Thermal stability of natural dye lakes from Canadian Goldenrod and onion peel as sustainable pigments

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ABSTRACT
The transformation of petrol based polymers towards more sustainable and biodegradable materials includes the development of bio-based pigments for mass coloration. Dye lakes prepared from aqueous plant sources could allow a substitution of synthetic pigments with bio-based material. The shaping of thermoplastic polymers includes a melt extrusion step at higher temperature e.g. 245 °C for polyamide 6, thus suitable natural dye lakes must exhibit sufficient thermal stability. Thermogravimetric analysis and differential scanning calorimetry experiments with aluminium based dye lakes from canadian goldenrod and onion peel demonstrated thermal stability of the lakes up to 245 °C. In isothermal treatment experiments the onset temperature for colour change was found near 220 °C, where only minor colour changes CIELab colour coordinates were observed. Thermally treated dye lakes also were tested in miniaturised dyeing experiments using wool as substrate. Remarkably the colour of the test dyeings on wool samples remained constant up to a treatment temperature of 245 °C. The thermal stability of the studied natural dye lakes was found sufficient to withstand temperatures applied in melt extrusion of polylactic acid or polyamide 6. Thus substitution of synthetic pigments by selected dye lakes from renewable resources could be a promising step towards greener polymers.

1. Introduction
Concerns about disposal of used synthetic polymers and release of micro-plastics into the environment have led to an increasing awareness for all aspects of material sustainability and recycling.(European Commission, 2019), (Scudo, 2017), (González-Pleiter et al., 2020) While substantial research efforts have led to achievements in sustainability of polymer material (Li et al., 2009), only limited research activities have addressed pigments used to colour polymeric material(Srisuk et al., 2020). For 2019 the annual production of pigments can be estimated with 10² metric tons, mainly TiO₂ and carbon black. The volume of other inorganic and organic pigments still accounts for nearly 1 million tons per year(Ceresana, 2020). During biological mineralisation of biodegradable polymers this amount of mainly non-biodegradable pigments will be released into the environment.

Prior to the development of cheap and brilliant synthetic organic colorants, natural colorants and pigments were used for purposes of coloration almost exclusively(Schwepppe, 1993). Plant material represented the main source for extraction of dyes, to a minor extent, insects (lac, cochenille) and snails (tyrian purpur) were utilised for dye production(Bechtold and Mussak, 2009). Organic and inorganic pigments were prepared by artists for their artwork.(Campanella et al., 2018), (Bourhis et al., 2011) These organic pigments often were prepared as insoluble dye lake(Pronti et al., 2018). Such lakes were prepared as metal complexes by addition of a metal salt to the solution of the extracted natural dye,(Jimtaisong, 2012), (Wongwad et al., 2012) Extracted water soluble dyes were used for coloring of clothing, mainly wool, silk, linen, hemp, and cotton. Frequently the application of the dye extract included mordanting(Manian et al., 2016). By addition of a mordant (e.g. metal salts, tannin) the binding of the dye to the fibre was strengthened and in many cases higher wash fastness of the dyeing could be achieved(Rather et al., 2016). Metal mordanting led to formation of a dye-metal complex, which remained adsorbed or deposited at the fibre surface. The direct use of dye lakes for purposes of textile dyeing was not possible, as dye lakes do not exhibit an affinity to the fibre substrate. Thus their application in textile dyeing requires the addition of a binder system to fix the pigment on the fibre surface, e.g. polyacrylate or polyurethane based binder polymers(Bechtold and
The invention of synthetic polymers occurred later than the development of the synthetic dyes and pigments, thus coloration of synthetic polymers exclusively relied on synthetic pigments. While bio-based and biodegradable polymers e.g. polyactic acid (PLA) or poly-hydroxybutyric acid (PHBA) have been developed as alternative for non-biodegradable petrol based synthetic polymers, the replacement of synthetic colorants by plant based material for mass coloration of polymer material still is almost unexplored (Ujjin and Jantip, 2012).

