Validation of near infrared spectroscopy as an age-prediction method for plastics

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Abstract: This work has two aims. Firstly, to validate the ability of experimental models derived through near infrared spectroscopy for acrylonitrile butadiene styrene (ABS), low-density polyethylene (LDPE), polyethylene terephthalate (PET), and polypropylene (PP) in predicting polymers' aging; focusing on the degree of oxidation. Secondly, to assess the reliability of non-invasive age-predictive models on waste plastic samples and on mechanically recycled samples. Aging time, temperature and number of extrusion cycles were selected as independent variables to build the aging-prediction models, where they were calibrated on samples subjected to controlled conditions. The accuracy of the prediction models was assessed on external samples (aged under known conditions) through the cross correlation technique and the Root Mean Square Error (RMSE). The models exhibited good collinearity for the aging temperature and the number of extrusion cycles factors for all tested polymers, but not for the aging time factor. The RSME value of the aging time factor was far from zero for all polymers. Plastic waste samples provided analogous results; the aging time estimation was mostly negative in value. The estimations of aging time and number of extrusion cycles were always positive in values, where the most reasonable aging factor estimation was the number of extrusion cycles.

- We investigated NIR spectroscopy ability to predict the oxidation degree of polymers
- Aging-prediction models were experimentally derived for ABS, PE, PET and PP
- Aging time, temperature and no. of extrusion cycles were the independent variables
- The models were calibrated on artificially aged samples and waste polymers
- The no. of extrusion cycles proved to be a key parameter for the reliability of the models

Validation of near infrared spectroscopy as an age-prediction method for plastics

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Abstract

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prediction models was assessed on external samples (aged under known conditions) through the cross correlation technique and the Root Mean Square Error (RMSE). The models exhibited good collinearity for the aging temperature and the number of extrusion cycles factors for all tested polymers, but not for the aging time factor. The RSME value of the aging time factor was far from zero for all polymers. Plastic waste samples provided analogous results; the aging time estimation was mostly negative in value. The estimations of aging time and number of extrusion cycles were always positive in values, where the most reasonable aging factor estimation was the number of extrusion cycles.

Keywords: FTNIR spectroscopy; polymer aging; polymer degradation; plastic waste; prediction models

1. Introduction

Plastics have become an environmental challenge, even though they do not generally possess a direct hazard to the environment. Their environmental footprint results from the consumption of non-renewable resources, in addition to being non-degradable (Sánchez and Collinson 2011). The extensive application of plastics creates a challenge connected to the waste management of the related flows. Moreover, the fact that a considerable fraction of the produced plastic is intended for single-use disposable applications (Hopewell et al. 2009) and mainly in form of films for household and industrial applications (Horodytska et al. 2018) exacerbates an already critical framework. Municipal solid waste management integrated systems are generally defined through the hierarchy of prevention, reuse, recycling, and recovery and disposal, in decreasing order of priority (Denise Reike et al. 2018). The adoption of the circular-

economy concept on waste plastics compels the application of recycling activities (M.K. Eriksen et al. 2018).

There are essentially four types of plastic recycling, categorized as primary (re-extrusion), secondary (mechanical), tertiary (chemical recycling) and quaternary (energy recovery) (Yu et al. 2016; Al-Salem et al. 2009). Mechanical recycling of plastics is most appropriate when polymers are separately collected from contaminated source (Ragaert et al. 2017). Chemical recycling represents processes able to recover synthesis monomers or feedstock chemicals by depolymerization. Whereas quaternary recycling or energy recovery is particularly utilized if plastics cannot be mechanically recycled or re-extruded due to contamination, separation difficulties, or significant degradation (Ragaert et al. 2017). This study focused on the mechanical recycling of plastics, since this process is by far the most commonly applied at industrial level for material recovery (Al-Salem et al. 2009). Generally, material's quality should be maintained during reprocessing and use as a subsequent product; therefore mechanical recycling is often limited to selected types of plastic wastes such as Polyethylene terephthalate (PET) bottles (Barlow and Morgan, 2013). The recycling of other types of polymers can be more complex, due to the wide variety of grades, poor recovery, cross-contamination, and downgrading in quality (Hopewell et al. 2009). The common difficulties related to mechanical recycling are the heterogeneity of plastic wastes and the deterioration in polymers' properties due to use and aging (Brandrup 1996; Perugini et al. 2005; Ragaert et al. 2017). Polymer degradation can cause changes in chemical, physical and mechanical features (Beninia et al. 2011; Anne Shayene Campos de Bomfim et al. 2019). Polymeric surface can also be attacked by material weathering (temperature, humidity and light), microorganisms and chemical solutions (Alassali et al. 2018a;

Picuno et al. 2019a; Picuno et al. 2019b). Polymer degradation; occurring due to thermal oxidation mechanisms is the focus of this study, as these mechanisms are typically activated when the polymer is exposed to environmental conditions as well as to elevated temperatures (i.e. during extrusion), in presence of oxygen (Izdebska 2016). As a consequence, integrating systems that are able to determine the material quality and degree of degradation in the industrial recycling scheme could strongly improve the recycling process.

In a previous study, Near Infrared (NIR) spectroscopy was employed to propose polymers' degradation-prediction models, those able to predict plastic aging by focusing on the degree of oxidation (Alassali et al. 2018b). NIR spectroscopy was chosen due to its wide application in plastic sorting facilities (Huth-Fehre et al. 1995; Wahab et al. 2006; Masoumi et al. 2012; S. Brunner et al. 2015) and due to its fast, accurate, and non-destructive features (Blanco and Villarroya 2002). This work is a follow-up to the previously conducted study by (Alassali et al. 2018b) and it aims at validating the generated models and their ability in predicting polymers' degree of thermal oxidation. In details, the prediction capability of the generated models was verified by the cross-validation technique (Pasquini 2003), a basic statistical technique used for estimating the predictive performance of a model (Bishop 2006) that typically relies on a small dataset (Goodfellow et al. 2016). In order to achieve the validation of the aging-prediction models—generated for the polymers polypropylene (PP), low-density polyethylene (LDPE), polyethylene terephthalate (PET), and acrylonitrile butadiene styrene (ABS), discretely—four sets of samples of virgin polymers were aged under controlled conditions. The applied aging method simulates environmental conditions, yet accelerated. At molecular level, the thermo-oxidative degradation of the studied

polymers is a process accomplished with exposing the material to elevated temperatures in the presence of oxygen (Song et al. 2014). Consequently, a variation in the polymeric structure is provided as a result of compound's oxidation. The thermal oxidation rate and extent of each polymer are unique, which generally depend on the chemical structure and the stability of the polymeric chains (Alassali et al. 2018b). In this study, virgin material (free of additives and stabilizers) was used. This was important to decrease the number of variables in building the aging models. Certainly, different additives, stabilizers and coloring agents may contribute to the degree of degradation and hence to the generated mathematical models. However, this study focused on evaluating the possibility of producing aging-prediction models, and re-applying them on external samples (treated differently).

