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The synthesis of coloured diaminoanthraquinone cross linked epoxy resins and their assessments in paint and selected polymers

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Novel polymeric pigments were synthesized in xylene by cross linking epoxy resin with 1,4 and 1,5-diaminoanthraquinones, by varying weight fractions from 5% to 20% of the diaminoanthraquinone derivatives. FTIR, GC/MS, UV and solubility tests were carried out. The pigments were then used to colour PLA, PMMA, PE and also in emulsion paints using polyvinyl alcohol as binder. Their light fastness, surface drying time and surface hardening time were assessed. It was found that λ_{\max} of the 1,4-diaminoanthraquinone shifted towards longer wavelength after the cross linkage, in contrast to the 1,5-diaminoanthraquinone which suffered a blue shift. However in all the cases, the λ_{\max} was not affected by the weight fractions of the anthraquinones, but the absorptivity coefficients was significantly increased as the weight fractions of the anthraquinones increased. The light fastness properties of the coloured plastics varied from 4 to 7 and indicating a trend of increase with the weight fractions of the anthraquinones. Similar observations were seen with the emulsion paints produced, in all the cases, the 1,4-diaminoanthraquinone producing better result.

Keyword: Epoxy resin, Diaminoanthraquinone, Chromophore, Pigments, PMMA, PLA

1. Introduction

Studies on the synthesis and application of polymeric dyes have aroused interest in recent years. Polymeric dyes due to high molecular size do not sublime, are nonabrasive, and generally have low toxicity^[1]. They have been widely applied on fibres because of certain essential dye properties such as fast leveling, fastness to light and wet treatments and very good thermal and chemical resistance^[2, 3, 4]. They are reported to have excellent brightness and are extremely fadeless^[4]. They have been used in food coloration and surface coating of plastic objects, as hair dyes^[5], solid state laser dyes^[6] and in jet printing^[1, 7]. Polymeric dyes constituting polyurethanes and polystyrene have been reported several years ago^[8, 9, 10]. Research activity in the area include: polymeric dyes containing anthraquinone^[11] structure and their application on polyethylene terephthalate^[10], synthesis and light

emitting properties of polymeric metal complex dyes based on hydroxyquinoline moiety^[12], polymeric dyes for photovoltaic applications^[13] and synthesis of novel water soluble cross-linked polymeric dyes with good dyeing properties^[14, 15]^[12-15]; others include the synthesis of coloured polyureas^[16]^[12-14] polyurethane derivatives^[3].

According to a recent work, polymeric colorants offer the advantage of allowing tunability in a range of physical properties such as solubility, absorption, migration, and viscosity. They do not sublime, are non-abrasive, and generally have low toxicity^[15]. Epoxy resins have been used for several years in the manufacture of high performance coatings and paints^[17]. It is with this belief in mind that we attempt the synthesis of coloured epoxy resins and explore their application for the coloration of plastics and use as a pigment in emulsion paint formulation. To the best of

our knowledge and extensive literature search, this is the first attempt of this nature.

2. Materials and Methods

2.1 Synthesis of Polymeric Dyes/ Pigments.

The synthesis of the pigments was done by a step growth condensation polymerization of specified ratio of 1,4-diaminoanthraquinone (1,4-DAQ), 1,5-diaminoanthraquinone(1,5-DAQ) and Poly (Bisphenol A-co-epichlorohydrin (EPCH) as summarized in Table 1.

Table 1: The formulation recipe for the polymeric dyes.

| Quantity of EPCH | | Quantity of 1,4 and 1,5-DAQ | | Pigment Code Number |
|------------------|------------------|-----------------------------|------------------|---------------------|
| Mass(g) | %Weight Fraction | Mass(g) | %Weight Fraction | |
| 6.25 | 95 | 0.33 | 5 | P5 |
| 6.25 | 90 | 0.70 | 10 | P10 |
| 6.25 | 85 | 1.11 | 15 | P15 |
| 6.25 | 80 | 1.57 | 20 | P20 |

