator consumption variable (θ)

In order to predict the consumption of the photoinitiator system, θ must be modelled. Once the values of A_{B_λ} and A_{0_λ} have been obtained, the values of θ can be determined by fitting them with the curve of the experimental values of A_λ (Figure 3). Figure 6a shows the values of θ for different thickness and I_0 . As it can be observed, θ decrease exponentially when the thickness increases. This behaviour can be justified due to the higher quantity of photoinitiators to be decomposed. On the other hand, when I_0 increases the values of θ increase. The photoinitiators use the absorbed energy to produce free radicals [12]. Thus, as more energy dose is applied on the exposed surface of the composite, the energy transmitted through the thickness is higher, and therefore, the photoinitiators are able to absorb more energy [30]. This fact is analytically modelled by the variable ω (Figure 6b), which increase linearly

with I_0 . The slope of the curve is the constant ω_0 and for the result, the following equations are proposed:

$$\theta = \omega \cdot e^{(-\psi \cdot z)} \quad (9)$$

$$\omega = \omega_0 \cdot I_0 \quad (10)$$

where, ψ is a constant experimentally determined.

Hence, the experimental constants ψ and ω_0 determine the consumption of the photoinitiator system, which can be determined by the regression shown in Figure 6a and 6b, respectively.

Insert Figure 6

3.2.2. Optical model validation

Once the experimental parameters have been obtained, equation 4 can be applied in order to obtain the evolution of the absorbance for different wavelengths, thicknesses and incident UV intensities. And, consequently, I_T evolution (equation 1) and I_T spectrum evolution (equation 3) can be obtained.

Figure 7a, 7b and 7c show the experimental and predicted I_T as a function of time of all the analysed I_0 and thicknesses. I_T decreases when the thickness increases, following the exponential behaviour according to the Beer-Lambert law. The thickness also influences the consumption of the photoinitiator system, which affects considerably to the transmitted intensity. This behaviour can also be observed when different I_0 are compared. Consequently, when thicker composites are cured or low I_0 is applied, more exposure time is needed in order to decompose the photoinitiators. Figure 7d presents the fitting between the experimental and predicted spectrum evolution of 1 mm thick specimen and 1758 W/m^2 at different exposure times. The effect of the absorbance of the photoinitiator system at different wavelengths can be noticed in the shape of the I_T spectrums, which has been also predicted with the optical model. As it can be observed in Figure 7 the optical model presents an accurate prediction in the whole range studied. Thus, it can be stated that the optical model developed in this study is able to predict the intensity spectrum evolution through the thickness of the composite for different I_0 .

Insert Figure 7

3.2.3. Absorbed intensity by the photoinitiator system (I_p)

As it has been commented before, the incident intensity (I_0) is reduced when it crosses the composite due to the absorbance of the photoinitiator system and the absorbance of the resin and the reinforcement.

However, only the absorbed intensity by the photoinitiator system (I_p) is used to start the photopolymerisation process, and therefore, the kinetic model must be fed by this intensity. In order to obtain I_p , two equal composites exposed to the same I_0 can be compared, but one of them with photoinitiators and the other one without photoinitiators (Figure 8). As the resin, the reinforcement and the I_0 are the same for both composites, the difference between the transmitted intensities is I_p (equation 11).

$$I_p = \int (I_{B_i} - I_{T_i}) d\lambda \quad (11)$$

Insert Figure 8

3.3. Curing kinetic model

The autocatalytic kinetic model has been selected as the reference model, which has been proved to be a proper model for photo-polymerisation process [4,9,16]. The equation governing the UV curing of a polymer is:

$$\frac{d\alpha}{dt} = k \cdot \alpha^m (1-\alpha)^n \quad (12)$$

where, α is the degree of cure at any time; m is the autocatalytic exponent; n is the reaction order and k is the rate constant. The rate constant can be related to the UV intensity and temperature based on the following equation [27]:

$$k = k_0(T) \cdot I_p^\beta \quad (13)$$

where, β is a constant exponent associated with the termination mechanism of the reaction [4,9,25]; k_0 is a temperature dependent kinetics constant; and T is the temperature.

3.3.1. Experimental parameters of the kinetic model

Once the experimental values from the DC sensor have been obtained, the main parameters of the autocatalytic model (equation 12) can be calculated. To that end, as it has been explained earlier, it has been considered the evolution of the absorbed intensity by the photoinitiator system during the UV curing process.

The values of autocatalytic exponent m are close to 0.5 and the reaction order n presents values close to 0.8, with a slight decrease as the intensity increases, and as the thickness decrease (Figure 9). As similar values are found for all the specimens, it can be stated that the overall reaction order ($m+n$) has not been affected by the thickness of the composite or by the incident intensity.