The second aim of this study was to utilize the validated age-prediction models to forecast the degree of thermal oxidation (aging) of plastic waste samples (deriving from e-waste) as well as on mechanically recycled samples, in order to test the viability of implementing the models on industrial-scale for the purpose of material recovery for recycling. To our knowledge this study is the first to investigate the reliability of non-invasive age-predictive models on waste plastics. Compared to the previous study (Alassali et al., 2018a), this work exhibits the following progresses: (I) a different and more complex validation approach was adopted, (II) a significant factor (number of extrusion cycles) was included to account for plastic aging by processing, and (III) the generated models were tested on real waste samples (derived from waste electrical and electronic equipment)

2. Materials and Methods

2.1. Materials

2.1.1. Virgin plastic samples under controlled aging condition

Virgin polymers (i.e. polymers free of additives) were either oven-aged under controlled conditions—which means at defined temperature and duration (to simulate thermo-oxidative effects)—or extruded (to simulate plastic mechanical processing) for the purpose of validation. The same materials used in creating the aging models (Alassali et al. 2018b) were also used for their cross-validation:

- cylindrical granules of ABS from POLYLAC PA-747 - CHI MEI CORPORATION;
- granules of PET, provided from NEOPET 82 FR - INEOS Olefins and Polymers Europe;
- cylindrical granules of LD-PE, provided from INEOS Olefins and Polymers Europe; and
- pellets of PP, provided from Olefins and Polymers Europe.

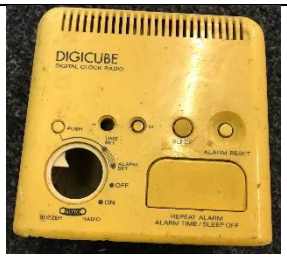
2.1.2. Plastic waste samples

The second set of samples was obtained from an e-waste collection point in the city of Hamburg (Germany). Ten items of different brands were selected, and only their plastic components were considered in this study (see Table 1). The polymers of each component were identified as specified in section 2.5.2.

Table 1. Description of the plastic waste samples deriving from e-waste units

Identified in the	e-waste unit	Image	Color	Polymer

study as				**type**
PP-1	Lamp cup		White	PP
PP-2	Water container of coffee maker		Transparent	PP
PP-3	Base of coffee maker		White	PP
PP-4	Closure of a juicer		White	PP
PP-5	Water container of an iron		White to transparent	PP
PP-6	Inner part of an iron		White	PP

ABS-1	Hand mixer		White	ABS
ABS-2	Case of digital clock radio		White-yellowish	ABS
ABS-3	Router case		White	ABS
ABS-4	Router case		White	ABS

143

144 **2.2. Plastic aging-prediction models**

145 As was explained in (Alassali et al. 2018b), aging-prediction models were created
146 utilizing the NIR spectra (obtained from a Bruker Optics FT-NIR spectrometer MPA,
147 Multi-Purpose Analyzer) of differently aged virgin polymers.

148 As a first step, controlled thermal aging of the material was conducted in a BINDER

oven, where two aging factors were considered (i.e., temperature and time), to simulate the thermo-oxidative degradation of plastics during their use in accordance with ASTM-F1980-07. The plastic aging-prediction models were generated depending on the relation between the experimental aging parameters (i.e., time (h) and temperature (°C)) and the NIR spectra. The NIR spectra of differently aged polymers exhibited specific variations in the absorbance intensity, related to changes taking place in the materials chemical structure due to oxidation, in other words degradation. This can be assumed with confidence, since the material used to build the models is virgin, without any additives and stabilizers. The dependent variable was the absorbance at a number of wavelengths, while the independent variables were the properties identified for the study: time of exposure and temperature. PLS (Partial Least Squares) chemometric algorithm could derive the empirical spectroscopic models for each polymeric material (PET, ABS, LDPE and PP) after being aged at different conditions. This procedure simultaneously reduced the amount of the spectral data and tried to find a regression over the data. The underlying basis for the models and putative mechanisms of oxidation was based on the observed spectral changes and by applying the principal component analysis (PCA). After collecting the spectra, the modelling procedure was realized using OPUS software. The “Quant 2 Method” option was used to apply a PLS regression on the data points, where the aging parameters were inserted in relation to the NIR spectra by the operator. Furthermore, the models were optimized through processing the data points by the software OPUS to enhance the data fitting. The processing included data pre-treatment. The different pre-treatment methods were semi-automatically selected, where the PLS model (created by OPUS) provided suggestions (by proposing data treatment methods and selecting regions of wavenumbers), after which, the operator

optimized the selection based on the obtained statistical evaluation. As a result, and due to considering two aging factors, two linear models for every polymer were generated; estimated aging time (h) and aging temperature (°C) of each sample could be obtained by mathematical relations.

To get one linear relation between model-predicted parameters and experimental parameters, thermo-oxidative aging time was calculated following Equation (1); once applying the model-predicted aging parameters and a second time applying the experimental aging parameters, finally they were plotted against each other. Thermo-oxidative aging was calculated applying the concepts of chemical reaction kinetics (Murray et al. 2013). It was assumed that the accelerated thermo-oxidative aging roughly corresponds to doubling the aging rate for each increase of 10 °C (Shimada and Kabuki 1968; Boldizar and Möller 2003), hence, a Q10 value of 2 was used in Equation (1) (Mandal et al. 2014; Alassali et al. 2018b; Alassali et al. 2018a). This relation is polymer dependent; hence different models are expected to be obtained for different polymers.

$$t_{(accelerated)} = t_{real} \times Q10^{(T_{aging} - T_{ambient})/10} \qquad (1)$$

Where,

$t_{(accelerated)}$: accelerated aging time (in days),

$t_{(real)}$: the real aging time applied, using accelerated conditions (in days),

Q10: accelerated aging factor (here 2 is considered (Murray et al. 2013)),

$T_{(aging)}$: the aging temperature applied in the treatment process (°C),

$T_{(ambient)}$: the ambient temperature (°C).

The aging-prediction models explained in (Alassali et al. 2018b) (see Figure 1) were used in this study with the aim of cross-validation (Equations 2-5), by predicting real (i.e. experimental) aging parameters from the provided model-proposed aging parameters.

