Influence of curcumin natural dye colorant with PMMA-acrylic polyol blended polymer

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Abstract

Purpose – The purpose of this work is to investigate the influence of curcumin dye natural colorant on adhesion, mechanical, thermal and electrochemical properties of blend poly (methyl methacrylate) (PMMA) – acrylic polyol.

Design/methodology/approach – Extracted curcumin yellow dye colorant from Curcuma Demostica was mixed with PMMA-acrylic polyol blended polymer in the volume ratios of 9:1, 8:2 and 7:3. The mixtures were applied on pre-treated cold-roll mild steel panels. All of the paint coating samples were subjected to potential time measurement (PTM), rapid impact deformation, differential scanning calorimetry (DSC), cross hatch and Fourier transform infrared spectroscopy (FTIR) tests.

Findings – The addition of curcumin dye colorant was able to improve the adhesion, flexibilities and resistance against electrolytes penetration of the blended poly (methyl methacrylate) (PMMA) – acrylic polyol polymer paint system. Cross hatch test studies showed that high amount of curcumin dye colorant (AP30 paint system) had the lowest peel-off coating area from the substrate. The FTIR test had confirmed the high concentration of hydroxyl group in the AP30 sample. The hydroxyl group was able to promote hydrogen bonding between coating substrate interface. The AP30 sample had the highest coating flexibilities when tested with rapid impact test. This was due to the lowest glass transition value Tg which indicated lowest cross linking density in the coating molecules structure. In the PTM test, AP30 paint system had shown the highest rate electrolytes penetration within the AP sample.

Research limitations/implications – The composition of curcumin dye colorant in the polymer blend is limited from 10 percent to 30 percent pigment volume concentration. Increasing the amount of lawsone pigment will result inhomogeneous mixtures.

Originality/value – The AP paint system is suitable for interior applications. This paint system has to be mixed with suitable additive materials to improve its performance for exterior purpose.

Keywords Curcuma Demostica, PMMA, Acrylic polyol, Adhesion, Impact strength, Structural properties, Thermal analysis, Structural analysis, Dyes

Paper type Research paper

Introduction

Recently, several researchers have developed renewable and environmental friendly materials for resin and coating application. The increasing interest is due to easy excess and low cost of agricultural raw materials. For example, linseed oil obtained from the seeds of the flax plant (Linumusitatissimum) has been used as a main ingredient in paint and varnishes (Derksen et al., 1996). Poly (urethane fatty amide) resin from linseed oil has been used in coating application (Ahmad et al., 2009). Furan has been used and extracted from vegetable as a replacement of petroleum-based polymers in latex paints (Hussain et al., 2002). Poly (urethane fatty amide) resin from linseed oil has been used in coating application (Ahmad et al., 2009). Furan has been used and extracted from vegetable as a replacement of petroleum-based polymers in latex paints (Hussain et al., 2002). The potential of rice bran has been found as an adhesive modified with potassium permanganate and poly (vinyl alcohol) for wood industry (Wang et al., 2010).

However, fewer studies have been made on the agricultural natural pigment as a colour property of paint coating system. Carotenoids and anthocyanin (natural pigments) are active materials in Gongronemalatifolium for corrosion inhibitions on mild steel in H2SO4 (Eddy and Ebenso, 2010). In our previous work, a new paint system from agricultural resource has developed using curcumin dye colorant and dammar-acrylic resin mixture (Abidin et al., 2006b). The stability of curcumin dye colorant in mixed dammar-acrylic resin and the improvement of paint system with the addition of dammar have been discovered.

Poly (methyl methacrylate) (PMMA) has low adhesion property due to its low surface energy. Extensive studies have been made to improve PMMA adhesion property by adding co-polymer, surface treatment modification, hybrid coating, etc. However, the use of acrylic polyol resin and especially agricultural resources are needed to be researched. Additionally, curcumin dye colorant has high adhesion properties which is the ability to stick on any substrate surfaces.
Curcumin (diferuoylmethane) is the pigment in turmeric (Curcuma domestica/longa) widely used as a spice and responsible for the yellow color of curry (Figure 1). Curcumin is the only natural pigment belongs to diaroylmethane compounds. Curcumin is a pigment in the roots and shoots of Curcuma domestica, C. longa, C. tinstori, C. rotunda, and C. viridiflora, which grow as wild plants in tropical Asia and are cultivated in China, Cochin China and East Indies. Curcuma trees usually possess an odor of ginger and a burning taste and contain oil and a further brown coloring matter in addition to curcumin. The addition of acrylic polyol is to enhance the adhesion property of PMMA (Figure 2). It represents a special group of amorphous polyols with presence of hydroxyl group that is able to promote the hydrogen bonding between coating and substrate interface.