Use of plant dyes e.g. indigo, madder and nut shell extracts already has been studied for dyeing of textiles made from synthetic polymers. (Mirjalili and Karimi, 2013), (Raisanen et al., 2001) Also dyeing of PLA with lycopene has been reported in the literature (Asadi and Pirsa, 2020). Coloration of solvent casted polycarbonate films by natural melanin has been studied as UV-blocking additive (Wang et al., 2018). Recently concentrated dye lakes have been proposed as an intermediate product to re-introduce plant dyes into technical textile dyeing operations (Mahmud-Ali et al., 2012), (Leitner et al., 2012) For this purpose an efficient procedure to form aluminium salt based dye lakes has been reported, which bases on aqueous extraction of plant material followed by precipitation of the dye lake (Mahmud-Ali et al., 2012), (Leitner et al., 2012).

The biodegradation of synthetic biopolymer wastes has been considered in the literature thoroughly (Saracusa, 2019). After the organic polymer matrix has been biodegraded into small fragments or has been mineralised completely the rather persistent organic pigments will be released as insoluble particles. Often decolourisation of synthetic dyes is taken as an indication of biodegradation, however formation of colourless products require serious consideration of potential hazards arising from the degradation products (Ali, 2010), (Khan et al., 2013).

The preparation of a dye lake could be an economically and ecologically useful route leading to a sustainable plant based pigment. These pigments then could be applied in mass coloration of plastics e.g. PLA, PP, PA, provided the pigments exhibit sufficient thermal stability to withstand the temperatures of melt extrusion without decomposition. With biodegradation of the polymer matrix the dye lake will be released into the environment. Representative values for the aluminium content in the dye lake are between 2 %wt and 5 %wt Al (Mahmud-Ali et al., 2012). When a pigment content of 3 %wt is used in polymer coloration, the total aluminium content in the polymer will be between 0.6 %wt and 0.15 %wt which will corresponds to 600 ppm and 1500 ppm of aluminium respectively. Due to its abundance the plant toxicity of aluminium has been investigated extensively, major factors being soil acidification, type of aluminium source and aluminium tolerance of a plant. (Neenu and Kathika, 2019), (Bojorquez-Quintal et al., 2017)

The aluminium content in soil ranges between 1 %wt and 25 %wt, however its exceptionally low solubility in the pH range of 5–9 limits the aluminium concentration in water to 60–300 μg L⁻¹ in water and around 1 μg L⁻¹ in sea water (Barabasz et al., 2002). The biodegradation of the aluminium lake will end up in the precipitation of Al(OH)₃, which thus remains practically insoluble, as long as no soil acidification occurs.

The introduction of plant based dye lakes in form of a colour master batch thus requires information about the thermal stability of natural dye lakes at the respective temperatures applied during polymer extrusion (Pajraoui et al., 2019).

Quercetin is a major constituent in plant extracts from onion peel or canadian goldenrod (Schwepp, 1995). For quercetin the presence of a quercetin-aluminium(III) complex with Mn stoichiometry of 1:1 has been proposed for neutral to slightly acidic solution. (Bourhis et al., 2011), (Guibin et al., 2005), (Puria et al., 2014).

The thermal stability of selected natural flavonoid compounds i.e. quercetin has been studied extensively. Analysis of various quercetin hydrates with differential scanning calorimetry and variable temperature-powder X-ray diffraction indicated a phase of dehydration and molecular rearrangement at temperatures up to 110 °C and a second phase transition between 250 and 270 °C, followed by melting above 270 °C (Borghetti et al., 2012). Similar results also were obtained with thermogravimetric and photovisual analysis of quercetin (da Costa et al., 2002). Quercetin-3,4′-O-diglucoside and quercetin-4′-O-glucoside account for 85–87% of total flavonol components in onion (Lu et al., 2011). Different thermal stability was reported for quercetin mono- and di-glycosides, where dependency of the thermal stability on the position of the sugar moiety was observed (Rohn et al., 2007). The final product of the thermal deglycolisation then was the aglycone quercetin.

In this work we present to our knowledge for the first time a systematic investigation of the thermal stability of two aluminium based plant dye lakes as model substances for plant based pigments. Thermal stability was studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). An adapted experimental TGA methodology was used to assess colour degradation as function of temperature. Colour change of the thermally processed dye lake was investigated with determination of the CIELab colour coordinates and thermal decomposition was monitored by FTIR analysis. The thermally treated pigments were dissolved for miniaturised dyeing experiments to indentify temperature dependent losses in colour strength and shift in colour coordinates. The presented results report a first study of the temperature stability of representative dye lakes. In addition a new methodology is presented, how to determine the temperature tolerance of a natural dye pigment under simulated thermal conditions of polymer melt extrusion.

