Development of a Chitosan Enhanced Alkyd Resin Coating for Automobile Surfaces

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ABSTRACT

An auto-based paint was successfully synthesized by dispersing TiO, pigment into a mineral spirit solvent which was then bound with an alkyd resin binder along with additives including; genoper, natrosol, calcium carbonate and ammonia. The formulated paint was characterized and compared with ASTM and NIS standards. The synthesized paint sample was then modified by blending it with chitosan copolymer of 98% Degree of deacetylation to enhance its properties. The result obtained from experimental analysis indicated that chitosan of high degree of deacetylation plays significant role on the improvement and solubility of the chitosan in the formulated paints. From the analyses carried out, the overall performance of the chitosan-modified paint when subjected to physicochemical and physicomechanical analyses gave indication of increase in density ($1.1 g/cm^3$), viscosity (35cp), filler content (71.6%) and film thickness (7.4μm) and a decrease in drying time (33mins) and alkalinity (7.8) was observed, clearly indicating an improvement in the properties of the modified paints enabling better industrial applications such as self-healing.

Keywords: Chitosan, Oil Paints, Alkyd resin

INTRODUCTION

Chitosan, with a molecular structure similar to cellulose, is attracting an increasing amount of research interest in the process industries because of its varied applications in food, agriculture, biomedicine, textile, water treatment and pharmaceuticals (Kim et al., 2001).

Chitosan is obtained by alkaline deacetylation of chitin giving an amino group. It is usually found as polymer chains containing a unique monomer (N acetyl- D-glucosamine or D-glucosamine) (Kumar, 2000). Chitosan and its derivatives are typically obtained from demineralization, deproteinization and deacetylation processes. The capacity of chitosan to dissolve in dilute aqueous solutions is the commonly accepted criterion to differentiate it from chitin (Rabea et al., 2003).

Chitosan is a semi-crystalline biopolymer; hence because of its rigid crystalline structure, it is not soluble in most of the solvents like water, alkali or aqueous solution and common organic solvents. At certain pH values under continuous stirring, chitosan is soluble in few acids such as hydrochloric, lactic, propionic, formic and acetic acids (Chung et al., 2005). Brine and Austin (1981) stated that lower solubility values suggest incomplete removal of protein.

In this research, chitosan was used as a modifying additive to enhance the self-healing properties of a paint emulsion. Self-healing materials address the degradation issue of surfaces through the inclusion of an active phase that responds to the damage by initiating a repair mechanism. The inspiration of self-healing materials comes from biological systems, which have the ability to heal after being wounded. A material that can intrinsically correct damage can lower production costs of a number of different industrial processes, reduce inefficiency over time caused by degradation, and prevent costs incurred by material failure (Yuan et al., 2008).

Chitosan is one of the self-healing materials which have been undergoing investigations and researches for several years now. To elucidate some properties of chitosan, a group of scientists

completed a research on self-healing coatings which repair small scratches after being exposed to sunlight. The sunlight caused the chitosan molecules to react with split oxetane rings (a combination of polyurethane paint, chitosan molecules, and a ring-shaped molecule) which in turn closed the split, essentially healing the surface (Trask et al., 2007). Ghosh and Urban (2009) developed a polyurethane network that exhibited self-healing traits on exposure to ultraviolet light. The network consisted of oxetane-substituted chitosan precursor incorporated into two-component polyurethane. Upon mechanical damage of the network, a four-member oxetane ring opened to create two reactive ends. On exposure to ultraviolet light, chitosan chain scission occured, which formed a cross-link with the reactive oxetane ends, thus repairing the network. These materials are capable of repairing themselves and can be used in many coatings applications, ranging from transportation to packaging, fashion and biomedical industries (Gosh and Urban, 2009). In this present study, paint was produced and characterized and then was incorporated with chitosan polymer for enhancement of its properties in surface coatings.

MATERIALS AND METHODS
Characterization of Chitosan
Solubility Determination
0.1g of dried chitosan sample was weighed and dissolved in 10ml of 1% acetic acid followed by stirring and then filtration. The time taken for the dissolution was determined using ASTM method (2009).

