Pigment & Resin Technology

Thermal and UV degradation of roselle anthocyanin extract and its mixtures with poly(vinyl alcohol) in different acid

Article information:
To cite this document:
Permanent link to this document:
http://dx.doi.org/10.1108/PRT-03-2014-0025

Downloaded on: 03 June 2015, At: 20:32 (PT)
References: this document contains references to 24 other documents.
To copy this document: permissions@emeraldinsight.com
The fulltext of this document has been downloaded 56 times since 2015*

Users who downloaded this article also downloaded:

Access to this document was granted through an Emerald subscription provided by 376953 []

For Authors
If you would like to write for this, or any other Emerald publication, then please use our Emerald for Authors service information about how to choose which publication to write for and submission guidelines are available for all. Please visit www.emeraldinsight.com/authors for more information.

About Emerald www.emeraldinsight.com
Emerald is a global publisher linking research and practice to the benefit of society. The company manages a portfolio of more than 290 journals and over 2,350 books and book series volumes, as well as providing an extensive range of online products and additional customer resources and services.

Emerald is both COUNTER 4 and TRANSFER compliant. The organization is a partner of the Committee on Publication Ethics (COPE) and also works with Portico and the LOCKSS initiative for digital archive preservation.

*Related content and download information correct at time of download.
Thermal and UV degradation of roselle anthocyanin extract and its mixtures with poly(vinyl alcohol) in different acid

S.V. Lee, A.N. Hadi, Z.H.Z. Zainal Abidin and N.A. Mazni
Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia

N.A. Halim
Centre of Defence Foundation Studies, National Defence University of Malaysia, Sungai Besi Camp, Kuala Lumpur, Malaysia, and

R. Usop, H.C. Hassan, S.R. Majid and A.K. Arof
Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia

Abstract
Purpose – The purpose of this paper is to observe the colour and thermal stability of natural red dye consisting of anthocyanin with addition of different aqueous acids and applied as coating films.

Design/methodology/approach – The natural red dye was extracted from Hibiscus sabdariffa L. (roselle) flowers and mixed with 1 per cent hydrochloric acid, 5 per cent acetic acid, 5 per cent citric acid and 5 per cent oxalic acid. All the dye samples were exposed to heat and UV-B to observe the colour stability by calculating the half-life and rate of reaction. In coating film application, each of the dye samples was mixed with 25 wt% of poly(vinyl alcohol) (PVA) and applied on to a glass substrate. The coating samples' colour stability was observed by using CIE L’ab colour space coordinates. The coating films’ weight loss stability against temperature was observed by using thermogravimetric analysis.

Findings – Addition of hydrochloric acid enhances the thermal and UV stability of the anthocyanin natural dye. This can be observed from the calculation of the half-life of the dye. The half-life values for the thermal and UV stability studies were 1,155 hours and 210 hours, respectively. In coating films, the sample with addition of acetic acid showed the highest colour stability with colour difference (ΔE*) value 8.95.

Research limitations/implications – The coating films developed in this work are not suitable to be applied on metal substrates due to the presence of water, which can contribute to the corrosion formation.

Practical implications – The coating films developed in this work are suitable for washable coating application. In other words, they are non-permanent coatings applied on a glass substrate.

Originality/value – Development of water-based coatings from PVA binder with anthocyanin colourant is introduced in this study.

Keywords Anthocyanin, Poly(vinyl alcohol), Roselle, Thermal degradation, UV degradation

Paper type Research paper

Introduction
Natural dyes extracted from plants and animals were used widely as colourants for fabrics and as food colourants before the invention of artificial colours. The lack of use of natural dyes in both applications is mainly due to poor colour stability. However, in the past decade, natural dyes have been used not only as food colourants but also in solar cell (Huihzi et al., 2011) and coating paint (Abidin et al., 2013) technologies.

Anthocyanin is a water-soluble molecule and is responsible for the variety of colours found primarily in flowers and fruits of higher plants, ranging from red, purple to blue. It has gained much attention in the past few decades and many studies were conducted on its properties. In the food industry, anthocyanin has exhibited a function as a natural dye to replace artificial food colourants (Bridle and Timberlake, 1997). Anthocyanin has also gained interest in medical applications owing to its antioxidant and antiradical properties (Tsai et al., 2002).

