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Thermo-oxidative and weathering degradation affecting coloration performance of lac dye

Prapaipim Nacowong and Sunan Saikrasun*

*Correspondence:
sunan.s@msu.ac.th
Creative Chemistry
Research Unit,
Department of Chemistry
and Center of Excellence
for Innovation in Chemistry,
Faculty of Science,
Mahasarakham University,
Mahasarakham 44150,
Thailand

Abstract

Thermo-oxidative stability of lac dye was studied by simultaneous thermogravimetry (TG) and differential scanning calorimetry under nonisothermal and isothermal modes in air. The thermal stability change of lac dye was characterized by FTIR and UV-Vis spectroscopy. The TG profiles of lac dye showed at least three steps of mass loss. The first mass loss (about 8 %) found in the range of 40–150 °C mainly corresponded to the evaporation of moisture whereas the next two major steps were found with mass losses of 50 (150–440 °C) and 25 % (440–550 °C). The FTIR results indicate that the degradation of the major mass loss step (150–440 °C) mainly involved the thermo-oxidative reaction at carboxylic groups in conjugation with the C=C bonds of the anthraquinone ring. The absorbance profiles of lac dye solutions showed that the remarkable drop of absorbability was observed when the dye was heated to elevated temperatures (>150 °C). The results obtained from isothermal investigation also indicated the thermo-oxidative stability dependence of heating temperature. The apparent activation energy of lac dye calculated using isoconversional methods was higher under dynamic than under isothermal heating. Long period of weathering exposure mainly affected the O–H bonds of hydroxyl and carboxylic groups, and hence lowering the absorbability of lac dye. These results provided helpful information that can give support in the maintenance, preparation, dyeing and application stages of lac dye.

Keywords: Lac, Thermogravimetry, Degradation, Absorbance, Kinetics

Introduction

The natural dyes have been widely used, especially for textile dyeing, coloring food, painting and in printing. However, with the rapid incursion of synthetic dyes, natural dyes undergo a setback. During the past few decades, the problems concerning the environmentally harmful effects and serious health hazards have been raised regarding the use of synthetic dyes. Therefore, the use of natural dyes is considerable current interest as these dyes are eco-friendly, safe for body contact, unsophisticated, harmonized and renewable (Nayar et al. 1994; Downham and Collins 2000).

For the dye molecules, the chemical structure is normally divided as the chromophore (main skeleton) and auxochrome (substituent groups) parts. The chromophore part generally determines the light fastness properties. Oppositely, the change in fastness properties is dominated by the auxochromes (Cristea and Vilarem 2006). Flavonoid

compounds are mostly found as the main components in natural dyes and the remaining components anthraquinones, naphthoquinones and indigoids. Anthraquinones and indigoids typically exhibit superior light fastness. Although the numerous advantages have been gained from the natural dyes, the color fading due to the degradation of dye is still be one of the major problems in textile color. Normally, the color fading directly affects in the loss of intact dye molecule resulting in the change of original dye color (Ahn et al. 2014). In general, the stability of natural dye is mostly influenced by the chemical and physical states of the dye. Moreover, the source and the intensity of illumination, humidity, temperature (heat), and the atmospheric pollution as the external factors can affect the stability of natural dyes as well. The light source containing UV radiation is one of the important factors that affect the stability of the dyes by photofading process (McLaren 1956; Padfield and Landi 1996; Gantz and Sumner 1957). Under exposing to light, both temperature and humidity can influence the fading rate of dyed textiles (Egerton and Morgan 1970). In addition, the natural dyes can react with gas contaminants in the atmosphere, e.g., sulfur dioxide and oxides of nitrogen and ozone even in the absence of light. In terms of thermal affecting stability, it is known that higher temperature accelerates the oxidation of the natural dyes. It has been reported that the oxidation reaction of amor cork tree dye is accelerated two times by every 2 °C increase in temperature under heating in 100 °C oven (Ramos et al. 1995; Ahn 2011). Thermal degradation behavior of the alizarin and *Phellodendron* bark, alizarin and indirubin has also been studied by GC-MS and HPLC-DAD-MS (Ahn 2011; Ahn and Obendorf 2004). In addition, Ahn et al. (2014) investigated the thermal resistance of the natural dyes. The thermal stabilizing performance of alizarin and purpurin was attributed to the formation of fiber-metal-dye chelated complex by aluminum or iron ions mordanting prior to dyeing.

Stick lac, a secretion of the insect *Coccus laccae* (*Laccifer lacca* Kerr), is a natural material used for preparation of lac dye (Moeyes 1993). The lac dye extracted from the stick lac has high potential in many fields of applications. For example, it is used as a cosmetics ingredient, for coloring food, oil painting and dyeing textiles (Moeyes 1993; Chairat et al. 2005; Janhom et al. 2004; Kongkachuichay et al. 2002; Kamel et al. 2007; Boonla and Saikrasun 2013; Sribenja and Saikrasun 2015). The main components in the soluble part of the stick lac are consisted of anthraquinone-based components. These are laccaic acids A (40 %), B (15 %) and C (10 %) (w/v) (Oka et al. 1998). The chemical structures of laccaic acids A-C are shown in Fig. 1. However, although lac dye is extensively used as natural colorants for many application routes, to the best of our knowledge, the systematic studies on thermo-oxidative and weathering degradations of lac dye have not been reported. In the present study, the effects of dynamic and isothermal heating and weathering on stability of lac dye were investigated. The FTIR and UV-Vis spectroscopy were used to monitor chemical changes in relation to the absorbability of lac dye. The obtained results are useful for prolonging the material lifetime under stability awareness during every stages material utilizations, especially in textile dyeing applications.

FTIR characterization

The structural change of lac dye was characterized by FT-IR spectroscopy (Spectrum GX-1, Perkin Elmer Co., Ltd., UK). A resolution of 4 cm^{-1} and 32 scans from 4000 to 400 cm^{-1} were used for each sample.