The requisite quantity of the epoxy (EPCH), 6.25 g; was dissolved in 5ml xylene and added to the calculated amount of the anthraquinone also in 5 ml xylene drop wise for 15 minutes. After a homogenous solution was obtained, 5ml of xylene was added with constant stirring with a mechanical shaker. The mixture was then warmed to 60 °C in a water bath and maintained for 2 hrs. The temperature was raised to 80 °C and maintained for another 2 hrs, then poured into a beaker and placed in an oven set at 120 °C for 4 hrs. Different ratios of the epoxy resin to the diaminoanthraquinone were used, 5 to 20% weight fractions at 5% intervals as shown in Table 1. A portion of 50 mls, Sodium carbonate solution (1%) was used for solvent extraction to purify the pigment until the aqueous layer was colourless.

2.2 UV-Vis spectroscopy of pigments

Visible absorption spectra of the pigments were measured using Colorimeter 253 spectrophotometer. Xylene was used as solvent. The results obtained were summarized in Table 2.

Table 2: The UV-Visible Spectrophotometer data

| Pigment | $\lambda(\text{nm})_{\text{max}}$ | A unit | $a_{1\text{cm}}^{1\%}$ | $\epsilon(\text{lmol}^{-1}\text{cm}^{-1})$ |
|-----------|-----------------------------------|--------|------------------------|--|
| PURE(1,4) | 520 | 1.000 | 100 | 238.00 |
| 4P5 | 585 | 0.543 | 54.3 | - |
| 4P10 | 585 | 0.577 | 57.7 | - |
| 4P15 | 585 | 0.674 | 67.40 | - |
| 4P20 | 585 | 0.897 | 89.70 | - |
| PURE(1,5) | 495 | 0.897 | 89 | 213.40 |
| 5P5 | 480 | 0.321 | 32.10 | - |
| 5P10 | 480 | 0.459 | 45.90 | - |
| 5P15 | 480 | 0.464 | 46.40 | - |
| 5P20 | 480 | 0.615 | 61.50 | - |

2.3 Solubility Test

The solubility test was carried out by using common laboratory solvents at room temperature (25 °C). A small amount of the pigment was placed in a watch glass and the solvent added with continuous stirring with a glass rod for over 3 minutes, the solubility was indicated when one layer is obtained. The results are shown in Table 4.

2.4 IR spectroscopy

The samples were characterized using KBr disc sampling method. The disks were prepared by grinding the sample (2% by weight) in KBr which was then compressed into a disk and analyzed with the spectrophotometer. All the spectra were recorded over the range 4000 - 400 cm^{-1} .

2.5 GC/MS Spectra

GC/MS spectra of the pigments were analysed with a GC/MS-QP10010 PLUS, SHIMADZU, JAPAN obtained at NARICT Basawa Zaria.

2.6 Application of the synthesised Polymeric dyes / Pigment on some Polymers.

The synthesised pigments were applied to PMMA and PLA by solution casting in xylene and unto PE by melt casting at 120 °C.

2.7 Paint Formulation

Polyvinyl acetate (PVAc); 150 g, was dissolved in ethanol; 750 ml, at room temperature for 5 hours with constant stirring to obtain a homogenous solution. From this stock solution of PVAc, 5 ml was mixed with ammonia (0.02 ml), formaldehyde (0.1 ml), kaolin (0.2 g), CaCO₃ (0.2 g) and pigment (0.33 g) and stirred for an hour at 35 °C. Grinding of pigment/mixing of paint was achieved using a ceramic pestle and mortar. The mixture was milled and stirred vigorously for 1 hour. The resultant paint was poured into a clean and air tight container for further characterization ^[18].

2.8 Application of Paints to Substrate

The paints were applied on a particle ceiling board popularly known as Duratex a Brazil ceiling board acquired from Samaru Market, Zaria, Nigeria. The samples each measuring 150 mm x 30 mm were cut and ensured to be clean, dry and free from imperfections. One inch (1”) Chuto bristle hand brush was used for the application of the paints. Four (4) coated samples were produced from the corresponding four (4) paints formulated plus one (1) market sample (control).