Insert Figure 9

By fitting these parameters with equations 12 and 13, β and k_0 can be calculated. The constant exponent β presents the similar value than the obtained for the same formulation in another research study, 0.260 [4]. As $\beta < 0.5$, it can be stated that the predominant termination mechanism of the reaction is primary radical termination [4,9,16]. In order to obtain k_0 , the relation between temperature and curing kinetics has been analysed by the results of photo-DSC for different isothermal temperatures (Figure 10a). It can be noticed that the higher is the temperature the faster is the conversion rate of the vinyl ester resin, since there is a higher mobility of the polymeric chain, and higher quantity of unsaturation sites are accessible for the polymerisation [25]. As it can be observed in the example shown in Figure 10b, the temperature through the thickness of the 1.5 mm thick composite presents a slight variation. This fact supports the assumption that in the range of the studied intensities and thicknesses, the temperature remains constant through the thickness of the composite and it is only dependent of the total thickness of the composite. This temperature-total thickness dependency is presented in Figure 10c. All the curves present a peak between 20 s and 30 s, which is related to the exothermic peak of the reaction and it is located close to the maximum conversion rate instant. Even when the exothermic contribution of curing is finished, temperature increases due to the heat flow of the UV source. Regarding the effect of the thickness, temperature increases with thickness, due to the bulk effect. Thicker composites imply more material that reacts, but also that heat transfer is slower. Hence, the value of k_0 can be indirectly calculated with the maximum thickness of the composite. Therefore, a modification of the equation 13 is proposed, where k_0 is dependent on the total thickness of the composite (z_{\max}):

$$k_0(z) = \zeta \cdot e^{(\mu \cdot z_{\max})} \quad (14)$$

where, ζ and μ are constants experimentally obtained.

Figure 10d shows that the experimental values fit accurately with the proposed equation. The value of the experimental constant ζ is 0.1513 s^{-1} and the value of μ is 0.4072 mm^{-1} . In addition, as the value of k_0 depends on the maximum thickness of the composite, the same k_0 can be used to calculate the distribution of the degree of cure through the thickness of a defined composite.

Insert Figure 10

Once the parameters of equation 14 have been obtained, the evolution of k during the UV curing process can be calculated. Figure 11 shows a comparison of the evolution of k with time at a depth of 0.5 mm for different thickness and a constant I_0 (2910 W/m^2). The value of k increases until reach a maximum value, which is the point where the maximum UV light is absorbed by the photoinitiator system. After that, the value of k decrease with the absorbed UV light due to the consumption of photoinitiators. This is the moment where the evolution of the degree of cure tends to an asymptote. Finally, the values of k are low and the changes in the degree of cure occurs slowly. On the other hand, the values of k increase when the maximum thickness increases, since k_0 depends on temperature (Figure 10).

Insert Figure 11

3.3.2. Kinetic model validation

Figure 12a, 12b and 12c present the evolution as a function of time of the experimental and predicted conversion with different I_0 for 1 mm and 2 mm of thickness. Analysing these figures, it can be noticed that when I_0 increases the composite needs less time to achieve the final degree of cure. In the same way, when the thickness decreases the time that the composite needs to achieve the final degree of cure decreases. It must be remarked that the prediction fits accurately with the experimental values in all the studied thicknesses, within the experimental scatter. Thus, it can be stated that in the studied range, the model is able to predict the evolution of the degree of cure through the thickness of the composite for different I_0 . In this way, Figure 12d shows the prediction of the evolution of the conversion with time and thickness of a 2 mm of maximum thickness composite and with an I_0 of 2910 W/m^2 . The prediction has been applied from the first layer of composite (0.25 mm) to the last layer of composite (2 mm). It can be noticed that as move deeper from the exposed surface, the layers of the composite need more exposure

time to achieve the final degree of cure. This fact is due to the evolution in time of I_T and is more remarkable when the thickness increase.

Insert Figure 12

4. Conclusions

A kinetic model able to predict the evolution of the through-thickness degree of cure during the photopolymerisation process of composites has been developed and validated. To that propose, the autocatalytic kinetic model has been fed with the absorbed intensity by the photoinitiator system predicted with an optical model, which divides this intensity into discrete values of wavelengths.

The results show that in the studied range of thicknesses and intensities, the temperature remains constant in all the sample, and it increases with thickness. Thus, the temperature of the autocatalytic model can be substituted indirectly by the thickness of the composite. Regarding the intensity absorbed by the photoinitiator system, it depends on the emission spectrum of the UV source, the material (resin and reinforcement), the thickness of the composite and the photoinitiator system (absorbance range and consumption).

In order to obtain the main values of the model, two techniques must be applied during the UV curing process: spectrometry to measure the transmitted intensity spectrum, and the analysis of the electric resistance of the composite to obtain the experimental curves of the degree of cure. From the experimental data measured by the spectrometer, the following values of the optical model must be obtained:

- The attenuation coefficient at a specific wavelength (k_λ), which models the attenuation due to the material as a function of thickness.
- The molar extinction coefficient of the photoinitiator system in a specific wavelength at a fixed concentration (\mathcal{E}_{c_λ}), which determines the absorbance range of the photoinitiator system.
- The constant ψ , which determines the consumption of photoinitiator system due to the thickness.
- The constant ω_0 , which determines the consumption of the photoinitiator system due to the incident intensity.

From the measurements of the electric resistance, the following values must be obtained:

- The autocatalytic exponent m and the reaction order n , which determine the overall reaction order of the reaction ($m+n$).
- The exponential constant β , which determines the predominant termination mechanism of the reaction.
- The constants ζ and μ , that relate the temperature dependent kinetic constant, k_0 , with the total thickness of the composite.

It has to be remarked that the differences between the experimental results and the predicted values of the kinetic model are acceptable. Therefore, the methodology and the curing model developed in this study can be applied in the design and development of UV cured composite parts. The maximum thickness of the part, the UV sources, the formulation of the matrix or even the cycle time can be estimated for any kind of manufacturing process where the UV light is used as curing technology (for instance, UV cured pultrusion or additive manufacturing).