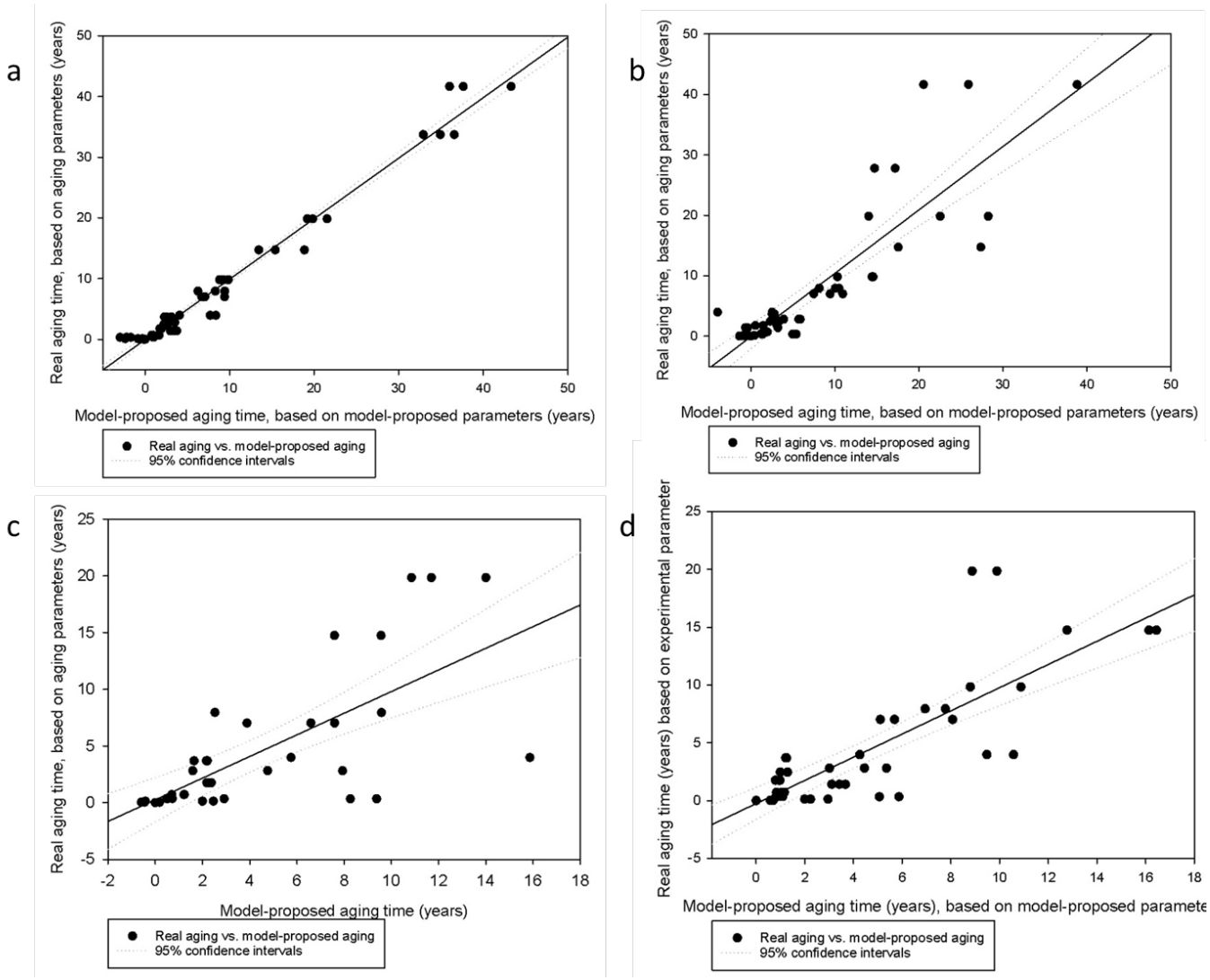


Figure 1. Calculated real aging time versus calculated model-proposed aging time: (a) ABS, (b) PET, (c) PP and (d) PE (Alassali et al. 2018b).

$$\text{ABS: } Real\ ageing = 0.9961\ x\ Model\ predicted\ aging - 0.023 \quad (2)$$

$$\text{PET: } Real\ ageing = 1.049\ x\ Model\ predicted\ aging - 0.0771 \quad (3)$$

$$\text{PP: } Real\ ageing = 1.0832\ x\ Model\ predicted\ aging - 0.341 \quad (4)$$

$$\text{PE: } Real\ ageing = 1.0016\ x\ Model\ predicted\ aging - 0.251 \quad (5)$$

2.3. Description of the models' validation technique

The objective of validating the generated NIR-based aging models, as any other analytical procedure, is to demonstrate that it is suitable for its intended purpose (Broad et al. 2002). Hence, the accuracy of the generated models needed to be evaluated (Pojić et al. 2012), in this case by measuring how well the NIR prediction value match a given reference value that is experimentally obtained. In many applications based on statistical analysis, cross-validation is one of the simplest and most commonly reproduced methods for estimating the prediction accuracy, therefore the error of a model (Hastie et al. 2009). Given a specific and sufficiently large set of data, a fraction of the dataset could theoretically be used for building the model, whereas the other part of the dataset could be utilized as a validation test set. Moreover, there is another method for cross-validation, which is called leave one out cross-validation (Öğütcü et al. 2012). However, it is often the case in studies, like the present one, where the dataset is not big enough to allow for its splitting. In order to overcome this issue and still be able to validate the models in this study, the following 6-steps validation technique was applied to test the models' accuracy:

1. The models to be validated were identified and equations describing each model were derived (Equations 2-5);
2. New, independent sample sets of virgin and pure material were assimilated by the application of thermal aging under defined conditions;
3. The newly created independent test sets were cross-validated with the before generated PLS aging-prediction models;

4. The OPUS software was used to transform the NIR spectra into numerical values;
5. The model-proposed parameters were used to calculate the real aging parameters following the linear mathematical relation created for age-prediction (Equation 2-5);
6. The real aging parameters (as were calculated in step 5) were compared to experimental aging parameters (applied in the lab) and the accuracy was statistically tested.

The above-mentioned steps are described in detail in section 2.4.

2.4. Model's accuracy statistical evaluation by cross-validation

A test set of pure samples was acquired for each material by applying specific aging temperature and aging time in a BINDER oven, as described in Table A in the supplementary data. The test samples were analyzed through a Bruker Optics Fourier Transform near infrared (FT-NIR) spectrometer MPA (Multi-Purpose Analyzer) and acquired spectra were further processed and analyzed with OPUS spectroscopy software from Bruker. The spectra of each test sample (described in Table A) were cross validated with the corresponding aging models resulting in model-proposed aging time (h) and model-proposed aging temperature (°C). Equation (1) was applied to combine both parameters to calculate the model-proposed thermo-oxidative aging time (expressed in years). The real thermo-oxidative aging time values for each polymer were then calculated following the Equations 2, 3, 4 and 5 respectively, which results were compared to the thermo-oxidative aging time calculated from the experimental

parameters (see the data repository, Table A) to calculate the models' aging-prediction accuracy.

The accuracy of age prediction was assessed by calculating the mean error (ME) and mean square error (MSE) (Prestwich et al. 2014; Azadi and Karimi-Jashni 2016), shown in Equation (6) and Equation (7), respectively.

$$ME = \frac{1}{n} \sum_{i=1}^{n} (y_i' - y_i) \quad (6)$$

$$MSE = \frac{1}{n} \sum_{i=1}^{n} (y_i' - y_i)^2 \quad (7)$$

Furthermore, the Root Mean Square Error of Cross-Validation (RMSECV) (Equation (8) (Chai and Draxler 2014)) was calculated for the test samples to characterize the model's prediction accuracy.

$$RMSECV = \sqrt{\frac{\sum_{i=1}^{n} (y_i' - y_i)^2}{n}} \quad (8)$$

where:

y_i = *real thermo-oxidative aging time (using experimental values)*

y_i' = *real thermo-oxidative aging time estimated by the generated model*

n = *number of data points*

2.5. Creating a global polymer aging-prediction model

2.5.1. Including the extrusion effect in the polymer thermo-oxidative aging model

Mechanical recycling of post-consumer plastics consists of sorting the material by polymer type and color, shredding, washing, drying, possibly sorting once more the resulting flakes and then extruding them in order to be transformed into granules. The generated granules can be further molded to form specific consumer products. In the

context of this research, three extrusion cycles were performed. The first extrusion cycle of virgin granules represented the first production process. The second extrusion cycle was considered as a first recycling cycle, and the third extrusion resembled a second cycle of recycling. Mechanical extrusion was performed using HAAKE^{TM} Rheomex CTW 100 OS Twin Screw Extruder.

First, the abovementioned models were applied to predict the age of extruded samples to evaluate for the possibility of using the same models to predict the age (degree of oxidation) of extruded polymers. As the models failed to efficiently and reproducibly predict material aging after being extruded, new aging models were built, this time including three parameters instead of two: heating temperature (°C), heating time (h) and the number of extrusion cycles. These three parameters could not be combined in one equation, therefore Equation (1) was not utilized and a model for each parameter was independently built.

