



Research paper

# Prediction of the thermal degradation-induced colour change of acrylonitrile butadiene styrene products as a function of temperature and titanium dioxide content

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## ABSTRACT

In this study, we examined the thermal degradation-induced colour change of acrylonitrile butadiene styrene (ABS)-based titanium dioxide (TiO<sub>2</sub>)-doped products as a function of TiO<sub>2</sub> content and temperature. Based on the time-temperature superposition (TTS) principle and the CIELAB colour space, we proposed a methodology for developing a robust model to estimate the long-term colour change of polymers doped with TiO<sub>2</sub> at elevated temperatures. We used 800 h of measurement data to develop the model and validated the colour change predictions of the model in 1600 h. The average colour difference between the measured and modelled results at the application temperature range (below 80 °C) was <1.5, smaller than the just noticeable difference (JND) in the CIELAB colour space. We found that above a certain TiO<sub>2</sub> content (approximately 3 wt%), the colour retention of the ABS/TiO<sub>2</sub> specimens can no longer be improved by increasing their TiO<sub>2</sub> content. To show the applicability of the model, we present two simple case studies predicting the colour and appearance of a polymer product under constant and variable heat loads. The proposed methodology provides an excellent tool for design, as it can be used to determine the optimum amount of TiO<sub>2</sub>. Moreover, it accelerates and simplifies the design process.

## 1. Introduction

A product's colour is a key design element in many industrial applications. From a marketing perspective, colour strongly shapes the consumer's view of a product as it can affect the purchase intention [1] by influencing the perception of several properties, such as healthfulness [2], flavour [3], or size/portion [4]. From an engineering point of view, colour change is crucial, as several processes/treatments and environmental effects can result in a change of colour, e.g. radiation [5] and heat [6] treatments or fermentation processes [7]. For this reason, colour (specifically colour change) is often used as an indicator. There is a wide range of applications for process monitoring and product rating based on colour change, from the quality control of heat-treated wood products [8] through the condition monitoring of synthetic hydraulic oils [9] to high-performance colourimetric humidity sensors [10–13].

The primary colour of a polymer product can be modified by fillers/reinforcing materials [14] and colouring agents such as dyes or colourants [15,16]. However, due to different environmental influences,

polymer products may change colour. This colour change (most often yellowing in the case of polymers) can severely limit a product's acceptance by users or even functional use in areas where transparency and clear white colour are required.

Yellowing has two main causes. The first reason may be the degradation of the polymer itself, especially in the case of polyaromatics (e.g. polyesters, epoxy amines or polystyrene). The degradation of the polymer can occur during melt processing or end-use [17]. Secondly, the discolouration can be caused by the by-products of additives. The structural stability of thermal antioxidants used for stabilisation influences the rate of yellowing [18]. Pastorelli et al. [19] investigated the effects of different environmental parameters on polymer degradation and discolouration. Their study on 17 different polymers showed that light and nitrogen dioxide concentration are the dominant factors for colour change. Wu et al. [20] studied the thermal and ultra-violet (UV) light-induced yellowing of epoxy and vinyl ester resins. Thermal ageing produced a darker colour (higher yellowness index) with the same exposure time. They found that a radical oxidation reaction causes the

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yellowing of the resins, and it can be prevented or reduced with coatings, antioxidants, and UV absorbers.

The extent of yellowing can be estimated with appropriate models if the environmental effect causing it is known. Achtioui et al. [21] presented a model to predict the yellowing of styrene-stat-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) during processing with an internal mixer. The effects of temperature, rotation speed and residence time were considered, and a good correlation was found between yellowing and mixing energy. Matsuo et al. [22] conducted accelerated ageing treatment on hinoki wood and analysed the colour changes. The time–temperature superposition (tTS) principle was applied to describe the temperature dependence of the reaction rate. Then, they used kinetic analysis to predict the time–dependent changes of the CIELAB colour coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ) caused by thermal oxidation during natural ageing. Mochizuki and Takayama [23] also applied tTS to predict colour changes in liquid formulations. The authors applied accelerated ageing treatment at elevated temperatures and measured the CIELAB colour coordinates. The tTS principle gave reliable predictions for colour change over time. Wu et al. [24] constructed back propagation artificial neural networks (BP-ANNs) to predict the degradation of polycarbonate (PC) in different environments. Significant environmental parameters were determined, and the results were verified with weathering tests in new locations. The authors presented a predictive map for PC degradation based on the yellowness index (YI). Liu et al. [25] investigated the effects of UV light on photovoltaic modules (solar panels). The authors quantified colour change with the YI and found a linear relationship between the YI and UV irradiation dose.

Additives are often used to overcome discolouration in polymer products. Titanium dioxide ( $\text{TiO}_2$ ) has been widely studied for its photocatalytic effects and is commonly used as a colouring (whitening) agent for polymers [26–28]. R.E. Day [29] investigated the effects of  $\text{TiO}_2$  pigments on thermoplastic polymers. They showed that due to its good UV absorbing capability,  $\text{TiO}_2$  can prevent photoaging and mask the yellowing effect. Semperger et al. [30] also demonstrated the positive effects of  $\text{TiO}_2$  as a UV stabiliser in the case of PA6. Asiaban et al. [31] found that  $\text{TiO}_2$  pigments can reduce the intrinsic yellowness of ABS. However, the pigment can decrease impact strength and hardness when applied in higher amounts (above 1.5 wt%). Han et al. [32] showed that  $\text{TiO}_2$  can promote hydrophilicity when added to ABS. Therefore,  $\text{TiO}_2$ -ABS composites have the potential to be membranes for oil/water separation.

While  $\text{TiO}_2$  is extensively used as an additive in the plastics industry, no established models exist to predict the heat-induced colour change in  $\text{TiO}_2$ -doped plastic products, marking a knowledge gap in the literature. This study addresses this gap by introducing a novel modelling approach to predict the colour change in ABS products over time based on temperature and  $\text{TiO}_2$  concentration. For this purpose, ABS/ $\text{TiO}_2$  injection-moulded plates with six different  $\text{TiO}_2$  concentrations were produced, subjected to thermal ageing at five distinct temperatures, and monitored for colour change using CIELAB measurements over an 800-hour period. This comprehensive dataset enabled the development of a predictive model, followed by two case studies demonstrating its practical application in a simulation environment. The model's development and validation through 1600 h of CIELAB colour measurements under controlled thermal ageing provides a robust foundation for its use in simulation environments. This application enables manufacturers to forecast product appearance changes before production, supporting quality control and material optimisation for long-term aesthetics and stability.

## 2. Materials and methods

### 2.1. Materials

The acrylonitrile butadiene styrene (ABS) used in this study was an

injection moulding grade

ABS, namely Terluran GP 35 (supplied by INEOS Styrolution, Frankfurt am Main, Germany), with a density of  $1.04 \text{ g/cm}^3$  and a melt volume rate ( $220 \text{ }^\circ\text{C}/10 \text{ kg}$ ) of  $34 \text{ cm}^3/10 \text{ min}$  according to the manufacturer's data. As a whitening agent, we used rutile-type titanium dioxide ( $\text{TiO}_2$ ) KTR600 supplied by Ixom Operations Pty Ltd. (Auckland, New Zealand), which has the following CIELAB colour values (according to the manufacturer's data):  $L^*=97.78$ ,  $a^*=-0.34$ ,  $b^*=2.62$ .