2. Experimental

2.1. Chemicals and material

Air dried yellow onion peel (Allium cepa) was collected during packaging of onions at a local onion producer. Canadian goldenrod (Solidago canadensis) was collected from wild growth in the western region of Austria, air dried and stored in dark. The full plant including stem, leaves and flowers was used for extraction.

Analytical grade chemicals were used for the dyeing processes: Oxalic acid H₂C₉O₄.2H₂O (Roth, Karlsruhe, Germany), FeSO₄.7H₂O (Zeller GmbH, Hohenems, Austria) and alum KAl(SO₄)₂.12H₂O (Roth, Karlsruhe, Germany). Technical grade Al₂(SO₄)₃.14–15 H₂O and NaOH 50 %wt (Deuring, Hoerbranz, Austria) were used for lake production.

The dyeing experiments were carried out on bleached wool yarn (metrical number 28/2 m/g; 71.4 tex) kindly supplied by Schoeller GmbH & CoKG (Hard, Austria). The wool yarn was used in form of small hanks.

2.2. Plant material – extraction of dye and formation of lake

A mass of 2.1 kg air dried onion peel was placed in an open cotton bag and extracted with 45 L soft water for 30 min at 80 °C. During extraction temperature was allowed to decrease to 60 °C. Photographs of the extraction are shown in the supplementary information, Fig. S1 and Fig. S2. Then 200 g Al₂(SO₄)₃.14–15 H₂O were dissolved in 1.2 L soft water and added to the plant extract (40 L) to precipitate the aluminium lake at a concentration of 5 g/L Al₂(SO₄)₃.14–15 H₂O. The solution pH of 2.4 then was adjusted to pH 5.3 by addition of NaOH solution. The lake was allowed to settle for 2 day at room temperature. The precipitate was collected by filtration using a paper filter (Kaffeepapier Melitta Bambus 60% 1 x 6, Melitta, Minden, Germany) and dried at 60 °C in a laboratory oven. A mass of 199.12 g dried aluminium lake was obtained after drying.

The full plant of air dried canadian goldenrod was used including buds, upper part of stem and leaves. Hot water (90 L, 90 °C) was used for the extraction of 4.5 kg of plant material. During the 30 min period of extraction the solution was allowed to cool down to 60 °C. At the end of the extraction step the plant material was removed and the extract was filtered through a cotton fabric. Pre-dissolved Al₂(SO₄)₃.14–15H₂O (270 g in 2 L) was added to 85 L of extract, to achieve a final
concentration of 3 g/L Al₂(SO₄)₃·14–15H₂O. The pH value was adjusted to pH 7.1 by addition of NaOH solution. The collection of the precipitate was performed after 1 day of settling analogous to the procedure described above for the onion peel. A total mass of 287.4 g of dye lake was obtained after drying.

For characterisation of the thermal stability and the dyeing experiments the dried lakes were milled to a fine powder.

2.3. Thermal analysis

The DSC curves of specimens were measured on a Differential Scanning Calorimeter (DSC 3, Mettler Toledo, Columbus, USA) under nitrogen flow of 50 mL/min in the temperature range of 25–300 °C with heating and cooling rates of 10 °C/min, on samples in 40 μL aluminium crucibles sealed with pierced lids. The data were analysed with the on-board software STAREe Evaluation Software (Version 15.01).

Thermogravimetric Analysis (TGA) was performed using the Thermogravimetric Analyser TGA 2 (Mettler Toledo, Columbus, USA). Thermograms were recorded in the temperature range of 25–800 °C under N₂ atmosphere at a heating rate of 10–20 °C/min. The data were analysed with the on-board software STAREe Evaluation Software (Version 15.01).