Weathering procedure and instruments

The powder dye sample of 0.250 g was loaded in a ceramic container. Each sample was kept out-door under the realistic atmosphere for 5, 10, 15 and 50 days. UV-Vis spectrophotometry (Thermo Scientific 4001/4, Thermo Electron Co., Ltd., MA, USA) was used to measure the absorbance of aqueous lac dye solution. The absorbance of aqueous dye solution with a fixed concentration of 0.15 g/L (150 ppm) was scanned from 100 – 900 nm . The optical images of the lac dye solutions were examined using digital camera (Canon, EOS-500D, Tokyo, Japan). The data of weathering investigation were gained from three measurements.

Results and discussion

Nonisothermal decomposition

Figure 2 shows the TG curves of lac dye after dynamic heating from room temperature to the selected temperatures as 60 , 90 , 150 , 250 and $350\text{ }^{\circ}\text{C}$ in air atmosphere. At temperature less than $150\text{ }^{\circ}\text{C}$, the first mass-loss step occurs in the range of 40 – $150\text{ }^{\circ}\text{C}$ and a mass loss of about 8% is observed (Fig. 2a–c). The first mass-loss stage mainly involves the evaporation of moisture in the materials. Generally, the hydrophilic substances tend to absorb and retain the moisture during the isolation and storing processes. From the polar structures of the main components in lac dye, it is the fact that the laccaic acids are hydrophilic and tend to retain the moistures in the intermolecular space. The moistures are mostly evaporated during heating from ambient temperature to $\sim 150\text{ }^{\circ}\text{C}$, resulting in the mass loss as observed from the TG profiles. After dynamic heating to $150\text{ }^{\circ}\text{C}$, the deflection of mass change (see arrows in Fig. 2d–f) is clearly observed, indicating the

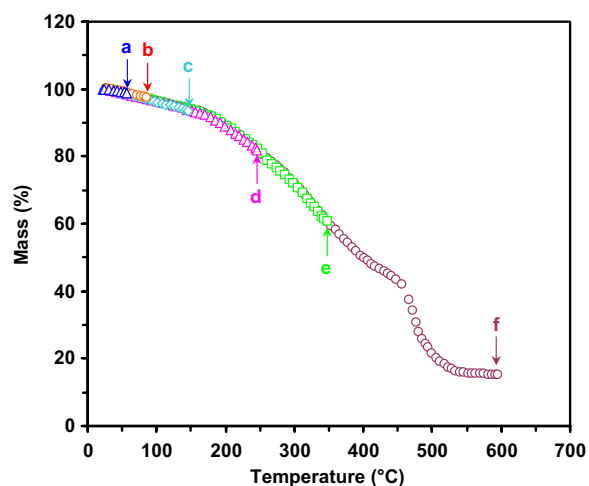
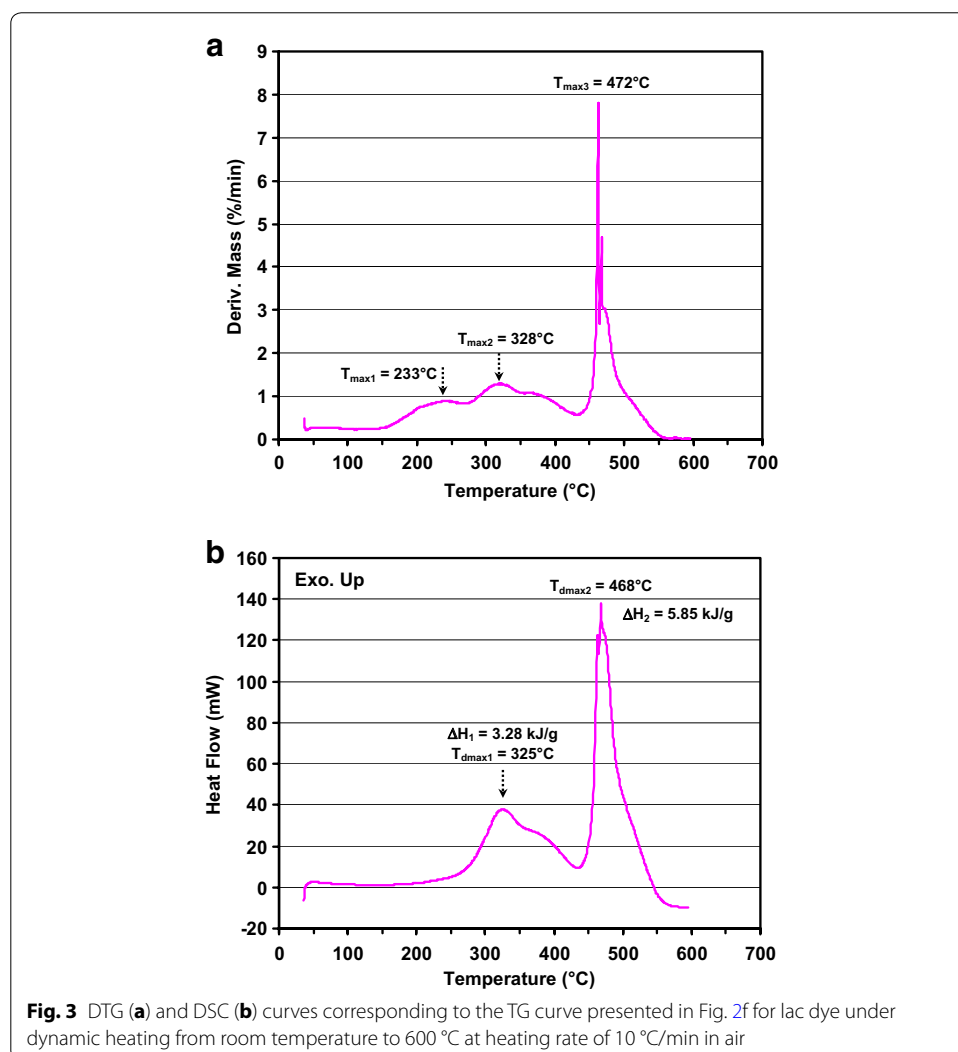


Fig. 2 TG profiles of lac dye under dynamic heating from room temperature to a 60 , b 90 , c 150 , d 250 , e 350 and f $600\text{ }^{\circ}\text{C}$ at heating rate of $10\text{ }^{\circ}\text{C/min}$ in air

change of mass-loss rate. Beyond this temperature, the degradation progressively occurs and next major change in mass loss rate is additionally observed around 440 °C (Fig. 2f). At temperature range of 150–440 °C, the TG profile shows the mass loss of about 50 %. The rapid degradation with the mass loss of 25 % is found at temperature higher than 440 °C. Moreover, the char left content after degradation is found to be ~17 %. In general, most organic materials thermally degraded and left small amount of char (less than 5 %). However, due to the lac dye sample studied in this work mainly contains multi-components of laccic acids, the further reactions of the gas products may occur and/or these gas products may promote the char formation process during degradation. Hence, the relatively high amount of char is observed.