2.9 Light Fastness

The pigmented polymers, were prepared for the light fastness test by compressing the polymers in a compression moulding machine in NILEST Samaru, Zaria. The conditions for the compression are 150 °C and 5x10⁶ kg for 4 minutes respectively. Light fastness test was carried out by the help of natural Sunlight source. Exposure was carried out for 1 ½ month for the painted specimens as in Table 5. Light fastness test of the painted samples was carried out by the use of direct sunlight. The procedure involved

aligning both the eight dyed wool standards together with the painted specimen on a cardboard. 2/3 of both the wool standards and the samples were covered with opaque cardboard while the rest was exposed to direct sunlight. Exposure was carried out until the last specimen to fade had faded to the extent of standard three of the standard grey scale for evaluating change in colour. The rating of the painted sample is that of the wool dyed sample, which faded to the same extent as the sample at the same time.

2.10 Surface Drying Time

This measures the relative degree of cure (dry to touch). It was measured by the quantitative finger marking test. The time taken for a coated sample to dry was measured by sporadically touching the coating with small white paper until there was no stain noticed on the paper. The experiment was repeated for the other three samples while the commercial paint served as control. The results are shown in Table 6

2.11 Hard Drying Time

This was the time taken for the coated sample to be completely dried and could withstand or resist gentle scratch. The hard drying times for all samples were recorded and compared with the commercial paint. The results are shown in Table 6.

3. Results and Discussion

3.1 UV- Visible Interpretation

The UV spectra of the pigments indicated in Table 1 showed that the pigments derived from 1,4-DAQ dissolved in xylene generally indicated a bathochromic shift of around 65 nm. The λ_{max} of the 1,4-DAQ was 520 nm compared to the epoxidized one which recorded 585 nm. The variation in the ratio of the anthraquinone to the epoxy didn't cause any change in λ_{max} . However, the absorptivity coefficients of the pigments did show a trend of increase with the ratio of the anthraquinone to the epoxy. The pigments are in the bluish-red range and their absorption varies with the concentrations. It also shows that those obtained from 1,5-DAQ have their λ_{max} at 480 nm (after cross linking with epoxy) whilst pure 1,5-DAQ had λ_{max} 495 nm, a hypsochromic shift of about 15nm. While explaining the UV-Vis spectra of 1,4-anthraquinone embedded in Polyurethane, Hu, *et al.*,

(2004) assigned the observed three absorptions at 555, 600 and 650 nm, to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions respectively. The absorption peak weakened with the decrease of molecular weight of aqueous dispersions.

From the results obtained it shows that pigments made from 1,4-DAQ have the higher absorptivity coefficients compared to 1,5-DAQ pigments. The one with the higher concentration of 1,4-DAQ cross linked epoxy resin is the best of all. This could be due to the planarity nature of 1,4-DAQ compared to the 1,5-DAQ.

3.2 IR Interpretation

FTIR spectroscopy was used to characterize the structure of pure epoxy resin and the modified epoxy resins. For pure epoxy resin, the band at 3500 cm^{-1} is assigned to -OH stretching. The bands at 2965 and 1383 cm^{-1} are characteristic of -CH_3 asymmetric and symmetric stretching, and the bands at 2877 and 1457 cm^{-1} are assigned to asymmetric and symmetric stretching mode of -CH_2 . The band at 915 cm^{-1} is the characteristic absorption of epoxide groups. The band at 1235 cm^{-1} is assigned to the ether bonds in epoxide groups. The absorption peaks at 1607 , 1508 and 828 cm^{-1} are characteristics of substituted aromatic rings in epoxy resin.

The fundamental reaction of concern in this analysis involved the condensation of the amine functional group -NH_2 in the diaminoanthraquinone with the epoxy resin to form the pigments. The aromatic ring benzene bands is weak compared to C=C in aliphatic systems. Hexa-substituted 3030 cm^{-1} aromatic stretching, $1613\text{-}1471 \text{ cm}^{-1}$ ring skeletal vibration, C=C - strong peak at 1461 cm^{-1} [19, 20, 21] also giving a total of $1590\text{-}1615 \text{ cm}^{-1}$ strong. In all the compounds they indicate -NH absorption bands at $2500\text{-}3600 \text{ cm}^{-1}$ and absorptions around $1630\text{-}1680 \text{ cm}^{-1}$ attributed to -C=N bonds [22] which could indicate some sought of tautomerism with the transfer of a proton from the NH group to the carbonyl oxygen on the anthraquinone. The $1630\text{-}1680 \text{ cm}^{-1}$ could also be attributed to intra-molecular hydrogen bonds [23].