2.4. Dyeing experiments

For the miniaturised dyeing experiments a mass of 15 mg of powdered dye lake was dissolved in 0.3 mL 0.079 M oxalic acid in a test tube and filled to 6 mL dyebath volume with warm deionised water. A mass of 300 mg wool yarn then was dyed in the solution. Thus liquor ratio 1:20 (1 g of samples/20 mL of dyebath) was used for the dyeing experiments. The mixture was heated in a water bath for 30 min at 60 °C to complete dyestuff dissolution. The wool sample then was immersed into the dyebath, which then was heated to 95 °C by means of a water bath. After dyeing for 15 min at 95 °C, a concentrated solution of KAl(SO₄)₂·12H₂O (50 g/L) was added to the dyebath, to achieve the final concentration of 5 g/L mordant. The total amount of mordant used thus corresponds to 10% of sample weight. The dyebath was kept at 95 °C for further 30 min. After cooling down to approximately 60 °C, samples were removed from the dyebath, rinsed three times for about 5 min in cold water and dried at room temperature for 24 h. The absorbance of the exhausted dyebath was measured after appropriate dilution with deionised water using a 10 mm cuvette and a diode-array spectrophotometer (Zeiss CLH 500/MCS521 UV/VIS, Carl Zeiss, Jena, Germany).

2.5. Spectroscopic analysis and colour measurement

The powdered dye lake was pressed to a pellet using KBr. The Fourier Transform Infrared Spectra (FTIR) were recorded in transmittance mode on a Bruker Vector 22 instrument (Karlruhe, Germany). A total of 50 scans were collected for each spectrum from 600 cm⁻¹ to 4000 cm⁻¹ at a scan resolution of 2 cm⁻¹. For photomicrographs of the lakes 3D-laser scanning confocal microscopy (VK-X200 Keyence, Osaka, Japan) was used.

Diffuse reflectance of the thermally treated dye lakes and of the dyed wool samples was measured in the range of 400–740 nm to calculate the CIELab colour coordinates and the Kubelka-Munk K/S value at 400 nm (Konica Minolta Spectrophotometer CM-3610d, sample diameter 4 mm, geometry d/8°, Konica, Japan). The L*, a*, b* values were calculated for illumination D65. Measurements were done in triplicate. Values are given as mean and standard deviation (error bars). The L* coordinate describes the lightness of a sample (L* 100 = white, 0 = black), the a* coordinate the position on the red – green axis (positive a* = red, negative a* = green) and the b* coordinate the position on the yellow – blue axis (positive b* = yellow, negative b* = blue). The K/S value describes the overall colour strength of a pigment.

Melt extrusion of thermoplastic polymers requires considerably high processing temperatures, e.g. 245 °C for polylamide 6 (PA 6) or 180–200 °C for polylactic acid (PLA). Thus thermal stability and colour change of representative natural dye lakes was investigated up to a temperature of 245 °C.

Aluminium based dye lakes from onion peel (Allium cepa) and Canadian goldenrod (Solidago canadensis) were used as representative lakes. In Europe Canadian goldenrod grows extensively on ruderal areas and possible utilisation as crop would contribute to the control of this invasive alien species. Besides extraction of phytopharmaceutics Canadian goldenrod also is of interest for preparation of infusions.(Zihare and Blumberga, 2017) (Weber, 2003) Loose onion peels are removed by farmers during packing of onions as food product. Thus no significant health hazards are expected to arise from the plant material used in this study or its aqueous extracts.

Extraction must be performed with water exclusively, as for both plants the major part of plant material will remain as solid residue after extraction and thus can be composted(Bechtold et al., 2006). The environmental impact of the lake preparation will be low as only a hot water extraction is required. Aluminium salts were selected for the lake formation and these salts also are widely used for flocculation in drinking water preparation. A concentration of up to 0.2 mg/L Al³⁺ has been defined by the WHO for drinking water.(Schacke, 1994), (Herschy and Blumberga, 2017) Selected aluminium based lakes have been approved by the Federal Food, Drug and Cosmetic Act (FD&C) thus there is no indication of potential health hazards to arise from the use of the aluminium lakes studied in this work.