The mass loss rate and simultaneous DSC profiles corresponding to the TG curve (Fig. 2f) of lac dye dynamic heated to 600 °C are presented in Fig. 3a, b, respectively. It is seen that the constant rate concerning with the evaporation of moisture is observed under heating from room temperature to 150 °C. At higher temperatures, the decomposition rate gradually increases to ~1 %/min and a broad DTG curve containing



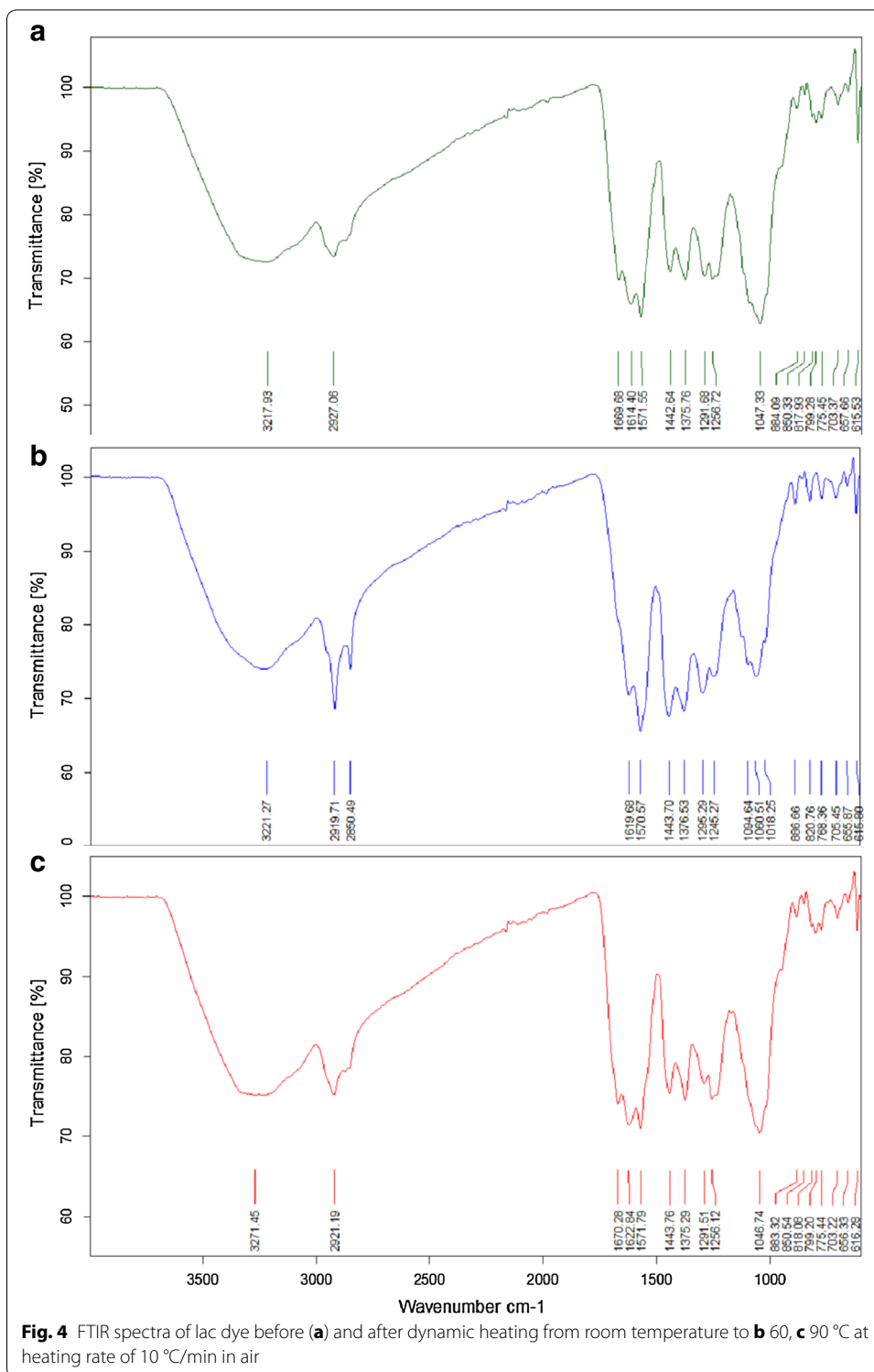
multi-peaks with stretching up to 440 °C is observed. However, the rapid increase in mass-loss rate is observed beyond ~450 °C and the degradation shows the maximum rate of 7.8 %/min at 472 °C. In fact, the lac dye used in this study contains multi-components and therefore the complex thermo-oxidative decomposition can be expected. As stated that the first mass loss step mainly involves the evaporation of moisture, the next two major steps of mass loss would correspond the decomposition of lac dye. As seen from simultaneous DSC curve in Fig. 3, the thermo-oxidative decomposition of lac dye is exothermic process. This is normal for the degradation process in air which tends to involve the formation reaction. Moreover, two exothermic peaks of lac dye corresponding to the second and third major mass-loss steps are observed with possessing enthalpy changes of 3.28 and 5.85 kJ/g, respectively.