3.3 Solubility Test of synthesized pigments

The solubility of the pigments was tested using some common laboratory solvents such as acetone, tetrahydrofuran and xylene. The results are as in the Table 4.

Table 4 shows that the pigments were more soluble in xylene than any of the three solvents tested. The order of decreasing solubility is xylene, tetrahydrofuran, acetone.

Table 3: The solubility behavior of the pigments

| Sample | Acetone | Tetrahydrofuran | Xylene |
|--------|------------------|------------------|----------------|
| 4P5 | Soluble | Soluble | Very Soluble |
| 4P10 | Soluble | Fairly Soluble | Very Soluble |
| 4P15 | Slightly Soluble | Fairly Soluble | Soluble |
| 4P20 | Slightly Soluble | Slightly Soluble | Soluble |
| 5P5 | Very Soluble | Very Soluble | Highly Soluble |
| 5P10 | Very Soluble | Soluble | Very Soluble |
| 5P15 | Soluble | Fairly Soluble | Very Soluble |
| 5P20 | Slightly Soluble | Slightly Soluble | Soluble |

3.4 Light Fastness Results

Table 4, shows the pigments obtained from (1,4)-diaminoAQ are more compatible with the polymers (PE, PLA, PMMA). This could be due to the fact that (1,4) diaminoAQ is more asymmetrical leading to its

shielding effect from the UV-rays, while (1,5)-diaminoAQ is less. This is reflected in the light fastness test results which show 1,4-diaminoAQ pigments to have higher light fastness than those obtained from 1,5-diaminoAQ.

Table 4: The lightfastness result of the pigments in the Polymers and Paint

| Pigment | PLA | PE | PMMA | PAINT |
|---------|-----|----|------|-------|
| 4P5 | 5 | 5 | 4 | 6 |
| 4P10 | 6 | 5 | 4 | 5 |
| 4P15 | 6 | 6 | 5 | 6 |
| 4P20 | 7 | 7 | 7 | 7 |
| 5P5 | 5 | 5 | 4 | 5 |
| 5P10 | 6 | 5 | 4 | 5 |
| 5P15 | 6 | 6 | 5 | 6 |
| 5P20 | 7 | 6 | 6 | 6 |
| SHARON | - | - | - | 5 |

3.5 Paint Surface Drying Time/ Paint surface hardening Time

Table 4, gave the surface drying and hardening times of the paints. The paints from the pigments have good and short surface drying time and surface hardening time though this is also the effect of the pigment molecular weight. The surface drying and hardening time is increasing in the sequence of degree of H-atom substitution by the epoxy resins in the anthraquinones derivatives.

Table 5: Surface Drying and hardening time.

| Pigments of Paint | Surface Drying Time | Surface Hardening Time |
|-------------------|---------------------|------------------------|
| 4P5 | 45 | 90 |
| 4P10 | 48 | 87 |
| 4P15 | 54 | 83 |
| 4P20 | 49 | 69 |
| 5P5 | 43 | 80 |
| 5P10 | 47 | 83 |
| 5P15 | 52 | 86 |
| 5P20 | 50 | 70 |

4. Conclusion

This work has shown that organic pigments can be synthesised by reacting epoxy resin with coloured diaminoanthraquinones. In this study, 1,4-diaminoanthraquinone and 1,5-diaminoanthraquinone were used. The coloured resins depicted hues not much different from the diaminoanthraquinone precursors. The pigments are produced with varying weight fractions, the result showed that the

absorptivity coefficients of the 20% weight fraction is more than 80% of the original diaminoanthraquinone. The preliminary assessments of the pigments as colorants for some thermoplastics and in paints showed some good promise. Generally speaking the light fastness result is good to very good. The 1,4-anthraquinone produced pigment with better result than the 1,5-anthraquinone.

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