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The colour stability of natural dye coating films consisting of chlorophyll after exposed to UV-A

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Abstract
Purpose – This paper aims to study the colour stability of chlorophyll and the effect of copper (II) nitrate – Cu(NO₃)₂ – as an additive in natural dye coating films after being exposed to ultraviolet-A (UV-A).

Design/methodology/approach – The natural dye was extracted from the leaves of Cassia alata L. using absolute ethanol as the solvent. The extract was divided into two parts and, one of it was added with 3 wt.% Cu(NO₃)₂ as an additive. The polymer blend of poly(methyl methacrylate) (PMMA) and acrylic polyol was used as the coating binder. Both parts of the dye with and without additive were mixed with the blended polymer in a specific ratio. The resulted mixtures were applied as coating films on glass substrates. The colour stability of the coating films on exposure to UV-A with the time of exposure was observed with Commission internationale de l’éclairage (CIE) L’a’b’ colour coordinates. The hidden power by the means of reflectivity and glossiness of the coatings was also studied. Statistical standard deviation (STD) was used to analyse the data.

Findings – The test showed that the coating films containing Cu(NO₃)₂ had smaller colour differences, (ΔE*), indicating higher colour stability. The analysis on hidden power also showed that the coating film with Cu(NO₃)₂ was 1.6 times more stable than the film without additive. All the measurements in this study were observed within 35 days of duration.

Research limitations/implications – This paper implies the potential of using natural dye extracted from Cassia alata L. leaves as a stable dye colourant for coating applications.

Practical implications – The coating film developed in this study is suitable for glass substrate applications.

Originality/value – A new method of preparing solvent-based coating film from PMMA–acrylic polyol with chlorophyll colourant is introduced in this study.

Keywords Chlorophyll, CIEL’a’b’, Colour stability, Natural dye coating film

Paper type Research paper

Introduction

There are 600 species of Cassia plants. Cassia alata is a bush tree and widely found on the road side in Malaysia. This tree can grow from 6- to 15-feet high. Cassia alata belongs to the Caesalpiniaceae family. Commonly known as “Gelenggang Besar” in Malaysia and is widely distributed in the tropical countries. Cassia alata has been reported to have antimicrobacterial substances (Khan et al., 2001). Phongpaichit et al. (2004) has reported that Cassia alata leaf extract contains an antimicrobial agent against Tichophyton rubrum fungus. It is well known that natural green dye extracts from plants consist of chlorophyll molecules that are mainly responsible for the visible colour appearance. In this work, the green dye extracts from Cassia alata leaves were used as colourants for coating films.

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Chlorophyll molecular structures are in the form of tetrapyroles that consist of four pyrrole rings with magnesium, Mg, at the centre. In solutions, chlorophyll molecules can undergo isomerisation and the magnesium comes out. Chlorophyll molecules are also easily destroyed by light, oxygen, heat, acid and alkali (Britton, 1983). These factors will cause fast degradation of the green colour visible appearance of the dye in less than 24 h (Matile and Hortensteiner, 1999). Despite the poor stability, there are several reports that have shown the potential of chlorophylls applied as photo-sensitisers in dye sensitised solar cells (Kay et al., 1994; Kalyanasundaram et al., 1987; Hassan et al., 2014). Traditionally, natural green dyes consisting chlorophylls also been used as fabric dyeing colourants before the innovation of synthetic colours (Lesch, 1969). In this work, we have investigated the colour stability of natural green dyes consisting of chlorophylls in coating films which were exposed to ultraviolet A (UV-A).

The natural green dye was extracted from Cassia alata leaves and was mixed with blended polymers poly(methyl methacrylate) (PMMA) and acrylic polyol. Such blended polymers were reported to be suitable as binders for natural dye coating films (Abidin et al., 2013).