Flavonoids represent the major dye constituents present in onion peel and Canadian goldenrod e.g. quercetin-glucoside (like quercitrin, isoquercitrin, rutin), quercetin, kaempferol and kaempferol-glucoside. (Schweppe, 1999), (Lu et al., 2011)

Representative examples are shown in Fig. 1. Thus during hot water treatment a number of different colorants becomes extracted from the plant material, part of these substances then is precipitated with alum. Due to the low concentration of colorants in the plant extract the formation of a dye lake is an essential step to prepare a product, which contains the colorants in higher concentration. In Fig. 2 photomicrographs from laser scanning microscopy and FTIR-spectra of the milled dye lakes are shown. The shape of the powdered lake particles results from the milling of the amorphous non crystalline structure of the dried lake, which contains of a number of different plant constituents.

The FTIR spectra exhibit characteristic absorptions for flavonoid dye
structures: 3289 cm⁻¹ for the phenolic O-H group, 1674 cm⁻¹ C=O for the carbonyl moiety, 1604 cm⁻¹, 1555 cm⁻¹ and 1520 cm⁻¹ for the aromatic double bond, stretching, 1377 cm⁻¹ for the stretching vibration of quercetin aromatic ring, 1321 cm⁻¹ for the =C-O-H stretching of phenolic group, 1260 cm⁻¹, 1161 cm⁻¹ and 815 cm⁻¹ for the stretching vibration of the catechol moiety and 1260 cm⁻¹, 1014 cm⁻¹ for the C=C-O aromatic ring vibration (Supplementary Information Table S1) (Porto et al., 2018). Characteristic absorbances for aluminium hydroxides are expected to appear at 1640 cm⁻¹ and 1064 cm⁻¹ (Koichumanova et al., 2015).

Simple techniques e.g. sedimentation and filtration have been selected, which will permit introduction of the extraction and precipitation step near the site of farming where the plant material is collected. (Leitner et al., 2012), (Mahmud-Ali et al., 2012) The dye lake contains a complex mixture of different colorants. The thermal stability of this mixture as a whole is of relevance as degradation of one major constituent will limit the thermal colour stability of the dye lake.

The DSC analysis of the natural dye lakes of Canadian goldenrod was carried out with three runs, first heating then cooling, followed by a second heating. Evaporation of moisture, degradation and melting of substances will be detected during the first heating. Changes in composition of the lakes will be indicated by differences between the first and the second heating phase. The DSC curves measured with the dye lake from Canadian goldenrod and onion peel are shown in Fig. 3a and 3b.

The DSC curve shows a large endothermic peak from 30°C to 240°C, whereby the first phase mainly is due to water evaporation. In analogy to the thermal stability reported for pure flavonoids melting, molecular rearrangement and decomposition of the dye lake is expected to take place during the second phase. (Borghetti et al., 2012), (da Costa et al., 2002) Many flavonoids exhibit a melting point in the temperature range of between 180°C and 200°C. For example, quercitrin melts at about 182–185°C. Rutin exhibits a melting point of about 195°C followed by decomposition temperature of about 214°C. Kaempferol-3-glucoside has a melting point of about 175–178°C. For the thermally more stable quercetin melting and degradation occur at near 314°C. (Schweppe, 1993), (Rohn et al., 2007), (Birkofer and Kaiser, n.d.)

Fig. 3b shows the DSC curve measured with the natural dye lake from onion peel, which exhibits a large endothermic peak from 30°C to 240°C, similar to the DSC obtained with lake form Canadian goldenrod. The endothermal event during the first heating cycle can be attributed to evaporation of bound water, irreversible molecular rearrangement and thermal degradation of the lake. In case of the dye lakes studied in this work thermal decomposition of the aluminium complexes is expected to occur instead of melting, which explains the absence of a distinct endothermal peak during both heating phases 1 and 2. No exothermal
event is observed during the cooling phase, thus crystallisation of molten phases is not detected.

By use of TGA the mass loss of a sample during controlled heating is recorded over time, which provides information about physical phenomena, such as phase transitions as well as chemical phenomena including release of volatile products and thermal decomposition. In Fig. 4a the TGA curve of natural dye lake from Canadian goldenrod is shown. The first phase (phase I) of weight loss near 120 °C can be attributed to the evaporation of adsorbed water, including hydrate and crystal water. During phase II between 120 °C and 250 °C a smaller weight loss of 6–7% can be allocated to chemical rearrangement processes and degradation of minor constituents in the natural dye lake, which is in agreement to observations reported for pure flavonoids (Borghetti et al., 2012). (Da Costa

Fig. 3. DSC measurement of aluminium dye lake from a) Canadian goldenrod, b) onion peel (Black curve: 1st heating, red curve: cooling, blue curve: 2nd heating). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
The begin of substantial decomposition reactions is indicated with higher weight loss in the temperature range of about 250 °C–340 °C (phase III), above 340 °C to 570 °C (phase IV) and 570 °C–800 °C (phase V) (Rohn et al., 2007).