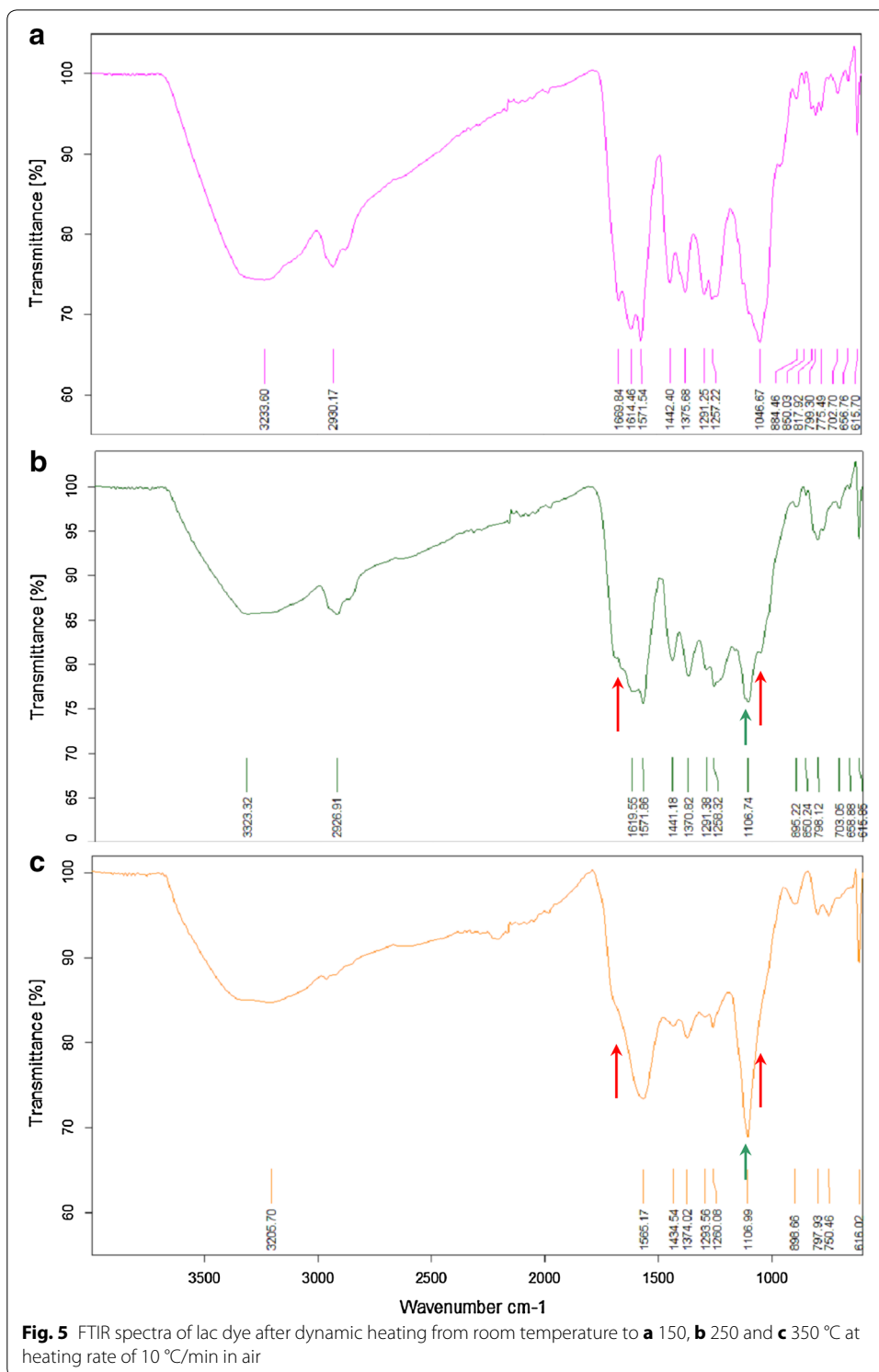
FTIR characterization of lac dye

FTIR is one of the spectroscopic methods widely used to characterize the functional groups and describe the interactions of molecules. Actually, the main coloring constituent of the lac dye is gained from the mixed laccic acids. However, laccic acid A, 3-[3-(2-acetamidoethyl)-6-hydroxyphenyl]-1,2,4,7-tetrahydroxyanthraquinone-5,6-dicarboxylic acid, is usually chosen as a representative for the lac dye to describe their kinetics and thermodynamics of adsorption. This is due to that the laccic A is a major component of lac dye. Therefore, in this work, the laccic acid A is also mainly considered in correlation with the thermo-oxidative decomposition behavior. The FTIR spectra of lac dye before and after dynamic heating to the selected temperatures are shown in Figs. 4, 5. The broadening FTIR spectra of lac dye are observed, resulting from that the dye has various functional groups that can form H-bonds (Dokmaisrijan et al. 2013). Also, the broad FTIR spectra observed might be contributing to the different conformers of the dye (Svobodová et al. 2012). Before and after dynamic heating to 60, 90 and 150 °C (Figs. 4a–c, 5a), slight change in FTIR spectra is observed. The FTIR spectra of lac dye appeared are primarily assigned as O–H rocking in hydroxyl and carboxylic groups (1100–1047 cm^{-1}), deformation vibrations of CH_2 and CH_3 groups (1500–350 cm^{-1}), C=O stretching for COO^- groups in conjugation with the C=C bonds in aromatic ring (1720–1570 cm^{-1}), C–H stretching (3000–2850 cm^{-1}) and vibration band of OH groups (around 3300 cm^{-1}). Under dynamic heating up to 250 °C (Fig. 5b), the significant change in FTIR spectra is clearly observed at the bands of ~1671 and ~1047 cm^{-1} (see arrows) corresponding to the decomposition of two carboxylic groups and C–O bonds, respectively. With heating to 350 °C (Fig. 5c), the stretching band of C–H at 2927 cm^{-1} is diminished indicating the decomposition of C–H bonds. Under heating to high temperatures (250, 350 °C), the sharp peak at ~1107 cm^{-1} , especially for the heated sample up to 350 °C, is appeared. This may be due to the formation of small solid products consisting =C–H bonds. However, due to the lac dye has many components with different chemical structures, the complex mechanisms would occur under thermo-oxidative condition.