### 2.2. Compounding

The ABS-based compounds were prepared with an LTE 26–44 twin-screw extruder (Labtech Engineering Co., Ltd., Thailand) with a length/diameter ratio ( $L/D$ ) of 44 and a screw diameter of 26 mm. Before processing, the ABS was dried in a Faithful WGLL-125 BE (Faithful Instrument (Hebei) Co., Ltd., Huanghua, China) hot air oven at  $80 \text{ }^\circ\text{C}$  for 4 h. Before extrusion, the  $\text{TiO}_2$  was added to the ABS by dry mixing at different percentages by weight: 0, 0.2, 0.5, 0.7, 1, 2.5, 5, 7.5 and 10 wt %. The temperature profile from hopper to die was:  $200\text{--}200\text{--}205\text{--}205\text{--}210\text{--}210\text{--}215\text{--}215\text{--}220\text{--}220 \text{ }^\circ\text{C}$ . The die temperature was  $220 \text{ }^\circ\text{C}$ , and the screw speed was 60 rpm. The extrudate was pelletised using an LZ-120/VS (Labtech Engineering, Thailand) granulator, and these pellets were used for injection moulding.

### 2.3. Injection moulding

Injection moulding was carried out using a two-cavity, cold runner mould with an Arburg Allrounder Advance 270S 400–170 (ARBURG GmbH, Germany, Lossburg) injection moulding machine. We produced  $80 \times 80 \text{ mm}$ , 2 mm thick plate specimens from the compounded pellets. The temperature profile from hopper to nozzle was 225, 230, 235, 240 and  $240 \text{ }^\circ\text{C}$ , while the mould temperature was  $30 \text{ }^\circ\text{C}$ . The screw ( $D = 30 \text{ mm}$ ,  $L/D = 20$ ) had a screw speed of 25 rpm, and shot volume was  $45 \text{ cm}^3$ . The injection rate was  $45 \text{ cm}^3/\text{s}$ , and the switchover was set to 8.5  $\text{cm}^3$ . Peak injection pressure reached 702 bar, and holding pressure was maintained at 500 bar for 5 s. The residual cooling time was 15 s. The total cycle time was 27.1 s.

### 2.4. Thermal ageing

The thermal ageing of the injection-moulded plate specimen containing 0, 1, 2.5, 5, 7.5 and 10 wt%  $\text{TiO}_2$  was carried out in a Faithful WGLL-125 BE hot-air oven (Faithful Instrument (Hebei) Co., Ltd., Huanghua, China), a Faithful DZ-3BCII hot-air oven (Faithful Instrument (Hebei) Co., Ltd., Huanghua, China) and a Venticell LISIS-B2V/VC55 hot-air oven (MMM Medcenter Einrichtungen GmbH, Planegg, Germany) at the following temperatures: 60, 70, 80, 90 and  $100 \text{ }^\circ\text{C}$ . In all cases, the heat exposure time was 800 h (~33 days). However, to validate our predictions to a certain extent, we continued the test at  $80 \text{ }^\circ\text{C}$  until 1600 h (~67 days).

### 2.5. Measurement of CIELAB colour values

To characterise the colour change of the tested samples, we used the CIELAB three-dimensional colour space with  $L^*$ ,  $a^*$  and  $b^*$  colour values.  $L^*$  refers to the achromatic colour (lightness or greyness) from 0 (black) to 100 (white).  $a^*$  and  $b^*$  represent redness ( $-a^*$ )/greenness ( $+a^*$ ) and blueness ( $-b^*$ )/yellowness ( $+b^*$ ), both indicating chromatic ("real") colour. Therefore, in this colour space, each colour is represented by a point with  $L^*$ ,  $a^*$  and  $b^*$  coordinates in the CIELAB colour space. The colour values were measured with a Gardner BYK colour guide sphere spectrophotometer (BYK-Gardner GmbH, Geretsried, Germany) under a D65 CIE standard illuminant light source at an observer angle of  $10^\circ$ . Colour measurements were taken on 3 different samples at 3 points per sample in every case, resulting in nine data points per material and treatment temperature. The maximum standard deviation of the nine

measurement points was 3.3, 0.9 and 1.6 for the  $L^*$ ,  $a^*$  and  $b^*$ , respectively. Based on the resulting standard deviations, the total colour difference ( $\Delta E_{ab}^*$ ), which is an industry-wide significant characteristic, can be considered.  $\Delta E_{ab}^*$  is the linear distance in CIELAB colour space between the two sets of coordinates ( $\Delta E_{ab}^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$ ). For the measured  $L^*$  colour coordinates having the highest standard deviation, if  $a^*$  and  $b^*$  were the same, this difference would result in a  $\Delta E_{ab}^* = 3.3$ . Depending on the field of industrial use, this value can be acceptable. Considering these, we used the average colour values in the calculations.

We measured the  $L^*$ ,  $a^*$  and  $b^*$  colour values of the samples, throughout the thermal ageing period, carrying out one measurement per weekday. Colour measurements on the specimen containing 0.2, 0.5, 0.7 wt%  $\text{TiO}_2$  were performed only at ageing time  $t = 0$  s.

### 2.6. Generating the master curve and modelling

Data analysis, model development and fitting were performed in Matlab R2021a software (Mathworks, Natick, MA, USA). We used the coefficient of determination ( $R^2$ ) and the root mean squared error (RMSE) to rate the goodness of fitting to the models.

## 3. Results and discussion

### 3.1. Development of a model to predict colour change

To predict the thermal degradation-induced colour change of ABS-based  $\text{TiO}_2$ -doped products as a function of  $\text{TiO}_2$  content ( $w$ ) and temperature ( $T$ ) at any arbitrary  $t > 0$  time point, we developed a robust model. The steps of developing the model are summarised in Fig. 1.

#### 3.1.1. Generating the master curve and determining the shift factor (temperature dependence)

As the first step, we applied the time-temperature superposition (tTS) principle (described in detail by Ferry [33]) to predict colour changes from a few hundred hours of measurements over a period of years. Using tTS, we constructed a master curve from the mean colour data ( $L^*$ ,  $a^*$ ,  $b^*$ ) measured at different temperatures for each  $w$ . The arbitrary colour value is hereafter denoted by  $X$ . The datasets measured at different temperatures were shifted along the time axis to coincide with the data obtained at the reference temperature,  $T_{ref} = 80$  °C, until a continuous curve was obtained. This procedure results in the concept of reduced time ( $t_{red}$ ), which is defined by Eq.1. Thus, data measured at temperatures other than  $T_{ref}$  can be "reduced" to  $T_{ref}$  with the use of Eq.1, resulting in the extension of the initial measurement time range (Fig. 2/a).

$$t_{red}|_{T=T_{ref}, w=const.} = \frac{t|_{T=const., w=const.}}{a_{T-X}(T)|_{w=const.}} \quad (1)$$

where  $a_{T-X}$  is the time shift factor for the  $X$  colour value at a given  $w$ .