The TGA curve of natural dye lake from onion peel shows similar behaviour as observed with the lake from Canadian goldenrod (Fig. 4b). Again weight loss near to 120 °C can be attributed to release of moisture and adsorbed water, while substantial degradation is indicated by weight loss above 250 °C.

In a modified TGA experiment the thermal stress prevalent during the masterbatch coloration was simulated. According to process conditions for PA 6 extrusion, the dye sample first was heated up to 245 °C, followed by 0–60 min isothermal treatment at 245 °C (Fig. 5a). Following to an initial mass loss of 20% of sample weight during the heating period only minor losses were measured during the isothermal phase at 245 °C, which indicates unexpectedly high thermal stability of the lake at 245 °C. Only a share of 7.6% of the initial sample mass disappears during a 60 min heating period at 245 °C. The TGA curves of the different experiments given in Fig. 5a overlap very closely which demonstrates the precision and reproducibility of the chosen methodology.

Colour change of the thermally treated samples then was analysed by measurement of the diffuse reflectance of the powdered pigment and calculation of the CIELab colour coordinates and by miniaturised dyeing experiments. The colour coordinates of the thermally treated dye lakes from Canadian goldenrod are shown in Fig. 5b. Major changes in colour appear during the heating phase, while only minor changes were observed during the isothermal period at 245 °C. A strong decrease in the $L^*$- and $b^*$-coordinate indicates a colour change from the initially brown colour of the concentrated lake in the direction of a darker tone. Remarkably the duration of treatment at 245 °C was of minor influence on changes of $L^*$- and $b^*$-values. Thus after an initial change in colour during the heating phase the lake exhibited thermal stability over 60
min at 245 °C, which is longer than the expected processing for PA 6 extrusion.

As major changes in colour had been observed during the heating period the influence of temperature in the interval from 160 °C to 240 °C was studied in more detail. Samples of the dye lake were heated by TGA to a predefined temperature, then after cooling, the CIELab colour coordinates of the respective sample were determined. The change in colour coordinates for lake from canadian goldenrod are shown in Fig. 6 a. Two peaks in colour change were observed, the first near 180 °C and a second near 220 °C. This observation is in agreement to findings reported in the literature for the thermal stability of flavonoids which begin to chemically rearrange and deglycosylate at such temperatures. (Borghetti et al., 2012), (da Costa et al., 2002), (Rohn et al., 2007) At about 245 °C the L*, a*, b* values decreased significantly, which comes along with a massive mass loss (Fig. 5 a). Two peaks in colour change were observed, the first near 180 °C and a second near 220 °C. This observation is in agreement to findings reported in the literature for the thermal stability of flavonoids which begin to chemically rearrange and deglycosylate at such temperatures. (Borghetti et al., 2012), (da Costa et al., 2002), (Rohn et al., 2007)

Fig. 6. CIELab coordinates L*, a* and b* and K/S values (400 nm) of thermally treated natural dye lake: a) canadian goldenrod, b) onion peel as function of the treatment temperature.

Fig. 7. FTIR spectra of the thermally treated natural dye lakes from onion peel in the wavenumber interval of a) 4000–500 cm⁻¹ and b) 1800–600 cm⁻¹. Treatment temperature: untreated (RT), 180 °C, 200 °C, 230 °C, 245 °C.

Within the investigated temperature range of up to 245 °C only minor changes in the IR spectra were observed. Intensity changes in the wavenumber interval between 1066 cm⁻¹ and 1100 cm⁻¹ (C-O single bonds) indicate molecular rearrangement, of minor flavonoid constituents present in the lake.