2.5.2. The application of the global aging-prediction models to forecast the degree of waste material oxidation

Plastic samples originated from e-waste were identified, sorted and separately shredded by a Retsch Cutting Mill SM 300 to a size below 4.0 mm. The shredded samples were analyzed by Bruker Optics FT-NIR spectrometer and acquired spectra were further processed and analyzed with OPUS spectroscopy software. The spectra were cross validated with the corresponding aging models, where a model-predicted aging time (h), aging temperature (°C) and number of extrusion cycles for each test sample were respectively provided.

3. Results and Discussion

After aging, changes in the chemical structure were observed, identified by changes in the absorbance intensity of the NIR spectra of differently aged polymers. Multivariate calibration algorithms like PLS correlate spectral intensity (absorbance values) in specified wavelength regions with experimentally obtained aging parameters (time and temperature in this study). The calibration work, entirely achieved by Quant 2 Method. The results were obtained as data points; provided value of the parameter of interest versus the model-predicted value. The applied relation was PLS, hence, the data points generated a linear mathematical relation (shown in Figure 1 and Equations 2-5). For the cross-validation, the method developed to generate the models was retrieved and the spectral data of the test samples were automatically processed (every polymer was separately processed by its own mathematical relation). The software returned values of respective aging parameters, as the model estimates. The model-predicted values were plotted against the real values; this is presented in Figures 2 (a, c) and 3 (a, c), as black stars. The deviation between the plotted test values and model's relation (Figures 2 (a, c) and 3 (a, c), grey circles) could give a quantifiable evaluation of the prediction accuracy.

3.1. Aging time and temperature effects on the calculated thermo-oxidative aging

Thermo-oxidative degradation becomes increasingly important as the exposure temperature and time increase, delivering distinctive changes for each polymer.

Overall, the model-predicted thermo-oxidative aging time increased by increasing each

of the applied aging factors. For all models, the model-predicted aging temperature (°C) was more accurately estimated than the model-predicted aging time (h). Moreover, at higher aging temperatures, the thermo-oxidative aging rate increased more significantly by increasing the experimental aging time. Simultaneously, the aging-prediction accuracy decreased when elevated temperatures were applied, as was indicated by the calculated RMSE values, especially for PET, PP and PE. The higher the RMSE value, the lower the model's accuracy. For PET, RMSE increased from 0.98 for samples aged at 85 °C to 9.01 for samples treated at 120 °C, for PP, RMSE increased from 0.85 for samples aged at 85 °C to 6.51 for samples treated at 120 °C and PE it increased from 1.15 for samples treated at 85 °C to 6.21 for samples treated at 120 °C. This indicates that the prediction accuracy decreases at higher aging temperatures, which could be attributed to the non-linear effect of elevated temperatures on the degradation rate of the tested polymers, where PLS method was assumed.

3.2. Aging models' accuracy assessment by cross-validation

3.2.1. ABS

Figure 2.a shows an accurate estimation of the model-predicted thermo-oxidative aging time of ABS (MSE = 0.90) at an experimental thermo-oxidative age lower than 5 years. Yet, the overall age-prediction accuracy of the selected sample-set showed a slight decrease (MSE = 2.42), which was due to the impreciseness in age estimation for the sample treated at 120 °C for 336 h, possibly due to range of material coloration. Cross-validation was performed by calculating the thermo-oxidative aging time twice:

(I) Using the experimental aging parameters (i.e., time and temperature);

(II) Using the model's estimated aging parameters to calculate relevant real aging

342 time (applying Equation (2); y = 0.9961 x + 0.023).

343 Values obtained from (I) and (II) were simultaneously plotted (see Figure 2.b). There is a
344 robust consistency in the values; they were generally overlapping. For the material aged
345 at 120 °C for 336 hours, the calculated model-based thermo-oxidative aging time was
346 higher by ~2 years for one sample and by ~4 years for another, indicating a range of
347 variation, yet less than what was observed by the rest of tested polymers. This variation
348 could be attributed to the possible non-linear oxidation behavior of the material, which
349 was interpreted by linear regression methods. The bias of the values was however
350 negligible (i.e., ME = 0.21). The overall RMSECV value (i.e., 1.51) shows a good age
351 estimation model.

352 *3.2.2. PET*

353 The cross-validation conducted on PET test samples indicated more compliance in the
354 aging region ≤11 years; model-predicted aging time varied for samples exposed to
355 thermo-oxidative aging parameters simulating aging time higher than 11 years (see
356 Figure 2.c). A high range of error between experimental thermo-oxidative aging time and
357 model-predicted thermo-oxidative aging time was obtained for the material aged at 120
358 °C for 408 h. The thermo-oxidative aging time calculated from the model's calibration
359 equation (y = 1.049 x – 0.0771 for PET) was plotted together with the real thermo-
360 oxidative aging time (calculated as per experimental parameters) to measure the degree
361 of agreement (see Figure 3.d). At aging temperature of 85 °C, the model showed high
362 prediction accuracy for all tested aging duration (bias values ranging between -0.94 and
363 1.01 only). For the thermo-oxidative aging at 120 °C, the aging time prediction accuracy
364 had an inverse relationship with the aging duration, where it was the lowest for the

365 material treated at 120 °C for 408 h. Generally, it was observed that the age prediction
366 accuracy decreased with increasing the severity of aging (see Figure 2.d). When the
367 samples treated at 120 °C for 408 h were excluded, the cross-validation of the PET
368 aging model provided high accuracy, with ME value of 0.64 and MSE value of 4.48. Yet,
369 the age-prediction accuracy of the PET aging model decreased significantly by cross-
370 validating the mentioned sample; the MSE increased to 46.96, with an overall cross-
371 validation RMSE value of 6.85. As well, this could be explained by the stability of PET
372 under the applied aging conditions, which did not result in a linear aging behavior as
373 estimated.