The aim of this work is to demonstrate the effect of curcumin dye colorant on the mechanical, thermal and electrochemical characteristics of PMMA-acrylic polyol blend polymer. Another aim of this work is to develop a new paint system using natural dye colorant (curcumin) as a pigment.

Experimental

Sample formulation
PMMA (Mw: 996,000 g mol\(^{-1}\), \(T_g: 125^\circ C\)) and acrylic polyol were purchased from Sigma Aldrich and Syntheses Malaysia Corporation, respectively. Blended polymer PMMA-acrylic polyol in volume ratio 9:1 with xylene as a solvent was mixed with liquid curcumin colorant extracted from Curcuma domestica root as shown in Table I. The curcumin yellow colorant was extracted from Curcuma domestica roots by immersing them in ethanol. All the mixtures were applied on cold roll steel Q-panel. The samples were left to dry for one week in room temperature 25°C.

Coating film adhesion test (ASTM D3359)
The coating film adhesion test was conducted by using American Standard Test Measurement ASTM D3359. The peel-off area of the coating in cm\(^2\) was also measured.

Infrared absorption spectroscopy
The samples infrared absorption spectroscopy’s behavior was observed by using Fourier transform infrared spectroscopy (FTIR) type Nicolet iS10. The purpose of conducting this experiment is to observed specific functional groups that presence in the coating systems that are able to promote the adhesion in between coating and substrate interface. The absorption relative peak intensity was also recorded as to predict the amount function group in the coating films. The estimation functional group amount was calculated by relative peak intensity (Yelil Arasi et al., 2012):

\[
\text{Relative intensity of functional group} (f_g) = \frac{A_{fg}}{A_{801}}
\]

Rapid impact deformation
Rapid impact deformation also known as impact resistance was conducted to evaluate the coating film flexibility characteristic. A 1 kg of weight was released from different heights onto the hemisphere indenter that rest on the coated panel surface. The maximum height of the weight was noted as the formation of crack occurs on the coating surface. A pinhole detector was used to detect the crack formation. In this test, we also observed the ability of the coating to withstand the compression (direct impact) and elongation (indirect impact) forces from the indenter (Figure 3).

Coating film glass transition temperature (\(T_g\))
METTLER TORLEDO DSC820 was used to determine the coating films glass transition temperature (\(T_g\)). 5-10 mg of coating sample was measured in hermetically sealed 40 µl aluminum crucibles in a self-generated atmosphere (Abidin et al., 2006a, c). The heating rate was 10°C/min from 0°C to 250°C. The \(T_g\) result will give the ideas how to correlate the molecules free volume concentration, with the flexibility and resistance against electrolytes penetration of coating films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PMMA-acrylic polyol 9:1 ratio (%)</th>
<th>Curcumin pigment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P90A10</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>AP10</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>AP20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>AP30</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

Table I Sample formulation in volume percentages

Figure 1 Curcumin molecular structure

Figure 2 PMMA structure

Figure 3 Impact test
Potential time measurement
The coating film ability against electrolytes penetration was evaluated by measuring the voltage across the film against time when expose to the salt water. The experimental setup for potential time measurement is shown in Figure 4. The voltage across the coated panel was recorded until $-0.43 \text{ mV}$ which equivalent to the voltage across the uncoated Q-panel. This voltage value of the immersed coated panel indicates the electrolytes are present in the coating substrate interface. 8.48 cm$^2$ of area of coating sample was exposed to 3 percent of sodium chloride (NaCl) solution (Abidin et al., 2006a, b).

Results and discussion
Sample formulation
A new formulation of natural paint system had been discovered in this work. Blended synthetic polymers PMMA – acrylic polyol can be mixed homogenously with curcumin yellow pigment. A smooth paint coating films surface was obtained after one week of application (Figure 5).

Coating film adhesion performance
The quantity changes of curcumin pigment played a role on the adhesion property of the blended polymer PMMA-acrylic polyol resins. 30 percent of curcumin colorant volume concentration had improved the adhesion property of AP30 paint system. It was predicted that the AP30 paint system had high amount of hydroxyl group in the $(1E, 6E)$-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione aromatic rings molecular structure and was able to create the hydrogen bonding with the oxide layer on cold roll steel Q-panel surface. A large amount of coating chipping had been found from the P90A10 and AP10 paint systems after the scratch test. This was due to the high amount of PMMA in both of the paint systems which caused higher brittleness characteristic behaviour (Table II).