We performed this procedure for all three colour values, and then fitted an exponential model (Eq.2) to the generated master curves (Fig. 2/b):

$$X(t_{red})|_{T=T_{ref}} = k_{1-X} + k_{2-X} \cdot e^{k_{3-X} \log(t_{red})} \quad (2)$$

where  $k_{1-X}$  was calculated as the mean of the first 150 points and  $k_{2-X}$ ,  $k_{3-X}$  are fitted constants.  $k_{1-X}$  indicates the initial colour value ( $k_{1-X} = X|_{t=0}$ ), and  $k_{2-X}$  and  $k_{3-X}$  determine the colour change rate. The master curves were generated with the mean values, but fitting was performed with the use of all the measured data.

In the second step, we investigated the temperature dependence of

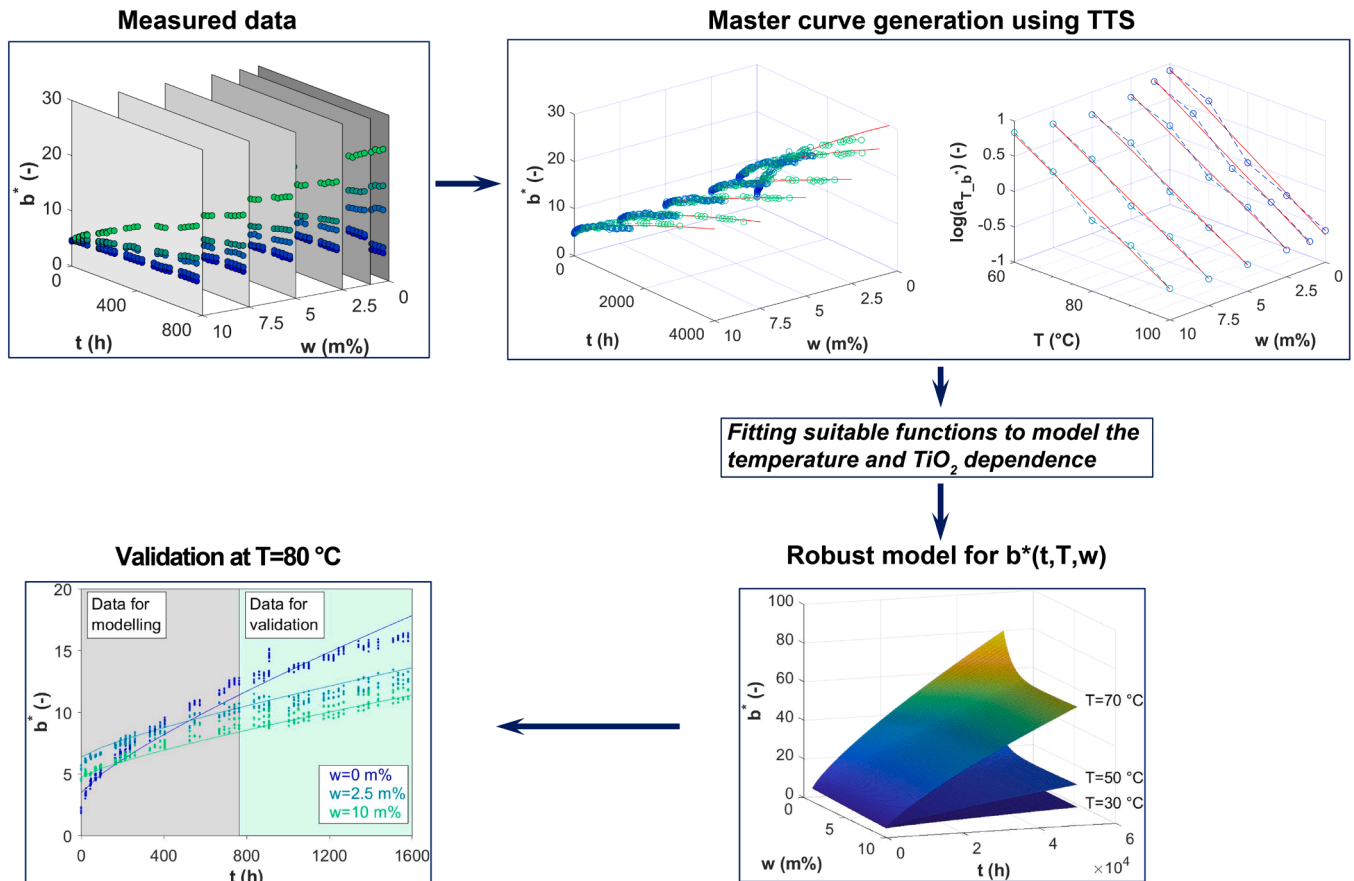


Fig. 1. Steps of developing the model to predict colour change as a function of temperature and titanium dioxide content presented for the  $b^*$  colour component.