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Figure 1. (a) Optical analysis setup scheme; (b) incident intensities and the photoinitiators absorbance spectrum.

Figure 2. (a) Evolution of the I_T spectrum during the UV curing process; (b) evolution of $I_{T_{395}}$ and A_{395} during the UV curing process.

Figure 3. Schematic view of equation 4.

Figure 4. (a) Beer-Lambert law curves in all the analysed I_0 for 395 nm; (b) experimental values of k_2 .

Figure 5. (a) Experimental fitting of A_{0_2} with respect to thickness for 395 nm wavelength; (b) experimental values of ε_{c_2} .

Figure 6. (a) θ values for different thickness and I_0 ; (b) ω evolution with I_0 .

Figure 7. Experimental and predicted curves of the optical model: (a) I_T evolution with time for 1758 W/m²; (b) I_T evolution with time for 1182 W/m²; (c) I_T evolution with time for 530 W/m²; (d) I_T spectrum at different UV exposure time of 1 mm thick composite and 1758 W/m².

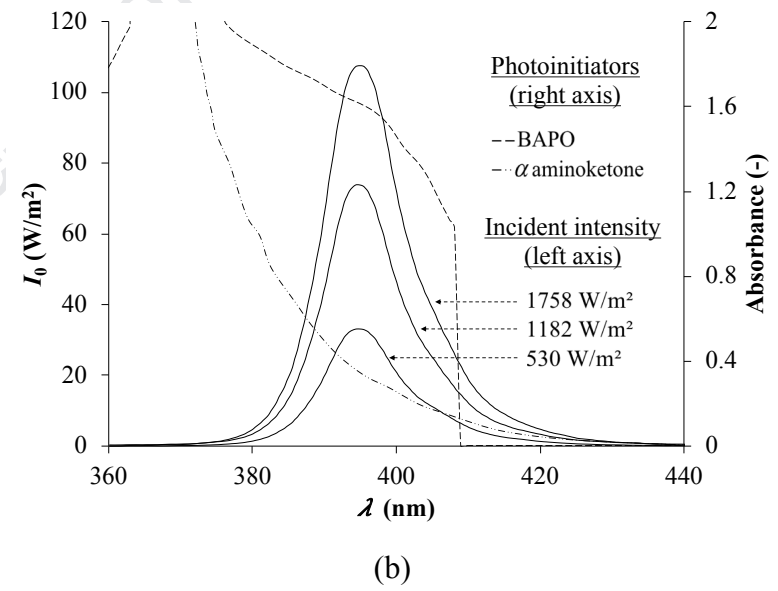
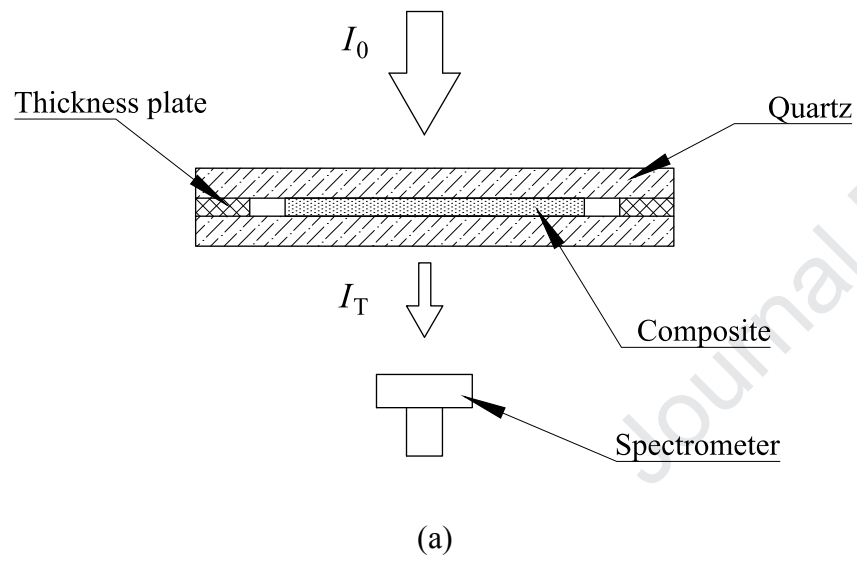
Figure 8. Schematic approach to estimate I_p .

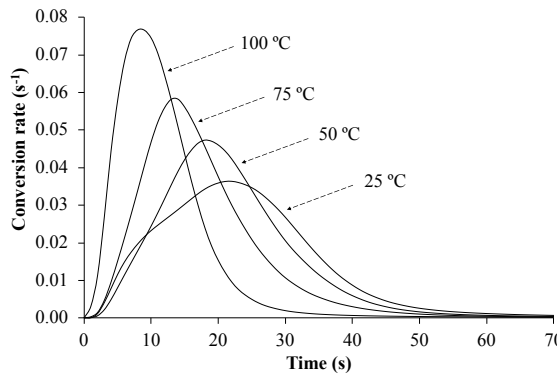
Figure 9. Autocatalytic exponent m and reaction order n .

Figure 10. (a) Conversion rate with respect to conversion from DSC analysis; (b) temperature evolution on the top, the bottom and the middle of the thickness of 1.5 mm thick composite; (c) measurements of temperature evolution with time and z_{\max} at the middle part of the thickness; (d) k_0 evolution with respect to the total thickness of the composite.