**Experimental**

**Sample preparation**

*Cassia alata* leaves were immersed in ethanol for 24 h. The extract was then filtered with Whatman filter paper to remove any impurities. The dye extract obtained was green in appearance. Another batch of the green dye was prepared by adding 3 wt. % of copper (II) nitrate – (Cu(NO₃)₂) – as an additive. Both types of these green dyes were mixed with blended polymer consisting of PMMA and commercial grade acrylic polyol. The blended polymer was prepared by mixing PMMA (Mw: 350,000 gmol⁻¹) and commercial grade Acrylic Polyol in the weight ratio 8:2 in xylene as a solvent. The PMMA and commercial grade acrylic polyol were obtained from Sigma Aldrich and Syntheses Malaysia Corporation respectively.

The green dyes and the blended polymer were mixed in 2:8 weight ratios. The constituents of the coating paints are shown in **Table I**. All the mixtures were applied on glass substrate and left to dry at room temperature, 27°C. Coating film samples were coded as Chlorophyll (CHR) and Copper-Chlorophyll (CHRCU) [the one containing Cu(NO₃)₂].

All the samples were exposed to UV light using 18 W Philips TL-D 18w/830 UV Fluorescent Lamp light source which was located at 15 cm above the surface of the samples.

**Table I** Constituents of natural green dye coating paints

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binder (wt.%)</th>
<th>Acrylic polyol</th>
<th>Dye content</th>
<th>Binder to dye (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHRCU</td>
<td>80</td>
<td>20</td>
<td>Chlorophyll + 3 wt.% of Cu(NO₃)₂</td>
<td>80:20</td>
</tr>
<tr>
<td>CHR</td>
<td>80</td>
<td>20</td>
<td>Chlorophyll</td>
<td>80:20</td>
</tr>
</tbody>
</table>

**Colour measurement**

Commission international de l’éclairage (CIE) 1976 colour space or scale L’a’b’ or popularly known as CIEL*a*b’ is a technique usually used to measure colour difference (Krishna Prasad et al., 1996). In this technique, the colour characteristic is measured from the transmittance spectrum of the object within the visible colour spectrum. The colour obtained is organised in coordinate space, as shown in **Figure 1**. The arrow direction in the coordinate space indicates the difference in colour composition intensity from the origin value (0,0). Total colour difference ΔE’ [equation (1)] is calculated to determine the coating film’s colour stability with reference to the Day 0 coating film samples:

\[ \Delta E' = \left( (\Delta a')^2 + (\Delta b')^2 + (\Delta L)^2 \right)^{1/2} \] (1)

The colour characteristics of the coating samples were measured using AvaSpec-2048 Fibre Optic Spectrometer and the analysis software used was AvaSoft 7.6.

**Reflectivity R_a**

Hiding power is the property of the coating film’s ability to hide the substrate. Incident light on the coating film surface will be partially transmitted and partially reflected. The light that reaches the substrate (which was transmitted by the coating film) will be partially transmitted and partially reflected by the substrates. This reflected light will visibly show the substrate pattern. Therefore, the reflectivity can be a measure of the hiding power of the coating films.

The coating films on glass panels were imposed on two standard backgrounds, black and white, to measure the coating film’s R_O and R_W values. Here, R_O and R_W values represent the reflectivity of the coating film on black and white background, respectively. The data obtained were used to calculate the hiding power in terms of reflectivity R_a. Equations (2) and (3) were used to calculate the R_a:

\[ R_a = a - (a^2 - 1)^{1/2} \] (2)

Where a is given by:

**Figure 1** CIEL’a’b’ colour coordinate space
$a = f(R_0, R_w, W) = \frac{1}{2} \left( R_w + \frac{R_0 + W - RW}{WR_0} \right)$

(3)

$W$ is the white substrate reflectance. The reflectivities of the coating films were measured as a function time. This is done to predict the effect of coating film colour changes on the hidden power stability. The coating film reflectivities were measured using the Rhopoint Novo-Shade Duo reflectometer at 45° angle.

**Glossiness**

Gloss values of the coating samples were measured at the incident angle 60° using a Novo Gloss Dual-glossmeter. The purpose of this test is to find out whether the exposure of the coating film towards UV light will cause alteration of the surface roughness or not (Mirabedini et al., 2011). This prediction is because of the ability of photon in the UV–visible light to initiate chemical reaction. Any changes on the coating film surface morphology will lead to the change of the glossy value.