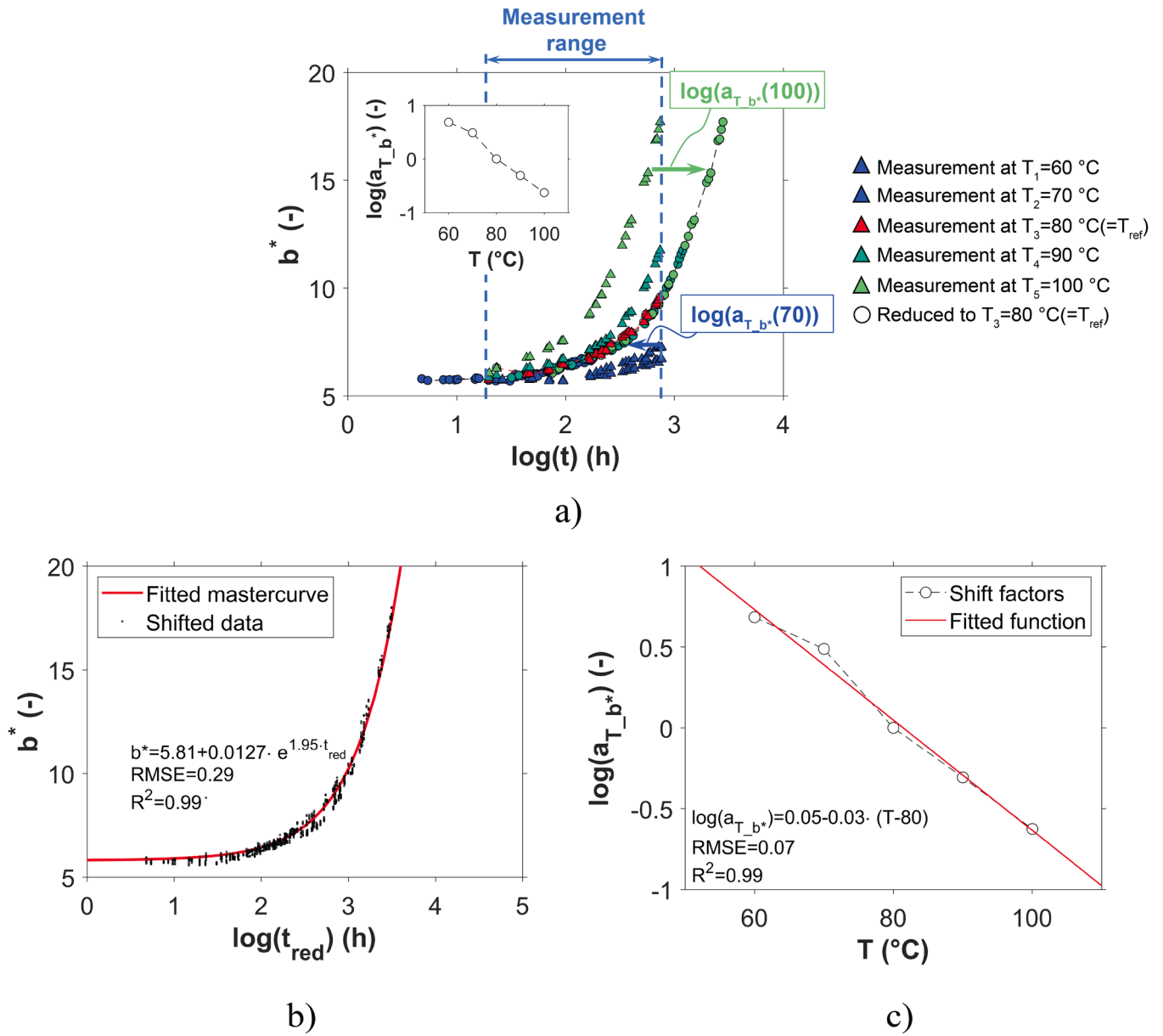


Fig. 2. Mean values of measured data (for  $w = 5$  wt%) and the generated master curve at  $T_{ref} = 80$  °C for the  $b^*$  colour component (a), exponential model fitted to the master curve with the use of all the measured data (b), fitted linear function to describe the temperature dependence of the shift factor (c).

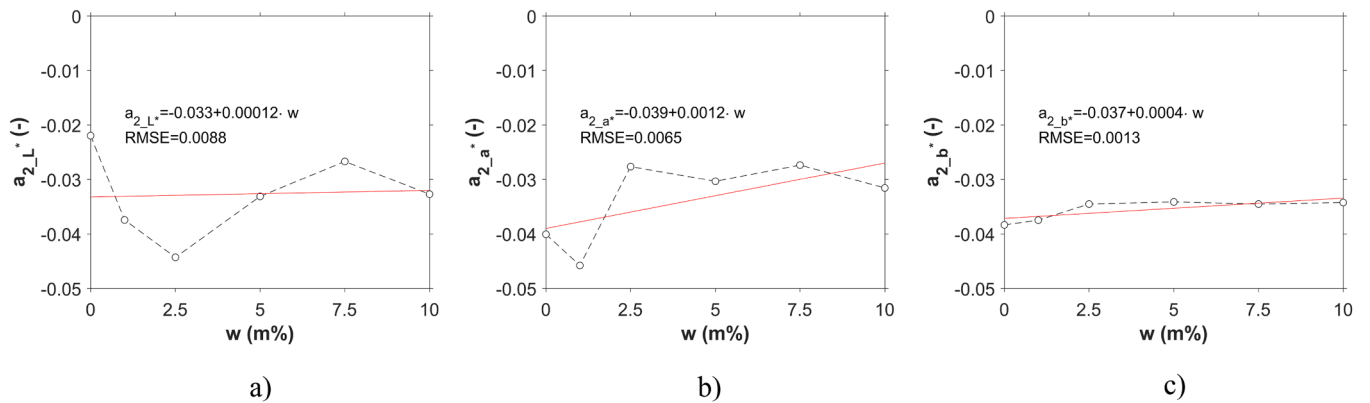


Fig. 3. Titanium dioxide content-dependence of the slope of the linear trend ( $a_{2,x}$ ), which describes the temperature dependence of the shift factors for the  $L^*$  (a),  $a^*$  (b) and  $b^*$  (c) colour values.

the resulting  $a_{T,X}$  for each  $w$ . We found that  $a_{T,X}(T)$  can be well described by Eq.3 for every  $w$  (Fig. 2/c):

$$\log(a_{T,X}(T)|_{w=const.}) = a_{1,X} + a_{2,X} \cdot (T - T_{ref}) \quad (3)$$

where  $a_{1,X}$  and  $a_{2,X}$  are fitted constants.  $a_{1,X}$  was included because the temperature may have fluctuated. Therefore, it was used for the fitting, but later on, we did not use it; only  $a_{2,X}$  was used for the model. As a result of the first two steps, we can predict the colour change of ABS-based TiO<sub>2</sub>-doped samples at different temperatures over a long period of time at a fixed  $w$ . To predict this colour change for any desired  $w$ , we need two further steps.

### 3.1.2. Investigating the effects of titanium dioxide content (titanium dioxide dependence)

In the third step, we investigated the TiO<sub>2</sub>-dependence of the slope of the linear trend ( $a_{2,X}$ ), which describes the temperature dependence of

the shift factors for all three colour values (Fig. 3). Based on previous results [34,35], we assumed that increasing TiO<sub>2</sub> content would reduce the effect of temperature on the samples' colour change. This means the absolute value of  $a_{2,X}$  parameters will decrease with increasing TiO<sub>2</sub> content. We assumed an increasing trend in the  $a_{2,a^*}$  and  $a_{2,b^*}$  parameters with increasing TiO<sub>2</sub> content. These results indicate that an increase in TiO<sub>2</sub> content reduces the change of the  $a^*$  and  $b^*$  colour values due to temperature. The results for  $a_{2,L^*}$  did not show a trendwise change. However, based on the work of Bersch et al. [36] whose results showed a linear trend in the change of  $L^*$  due to the increase in TiO<sub>2</sub> content, we approximated all of these dependencies with linear functions (Eq. (4)):

$$a_{2,X}(w) = a_{21,X} + a_{22,X} \cdot w \quad (4)$$

where  $a_{11,L^*}$ ,  $a_{12,L^*}$ ,  $a_{11,a^*}$ ,  $a_{12,a^*}$ ,  $a_{11,b^*}$ ,  $a_{12,b^*}$  are fitted constants. Based on Eqs.3 and 4, the T and TiO<sub>2</sub> content-dependent shift factor ( $a_{T,X}(T,w)$ ) can be determined.