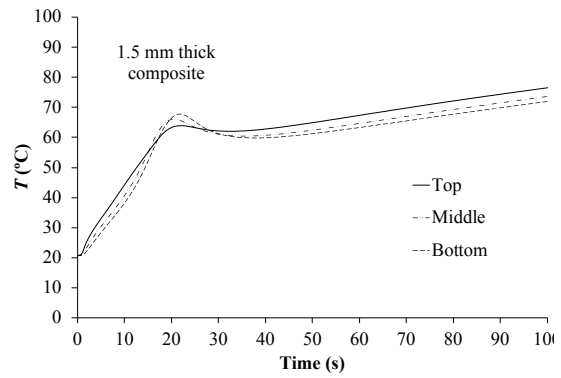
Figure 11. k evolution with time and thickness during the UV curing process in 0.5 mm and 2910 W/m².

Figure 12. Experimental and predicted values of the evolution of the degree of cure: (a) 2910 W/m²; (b) 4250 W/m²; (c) 5750 W/m²; (d) Evolution of the predicted degree of cure through the thickness of a composite with a maximum thickness of 2 mm and irradiated with 2910 W/m².

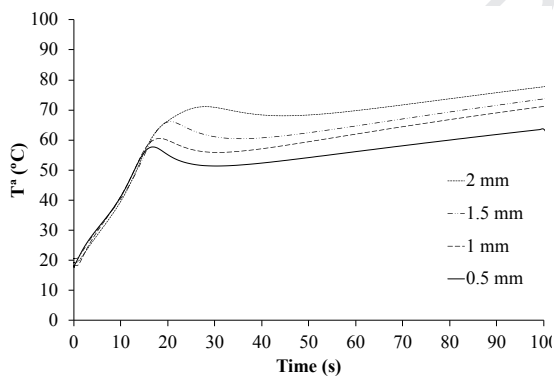




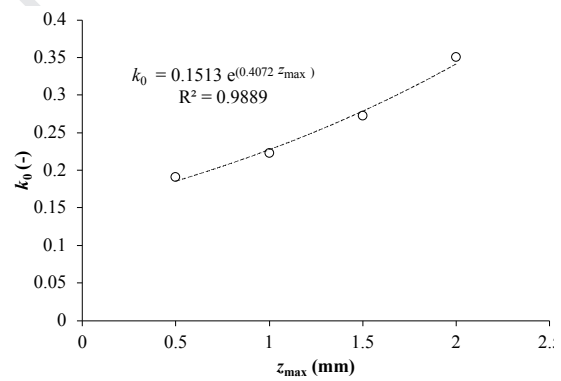
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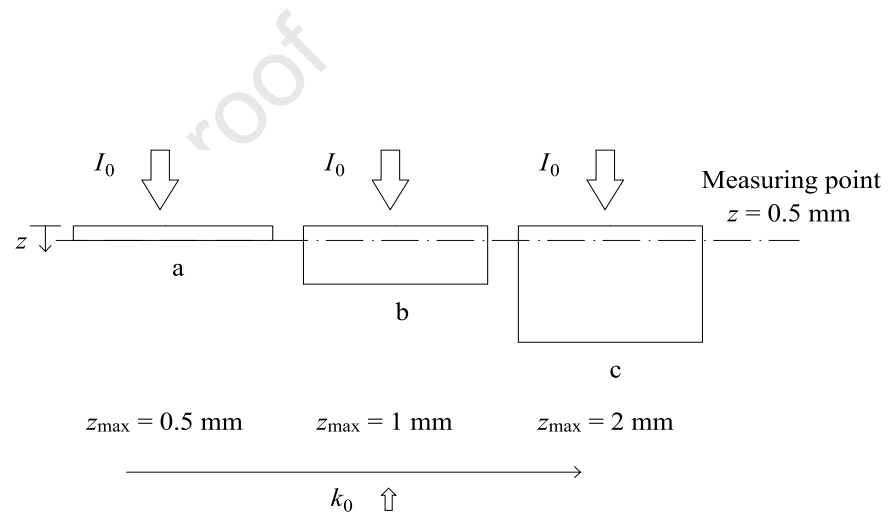
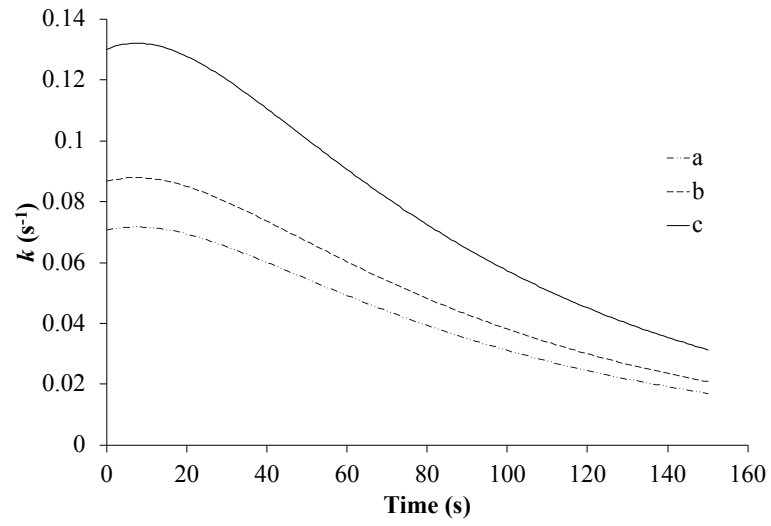
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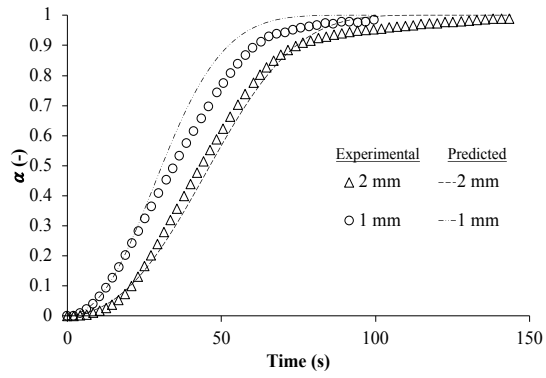