Also for canadian goldenrod lakes, only small changes were observed

3.2. FTIR analysis of thermally treated lakes

FTIR analysis was used to follow dye lake degradation during the thermal treatment. Characteristic absorptions of functional groups present in flavonoids are given in supporting information (Table S1). (Schweppe, 1993), (Heneczkowski et al., 2001), (Schönbichler et al., 2014), (Porto et al., 2018)

Fig. 7 shows the FTIR spectra of thermally treated dye lakes from onion peel. Lower absorbance was observed in the FTIR spectra of the dye lake in particular at 1025 cm⁻¹ (C-O bonding) when compared to the FTIR spectra of onion peel extract, which can be explained with the participation of phenolic hydroxyl groups in the metal complex formation (Lu et al., 2011).

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in the FTIR spectra between 1066 cm\(^{-1}\) and 1100 cm\(^{-1}\). This demonstrates thermal stability of the major constituents up to a treatment temperature of 245 °C (Supplementary Information Fig. S3).

These findings are in agreement with published studies for the thermal stability of flavonoid compounds. Quercetin hydrates have been reported to exhibit a first phase of dehydration and molecular rearrangement at near 110 °C, which apparently is not accompanied by structural decomposition, followed by a phase of degradation and melting at temperatures above 250 °C (Borghini et al., 2012), (da Costa et al., 2002). Roasting of quercetin glycosides at temperatures above 180 °C has been reported to induce deglycosylation and formation of the corresponding aglycone (Rohn et al., 2007).

3.3. Miniaturised wool dyeing

Miniaturised dyeing experiments on wool were performed to study the effect of thermal processing on the colour development. The dyeing experiments were designed to require only 15 mg of thermally treated dye lake. Thus the small dye samples collected from TGA experiments was sufficient for wool dyeing. The dyeings were characterised by colour measurement and K/S determination. The absorption spectra of exhausted dye liquor also were recorded using UV/VIS spectrophotometry.

Fig. 8a shows the CIELab colour coordinates of dyed wool samples which were obtained with different thermally treated lakes from Canadian goldenrod. The colour coordinates \(L^*, a^*, b^*\) remained virtually constant. Remarkably even after heating to 245 °C no significant loss in colour strength (K/S at 400 nm) or change in shade (\(L^*, a^*, b^*\) coordinates) was observed. Similar results were obtained with thermally treated natural dye lake from onion peel (Fig. 8b). No significant loss of colour strength or change in shade was indicated by the K/S value at 400 nm and the \(L^*, a^*, b^*\) coordinates up to a treatment temperature of 245 °C. Photographs of the respective samples are shown in Fig. 8c and d. Acceptable colour fastness properties of dyeings on wool have been reported for the two representatives tested in this work. Wash fastness of dyeings on wool with Canadian goldenrod peel extract and aluminium mordant was determined to reach a level of 4 (maximum score 5), and water fastness of similar dyeings with onion peel extracts was determined to reach a mark of 4–5 (maximum score 5) (Bechtold et al., 2004a), (Rapp et al., 2005). Only fastness to light for Canadian goldenrod dyeings on wool were limited (Bechtold et al., 2003), (Bechtold et al., 2004b).
During preparation of an aqueous plant dye extract a number of coloured substances becomes extracted and collected as dye lake, however only part of these coloured molecules adsorbs on the textile material e.g. wool (Bechtold et al., 2007). Coloured substances which do not absorb on the substrate will remain in the exhausted dyebath. Thus for a complete assessment of the thermal stability of all constituents in the dye lake also degradation of colorants remaining in the exhausted dyebath has to be taken into account.

The absorbance curves of dye liquor extracts collected at the end of the miniaturised dyeing experiments with thermally processed dye lake from canadian goldenrod are shown in Fig. 9a. The dyebath from a blank dyeing of wool without pigment (reference 1) exhibited only low absorbance, with a maximum at 300 nm (Fig. 9a). The absorbance curve obtained with a residual dyebath using untreated dye lake exhibited maxima near 300 and 400 nm (reference 2), which is in agreement to absorbance spectra reported in the literature for the aqueous extracts of canadian goldenrod (Leitner et al., 2012). The absorption curves obtained with thermally treated dye lakes exhibited a decrease in absorbance at 400 nm with rising treatment temperature. Only minor reduction in absorbance occurred up to a treatment temperature of 180 °C, however significant reduction of absorbance was observed after treatment above 180 °C.