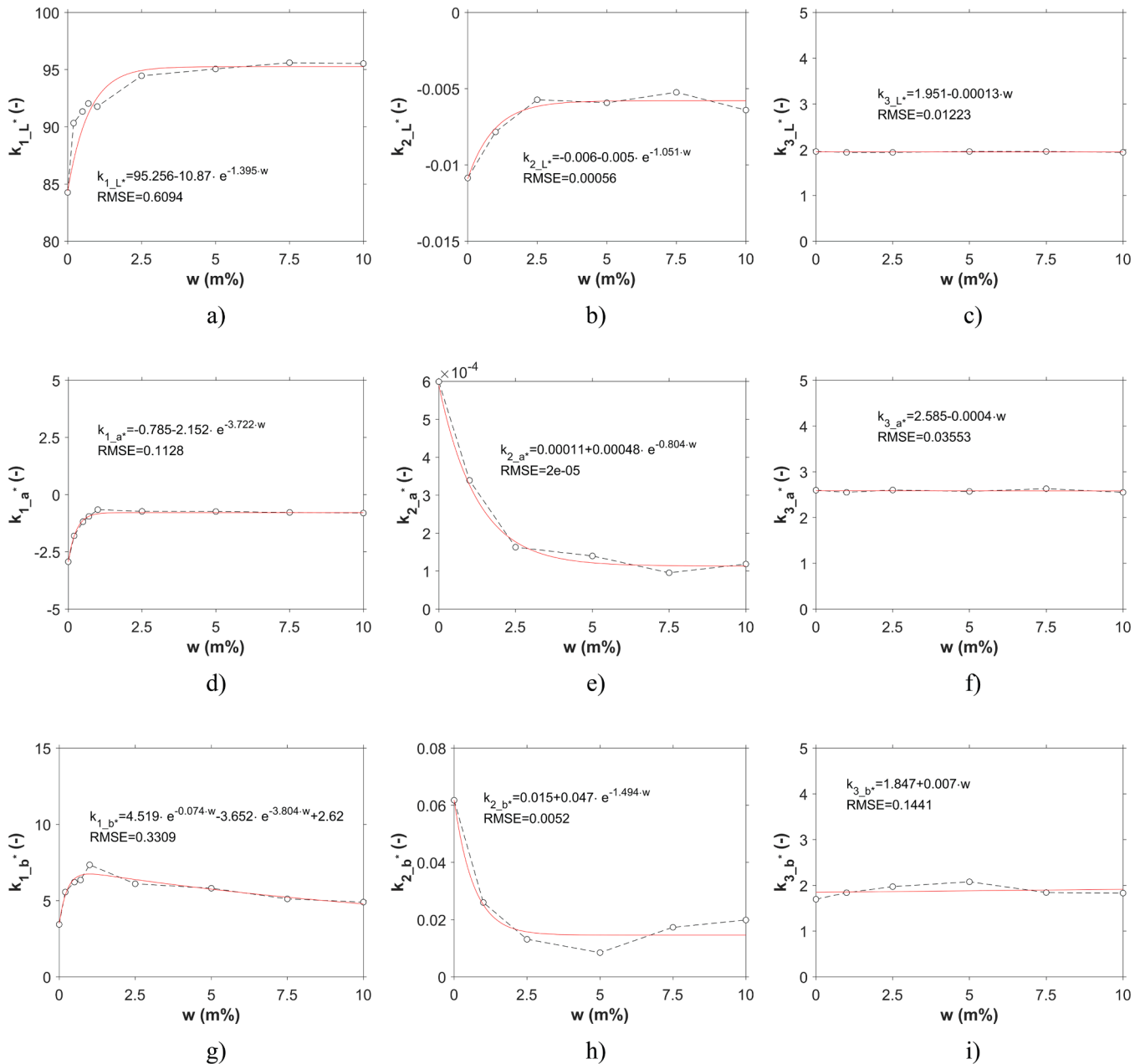


Fig. 4. Titanium dioxide content-dependence of the parameters of master curves describing the time-dependent change of colour values. The circles denote the exact values, continuous lines are the fitted suitable functions for  $L^*$ (a-c),  $a^*$ (d-f) and  $b^*$  (g-i) colour values.

In the fourth step, we examined the dependence of the master curve model parameters of Eq.2 on TiO<sub>2</sub> content (Fig. 4). These dependencies were approximated using suitable saturation and decay exponential and linear functions (Eq.5–9).

$$k_{1L^*}(w) = k_{11L^*} + k_{12L^*} \cdot e^{k_{13L^*} \cdot w} \quad (5)$$

$$k_{1a^*}(w) = k_{11a^*} + k_{12a^*} \cdot e^{k_{13a^*} \cdot w} \quad (6)$$

$$k_{1b^*}(w) = k_{11b^*} \cdot e^{k_{12b^*} \cdot w} + k_{13b^*} \cdot e^{k_{14b^*} \cdot w} + k_{15b^*} \quad (7)$$

$$k_{2X}(w) = k_{21X} + k_{22X} \cdot e^{k_{23X} \cdot w} \quad (8)$$

$$k_{3X}(w) = k_{31X} + k_{32X} \cdot w \quad (9)$$

where  $k_{1L^*}$ ,  $k_{1a^*}$  and  $k_{1b^*}$  are the initial  $L^*$ ,  $a^*$  and  $b^*$  colour values, respectively.  $k_{2X}$  and  $k_{3X}$  are the parameters characterising the degree of change in the given colour component. The parameters containing two numbers in the subscript are fitted values. For the  $k_{1L^*}$ ,  $k_{1a^*}$  and  $k_{1b^*}$  values to be correct, these values must be the  $L^*$ ,  $a^*$  and  $b^*$  colour values of TiO<sub>2</sub> at  $w = 100$ , respectively. Therefore, the colour component data of TiO<sub>2</sub> were used to fit the models.

Between 0 and 1 wt% TiO<sub>2</sub> content, we observed an abrupt change in the  $k_{1X}$  values (Fig. 4/a,d,g). We also determined the initial colour values for samples containing 0.2, 0.5 and 0.7 wt% TiO<sub>2</sub> to find suitable functions. With increasing TiO<sub>2</sub> content, the  $k_{1L^*}$  and  $k_{1a^*}$  parameters reach saturation at a certain level, while  $k_{1b^*}$  increases to 1 wt% and steadily decreases thereafter (Fig. 4/a,d). This suggests that with increasing TiO<sub>2</sub> content, the colour of the ABS sheets becomes lighter and slightly redder. In addition, up to 1 wt%, the colour tends to shift towards yellow and then increasingly towards blue. However, regarding the  $L^*$  and  $a^*$  colour values, these curves become saturated, i.e.

$$\Delta E_{avg} = \sqrt{\frac{1}{n} \sum_{i=1}^n (L_{model,i} - L_{measured,i})^2 + (a_{model,i} - a_{measured,i})^2 + (b_{model,i} - b_{measured,i})^2} \quad (11)$$

increasing the TiO<sub>2</sub> content above approximately 3 wt% does not lead to further changes in these colour values. At this amount, the values of  $L^*$  and  $a^*$  of the applied TiO<sub>2</sub> additive are already reached. The rate of change of the colour component due to heat can be reduced by TiO<sub>2</sub> doping above a certain TiO<sub>2</sub> content, but the temperature resistance of the specimen does not increase further.

After the decrease in absolute value, the  $k_{2X}$  parameters all saturate with increasing TiO<sub>2</sub> content (Fig. 4/b,e,h). This means that the rate of change of the colour component due to heat can be reduced by TiO<sub>2</sub> doping. But above a certain TiO<sub>2</sub> content (approximately 3 wt%), the colour retention of the ABS specimens is no longer improved. With increasing TiO<sub>2</sub> doping, the sample becomes less dark (increasing  $|L^*|$  values) and less shifted towards yellow (decreasing  $b^*$  values) or red (decreasing  $a^*$  values) due to thermal load.  $k_{3X}$  was found to be quasi-constant in all three cases (Fig. 4/c,f,i). Therefore, after fixing the values of  $k_{3X}$ , we performed the fitting of Eqs. (5)-(9) again and used the resulting fitting parameters for the model.