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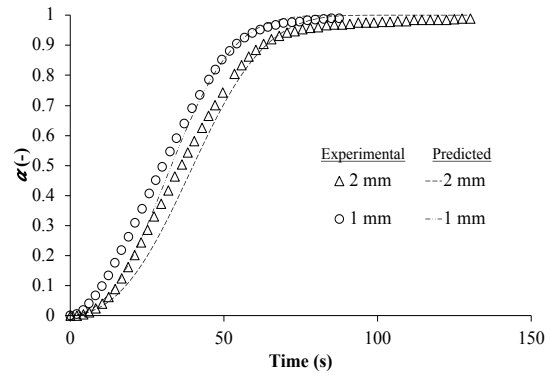


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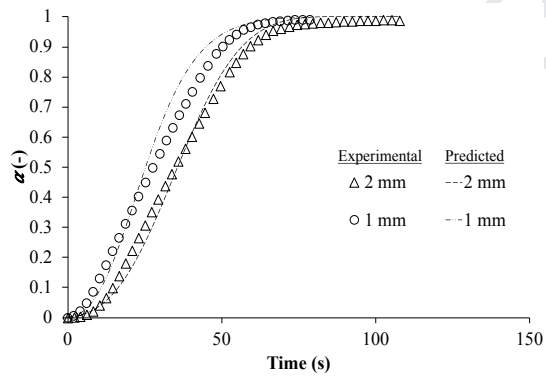