Similar results were observed from an analysis of the residual dye baths from dyeings with thermally treated dye lake from onion peel (Fig. 9b). Two peaks at about 300 nm and 400 nm wavelength were observed for the unprocessed dye lake. The absorption spectra of the exhausted dyeing liquor show a reduction of the absorption at 400 nm for lakes, which had been treated at a temperature above 180 °C and 200 °C for canadian goldenrod and for onion peel, respectively. After processing at temperatures of 230 °C and above, the absorbance at 400 nm reduces significantly. This can be explained with chemical rearrangement and degradation reactions which then occur during the thermal treatment of the dye lake.

Natural dye lakes represent a sustainable source of bio-based pigments. These pigments could be of high value for mass coloration of polymers made from renewable resources e.g. PLA and PA 11 as well as recycled PA 6. The shaping of these polymers is executed via melt extrusion processes above their respective melting temperature. For a possible use in mass coloration the dye lakes thus must exhibit sufficient thermal stability. In this study aluminium salt based dye lakes prepared from canadian goldenrod or onion peel extracts were used as representatives for flavonoid based natural pigments.

The dye lakes of canadian goldenrod and onion peel show a similar pattern in DSC analysis with a large endothermic peak from approx. 30 °C to approx. 250 °C, which can be attributed to water evaporation, chemical rearrangement and melting. Similar behaviour is observed in TGA investigations between 30 °C and 800 °C. The temperature dependent mass loss can be attributed to the hydrate water evaporation, and release of volatile decomposition products. The effect of a certain temperature on the colour of a lake was analysed by isothermal treatment and determination of the pigment colour in terms of CIELab coordinates. Results indicated a remarkable stability of the pigments up to 245 °C, which is sufficient for melt extrusion of PLA, PA 6 or PA 11. The duration of the thermal treatment was found to be of minor influence on the colour change of the pigment. In FTIR analysis of thermally treated natural dye lakes only a small change in absorption was detected at a wavenumber of about 1066 cm⁻¹.

4. Conclusions

Pigments used for mass coloration of plastics must withstand the thermal stress applied during thermoplastic shaping of the polymer. In many cases temperatures above 240 °C are used in melt extrusion processes. Thus natural dye lakes must exhibit sufficient thermal stability to survive the high temperatures in extrusion without substantial colour change.

Thermally treated natural dye lakes were used for miniaturised wool dyeing experiments. The CIELab colour coordinates of the dyed wool samples indicated surprisingly high thermal stability of the lakes. Even lakes which had been heated to 245 °C showed only small differences to the reference dyeing.

The investigated aluminium based flavonoid dye lakes exhibit unexpectedly high thermal stability, which makes these pigments suitable for mass coloration of thermoplastic polymers. The findings open a new avenue for replacement of synthetic pigments in coloration of plastics by bio-based pigments from plant sources, which will be of particular value for coloration of biodegradable polymers.

Future research should address more technical aspects of mass coloration, e.g. formulation of colour master batches and polymer coloration in extrusion processes. An insulation and detailed monitoring of the behaviour of individual substances was beyond the scope of this study and could be part of study to improve the thermal stability of a
certain lake further.

Supporting information

Photographs presenting the lake formation (Figs. S1 and S2).

FTIR spectra of thermally treated aluminium lake form Canadian goldenrod (Fig. S3).

Characteristic infrared absorption of flavonoid structures (Table S1).

Data statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

CRediT authorship contribution statement

Huong Lan Nguyen: conducting a research, Investigation, Methodology, Data curation, Writing – original draft.

Thomas Bechtold: formulation or evolution of overarching research goals and aims, methodology, Data curation, Writing – original draft.

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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Abbreviations

CIELab coordinates

Commission International de l’Eclairage L* a* b* coordinates

PLA Polyactic acid

PHBA Polyhydroxybutyric acid

PP Polypropylene

PA Polyamide

PA6, PA11 Polyamide 6, polyamide 11

DSC Differential Scanning Calorimetry

TGA Thermogravimetric Analysis

FTIR Fourier Transform Infrared Spectroscopy

K/S Kubelka Munk value

WHO World Health Organisation

FD&C Federal Food, Drug and Cosmetic Act

UV/VIS spectrophotometry Ultraviolet and Visible Light Spectrophotometry

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2021.128195.

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