### 3.1.3. Generating and validating the models

Based on the four steps described in Section 3.1.1 and 3.1.2, robust models can be defined, which express the colour values as a function of  $t$ ,  $T$  and TiO<sub>2</sub> content (Eq.10):

$$X(t, T, w) = k_{1X}(w) + k_{2X}(w) \cdot e^{k_{3X} \cdot \log\left(\frac{t}{a_{T-X}(T,w)}\right)} \quad (10)$$

where  $k_{1X}$  and  $k_{2X}$  are the initial value and the rate of the change in

colour component value, respectively (both are TiO<sub>2</sub> content-dependent parameters), while  $k_{3X}$  is independent of TiO<sub>2</sub> content, it only depends on the colour component. The model resulting from Sections 3.1.1 and 3.1.2 can predict the colour of ABS-based TiO<sub>2</sub>-doped products as a function of TiO<sub>2</sub> content ( $w$ ) and temperature ( $T$ ) at an arbitrary time  $t > 0$ . Fig. 5 shows the time-dependent and TiO<sub>2</sub> content-dependent surfaces generated from the model at different temperatures for each colour component.

We rated the goodness of fit for the model with several metrics. The root mean squared error (RMSE) values (Fig. 6/a-c) were  $<2.5$  in all the cases tested, except for the  $b^*$  colour component of the  $w = 0$  wt% sample at  $T = 100$  °C, where the error was 8.4. Note, that the glass transition temperature ( $T_g$ ) of ABS is around 105 °C [37] and near the  $T_g$  mechanical problems can already arise. Although it was important to carry out colour measurements at temperatures close to  $T_g$  for long-term tTS-based predictions, the real application temperature of ABS is below 80 °C. In the cases of real application temperatures the RMSE values for the  $b^*$  colour component were  $<1.4$  in all cases. Moreover, the RMSE values for  $a^*$  and  $L^*$  were significantly lower. These results suggest that all three colour values can be well estimated using the developed model. The largest deviation from the actual values obtained in the greenness/yellowness component, and there are actually marginal errors for the green/blue component and for the lightness. We also examined how the squared errors evolved with the samples measured at 80 °C, where we had data beyond the data used for modelling (data from 0 to 800 h). Based on Fig. 6/d-f, we found that the squared errors between 800 and 1600 h are even smaller, meaning that in this region our model gives an even more accurate prediction for each colour component. To rate the colour difference between the measured and the modelled results we calculated the average colour difference ( $\Delta E_{avg}$ ) from Eq. (11):

where  $n$  is the number of measured data for the given ( $t,w$ ) pairs.

Fig. 6/g shows that  $\Delta E_{avg}$  is  $<2.8$  in all cases, but the  $w = 0$  case at  $T = 100$  °C (where it is 7.0). Moreover, if we consider the actual application temperature range, i.e. below 80 °C,  $\Delta E_{avg}$  is  $<1.5$  in all cases. In the CIELAB colour space,  $\Delta E_{avg} = 2.3$  corresponds to the just noticeable difference (JND) value [38], which means that JND is the amount that a given colour has to be modified to obtain a noticeable difference. Therefore, within the actual application temperature range, the model can provide an accurate estimate with a colour difference smaller than JND.

Consequently, the proposed methodology can be used to estimate the long-term colour change of polymers doped with TiO<sub>2</sub> at elevated temperatures, as a function of the amount of TiO<sub>2</sub> added. Therefore, it is an excellent tool for design, as it can be used to estimate the appearance of a product exposed to elevated temperatures.

## 3.2. Practical application: case studies

### 3.2.1. The prediction of colour for a constant heat load

One possible application of the model is to determine the colour change of a polymer product under constant heat load. If we know the conditions under which our polymer product will be used (e.g. at what temperature and for how long it will be exposed to heat), we can use the model to estimate the colour change, even over years. Fig. 7/a shows the measurement points used for model fitting and the solid line provided by the model. Green dots indicate the four different time points at which

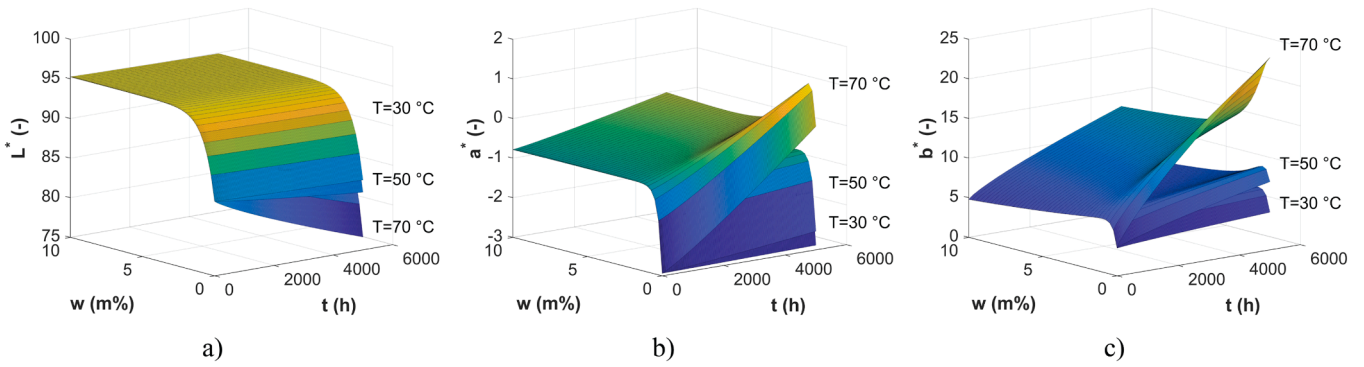


Fig. 5. The generated model represented as a surface for each colour component at different temperatures showing how the model depends on time and titanium dioxide content for  $L^*$  (a),  $a^*$  (b) and  $b^*$  (c) colour values.