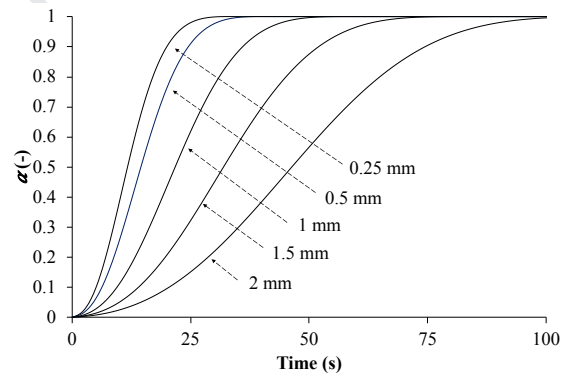
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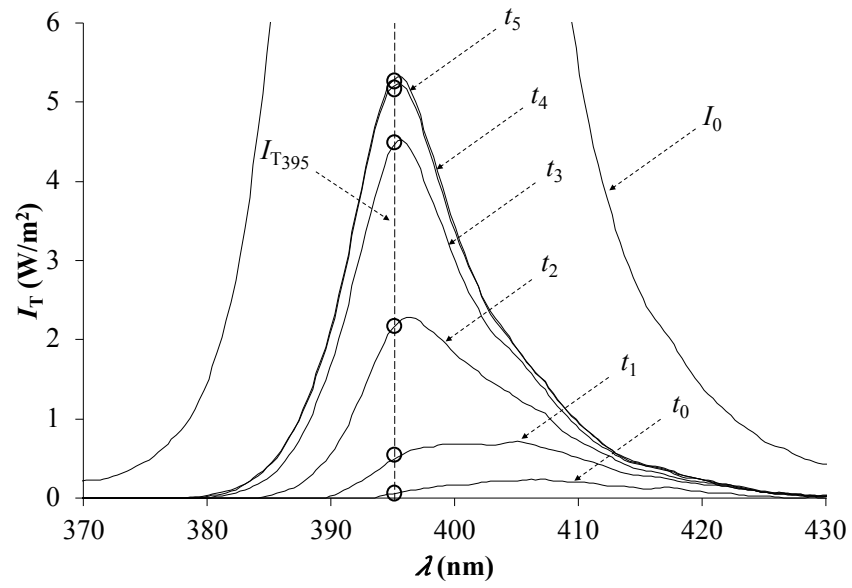
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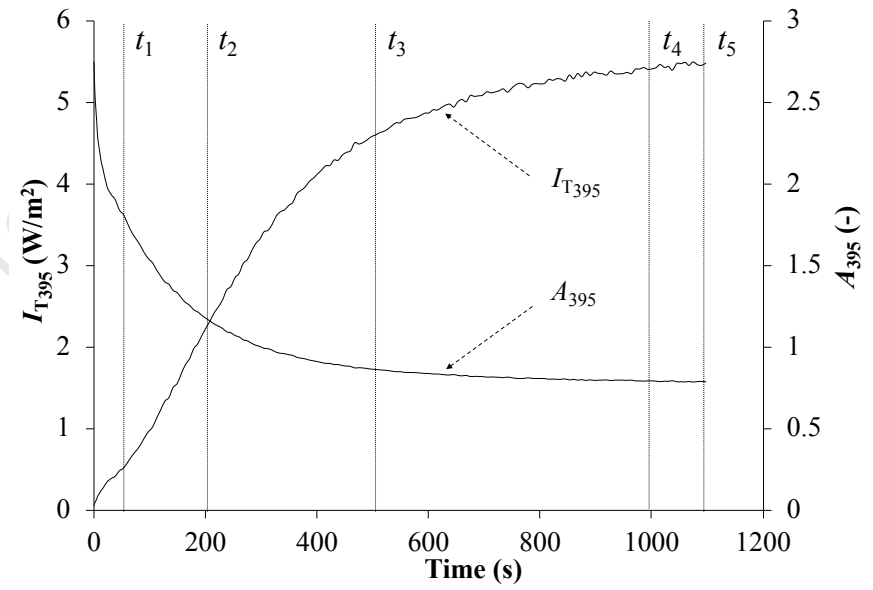
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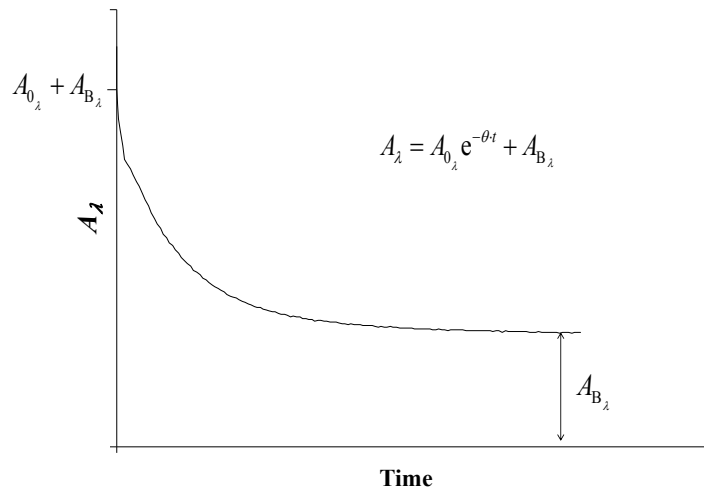
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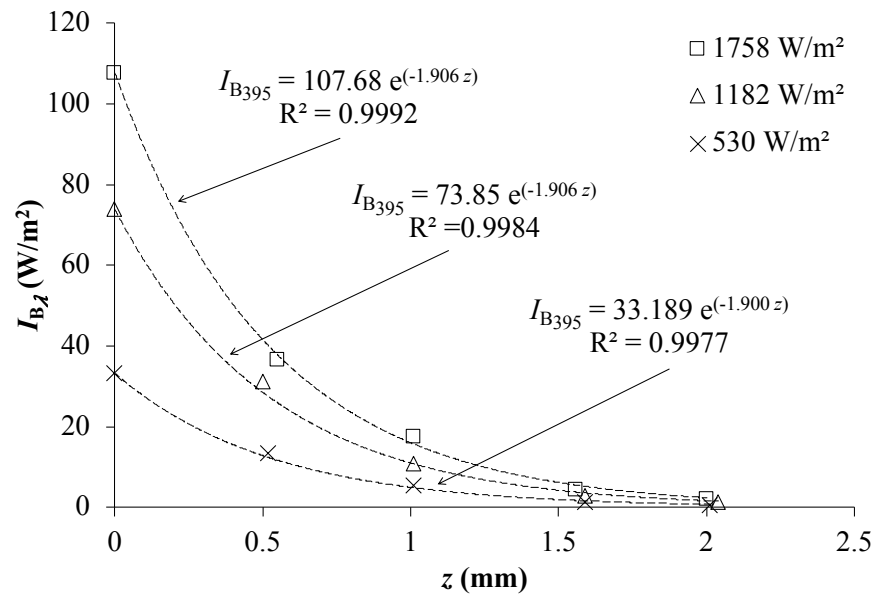
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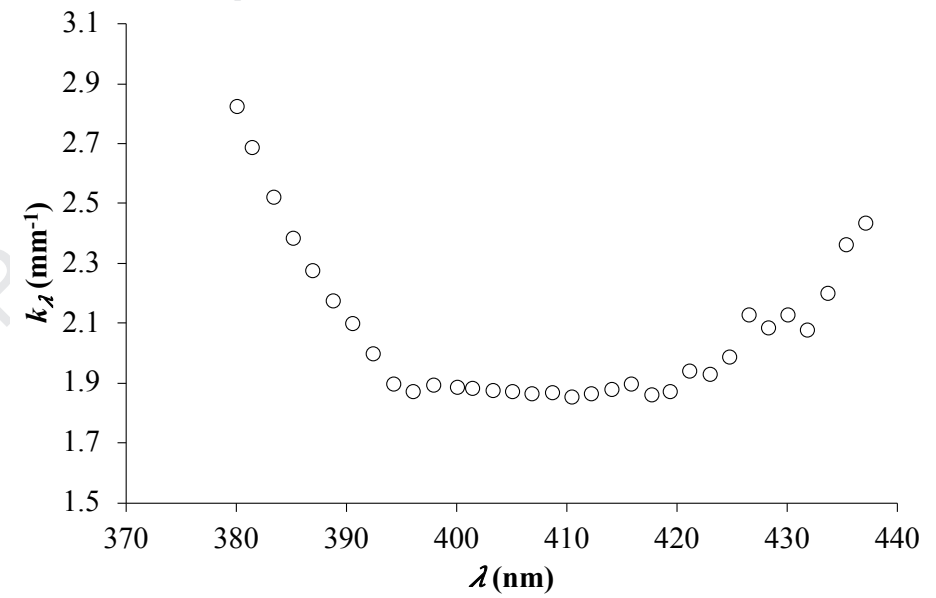