Roselle (Hibiscus sabdariffa L.), which belongs to the family Malvaceae, is a tropical plant commonly found in Asia and tropical Africa. Its calyxes, bright red in colour, are rich in anthocyanins. Du and Francis (1973) have reported two major, delphinidin-3-sambubioside and cyanidin-3-sambubioside, and two minor, delphinidin-3-glucoside and cyanidin-3-glucoside, anthocyanins in the calyxes of roselle. Anthocyanins from roselle have also shown potential for use as food colourants.

The current issue and full text archive of this journal is available on Emerald Insight at: www.emeraldinsight.com/0369-9420.htm

The authors would like to express their gratitude to the University of Malaya for research grants (RG249-12AFR) and (RP001D-13AFR) provided.

Received 25 March 2014
Revised 15 May 2014
Accepted 1 July 2014
Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer. It has been used in adhesives, paper coatings (Schumana et al., 2004), waste water treatment (Chang et al., 2005) and biomedical applications (Pourcie et al., 2005). Its non-toxic properties make it a viable candidate as an environment-friendly water-based coating. A first account of incorporation of natural plant pigments into coatings was given by Abidin et al. (2006). We have previously reported the incorporation of anthocyanin into poly(acrylamide-co-acrylic acid) (Lee et al., 2013). In this work, we studied the thermal and UV degradation of roselle anthocyanin extracts in different acids, and the coatings resulting from mixtures of the extracts with PVA.

**Experimental**

**Dye samples preparation**

Fresh roselle calyces were obtained from a local market in Kuala Lumpur. The plants were soaked for 3 hours in distilled water for anthocyanin extraction. The extract was filtered through a Whatman filter paper to remove insoluble particles. Acids introduced into the extract were 5 per cent acetic acid, 5 per cent citric acid, 5 per cent oxalic acid and 1 per cent hydrochloric acid. A dye not containing acid was also prepared in this work.

**Thermal degradation factor of anthocyanin dyes**

The five dyes mentioned above were stored in airtight laboratory bottles and placed in an oven at 50°C isothermal. Visible absorption spectroscopy was measured on all dye samples before and after the heating process and at 1-hour intervals up to 4 hours. The maximum absorption peaks from the visible absorption spectrum were marked as $A_i$ and $A$, indicating before and after the heating process, respectively. In this test, the dyes’ reaction rates and half-lives were calculated by using equations (1) and (2). The dye with the lowest reaction rate and the highest half-life has the least thermal degradation.

**Ultraviolet degradation factor of anthocyanin dyes**

Another set of five dyes as mentioned previously were exposed to UV light with wavelength 312 nm for 8 hours. Visible absorption spectra were obtained before exposure and at the 4th, 6th and 8th hour of exposure. The maximum absorption peaks from the visible absorption spectrum were also marked as $A_i$ and $A$, indicating before and after the heating process, respectively. The dyes’ reaction rates and half-lives were calculated by using the same equations (1) and (2). The dye with the lowest reaction rate and the highest half-life has the least UV degradation.

**Calculation of reaction rates and half-life**

It has been reported that degradation of anthocyanin follows first-order kinetics (Ozela et al., 2007; Yang et al., 2008). The reaction equation and half-life are given, respectively, as:

$$\ln \left( \frac{A}{A_0} \right) = -kt \quad (1)$$

$$t_{1/2} = \frac{0.693}{k} \quad (2)$$

Where $t$, maximum absorption peak after exposure at specific time, $A_i$: initial maximum absorption peak before exposure, $A$: reaction rate, $k$.