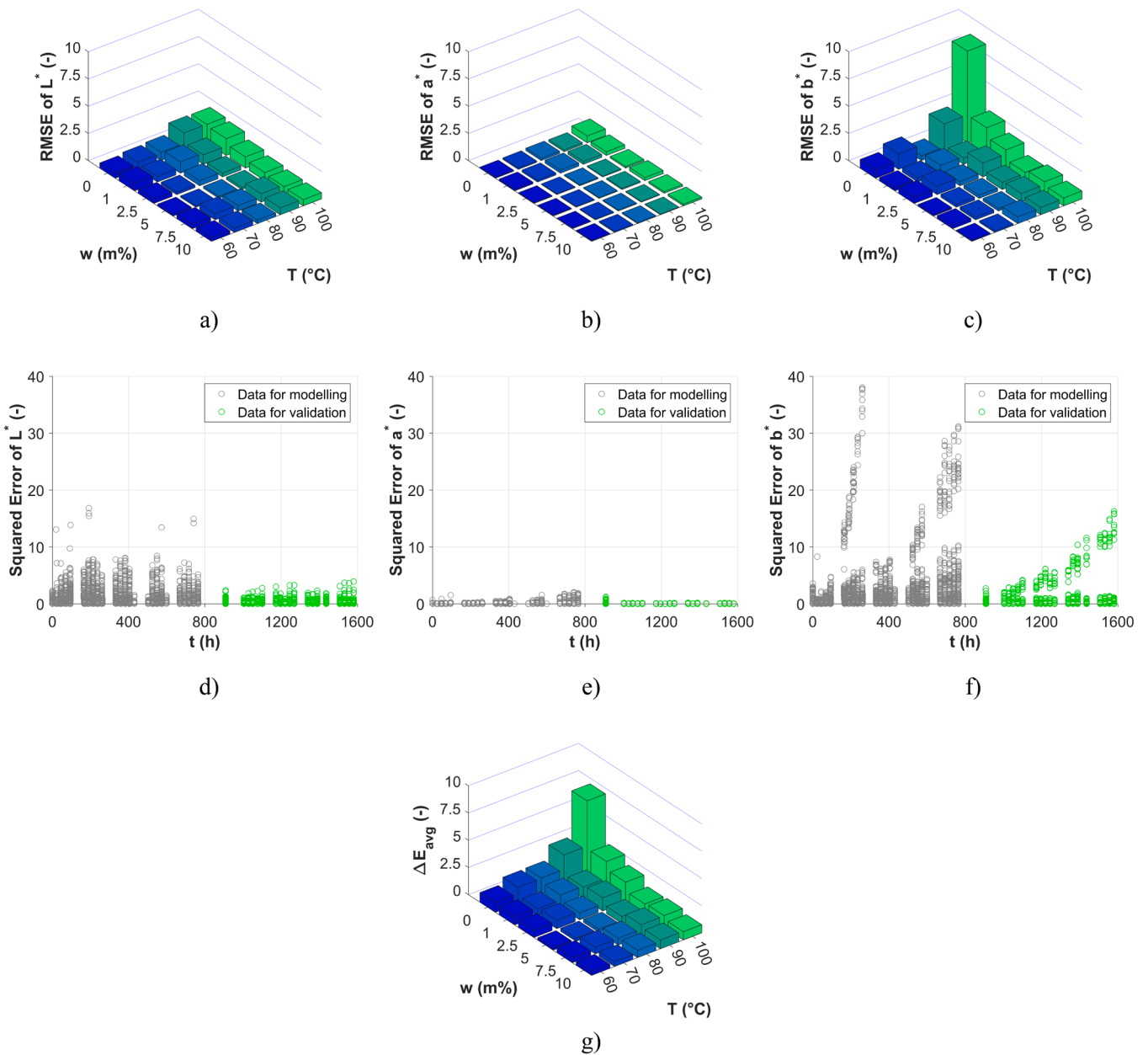


Fig. 6. Root mean squared errors (RMSE) of the model for the data used for modelling for  $L^*$  (a),  $a^*$  (b) and  $b^*$  (c) colour values the squared errors for modelling and validation for  $L^*$  (d),  $a^*$  (e) and  $b^*$  (f) colour values, and the average colour difference ( $\Delta E_{avg}$ ) for every examined case (g).

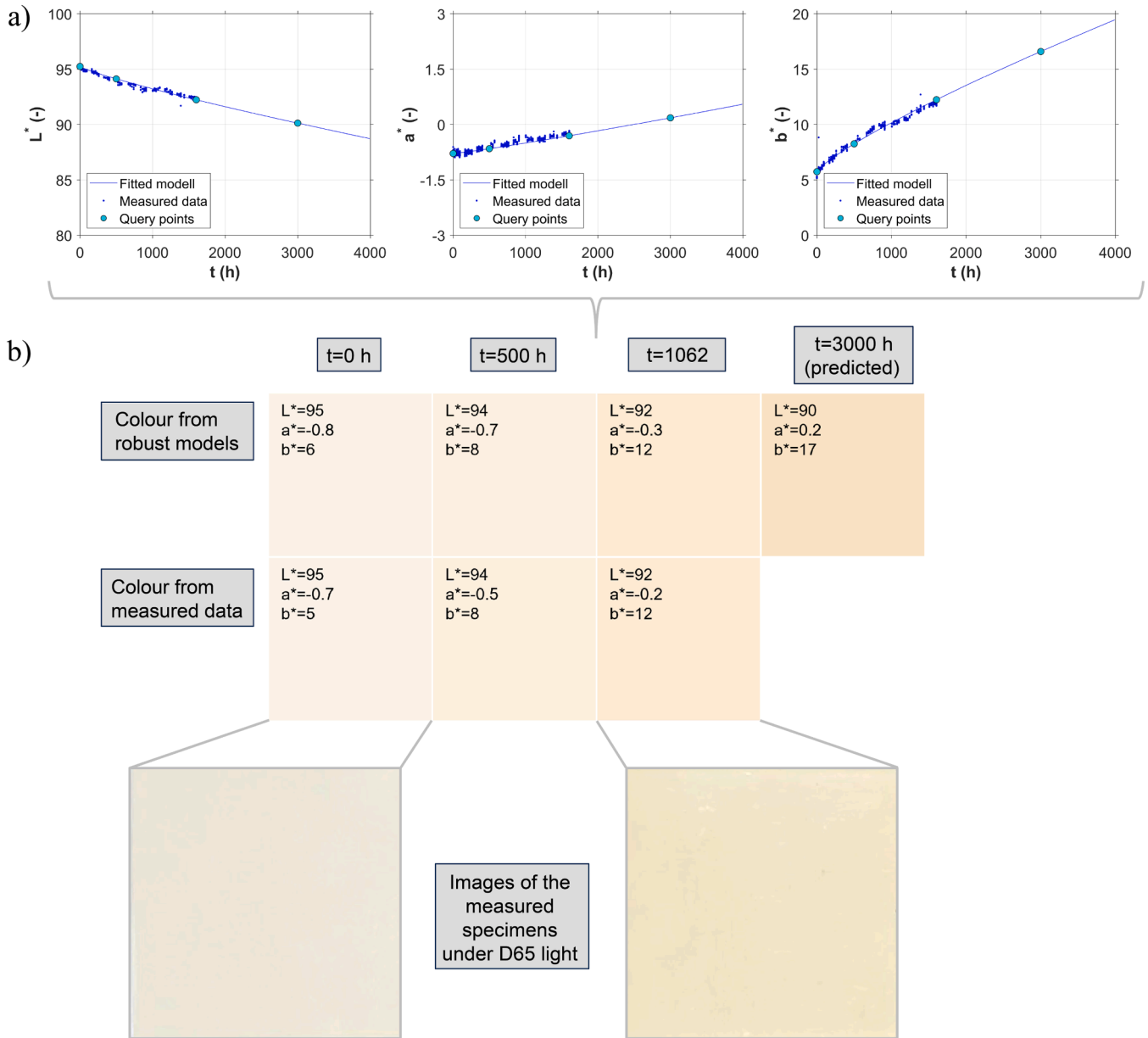


Fig. 7. Comparison of the predicted colour and the measured colour of the sample exposed to constant heat load for the  $w = 5$  wt% case at  $T = 80$  °C.

the estimated colour of the test specimen was obtained based on the model. The first three are the measured points, where the first two were used for model fitting and the third for validation. The fourth point shows the predicted colour change based on the model. Then, we compared the predicted colour values with the actual data. Based on the obtained colour values, we displayed the colour of the test specimens (Fig. 7/b). At the points where measured data were available, the discrepancy between the data estimated by the model and the measured data is negligible. Also, the plate exposed to a constant high temperature becomes visibly yellow over time. In this example, 3000 h was the furthest estimate, but the model can be used for longer estimates. The yellowing effect was visible on real test specimens photographed under D65 illumination.