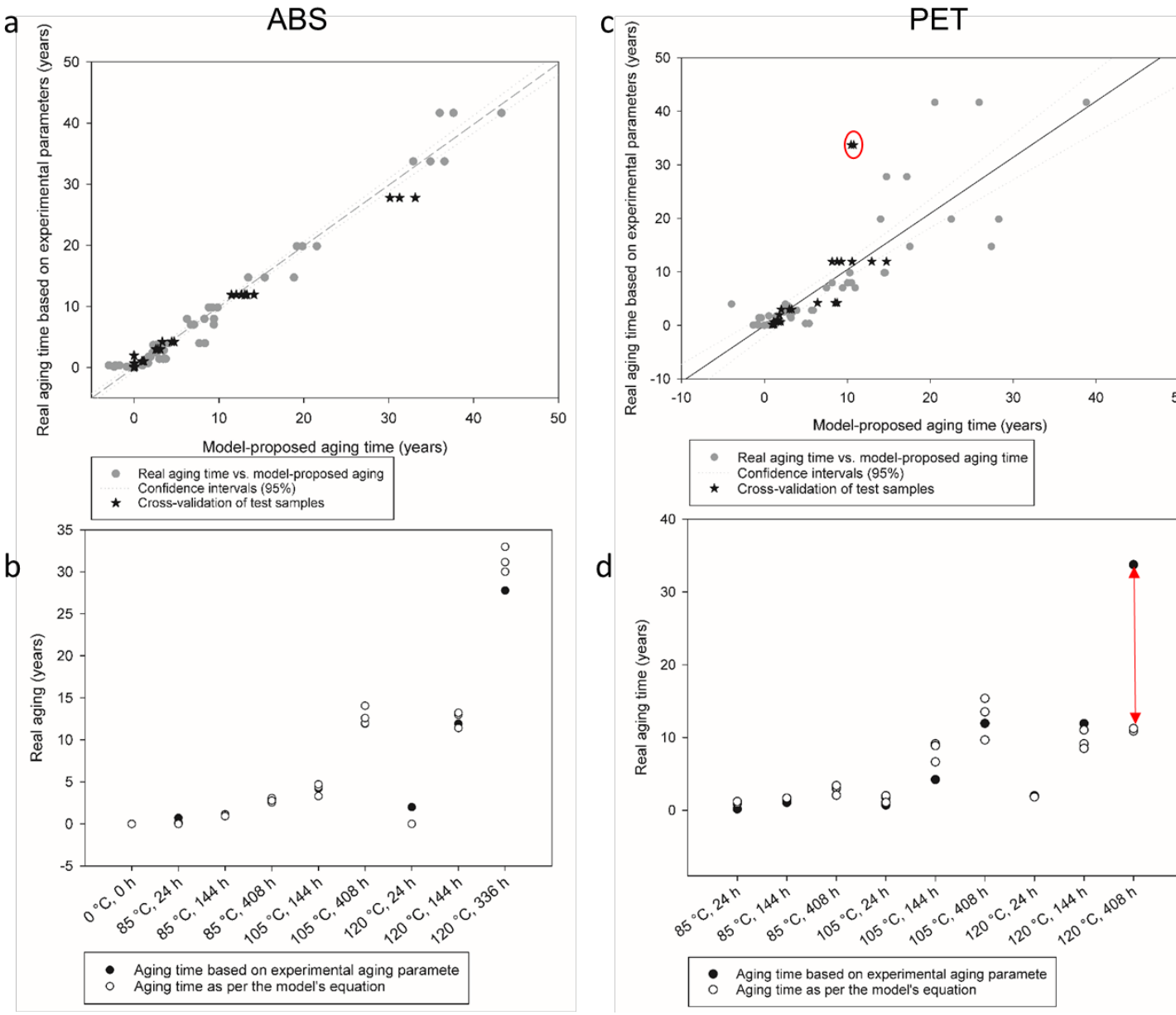


Figure 2. Left (a, b) for ABS and right (c, d) for PET: (a, c) Test samples cross-validated with the aging model, (b, d) comparison between real thermo-oxidative aging time obtained from experimental parameters and real thermo-oxidative aging time obtained from the generated regression model.

3.2.3. PP

The PP aging model had a low collinearity, R^2 = 0.64 (see Figure 1 and Equation (4)),

yet this value was sufficient for a screening with wider error intervals (Krapf 2013). As shown in Figure 3.a, higher aging-prediction accuracy of the test samples was obtained for those that underwent short thermo-oxidative aging period (≤ 2 years). The real thermo-oxidative aging of test samples was frequently accurately predicted applying the model's formula (y = 1.083 x – 0.341), except for samples treated at 120 °C (see Figure 3.b). The MSE of the cross-validation for all samples treated at 85 °C and 105 °C was 2.0, which increased by about 6 folds when the samples treated at 120 °C were included (i.e., MES value reached 11.83). This indicates that with increasing the severity of the treatment, age-prediction accuracy decreases, while the effect of aging temperature was more significant than the aging time. The overall cross-validation RMSE (3.44) value is yet acceptable.

3.2.4. PE

As indicated in Figure 1 and Equation (5), the collinearity of the relation between experimental thermo-oxidative aging time and model-predicted thermo-oxidative aging was relatively low for PE (i.e., 0.66). However, the PE aging model in comparison to real aging data showed good model estimation, with wider range of prediction error. As shown in Figure 3.c, the cross-validation of test samples falls in the region of model's confidence interval, except for the samples aged at 105 °C for 408 h and at 120 °C for 144 h, where the calculated thermo-oxidative aging for both conditions, applying Equation (1), is 11.9 years. The model's anticipated aging was overestimated (by 2 to 5 years) for the samples aged at 105 °C for 408 h, where an age underestimation (by 6 to 8 years) was provided by the PE aging model for the samples aged at 120 °C for 144 h.

Following the regression model generated formula ($y = 1.016\ x - 0.251$), the calculated real thermo-oxidative aging time showed negligible variations in comparison to the experimental thermo-oxidative aging time for all test points, except for the above mentioned two samples (see Figure 3.d). The overall cross-validation ME was insignificant (i.e., 0.0182), yet the overall age-prediction accuracy was lower than what was provided by the ABS aging model (MSE of 6.01). The calculated RMSE value for the cross-validated samples indicated higher oxidation-prediction accuracy (i.e., 2.45) in comparison to PET and PP aging models.