Molecular Weight Determination
The molecular weight of the chitosan sample was determined using the Mark-Houwink equation

$$: [\eta] = KMW^a \qquad (1)$$

$$\eta = \frac{\eta - \eta_0}{\eta_0 C} \qquad (2)$$

Where MW is the viscosity average molecular weight for the given polymer; K and a are constants.

In addition, $[\eta]$ is intrinsic viscosity (dL/g) and [C] is the solute mass concentration (C), g/dL).

Degree of Deacetylation

The degree of deacetylation of the chitosan sample was determined according to Rout, (2001).

$$DD = 118.883 - \left[40.164 \times \left(\frac{A_{1655}}{A_{3450}}\right)\right] \qquad (3)$$

Determination of viscosity
The viscosity of chitosan was carried out using a capillary viscometer (model GMBH – D6579) and the efflux time of the solution recorded at constant bath temperature (25 ± 0.1°C). Chitosan samples were dissolved in a 0.1 M acetic acid/0.2 M sodium chloride and water (Brugnerotto et al., 2001).

Determination of ash value

To determine the ash value of chitosan, 2.0g of chitosan sample was placed into previously ignited, cooled, and tarred crucible. The sample was heated in a furnace that was preheated to 650°C for 4 hrs. The crucible was then allowed to cool to less than 200°C. Percentage of ash value was calculated using equation (4).

$$\% \, Ash = \frac{(Weight \, of \, Residue) \times 100}{(Sample \, Weight) \, g} \qquad (4)$$

Paint formulation
70ml of mineral spirit (solvent) was measured into a beaker and was placed on continuous stirring with a magnetic stirrer. 1.35ml of the anti-settler was introduced into the solvent to ensure that the solid components that will be introduced into the mixture will be kept in suspension for uniform mixing without settling down. 200ml of TiO_2 pigment was poured into the mixture and thoroughly stirred until all lumps were dissolved. This stirring process lasted for about 100minutes. At the stabilization stage, 90ml of alkyd resin (Binder) was introduced as the vehicle which was also thoroughly stirred in the mixture to ensure good quality as recommended by Oragwu (2013). At the 'Let down stage' other additives were then incorporated into the paint formulation including Calcium for accelerating drying of the paints, Genoper (anti-foam), Natrosol (thickener) which was dissolved in a little quantity of water before addition into the mixture, $CaCO_3$

(filler), Ammonia (pH adjuster), Calgon (dispersant) and preservatives. Each of the individual additives was 1.5% of the core paint formulation as specified by Abdullahi (2015). The paint formulation was then subjected to filtration to remove the undissolved pigments after which it was allowed to cool to about 28^0C before storage. The same procedure was followed for the modified automobile alkyd resin paint by adding 1.5 % chitosan concentration (Abdullahi, 2015).

Analysis of formulated paints

The quality control tests were carried out on the paint samples and compared to the commercial Berger auto paint. The various tests were according to the American Society for Testing Materials (ASTM) standard (2009).

Density

The density of the paint solutions were determined gravimetrically using a density bottle. The mass of the empty bottle was first determined as well as that of the density bottle filled with the paint solution and also when filled with water.

Where;
w_0 = Mass of empty density bottle (g)
w_1 = Mass of density bottle with water (g)
w_2 = Mass of density bottle with paint solution (g)

$$Density\ (g/cm^3) = \frac{(w_2 - w_0)}{(w_1 - w_0)} \quad (5)$$

pH

The pH of the formulated paints was measured with the use of a pH meter by immersing the pH spindle from buffer solution into the paint sample, and the reading allowed to stabilize and then recorded. The (ASTM D 1208) standard methods were adopted.

Viscosity

The ASTM D 1200-10 test methods were used for the viscosity tests. 1ml of the paint formulation was introduced into 100ml solvent (deionized water) for the viscosity measurements. The flow time of the deionized water and that of the paint solution were represented as t_0 and t respectively and measurements were carried out at ambient temperature of 28^0C. This is given in equation (5).

$$l_2 = \frac{(l_1 t_0 \mu_2)}{(t\mu_1)} \quad (6)$$

Where,
t_1 = flow time of water (mins), t_2 = flow time of paint solution (mins), l_2 = viscosity of paint solution (kg/(m.s), l_1 = viscosity of water (kg/(m.s), μ_2 = density of paint solution (g/ml), μ_1 = density of water (g/ml).

Drying time

The drying time of the unmodified formulated paint and the chitosan-modified paint sample were determined by applying them individually on white cardboard substrates and their drying times determined by exposure to air and the records taken. ASTM D1640 (set-to-touch time) testing methods was followed.

Film thickness

The film thickness of the coated substrates was measured using a thickness gauge (Dual scope 359). Measurement was carried out three times and the average value taken. The test was conducted according to the Nigerian Industrial Standards, NIS (2008).

Cross-scratch

Two substrates; one coated with a chitosan-modified paint and the other with the unmodified auto-based paint were cleaned with a cotton wool that was wetted with a thinner, which was then allowed to dry and then the coated surfaces were cross-scratched with a cutting tool and the areas covered with an adhesive tape. The adhesive tape was forcefully pulled out of the scratched areas and then examined whether the coated paint will peel off along with the tape (i.e., if there is a paint stain in the adhesive tape). The result of this test was used to classify the paints using ASTM standard auto base specifications (ASTM, D5178).

Heat resistance

This test was used to ascertain the life span of the paints. The coated plates were immersed into a container with solution of acetic acid, ethanol, and demineralized water which was then heated in an oven at a temperature of 180^0C for 70 hours. After which they were cooled and examined for colour stability (NIS, 2008).

Chemical resistance

To evaluate the chemical resistance of the paint films according to ASTM D1308, flexible aluminium panels (150mm x0.3) were used as the test panel. A coat of paint using paint applicator was applied on the panel. One litter glass beaker was filled with 0.1 M NaCl solution to a depth of 150mm and the test piece immersed for 48 hours to a depth of approximately 120mm which was then removed, washed with running water and dried for 2 hours. The presence of any surface defects such as cracking, peeling or change in colour will indicate poor chemical resistance (ASTM, 2009).

Ash Test

Two grams of the paint samples was weighed into a dried porcelain crucible; which was heated in a muffle furnace at $650^{\circ}C$ for an hour. The crucible was weighed after they had been cooled to room temperature. The percentage ash was calculated using the following expression (ASTM, 2009).

$$\text{Ash (\%)} = \frac{\text{Weight of residue, g}}{\text{Sample weight, g}} \times 100 \qquad (6)$$

RESULTS AND DISCUSSIONS

Characterization of Chitosan

The purchased chitosan was soluble in acetic acid/ethanol mixture (5% chitosan, 8%acetic acid, and 35% ethanol) which enabled it to be blended into the synthesized paint as recommended by (Rau, (2009). Table 1.0 show the properties of synthesized chitosan which include viscosity, solubility, molecular weight, pH and Degree of Deacetylation (DD).

Table 1.0   Properties of analyzed chitosan.

Visc. (cPs)	Mol. wt. (g/mol)	DD(%)	pH	Solubility
6.6	2.01×10^5	96.06	6.9	soluble

The properties of chitosan in Table 1.0 significantly affect the physicochemical and biological functionality of chitosan, particularly the degree of deacetylation. No. et al., (2001) reported that viscosity of chitosan varied considerably depending on the species and the preparation path used. The viscosity value of chitosan that was obtained (6.6cps) was good as it easily dissolved

and mixed properly with the paint solution on vigorous stirring.

Using Mark Houwink equation, the molecular weight of the chitosan sample was calculated as shown in Table 1.0 which was similar to the values reported by Shahidi and Synowiecki, (1991). The importance of the molecular weight is that it affects the thermal stability of the end polymer. However, factors including high temperature, reaction time, particle size, dissolved oxygen concentration, shear stress and concentration of alkali also influence the molecular weight of the chitosan (Shahidi and Synowiecki, 1991).

The degree of deacetylation (DD) is an important parameter affecting solubility, chemical reactivity, and biodegradability. Depending on the source and preparation procedure, DD may range from 50% to 99 % (Martino et al., 2005). It is rare however to have the production of chitosan with 100% degree of deacetylation. Thus, chitosan with various degree of deacetylation in the range of 75–98% can be found in commercial quantity.

The degree of deacetylation (DD) was calculated using the Rout equation. Several studies show that chitosan DD affects both hydrolytic and thermal behavior of the polymer products (Mucha and Pawlak, 2002). Also, chitosan with higher DD has a less porous structure and lower water-uptake ability, which limits the rate of the degradation process in acidic environment (Varum et al., 2001). From the analysis of chitosan carried out, DD was obtained to be 96.06% which indicated a high removal rate of the protein constituent of chitosan (Brine and Austin, 1981). A high DD of chitosan is necessary for good solubility which is highly required for the incorporation of chitosan into solvent mixtures such as the synthesized paint formulation (Rout, 2001). In general, chitosan emulsions tend to be very stable and effective with chitosan of high degree of deacetylation than chitosans of low or intermediate degree of deacetylation (Fernandez-Kim, 2004).

Analysis of Formulated Paints

The viscosity of the automobile base paint according to Peugeot Automobile Nigeria, PAN (2013) is expected to be about 30 (±5) cp. The viscosity provides for good flow, flexibility and workability of the auto-paint. The viscosity of paint

must be low enough to allow for easy application and high enough to avoid a runny paint. Paints designed to be highly protective have higher viscosities (Baba et al., 2015). From Table 2.0, the viscosity of the chitosan-enhanced formulated auto base paint is within the recommended PAN range and can be easily adjusted by car manufacturers by dilution with a suitable solvent to suit their own application purposes. The chitosan-modified paint sample had a higher viscosity compared to the paint sample without chitosan indicating that the resistance of the modified paint to sagging during application is higher. The chitosan enhanced paint sample had a pH of 7.8 indicating its alkaline nature. This alkalinity was also reflected by the unmodified paint sample of pH 8.0 which falls within the standard value range for automobile paints (Obi, 2013). The expected pH range for water based paints is between 8.5 and 9.0, but there is no current reported literature on the pH specification of automobile paints, which is an oil based paint (Oragwu, 2013). The drying time was monitored under atmospheric conditions and the duration of film formation was recorded at 37 minutes for the unmodified paint sample and 33 minutes for the chitosan-enhanced paint. Hence, it can be inferred that that the presence of chitosan in the auto-based paints reduced the surface drying time compared to the unmodified paint samples. Both values are suitable for surface coatings, as stipulated by the Nigerian Industrial Standard (2008).

Table 2.0 Results of the u nmodified and modified auto base paint

Parameter	Unmodified	Modified	ASTM	NIS
Density (g/cm³)	0.9	1.1	-	1.01326
Viscosity (cp)	34	35	-	33.43
pH	8.0	7.8	-	-
Drying Time (mins)	37	33	-	20-30
Film thickness (µm)	7.1	7.4	7.2 ±0.8(2 coats)	-
Ash test (%)	71.60	70.47	76	-
Gloss (opacity)	84	84	85-95(High gloss)	-
Cross-scratch	Accepted	Accepted	ACCEPTED (1&2)	-
Chemical resistance	0	0	0 (no trace of stain)	-

The cross-scratch tests showed that both the chitosan-enhanced and unmodified auto-based paints exhited very good resistances which is obviously due to the type of binder used in the paint formulation. The ASTM grading standard for adherence of paints to the surface of a substrate without falling off is labelled 1 and 2 (ACCEPTED), while 3 and 4 both signify 'FAIL' indicating that there was a paint fall off from the surface of the substrate.

The film thickness is an important physico-mechanical property of paints that determines the quality of the end product (Joseph, 2012). A single coat of paint should cover an appreciable substrate surface area such as the ASTM standards of 7.2

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