### 3.2.2. The prediction of appearance for a varying heat load

Alternatively, we can predict the local colour change of a polymer product, if it is subjected to a known non-uniform heat load. This thermal load can be determined by measurement, analytical calculation or finite element simulation. For example, if heating pipes are placed over a

sheet-like product (Fig. 8/a) and the heat load that the pipes will transfer to the product is known (e.g. a sinusoidally varying load Fig. 8/b), then the local colour change of the surface of the product can be determined (Fig. 8/c).

Once this has been determined, we can test our product against the quality requirements. For example, if the maximum permitted colour deviation ( $\Delta E_{plate,max}$ ) cannot be greater than 5, then we need to compare the least and most yellowed areas of the plate. The colour difference ( $\Delta E_{plate}$ ) can be estimated from the colour values of these areas according to Eq. (12):

$$\Delta E_{plate} = \sqrt{(L_{max} - L_{min})^2 + (a_{max} - a_{min})^2 + (b_{max} - b_{min})^2} \quad (12)$$

Fig. 8/d shows the colour difference of the sheet-like product as a function of time and TiO<sub>2</sub> content. If we want to reduce the colour change of the sheet with TiO<sub>2</sub>, we can also obtain information on the amount of TiO<sub>2</sub>-doping, so the minimum amount of TiO<sub>2</sub> to be used to meet the colour change specifications for the product can be determined based on the lifetime of the product (Fig. 8/f). In the present case, TiO<sub>2</sub>



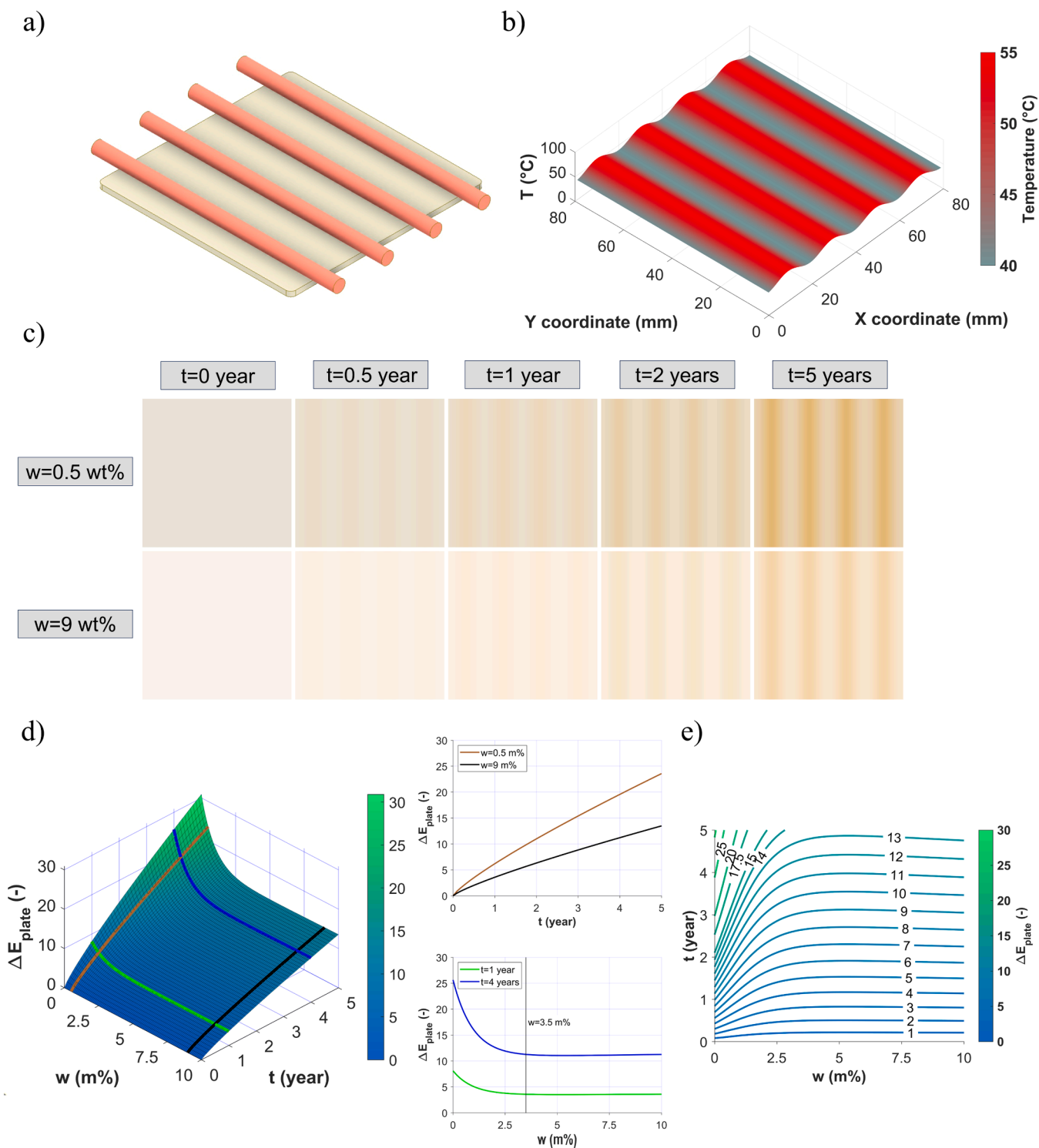


Fig. 8. Sheet-like product placed under heating pipes (a), heat load acting on the sheet-like product (b), surface colour predicted by the model for two different TiO<sub>2</sub> contents (c), surface plot for the colour difference of the sheet-like product (d) and nomogram to determine the optimal amount of TiO<sub>2</sub> (e).

doping higher than 3.5 wt% does not significantly improve temperature resistance. Using the methodology described above, nomograms can be generated to help determine the optimal amount of additives (Fig. 8/g). In engineering practice, such nomograms are very important as they simplify and accelerate the design process.

#### 4. Conclusion

Our goal was to predict the thermal degradation-induced, long-term colour change of ABS-based TiO<sub>2</sub>-doped products as a function of TiO<sub>2</sub> content and temperature. For this purpose, we investigated the colour change of ABS sheets doped with different levels of TiO<sub>2</sub> at five elevated temperatures between 60 and 100 °C. Applying the tTS principle and the CIELAB colour space, we proposed a methodology for developing a

robust model that can be used to estimate the long-term colour change of polymers doped with TiO<sub>2</sub>, at elevated temperatures. We used 800 h of measurement data for model development and validated the colour change predictions of the model for up to 1600 h. At the application temperature range (below 80 °C), the average colour difference was <1.5 in all the examined cases, which is smaller than the just noticeable difference (JND) in the CIELAB colour space. To show the applicability of the model, we presented two simple case studies predicting the colour and appearance of a polymer product under constant and variable heat loads. The model's development and validation through 1600 h of CIELAB colour measurements under controlled thermal ageing provides a robust foundation for its use in simulation environments. This application enables manufacturers to forecast product appearance changes before production, supporting quality control and material optimisation for long-term aesthetics and stability.

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**CRedit authorship contribution statement**

Ábris Dávid Virág: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. András Suplicz: Writing – review & editing, Funding acquisition, Conceptualization. Dániel Török: Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization.

**Declaration of competing interest**

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.

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**Data availability**

Data will be made available on request.

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