Hydrogen bonding in between coating substrate interface
Hydrogen bonding occurrence in between the polymer coating and substrate interface is the main contribution to the coating films adhesion property. The presence of three molecules groups which are hydroxyl (−OH), −CH$\text{\textsubscript{2}}$ and methyl (−CH$\text{\textsubscript{3}}$) have been observed with the infrared spectroscopy (Figure 6). It was predicted these functional groups are able to promote the hydrogen bonding in between coating substrate interface (Hong et al., 2010).

Hydroxyl group was detected within the range of 3,702-2,078 cm$^{-1}$. The presence of hydroxyl group (Figure 7) is mainly contribute by −OH at the end of the polyl chain, carboxylic acid R−C(==O)OH from the PMMA and −OH at the R$_2$ position of curcumin aromatic rings. The presence of the carboxylic acid is due to the PMMA, an ester material. It can be observed from Figure 7 that AP30 sample had shown highest relative absorption peak intensity of hydroxyl group. This indicates the 30 percent curcumin colorant had increased hydroxyl group in the AP30 paint system.

The bend vibration mode of CH$\text{\textsubscript{2}}$ and CH$\text{\textsubscript{3}}$ were observed in the 1,465 and 1,373 cm$^{-1}$, respectively, (Figure 7). There were

### Table II Group of coating based on percentage of peeled of area

<table>
<thead>
<tr>
<th>Group of coating based on percentage of peeled of area</th>
<th>Cross hatch result</th>
<th>ASTM D3359</th>
<th>Coating peeled off area in cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P90A10</td>
<td>0</td>
<td>1.595</td>
<td></td>
</tr>
<tr>
<td>AP10</td>
<td>1</td>
<td>1.456</td>
<td></td>
</tr>
<tr>
<td>AP20</td>
<td>2</td>
<td>1.213</td>
<td></td>
</tr>
<tr>
<td>AP30</td>
<td>3</td>
<td>0.822</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4 PTM test schematic diagram

![Figure 4 PTM test schematic diagram](image)

Figure 5 AP 10, AP 20 and AP 30 samples

![Figure 5 AP 10, AP 20 and AP 30 samples](image)
small changes in the relative absorption peak intensity of CH$_2$ and CH$_3$ as the composition curcumin colorant in the PMMA changed. PMMA monomer (methyl methacrylate) has two CH$_3$ and one CH$_2$ in the molecular structure. However, the presence of these two functional groups have less effect for the PMMA coating film adhesion property upon cold roll steel Q-panel. It can be observed from Figure 7 the peel-off coating area of samples decrease as the composition PMMA decreases. In order to support this assumption we had applied pure PMMA solution on to cold roll steel Q-panel surface. After one week of application, the coating film was peeled off naturally from the substrate which indicated the behavior of PMMA as free standing film (Figure 8).

In curcumin, the position of CH$_2$ is at centre of the molecular structure. The CH$_3$ molecules are at both sides of the curcumin aromatic rings. It is predicted the aromatic rings at the end of the curcumin molecular structure is able to promote the adhesion property in between the coating substrates interface (Sathyanarayana and Yaseen, 1995; Zhang, 2010). This is due to the hydrogen bonding between –CH at the aromatic rings with the oxide layer at the cold roll steel Q-panel surface.

It can be concluded the presence of hydroxyl, ethyl and methyl is able to improve the PMMA-acrylic polyol curcumin paint coating film adhesion property in this work. All these groups consist of hydrogen compound which is role as to produce hydrogen bonding between coating and substrate.

**Coating film flexibility**

Impact test was conducted on all three samples to evaluate the coating film resistivity against crack formation by rapid impact deformation. It can be observed from Figure 6 the quantity change of curcumin pigment colorant does not show any significant change to the coating film impact resistance. AP10 paint coating system had shown the lowest ability to resist the formation of crack cause by the direct impact and indirect
impact of the indenter. It was to our surprise that the increase amount of curcumin colorant had improved the mechanical strength of the paint coating film since curcumin molecules consists of two aromatic rings.

The presence of aromatic rings is able to increase the cross link density and lower the free volume concentration of a coating film (Wicks et al., 1992). Therefore, 30 percent of curcumin dye colorant in the AP30 (that consist of high amount of aromatic rings) paint system should contribute to the highest cross link density and lowest free volume concentration molecules structure. These molecule structures will reduce polymer mobilities during the rapid impact test and resulting the ease ability to form cracks during rapid impact test (Ward Wicks et al., 1994).