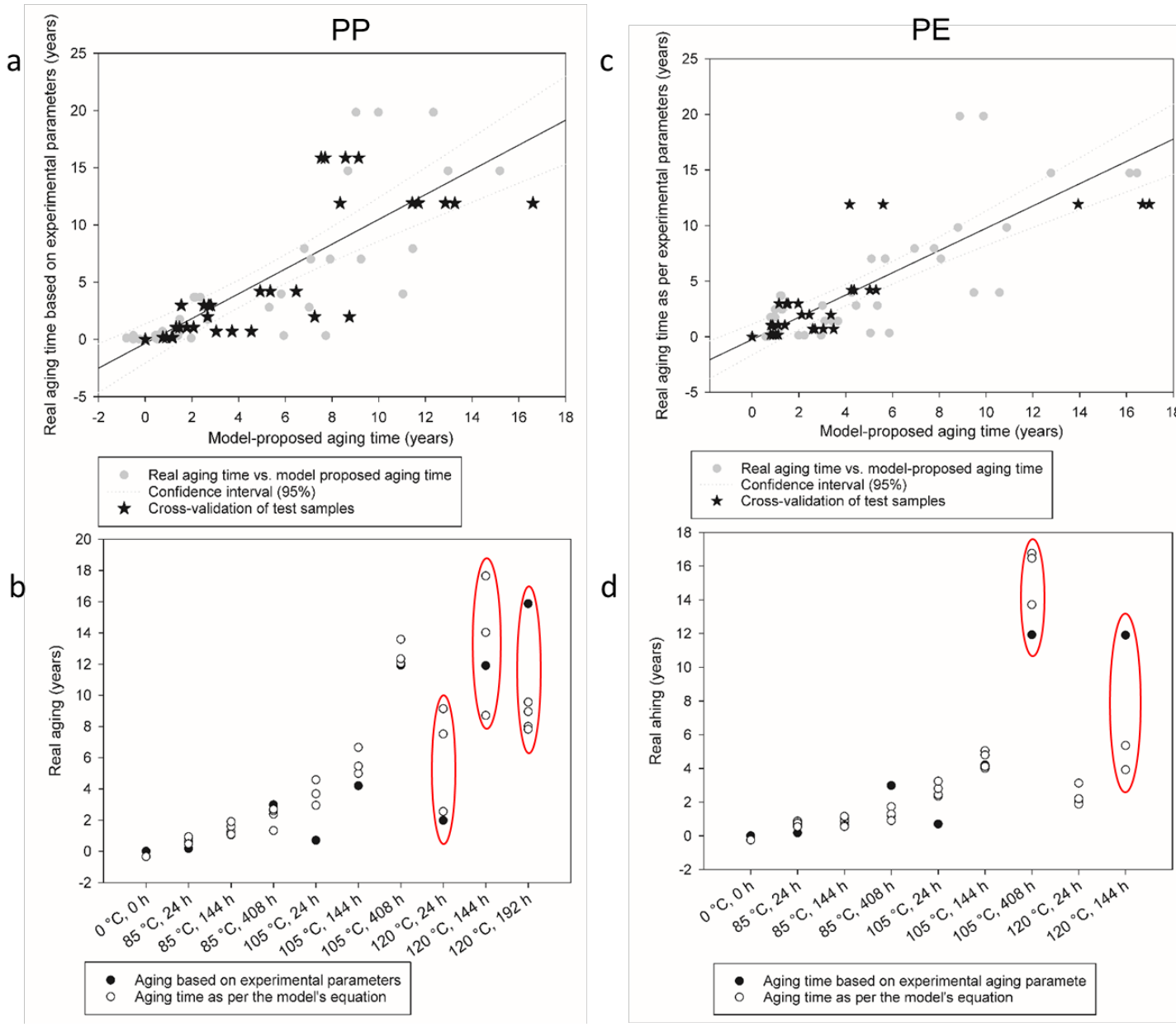


Figure 3. Left (a, b) for PP and right (c, d) for PE: (a, c) test samples cross-validated with the aging model, (b, d) comparison between real thermo-oxidative aging time obtained from experimental parameters and real thermo-oxidative aging time obtained from the generated regression model.

3.3. Comparison of the quality of the aging-prediction models

The aging-prediction models of different polymers (i.e., ABS, PET, PP and PE) were assessed by calculating the RMSECV of the test sets described in Table A in the supplementary material, which is calculated by weighing the deviation of the experimental thermo-oxidative aging values from the model's calculated thermo-oxidative aging time (using the created regression models in Figure 1). The RMSECV value calculated for the ABS aging model (1.51) was lower than the values calculated for PE and PP aging models (2.45 and 3.44, respectively), while the highest value was obtained for PET aging model (6.85). These results indicated that the performed cross-validation provided the best fitting for ABS aging model, however the model's quality decreased for other polymers aging models, to be the lowest for the PET aging model. Degradation process occurs due to the influence of thermal, chemical, mechanical, radiative and biochemical factors; resulting in deterioration of mechanical and physical properties of polymers. The degradation occurs due to changes in the main backbone or side groups of the polymer (Venkatachalam et al. 2012). The degradation of PE and PP could result in chain breakage and formation of radicals, which are easily oxidized. Therefore, it is expected to obtain an increase in C═C, C═O or C—OH bonds in the generated NIR spectra after material aging, in addition to the increase in the concentration of methyl groups (Alassali et al. 2018b). However, the models indicated that the oxidation rate of PE and PP is slower that what the model would predict, which resulted in low collinearity and reduced age estimation accuracy. In PET, the aromatic ring connected to a short aliphatic chain provides stiffness to the molecule. The lack of segmental mobility in the polymer chains results in relatively high thermal stability

443 (Venkatachalam et al. 2012). Nevertheless, the thermal degradation of PET was
444 reported to take place leading to cyclic oligomers and chain scission, resulting in vinyl
445 ester and acid end-groups (Holland and Hay 2002). As per the generated aging
446 prediction model for PET, the model aging time and aging temperature estimation had a
447 range of values, providing that the chemical stability of the polymer resulted in
448 inhomogeneous degradation performance. On the other hand, degradation of the
449 elastomeric polybutadiene phase (i.e., containing C═C) in ABS is initiated by hydrogen
450 abstraction from the carbon α to unsaturated bonds, resulting in hydroperoxide radicals
451 and producing carbonyl and hydroxyl products. Furthermore, degradation of the
452 styrene–acrylonitrile phase in ABS takes also place by thermo-oxidative degradation, yet
453 in lower rate (Tiganis et al. 2002a). Generally, the age-prediction model of ABS showed
454 a high accuracy and optimized linearity, which is attributed to the linear relation between
455 the degree of degradation of the polymer and the aging severity, which fits with the
456 linear regression methods being applied.
457 Comparing the RMSECV values of the test samples to what was obtained by the original
458 aging model described by (Alassali et al. 2018b), lower values were obtained for ABS,
459 PE and PP, whereas it was higher for PET. This could be attributed to the limited
460 number of test samples used in the cross-validation in comparison to the data points
461 used in constructing the models; having few samples, which were unable to capture the
462 model's trend, allowed for an elevated RMSECV value. Despite the bias in the predicted
463 thermo-oxidative aging time, the four models were able to provide an age estimation
464 tool.

3.4. The application of the original age-prediction models as a tool of age estimation of polymer samples

3.4.1. Extruded samples

The utilization of the age-prediction models was incompatible to predict degradation (i.e., aging) of extruded samples. As shown in the data repository, Table B, the predicted aging parameters were below zero, especially for ABS and PET. This was attributed to the great change in color of these two polymers after extrusion (see Figure 4).