Thermo-oxidative stability of lac dye under dynamic heating

As known that lac dye consists mainly of different types of laccic acids, the complex degradation mechanism of lac dye is expected to take place. To obtain the reliable kinetic





information for the solid state reactions of lac dye, the use of kinetic method without the knowledge of kinetic model is required. Flynn–Wall–Ozawa (F–W–O) isoconversional method (Ozawa 1965; Flynn and Wall 1966), is a relatively simple (model free) method of determining activation energy directly from mass versus temperature data, obtained

at several heating rates. After providing the mass loss-temperature data at several heating rates, the activation energy can then be determined from the following equation:

$$\ln \beta = \left[\frac{AE_a}{Rg(\alpha)} \right] - 5.3305 - 1.0516 \frac{E_a}{RT} \quad (1)$$

where $g(\alpha)$ is an integral reaction type of kinetic function, β is a heating rate in $^{\circ}\text{C}/\text{min}$, E_a is an activation energy (kJ/mol) of the concurrent chemical reaction and physical process (apparent activation energy), T is an absolute temperature (K), R is the universal gas constant (J/K mol), and A is a frequency factor. A change in E_a with increasing degree of conversion is an indication of a complex reaction mechanism. Figure 6 shows the heating rates dependence of TG curves (Fig. 6a) and the F–W–O plots of E_a versus conversion extent (α) (Fig. 6b) for lac dye. In the present work, the F–W–O calculation was selected in the temperature range of 150–300 $^{\circ}\text{C}$ corresponding to the major degradation step of lac dye and the TG curves appear without overlapping. The E_a values at various percent conversion extents are presented in Table 1. It is seen that the E_a value progressively

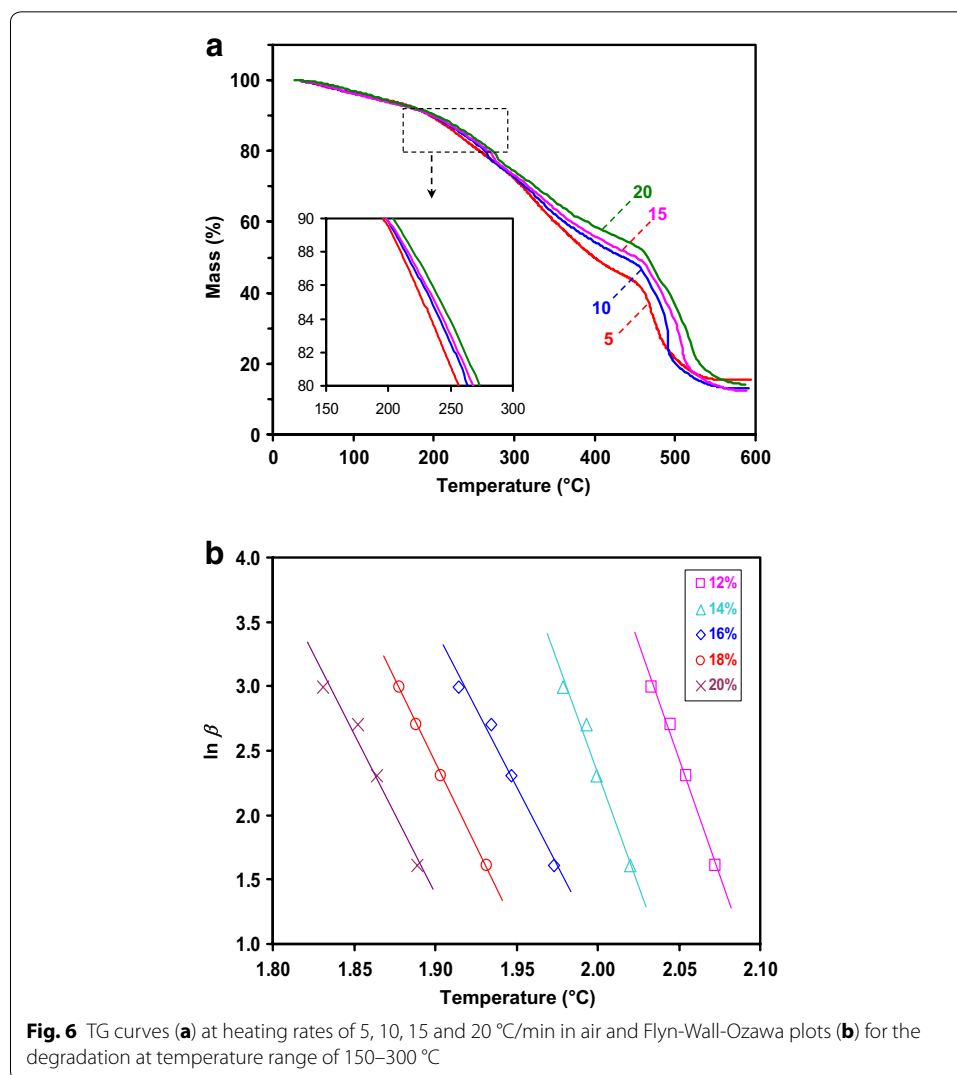


Fig. 6 TG curves (a) at heating rates of 5, 10, 15 and 20 $^{\circ}\text{C}/\text{min}$ in air and Flyn-Wall-Ozawa plots (b) for the degradation at temperature range of 150–300 $^{\circ}\text{C}$

Table 1 Thermo-oxidative activation energies (E_a) at various mass losses of lac dye

% Mass loss	E_a (kJ/mol)	r^{2*}
12	283	0.9900
14	275	0.9710
16	193	0.9780
18	205	0.9990
20	195	0.9680

* r^2 Means correlation coefficient for linear fit analysis

decreases as the conversion extent increases. However, the average E_a value of 230 kJ/mol suggests a high thermo-oxidative stability of lac dye under nonisothermal heating.

Thermo-oxidative stability of lac dye under isothermal heating

To gain a complete information of the degradation kinetics, isothermal TG analyses are also investigated. The isothermal decomposition behavior is shown in Fig. 7. The isothermal TG and DTG curves are shown in Fig. 7a, b, respectively. The TG and DTG profiles of lac dye are nearly the same under isothermal heating at 110, 130 and 150 °C for 0–10 min. This indicates that the mass loss mainly involve the evaporation of moisture during heating at 110, 130 and 150 °C for the first 10 min. After heating for longer time, it is seen that mass loss progressively increases with temperature. Under isothermal heating at 170 °C, lac dye obviously exhibits a rapid degradation during the first 25 min of isothermal heating. However, the mass loss content during the first 10 min of heating at 170 °C is clearly lower than those at 110, 130 and 150 °C. Note that, the time at maximum rate of decomposition (t_{max}) of the sample is increased with increasing isothermal temperature. In the case of simultaneous DSC curves (Fig. 7c), it is seen that the single endothermic peak is observed during heating time of 10–20 min. With increasing heating temperature, the exothermic peaks reveal at the higher heating time. Moreover, the enthalpy is mostly found to increase with higher heating temperature.

For solid state degradation reaction, the rate of decomposition ($d\alpha/dt$) can be described by (Tanaka 1995; Nam and Seferis 1991; Vyazovkin and Wight 1997).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where $k(T)$ and $f(\alpha)$ are the reaction rate constant and a conversion function, respectively. By replacing $k(T)$ using Arrhenius equation, $k(T) = Ae^{-E_a/RT}$, the rate of decomposition becomes.

$$\frac{d\alpha}{dt} = f(\alpha) Ae^{-E_a/RT} \quad (3)$$

By integration of Eq. (3), $g(\alpha)$, is obtained:

$$g(\alpha) = Ae^{-E_a/RT} t \quad (4)$$

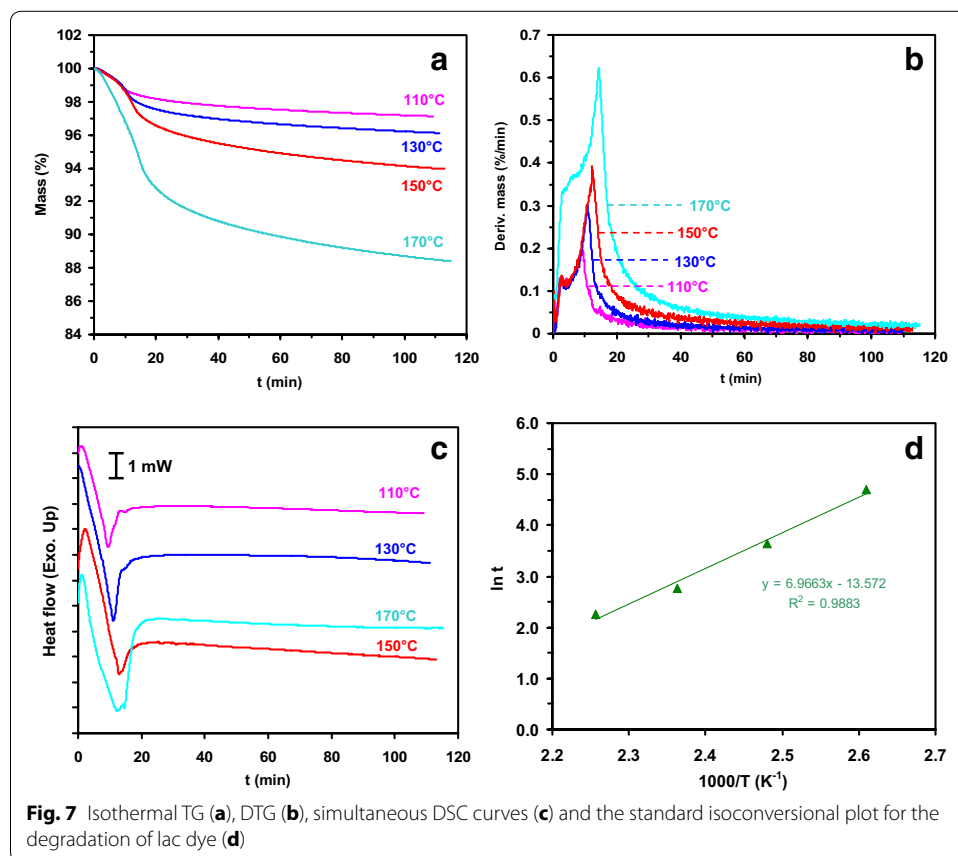
where t is a degradation time. By writing the Eq. (4) in the form of natural logarithmic expression, the following equation is obtained:

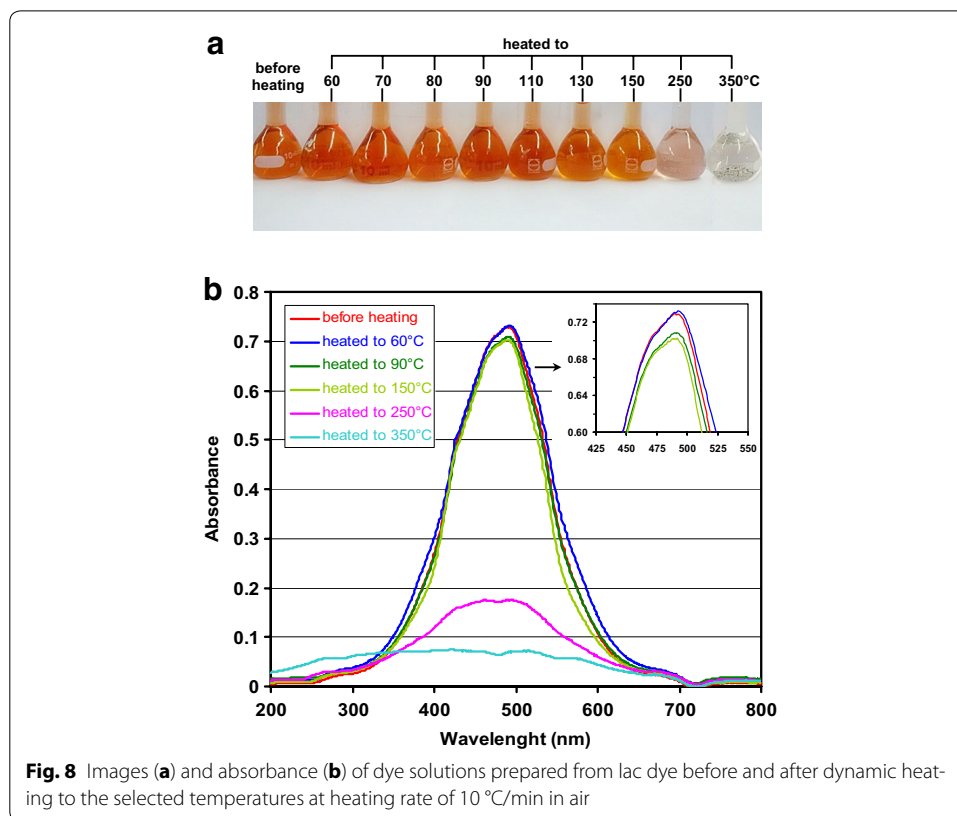
$$\ln t = \ln g(\alpha) - \ln A + \frac{E_a}{RT} \quad (5)$$

Equation (5) is known as a standard isoconversional method (Vyazovkin 2000). The $\ln t$ corresponding to a certain mass loss is linearly dependent on $1/T$. The E_a can be evaluated from the slope of the linear relationship of $\ln t$ versus $1/T$. For instance, the plot of $\ln t$ against $1/T$ corresponding to the mass losses of 3 % of lac dye is presented in Fig. 7d. The E_a value calculated from the slope of the straight line is 57.9 kJ/mol. It is seen that the isothermal activation energy of lac dye appears to be lower than those of the nonisothermal one, indicating a lower thermo-oxidative stability of lac dye under exposing to the isothermal heating.

Effect of dynamic heating on absorbability of lac dye solution

To investigate the influence of dynamic heating on the absorbability of lac dye, the measurement of absorbance using UV–Vis spectroscopic method for the dye solution was employed. After dynamic heating the lac dye to the selected temperatures, the absorbance of lac dye solutions in correlation with their colors is shown in Fig. 8. It is roughly seen that no significant change in fading of the dye solutions for the dye solution before and after dynamically heated at 60–150 °C. The remarkable fading of lac dye solution is clearly observed for the dye heated to 250 °C (Fig. 8a). Under dynamic heating to





350 °C or higher, the solution is colorless and some suspended residues or ashes were observed. The obtained results suggest that the lac dye clearly degrade under dynamic heating at the temperature >150 °C. The absorbance of the lac dye solution is presented in Fig. 8b. The major high absorption band at ~490 nm in the visible region is observed corresponding to the singlet $\pi \rightarrow \pi^*$ transition with 83 % MO contributions (Dokmaisrijan et al. 2013). Meanwhile, the HOMO and LUMO levels mainly differ at the delocalization at $^{**}\text{COOH}$ group. The transition involves an electron density transfers from anthraquinone ring to the carboxylic group ($^{*}\text{COOH}$) (see Fig. 1a). As seen from Fig. 8b, the maximum absorbance intensity (at $\lambda_{\text{max}} \sim 490$ nm) for the solutions containing lac dye before and after heating to 60–150 °C lies in the range of 0.70–0.75. Although the spectra for the solutions with the dye heated to 70 and 80 °C are not shown here, the shape and maximum intensity of both samples are respectively the same and comparable, compared to those of the solutions containing 90 °C-heated dye. Interestingly, for the solution of the dye samples heated to 250 and 350 °C, the remarkable drop in absorbance intensity is clearly observed. This arises from that the stability of the dye is not prolonged at very high temperatures. As compared from the FTIR spectra of lac dye before

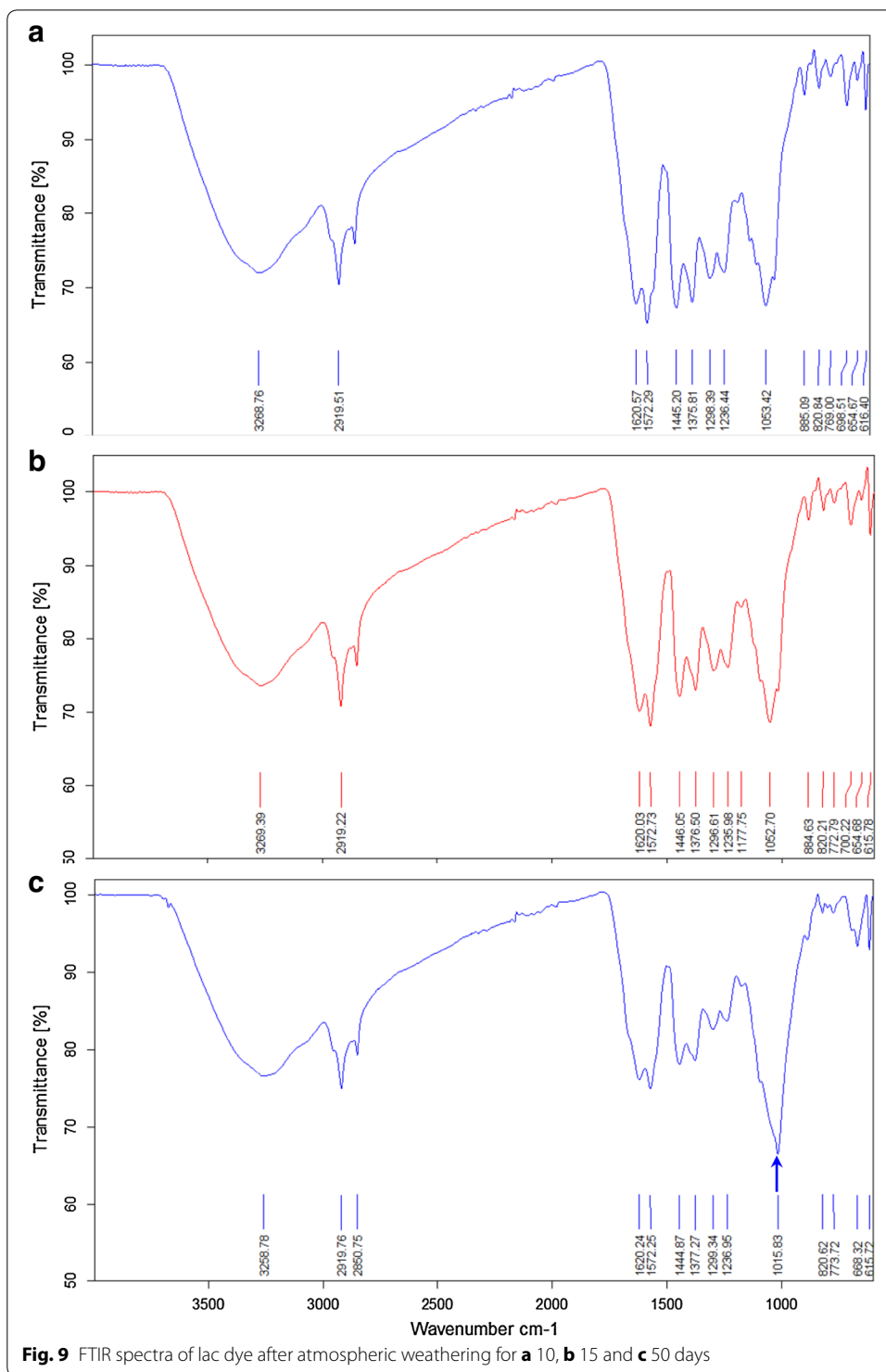
and after heating to 250 and 350 °C (Figs. 4, 5), the vibration bands of COOH groups conjugated with the C=C bonds of the anthraquinone ring (1720–1570 cm⁻¹) clearly change. The degradation of COOH groups directly affects the conjugated systems and lowers the ability of electron transfers from anthraquinone ring to COOH groups. The absorbance profiles of lac dye solutions obtained from the present study relate well with their fading properties as shown in Fig. 8a.

Effect of atmospheric weathering on absorbability of lac dye solutions

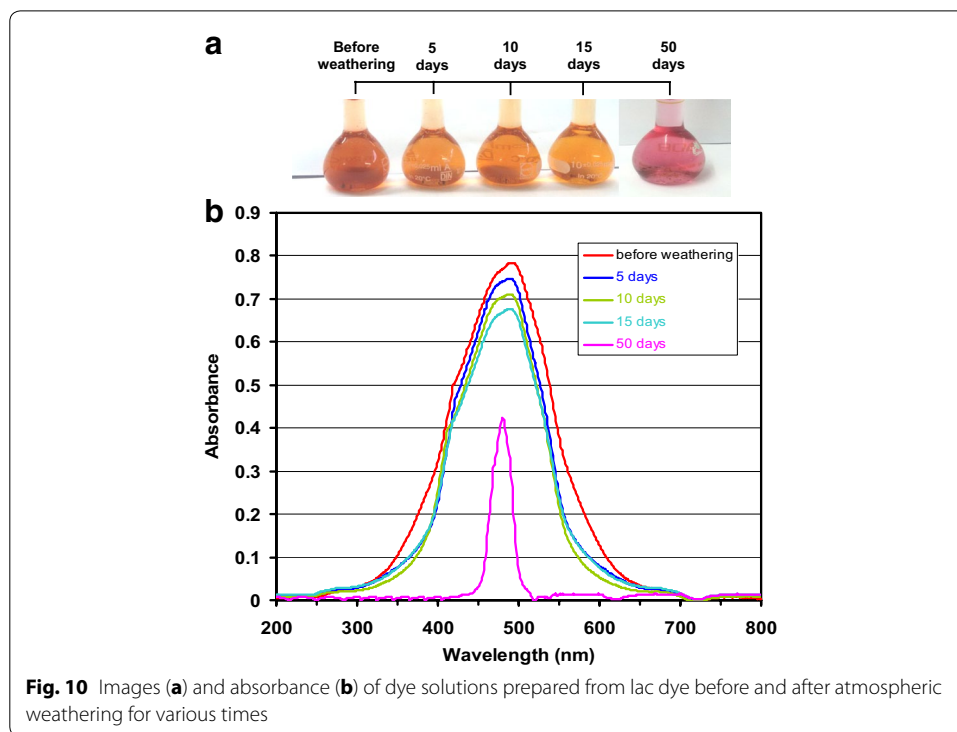
Normally, the natural dyes must encounter the degradation phenomena at almost every stage in storing, preparing, processing and application stages. Therefore, the understanding of stability of lac dye in relation with its coloring performance under realistic atmosphere is very important in suggesting their suitability of applications. Figure 9 shows the effect of out-door weathering under local atmosphere on FTIR spectra of lac dye. Under weathering for 10 and 15 days, no significant change in the FTIR spectra compared with the controlled sample is observed. Interestingly, the band at ~1063 cm⁻¹ is clearly shifted to ~1016 cm⁻¹ under weathering for 50 days. The results indicate that the weathering condition strongly affect the O–H bonds of hydroxyl and/or in carboxylic groups. This means that the initial reaction would mainly occur at these functional groups. However, although the reaction has been occurred at OH sites, the conjugated systems, especially for electron transfer from anthraquinone ring to COOH groups, are partly still existed. This is evident from the spectroscopic results as seen from Fig. 10. It is seen that the absorbance intensity progressively decreases (Fig. 10a) with weathering time which relate with color fading of dye solutions (Fig. 10b). The obvious change in absorbance profile is observed with weathering for 50 days. That is, small and sharp absorption peak is observed and the maximum absorbance intensity is much lower than those of other samples. This indicates that, under exposing to long weathering time, the reaction of lac dye mainly occurs at O–H bonds of carboxylic groups, resulting in the change of absorbability of red chromophores.

Conclusion

In this work, effects of thermo-oxidative heating and atmospheric weathering on stability of lac dye were investigated. Under dynamic heating, the lac dye started to degrade at temperatures higher than 150 °C which mainly involved the thermo-oxidative reaction at carboxylic groups in conjugation with the C=C bonds of the anthraquinone ring. Before and after dynamic heating to 60–150 °C, the absorbance profiles of each lac dye solution were not significantly different. Under heating the lac dye to higher temperatures, the absorbance significantly dropped resulting from the degradation of the chromophores. Under long weathering period, the chemical change mainly involved O–H bonds of



hydroxyl and carboxylic groups. This change also strongly lowered the absorbability of lac dye solution. The obtained results provided helpful information about thermo-oxidative and weathering stability of lac dye which is useful for maintenance, preparation, dyeing process and realistic applications.



Authors' contributions

Both authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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