**Results and discussion**

**Sample preparation**

It was found that samples prepared with compositions other than those shown in Table I were not suitable to be applied as coating films. Experiments showed that the coating films prepared with any other compositions caused bubbling and inhomogeneous colour distribution in the coating. Figure 2 shows the two coating films produced with contents as given in Table I illustrating the perfect nature of the films.

**Colour measurement**

Statistical standard deviation (STD) was used to analyse the colour stability of the coating film samples. Ideally, if the coating film has a high colour stability, it will show zero STD value. In a practical coating film with higher colour stability, the film will have a STD value closer to zero.

The CHR coating film had $-7.96$ a’ coordinate value and the CHRCU coating film had a corresponding value of $-13.03$ before exposure to the UV-A (Figures 3 and 4). These data showed that the CHRCU coating film was greener than the CHR coating film even before the exposure to the UV-A. The visible appearance of both samples showed that the CHR coating film is not able to maintain the original green dye colour for many days compared to the CHRCU coating film (Tables II and III). After 35 days of exposure to the UV-A, CHRCU coating film had a STD of 1.24 which is only 0.46 lower than that of the CHR coating film. However, it has to be noted that the CHR coating film’s STD value calculation is not based on the original green dye colour appearance, as the CHR coating film at Day 0 had already changed to yellow (Table III).

Before the exposure to the UV-A, both coating films had higher coordinates for b’ (in positive values) compared to their respective a’ values, as seen in Figures 3 and 4. These results indicate the higher yellowness colour component in the coating films. Despite the higher value of b’, CHRCU coating film did not show yellow colour appearance, as it has the greenness coordinate of $-13.03$ indicating that the green component was sufficient enough to hide the yellow colour component visibility. After 35 days exposure to the UV-A, the CHR coating film’s b’ STD value was 2.19 times higher than that of the CHRCU coating film. Hence, it can be assumed that the yellowness of the CHR coating film is 2 times less stable than that of the CHRCU coating film.

The L’ whiteness (or lightness) coordinate of CHRCU coating film is 1.43 times higher than that of the CHR coating film at Day 0. After 35 days of exposure to UV-A, from visual appearance of the lightness, both coating films do not show any significant changes in the colour visibilities (Figures 3 and 4).
Figure 4 CIE L*“a”“b” colour space coordinates for the CHRCU coating film

Table II Visible colour appearance of CHR and CHRCU pigments

<table>
<thead>
<tr>
<th>CHR</th>
<th>CHRCU</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Sample" /></td>
<td><img src="image2.png" alt="Sample" /></td>
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</table>

Table III Visible colour appearances for CHR and CHRCU coating films

<table>
<thead>
<tr>
<th>CHR</th>
<th>Day 0 (before UV exposure)</th>
<th>Day 7</th>
<th>Day 14</th>
<th>Day 21</th>
<th>Day 28</th>
<th>Day 35</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image8.png" alt="Sample" /></td>
<td><img src="image9.png" alt="Sample" /></td>
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</table>

<table>
<thead>
<tr>
<th>CHRCU</th>
<th>Day 0 (before UV exposure)</th>
<th>Day 7</th>
<th>Day 14</th>
<th>Day 21</th>
<th>Day 28</th>
<th>Day 35</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image12.png" alt="Sample" /></td>
<td><img src="image13.png" alt="Sample" /></td>
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<td><img src="image15.png" alt="Sample" /></td>
<td><img src="image16.png" alt="Sample" /></td>
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</tbody>
</table>
Chromaticity (C) also known as colour saturation in CIE L’a’b’ system is determined by the length of colour coordinate value to the (0,0) as shown in Figure 5. For the CHR coating film, the C values decrease and moving towards (0,0) with time of exposure (Figure 6). The Hue angle (H°) which is related to the C positions was maintained within the range 96.91° to 106.43° in quarter region II (Figure 7). In contrast with the CHRCU coating film, the C values show much smaller changes with the time of exposure compared to those of CHR coating film. The STD value of C for CHRCU coating film is 3.98 lower than that of the CHR coating film. As we can see from Figure 7, the H° value for CHRCU coating film is also smaller throughout the 35 days period with a STD value of 2.29.