However, from Figure 9 the impact resistance results are contradicting with the statement from the above paragraph. We predicted this was due to the curcumin aliphatic chain molecules in between the two aromatic rings and the high composition of PMMA in each sample have more dominant in contributing the coating film flexibility. Hence, the maximum flexibility of coating film AP30 in this work was able to withstand the impact by the falling indenter from the height of 9.0 cm.

The blended PMMA-acrylic polyol resin (without the present of dye curcumin colorant) had shown lowest resistivity against rapid deformation. The P90A10 sample can be concluded that it behaves more brittle and the addition of dye curcumin colorant was able to improve the coating film flexibility.

DSC test was conducted to observe the coating paint film glass transition temperature Tg. The Tg value will enable us to predict and compare the concentration crosslink density and free volume molecules structure for each of the samples (Menczel and Prime, 2009).

The glass transition temperature (T_g) effect on coating film flexibilities

Different quantity of curcumin colorant in the blended PMMA-acrylic polyol polymers coating film had shown slight changes on the glass transition temperature value (Table III). The PMMA Tg was equal to the Sigma-Aldrich web-catalog, referring to the code numbers data and the same Tg value for PMMA (Mw: 996,000 g mol⁻¹) was also reported as obtained in this work (Fu et al., 2008). The Tg values decreased with the increase of percentage volume of dye curcumin colourant in the blended polymer. The decrease of the glass transition temperature can lead to lower cross link density and higher flexibility of coating film. This trend of results are also valid (Vengadaesvaran et al., 2010). In this work, 10 percent volume concentration of curcumin colorant in blended polymer had highest Tg value compared with the other AP samples. This is an indicator that the sample consists of high cross link density and low free volume concentration in the molecules structure (Austen et al., 1996). Therefore, the AP10 sample had limitation of molecular motions during the rapid impact test. In other words, AP10 sample was able to absorb much of the quick energy from the fallen rapid impact indenter due to the limitation of flexibility. Therefore, the received energy is easily transferred to the formation of crack in AP10 coating paint film (Figure 10).

The coating film resistivity against electrolytes penetration

The -0.43 mV horizontal line in Figure 11 is used as an indicator for electrolytes reaching the coating substrate interface area. The -0.43 mV value is the potential difference measurement been made across the bare cold roll steel Q-panel surface. Once the recorded potential voltage graph trend lines crossing the -0.43 mV horizontal line, it indicates the failure of the coating film to resist the penetration of electrolytes through the coating substrate interface.

Most of the researchers agree with the assumption the higher Tg value of coating film indicates the lower free volume concentration and higher cross link density in the coating film (Wicks et al., 1992). The free volume is accessible for electrolytes to penetrate through the coating substrate interface (van der Wel and Adan, 1999). The P90A10 coating system had shown the high rates of electrolytes penetration when the sample was exposed to 3 percent NaCl. The concept of Tg with free volume concentration does not support the result of P90A10 electrolyte resistivity. Based on the observation of P90A10 coated panel, we found several blistering formation with the presence of corrosion on the substrate surface. It was predicted the low adhesion property of P90A10 coating film would ease the constructive and expensive internal stress processes (Funke and Negele, 1996). The formation of blistering and crack occurred on the coating film surface factor was caused by the low adhesion property of P90A10 coating film when exposed to the electrolytes.

Referring to Table III again, the lowest Tg value of AP30 indicated the lowest free volume concentration in the AP coating system. During the immersion of coating film in the 3 percent NaCl solution, AP30 experienced the higher rates of electrolytes penetration through the coating substrate interface which was within eight days of exposure (Figure 11).

Table III Sample formulation in volume percentages

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>110.00</td>
</tr>
<tr>
<td>P90 A10</td>
<td>100.12</td>
</tr>
<tr>
<td>AP10</td>
<td>52.34</td>
</tr>
<tr>
<td>AP20</td>
<td>51.35</td>
</tr>
<tr>
<td>AP30</td>
<td>50.82</td>
</tr>
<tr>
<td>Acrylic polyol</td>
<td>42.30</td>
</tr>
</tbody>
</table>

Conclusions

As renewable materials from agricultural resource, curcumin has the potential to improve the adhesion, flexibilities and electrolyte resistance properties of blended
Figure 10 Glass transition temperature ($T_g$)

(a) P90A10

(b) AP 10

(c) AP 20

(d) AP 30
polymer poly (methyl methacrylate) (PMMA) – acrylic polyol. However, increasing the amount of curcumin dye colorant pigment in the blended polymer did not increase the flexibility of coating paint film (AP30). Taking into account the flexibility of coating film, this curcumin dye colorant paint system is suitable for interior coating system application.

References

Further reading
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