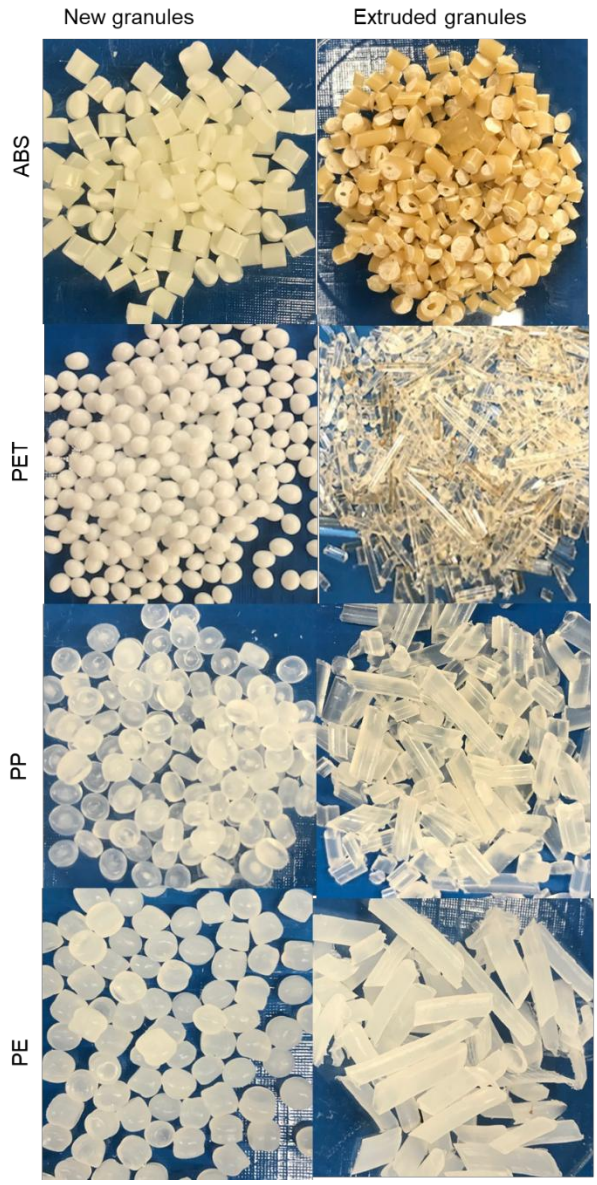


Figure 4. The change of color of polymers after extrusion

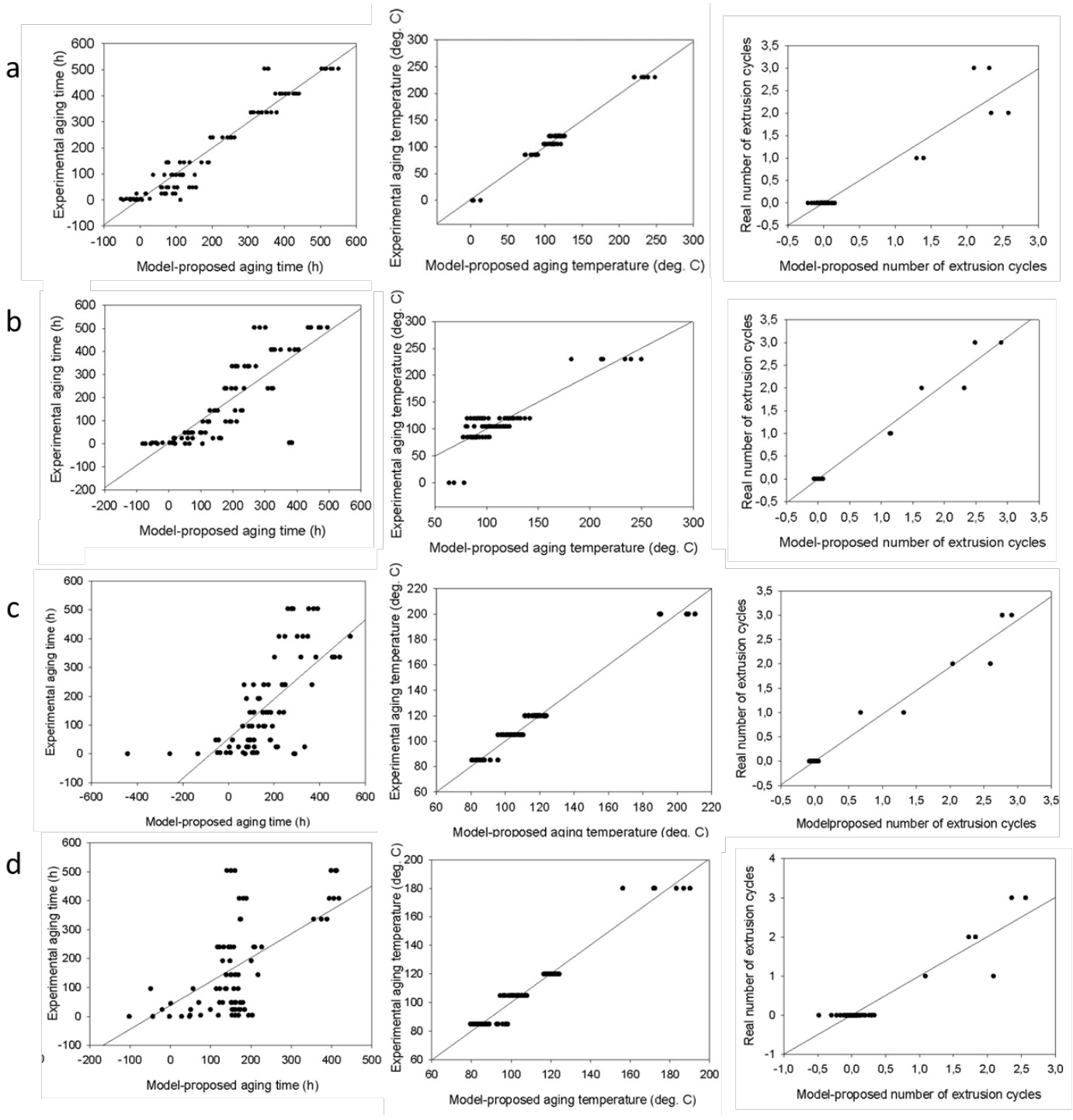
3.4.2. Waste samples

As the data in the data repository, Table B showed, the model predicted negative aging temperatures for samples PP-2 and PP-5 (from Table 1), which resulted in a negative thermo-oxidative aging time (years) estimation. The predicted aging temperature of PP-1, PP-3, PP-4 and PP-6 was too high (above 1000 °C), which resulted in an aging time overestimation, especially for PP-6. This could be attributed to the effect of extrusion

and molding taking place during production, which has accelerated the thermo-oxidation of the polymers and consequently resulted in intense coloration. For ABS, the aging temperature of the material was mostly estimated to be negative, resulting in negative values of thermo-oxidative aging time (years). The results support what was obtained in extruded samples, where the granules color changes significantly by extrusion and possibly molding. Not to forget the possible impact of stabilizers and antioxidants in the plastics formulations to provide protection during processing or fabrication into finished product (Dopico-García et al. 2011).

3.5. Building a global polymer aging model

In previous models, the effects of aging time and temperature were accounted. However, in the production phase, polymers undergo harsher processing conditions, where melting takes place during both, extrusion and molding. For this reason, the initial models (including time and temperature factors) did not have the capacity to properly predict thermo-oxidative behavior of consumer products (plastics derived from electrical waste). Hence, the factor of number of extrusion cycles was additionally evaluated. For this study, the number of extrusion cycles was restricted to 3. As can be seen in Figure 5, for each material (i.e., (a) ABS, (b) PET, (c) PP and (d) PE), three equations were extracted, one to predict the aging time (h), a second one to predict the aging temperature (°C) and a third one to predict the number of extrusion cycles (from left to right in Figure 5).



500

501 Figure 5. The global aging models created to predict materials' aging time (h), aging

502 temperature (°C) and number of extrusion cycles (from left to right) for (a) ABS, (b) PET,

503 (c) PP and (d) PE.

504 The generated models were evaluated by calculating the RMSE for each aging
505 parameter, which was calculated by accounting for the difference between the model-
506 proposed value and the experimental value for virgin test samples. The model
507 constructed for ABS was the most efficient in comparison to PET, PP and PE (see
508 Figure 6). The model was less accurate in estimating the aging time (h) in comparison to
509 all other parameters (components), for all tested materials (ABS, PET, PP and PE). The
510 RMSE value was, however, the lowest for ABS (47.48) and the highest for PP (125.56)
511 (Figure 6.a). Aging temperature prediction was significantly more precise for ABS, PP
512 and PE, where the RMSE of the PET model showed a significant increase (lowering the
513 model's estimation accuracy) (Figure 6.b). For all tested polymers, the estimation of the
514 number of extrusion cycles was considerably accurate (see Figure 6.c). This could be
515 attributed to the limited number of extrusion cycles applied (ranging from 0 to 3).
516 Moreover, the R^2 value was calculated for all parameters of the global aging models
517 (see Figure 6.d). For ABS the relation between experimental aging parameters and
518 model-proposed aging parameters was mostly collinear (i.e., 0.92 for aging time
519 component, 0.98 for aging temperature component and 0.91 for number of extrusion
520 cycles component). The collinearity of the relation between real aging time and model-
521 proposed aging time for PET was relatively low (0.66), yet allowing for the application of
522 approximate calibration (Krapf 2013). The R^2 value increased significantly for the
523 extrusion cycle component for the PET global aging model to reach 0.98. For PP and
524 PE, the global aging model indicated poor aging time estimation, the R^2 values for the
525 aging time component for PP and PE were 0.46 and 0.40, respectively. Yet, for the
526 aging temperature component and number of extrusion cycles components, the R^2
527 values were both 0.98 for PP, indicating the model's applicability. The R^2 values were

similarly high for PE (i.e., for aging temperature component: 0.95 and for number of extrusion cycles component: 0.90), allowing for the application of the model for different purposes, covering quality insurance applications.