The colour difference, ΔE*, was calculated by using colour space coordinate L’, a’ and b’ of coating films with Day 0 as reference. The ΔE* of CHR coating film showed drastic changes after three days of exposure to UV-A with values 2.04 times higher than those of CHRCU coating film (Figure 8). ΔE* values of CHR coating film showed continuous increment and ended at 36.21 on Day 35. Although for the CHRCU coating film, ΔE* values tend to remain constant and ended at 11.83 on Day 35. At the end of 35 days, CHR film had the ΔE* STD value that is 3.06 times higher than that of the value of the CHRCU film.

**Reflectivity R_o**

Figures 9 and 10 show the reflectivities of the coating films on standard black and white substrates, respectively. The CHRCU coating film showed constant values of R_o during 11 days of exposure to the UV-A. But the CHR coating film was only able to maintain constant R_o value up to seven days.

Both of the R_o graphs in Figure 9 had the same trends as the R_w results, as shown in Figure 11. However, all the R_o values do not affect significantly the values of R_w. This is because R_o values are too small compared to the R_w values (Figure 10) which are also included in the calculation of R_w. The increase in R_w values arises because of the decrease in the values of R_w.

Both coating films tend to show stable R_o values within the first two weeks of exposure (Figure 11). After 21 days of exposure, the reflectivity of the CHR coating film increased to 0.0214 which is 1.15 times higher than that of the CHRCU coating film. The R_w values for both coating films do not change significantly from Day 21 to Day 28, but increase rapidly beyond 28 days. The CHR and CHRCU coating films have STD values of 0.0044 and 0.0024, respectively. The higher STD value of CHR coating film is because of steeper rising of R_o value of CHR film compared to CHRCU coating film on Day 35.

**Glossiness**

Figure 12 shows that both coating film samples did not show any significant changes of their glossiness, GU, after six days of exposure to UV-A. For both films, the change in GU values with number of days shows the same trend and the values were found to decrease from Day 6 to Day 18. The lowest GU values for CHR and CHRCU coating samples were 148 and 115, respectively, and occurred on the same day (Day 18). The decrease of the GU values is expected because most of the incident light is absorbed by the coating film during the glossy measurement and less intensity is reflected for glossiness measurement compared to those of the respective Day 0

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**Figure 5** Chromaticity (C) and Hue angle in CIEL*a*b* colour coordinate space

**Figure 6** Chromaticity (C) for CHR and CHRCU coating films

**Figure 7** Chromaticity (C) and Hue angle in CIEL*a*b* colour coordinate space
sample. After 35 days, the STD values for CHR and CHRCU were 2.40 and 2.12, respectively.

**Conclusions**

Dye containing chlorophyll from *Cassia alata* leaves was successfully used as a colourant in blended PMMA-Acrylic Polyol for coating film application. (Cu(NO₃)₂) was added to the pigment to study its effect on the colour stability of the coating film. The colour measurement showed that yellowness of CHR coating film containing chlorophyll only was less stable compared to CHRCU coating film containing the Cu(NO₃)₂ additive indicating that the additive helps to
Figure 10 Reflectivities with a white tile background, $R_w$

Figure 11 Reflectivities of coating films

Figure 12 Gloss measurements of CHR and CHRCU coating samples at 60° angle
maintain the green colour of the chlorophyll in CHRCU. Meanwhile, the reflectivity of both samples showed that the stability of the colour remained for two weeks when exposed to UV-A, and the reflectivity started to increase after two weeks because of the colour degradation on longer exposure. The glossiness of CHRCU coating film was found to be more stable based on its STD value. Hence, it can be concluded that the addition of (Cu(NO₃)₂) as an additive to chlorophyll pigment from Cassia alata leaves can provide good colour stability in PMMA-acrylic polyol-based coating films.

References


electrolytes, solar cell and electrochemical double-layer capacitor).

**S.R. Majid** obtained her master’s degree and PhD degree in Advanced Materials Science at University of Malaya in 2000 and 2005, respectively. She is currently worked as Associate Professor in 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).

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