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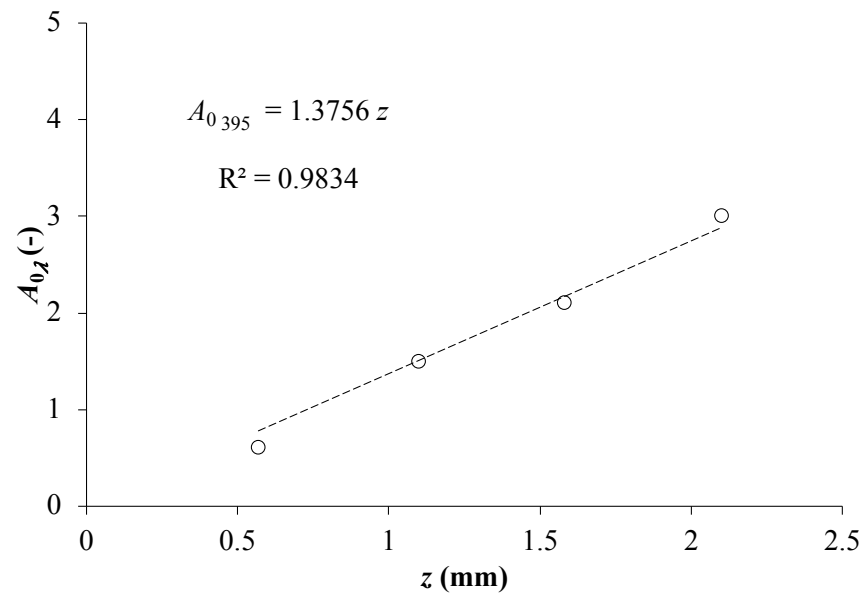
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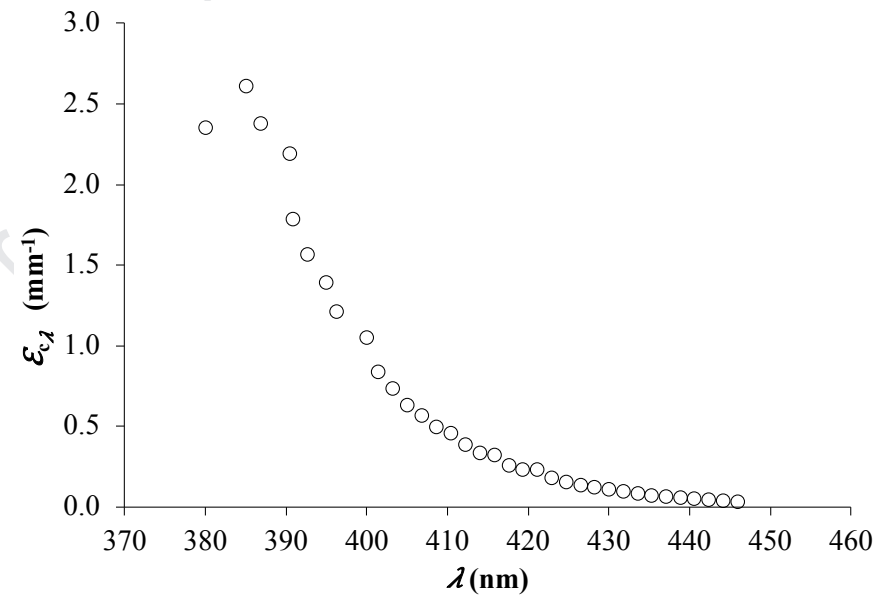
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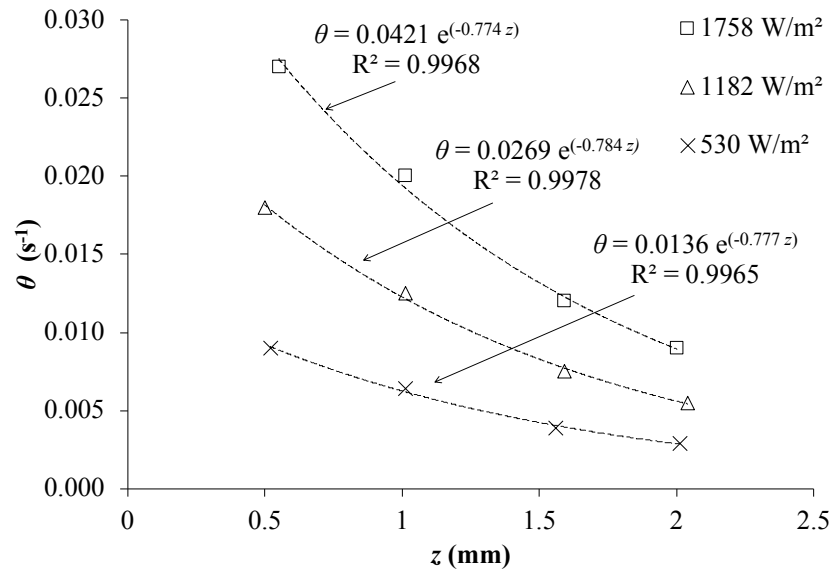
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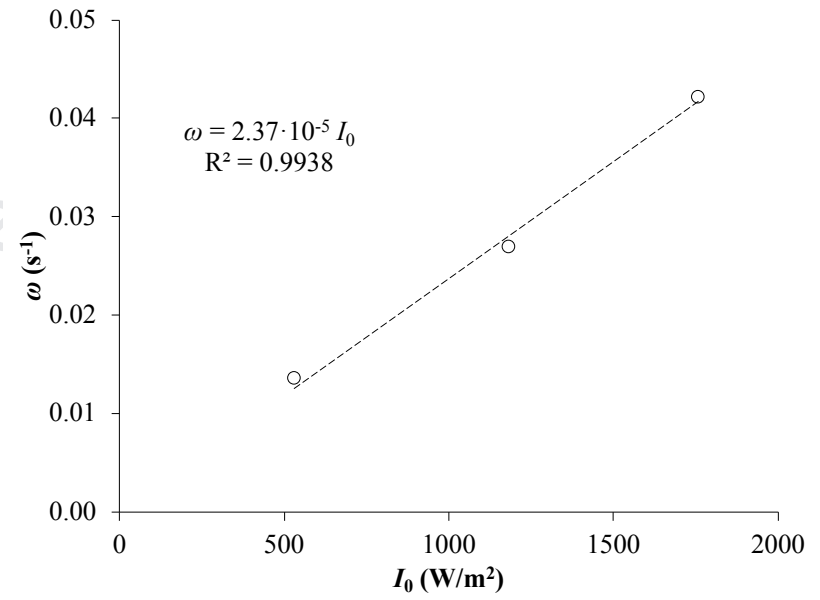
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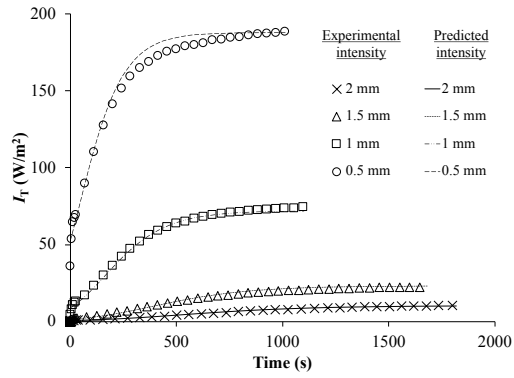