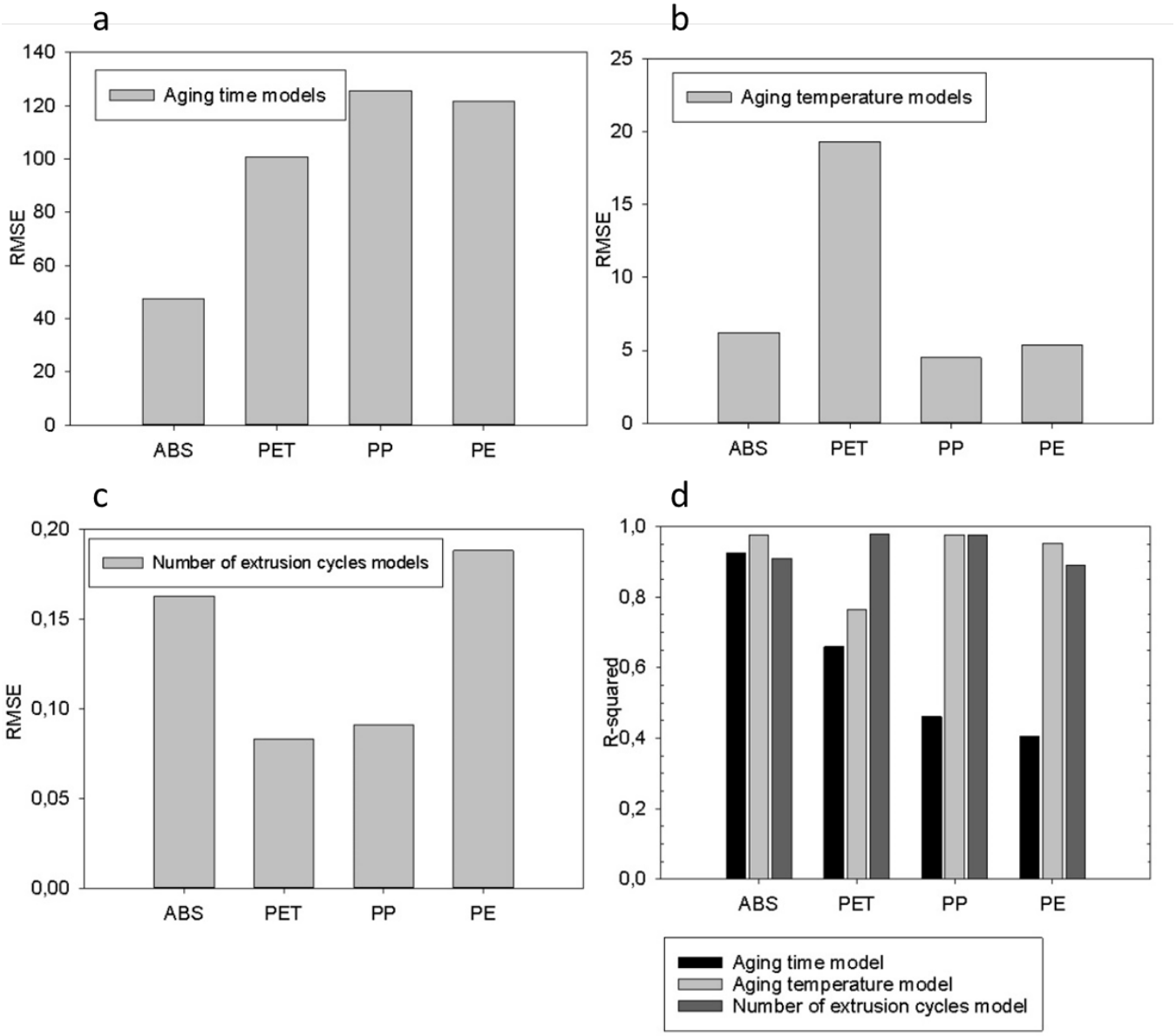


Figure 6. Evaluation of the global aging models for ABS, PET, PP and PE; (a) RMSE for the aging time component, (b) RMSE for the aging temperature component, (c) RMSE

for the number of extrusion cycles component and (d) R^2-value for the three mentioned components of the aging models.

3.5.1. The application of the global models to estimate the age of waste samples

The aim of creating global aging models is to develop a quality control tool to assess the quality of the recycling input material and, therefore, to improve the quality of recycled material. The model-proposed aging time, aging temperature and number of extrusion cycles were used to calculate the real aging time, aging temperature and number of extrusion cycles following the equations provided by the generated global models. It can be clearly seen from Table C (in supplementary material) that the models failed to estimate the aging duration of the material, where values were either below zero (especially for ABS polymer) or too high (PP-4 and PP-6). The predicted aging temperature for ABS was 3 to 5 folds higher than that for PP, which is ascribed to the material coloration. The estimation of the number of extrusion cycles for both materials was reasonably acceptable; positive values in acceptable ranges were obtained.

3.6. Economic and environmental considerations

This research has significant practical, economic and environmental consequences. Life Cycle Analysis assessed the environmental benefits of plastic recycling, compared to disposal in waste-to-energy facilities, and results were controversial (Huysveld et al. 2019; Faraca et al. 2019; Khoo 2019). Considering the economic outcomes, plastic recycling could easily become economically too expensive (if the recycled product exhibits low features and consequently low market value) to achieve a net benefit compared to disposal. However, as a general statement, policy interventions supporting

plastics recycling, as well as technological changes and a transparent communication and collaboration between all stakeholders are needed to enhance the recycling process (Hahladakis and Iacovidou 2019). Nowadays, recycling is usually associated with higher economic efforts than incineration due to higher labor needs and enhanced transport and sorting costs, hence, proposing an available technique (NIR sorting) in order to enhance the quality of plastic recycling should be of a great significance in industrial applications.

4. Conclusions

The aim of this study was to validate plastic aging-prediction models for their industrial applicability, especially for material quality identification for recycling. A recent study (Faraca et al. 2019) proved that if high quality of the recycled plastic is achieved, both environmental savings and financial revenues are possible. Therefore the here presented aging-prediction models could be of great help for material quality identification in plastic sorting facilities.

The generated models showed effectiveness in age-estimation of experimentally aged polymers. The ABS aging-prediction model was the most accurate among all tested polymers, which was attributed to the quantifiable changes in the chemical structure through aging. For other polymers (i.e., PET, PP and PE), although the accuracy of age-estimation was lower, the models could still be applicable to estimate the age of material, which was aged under controlled conditions. The original aging-prediction models provided negative aging values for extruded ABS and PET samples. Consequently, negative thermo-oxidative aging duration were calculated. Hence, new aging-prediction models (i.e. identified as global aging-prediction models) were created,

including the factor of ‘number of extrusion cycles’. Generally, these models exhibited a good collinearity for the ‘aging temperature’ factor and the ‘number of extrusion cycles’ factor. However, the ‘aging time’ factor of PET, PP and PE provided a collinearity lower than 0.70. The models’ estimation accuracy was also evaluated by calculating the RMSE for each of the mentioned factors. The aging time factor was far from zero for all tested polymers, yet the lowest value was obtained for ABS (47.48) and the highest for PP (125.56). This was replicated when plastic waste samples were tested; the aging time estimation was mostly negative in value, especially for ABS material. The estimations of ‘aging temperature and the ‘number of extrusion cycles’ were always positive in values, where the most reasonable aging factor estimation was the ‘number of extrusion cycles’. All in all, the generated models need to be extended to include a wider range of data, where further aging parameters, e.g. UV radiation (Picuno et al. 2019a) should be considered for the aim of including all possible forms and degrees of degradation.

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