**Results and discussion**

**Thermal degradation of anthocyanin extracts with acids**

It has been reported that anthocyanins degrade upon heating (Patrasa et al., 2010). Degradation of all dye samples followed first-order degradation kinetics, as shown in Figure 1. Table I shows the reaction rate ($k$) and half-life ($t_{1/2}$) of the samples.
The maximum absorption peaks were recorded at wavelengths ranging from 520 to 530 nm. Using equation (2), the lowest half-life of anthocyanin was determined to be 45 hours (Table I) at 50°C. Mourtzinos et al. (2008) reported a value of 16.5 hours at 60°C isothermal, whereas Wang and Xu (2007) reported a value of 8.8 hours at 70°C isothermal. Addition of hydrochloric acid increased the half-life of the anthocyanin dye to 26 times higher than the pure anthocyanin dye, thus making hydrochloric acid the most effective thermal stabilizer among other acids in this work.

Thermal degradation mechanism of anthocyanin has been proposed by Adams and Woodman (1973). It was reported that anthocyanin would decompose into chalcone form upon heating. All samples with acids can be considered to exhibit a lower degradation rate and an increased half-life. This indicated that addition of acid into an anthocyanin extract improved thermal stability and inhibited thermal degradation of the anthocyanin extract. Effects of acids on thermal stability of anthocyanin have been reported by many (Bakowska et al., 2003; Parisa et al., 2007).

**UV degradation of anthocyanin extracts with acids**

UV radiation has been reported to cause photodegradation of anthocyanin, further causing discolouration effects (Pala and Toklucu, 2011). In our study, UV degradation of anthocyanin extracts and extracts containing acid has shown to follow first-order kinetics (Figure 2). Table II shows the reaction rate (k) and half-life (t_{1/2}) of the samples on 8 hours of UV irradiation. Reaction rate of degradation and half-life of anthocyanin were calculated as 0.0219 hr^{-1} and 31.6 hours, respectively.

Dyes with hydrochloric acid and citric acid were able to avoid UV degradation with a lower degradation rate and higher half-life. Addition of hydrochloric acid increased the half-life by sevenfold to 210.0 hours and reduced the reaction rate to 0.0033 hr^{-1}, as compared to half-life of 31.6 hours and reaction rate of 0.0219 hr^{-1} for extract without acid. It was an unexpected result that addition of acetic and oxalic acids decreased the half-life compared to the pure anthocyanin dye. Therefore, both of the acids enhanced the UV degradation process of the anthocyanin dye. The extract with added oxalic acid showed the highest UV degradation rate, calculated at 0.1923 hr^{-1}.

According to Marco et al. (2011), degradation of anthocyanins by UV radiation is the transformation of flavylum cation into colourless carbinol and coloured quinoidal base at low pH.

**TGA of PVA–anthocyanin coatings**

Thermograms of all coating samples are depicted in Figure 3. Our results obtained for pure PVA were similar to that obtained by Raju et al. (2007). Weight loss at temperature below 100°C was due to water content. This loss was noticeable in all samples. Second degradation step at 200-300°C was due to thermal degradation of the PVA molecule, and third weight loss was due to PVA by-products (Chen et al., 2008). In our study, an additional step was observed in the thermogram of PVA with anthocyanin, which could be due to anthocyanin. More degradation steps could be observed in thermograms of other samples. Appearance of a degradation step at 200-250°C of coating samples with citric acid could be attributed to the fragments of citric acid (Hardy et al., 2003). Degradation steps at 150-300°C of samples with added oxalic acid may be due to...
evolution of oxalic acid. Samples containing hydrochloric acid, citric acid and oxalic acid showed a shift in the second degradation loss, recording at 300-350°C compared to 250-300°C in other samples. This indicated that those samples had higher thermal stability at a higher temperature. At a lower temperature, thermal degradation of the coating samples was similar, which was due to water evaporation.

Table II Reaction rate and half-life of anthocyanin extract and extracts with acid upon UV irradiation for 8 hours

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction rate (h⁻¹)</th>
<th>Half-life (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthocyanin</td>
<td>0.0219</td>
<td>31.6</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.0033</td>
<td>210.0</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.0256</td>
<td>27.0</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.0117</td>
<td>59.2</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.1923</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Figure 2 UV degradation of anthocyanins and anthocyanins with acids

Figure 3 Thermograms of pure PVA, PVA + anthocyanin and PVA + anthocyanin with acids

UV-induced colour degradation of PVA–anthocyanin coatings

Results of CIE L*, a*, b*, C* and ΔE values before and after 24 hours of UV irradiation on coating samples are tabulated in Table III. Visual colour changes of the coatings before and after UV irradiation are shown in Table IV. A minimum ΔE = 1 was assumed to be the basis for colour difference noticeable by human eye (Gonnet, 1998). It was observed that all samples showed an increase in lightness L* and a decrease in a*, b* and C* values. It can be deduced that UV irradiation increases lightness and lowers redness and blueness of PVA–anthocyanin coatings, which could be due to the degradation of anthocyanin in the coating. Yang et al. (2008) also reported the same trends of result in aqueous anthocyanins. It was reported that the decrease in a* value could be attributed to degradation of monomeric anthocyanins, while the increase in b* value indicated the formation of yellow chalcone species. Addition of hydrochloric
Acid, acetic acid and oxalic acid reduced the ΔE values compared to coating with anthocyanin only without acid, thus enhancing UV stability of the PVA–anthocyanin sample.

**Conclusions**

Development of PVA coating films with anthocyanin and different acids as additives was done in this work. It can be shown that addition of hydrochloric acid and citric acid enhanced thermal and UV stability of the anthocyanin extract. Thermal stability of the coating was enhanced by addition of hydrochloric acid, citric acid and oxalic acid, while UV-colour stability was enhanced by hydrochloric acid, acetic acid and oxalic acid.

**References**


About the authors

S.V. Lee obtained his first-year degree and master's degree in physics from the University of Malaya in 2009 and 2013, respectively. He is currently working as a Lecturer at UCSI University. His interests cover organic coating, pigment and technology resins.

A.N. Hadi obtained his bachelor's degree in physics from the University of Malaya in 2013. He is currently working as a Research Assistant and pursuing a master's degree in physics (materials science). His interests cover organic coating, pigment and resin technology.

Z.H.Z. Zainal Abidin obtained his bachelor's degree and PhD degree from the University of Malaya in 1999 and 2005, respectively. He is currently working as a Senior Lecturer at the Centre for Ionics, Physics Department, University of Malaya. His interests cover polymeric materials, advanced materials science, pigment and technology resins, biophysics and organic coating. Z.H.Z. Zainal Abidin is the corresponding author and can be contacted at: zul_hazrin@um.edu.my
N.A. Mazni obtained her bachelor’s degree in genetics from Universiti Kebangsaan Malaysia. She is currently pursuing a master’s degree in plant biotechnology at the Universiti Malaysia Kelantan while working as a Research Assistant at the University of Malaya. Her interests cover plant biotechnology, organic coating and pigment.

N.A. Halim obtained her bachelor’s degree and PhD degree from the University of Malaya in 1998 and 2010, respectively. She is currently working as a Lecturer at the Centre for Defence Foundation Studies, National Defence University of Malaysia (UPNM). She is also a collaboration member of the Centre for Ionics University of Malaya, Physics Department, University of Malaya. Her interests cover polymeric materials, organoclay, polymer nanoclay composites, advanced materials science and organic coating.

R. Usop obtained her bachelor’s degree in physics from Universiti Malaysia Terengganu in 2012, and is currently pursuing a master’s degree in physics (materials science). Her interests cover organic coating, pigment and resin technology.

H.C. Hassan obtained her bachelor’s degree in physics (electronics & instrumentation) from Universiti Malaysia Terengganu in 2012. She is currently pursuing a master’s degree in physics (advanced materials science). Her interest covers dye extraction process.

S.R. Majid obtained her master’s degree and PhD degree in advanced materials science from the University of Malaya in 2000 and 2005, respectively. She is currently working as an Associate Professor at the Centre for Ionics, Department of Physics, University of Malaya. Her interests cover polymer electrolytes (application of polymer electrolytes in proton and lithium ion batteries, electric double-layer capacitors, fuel cells, solar cells), energy storage and electro-active ceramics (lithium ion conducting ceramics materials).

A.K. Arof is currently the Head of the Centre for Ionics (CIUM), University of Malaya. He has been working in the University of Malaya since 1985 and has more than 100 publications. His field of strength and interest envelops areas pertaining to batteries, solid-state ionic and advanced materials.