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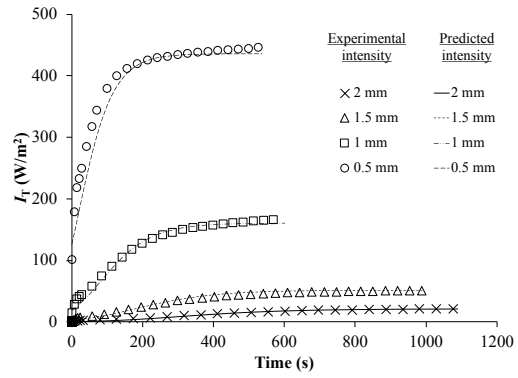
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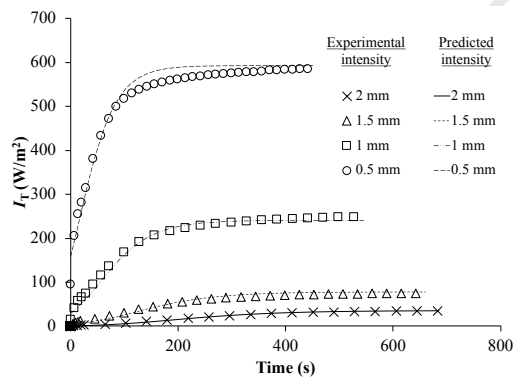
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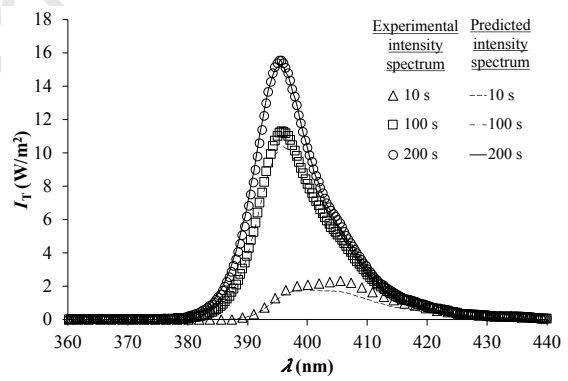
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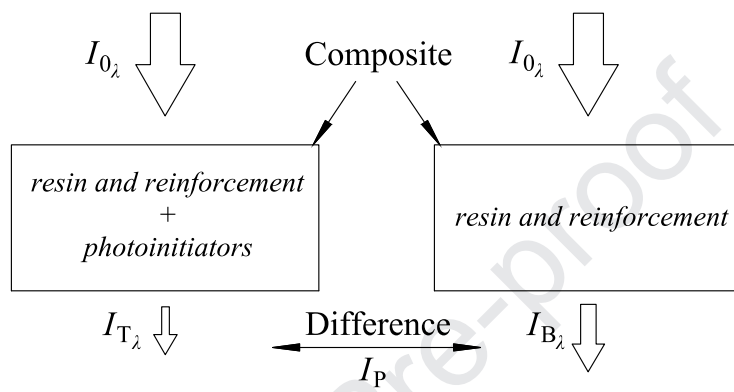
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(c)



(d)



Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: