Chitosan is one of self-healing materials which has been investigated in polymer technology. It is a linear polysaccharide obtained by extensive deacetylation of chitin. It is a biopolymer produced from the exoskeletons of shrimp and crustaceans, which would otherwise be discarded.It is mainly composed of two kinds of (1 → 4) linked structural units, namely, 2-amino-2-deoxyd- glucose and N-acetyl-2-amino-2-deoxy-d-glucose. Nonetheless, as much as it is virtually impossible to completely deacetylate chitin, what is usually known as chitosan is a family of chitins with different but always low degrees of acetylation. The capacity of chitosan to dissolve in dilute aqueous solutions is the commonly accepted criterion to differentiate it from chitin (Rabea *et al,* 2003; Mourya and Inamdar, 2008). Chitosan has a very wide application range everywhere in life. It is a very useful polymer for biomedical applications in terms of its biocompatibility, biodegradability, and low toxicity (Peniche, 2008). Recently the self-healing properties of chitosan have been investigated. To clarify the properties of chitosan, a group of scientists completed a research on a self-healing coating which repairs small scratches after being exposed to ultraviolet light. The ultraviolet light causes the chitosan molecules to react with split oxetane rings (a combination of polyurethane paint, chitosan molecules, and a ring-shaped molecule) which in turn closes the split, essentially healing the surface (Trask, 2007).

The coating of surfaces goes beyond protecting these objects but also adds to its decoration and fineness. Surface coatings include paints, drying oils and varnishes, synthetic clear coatings, and other products whose primary function is to protect the surface of an object from the environment (Christian, 2016). The terms "paints" and "coatings" are often used interchangeably. However, for the most part, paints are considered to be used primarily for aesthetics, while coatings are used principally to prevent substrate deterioration or for corrosion protection.

Paint is defined as an engineered material made of several ingredients such as resin, solvent, pigments and additives that are mixed together to create a specific product with its own unique properties (Rodger, 2008). It is classified based on purposes and area of applications. A paint whose diluent of formulation and medium of cleanliness is solvent is referred to as gloss paint. This type of paint can be formulated for car surface coating, refinery

equipment coating, road marking purposes, varnishes and so on (Rodger, 2008; Alireza *et al.*, 2009). Paint has been in existence for decades and there are standard formulation for its high quality, though there are no much published work on its detail experimental apart from the general knowledge of its product, this may be due to the products being mostly patented. However, it has been established that, mixing binder, solvent, pigments and additives in random proportion will result to paint product, but its certified quality depends on its ability to meet standard specification test, where its best performance after application tells and differentiate it from low quality product (Turner, 1999; DuPont, 2010; Shawn, 2011; PAN, 2013). Thus, having knowledge of the appropriate proportions of the different component of the paint to be added during formulation will give rise to a desired quality product as may be proved from analysis of its physio-chemical/physio-mechanical test before and after application (Alireza *et al.*, 2009).. Due to daily technology development most especially on polymer modification, satisfied quality car paint can as well be improved on as it has been done to other polymer materials that exhibit self-healing property. Self-healing car paint differs from ordinary car paint in that, it contains an autonomic healing materials capable of responding to harsh environmental effects which subsequently repair damages incurred on coating where it is been applied without external intervention (Chris *et al.*, 2011). Nonetheless, design of experiment technique incorporated with response surface methodology (RSM) can be used to generate runs of experiment by inputting desirable variable conditions that will result to optimum paint formulation from expected responses. The technique (RSM) is a widely used mathematical and statistical method of modeling and analyzing a process in which the response of interest is affected by various variables to accomplish the objective of maximization or minimization of the responses (Braimah, 2016)). Thus, the present investigation is on the production of self-healing car paint and chitosan was incorporated to enhance the self-healing properties.

EXPERIMENTAL PROCEDURE

Raw material – Chitosan

Chitosan sample was purchased from the market. 0.1g was weighed and dissolved in 10ml of a 2% acetic acid solution under stirring to check its solubility. The time taken for the dissolution was taken using ASTM method (2009). Also, the degree of deacetylation of the chitosan sample was determined using Rout equation.

Experimental design

The design expert 12.0.3 version was used in planning of the experiment to optimize the process parameters. The influence of the chosen key factors was studied experimentally with a central composite design (CCD). In this work, two factors were studied: Solvent (A), Binder (B) in relation to drying and coverage time response studied and a total number of 13 experimental runs were required. These variables at two levels, low and high: A (10g – 70g), B (10g – 160g) were selected and inputted respectively on the design of experiment interface tool. Table 3.1 shows the summary of the specifications.

Car paint formulation procedures

The experiment design provided unique values for the binder and solvent for all 13 runs while the additives such as pigment, anti-settling agent, anti-skinning agent, mixed dryer and preservative were kept constant during the formulation. In run one, 70g (90 ml) of mineral spirit was measured and transferred to the mixing unit while the mixer was powered on for stirring the raw materials coming in. This was followed by addition of anti-settling agent into the mixing unit to ensure that other solid components coming into the mixing unit were kept in suspension for proper and uniform mixing without settling down. As the mixing was continued, 10g of pigments (red (ii) oxide) was added and mixed until homogeneity was achieved, after which the solution was binded with 160g of medium oil alkyd resin as the mixing continued. This was followed by addition of mixed dryer to enhance quick drying process after application. Anti-skinning agent and preservative were then added to prevent the paint from sticking to its container and prevent it from micro-organisms attack. Each additive added was 7.5% of the total formulation as specified (Ali, 2005). The paint product obtained was filtered to remove undissolved pigment. This procedure was repeated for the other 12 runs as shown in Table 3.4. Thereafter, the following quality control tests were carried out on the samples; density, viscosity, pH, specific gravity, drying time and coverage responses were determined.

Self-healing car paint formulation

The optimized paint formulation out of 13 solutions obtained from response surface methodology as it combines drying time and coverage responses optimum values was used to formulate self-healing paint. The optimum formulation which contains 40g Solvent (petrol), 190g of binder (medium

alkyd resin) was mixed together in a mixer with 10g pigment red(ii) oxide,7.5% each of anti-settling agent, anti-skinning agent, preservative, 5% Mixed dryer of the total formulation. Four different paints of different chitosan content were formulated. The chitosan concentrations used were, 0.0g (which forms control paint), 5.0g, 7.5g and 10g respectively.

Investigation of self-healing property of the paint

Four 2mm by 2mm panels labelled 0.0g, 5.0g, 7.5g and 10g chitosan concentration were sprayed with the chitosan incorporated paint. These were allowed to dry, scratched with thin pin, and inserted inside a scanning electron microscope (SEM) machine to take their respective micrograph, which shows the extent of damages to the substrates. These were then exposed to ultra violet (UV) light from the sun for 60 minutes in each case and then taken back to the SEM machine to observe the extent of repair.

Fourier transforms infrared analysis

1g each of the raw chitosan, formulated paint without chitosan and self-healing formulated paint (i.e. the formulated paint with chitosan) were measured in each case and introduced into a cell of 10 cm length. These were transferred into potassium bromide disc, which was then charged into FTIR spectrophotometer for spectral analysis of all the functional groups present in each sample charged into the machine.

RESULTS AND DISCUSSIONS

Characterization of Chitosan

The raw chitosan was soluble in acetic acid which enabled it to be blended into the car paint formulated. Table 1.0 shows the properties of the analyzed chitosan.

Table 3.1 Properties of Chitosan Analyzed

Viscosity (cPs)	Mol wt. (g/mol)	DD (%)	pH	Solubility
6.6	2.01×10^5	94.5	6.9	soluble

The properties of the chitosan significantly affect its physiochemical and biological functionality, particularly the degree of deacetylation. The viscosity

value of chitosan that was obtained (6.6cps) was good as it easily dissolved and mixed properly with paint solution on vigorous stirring. The molecular weight of the chitosan sample as shown on table 1.0 was calculated using Mark Houwik equation. Factors such as high temperature, reaction time, particle size dissolved oxygen concentration of alkali and shear stress influence the molecular weight of the chitosan. However, the importance of molecular weight is that it affects the thermal stability of the end polymer (Abdullahi, 2015).

The degree of deacetylation (DD) is an important parameter which affects solubility, biodegradability and chemical reactivity. Degree of deacetylation may range from 50% to 99% depending on the source and the procedure used for preparation. It is rare however to have the production of chitosan with 100% degree of acetylation. From the analysis, DD was obtained to be 94.5% thus indicating a high removal rate of protein constituent of chitosan. Several studies show that chitosan DD affects both hydrolytic and thermal behavior of the polymer products and a high DD is necessary for good solubility which is highly required for the incorporation of chitosan into solvent mixtures such as the paint formulation (Abdullahi, 2015).

Design of Experiment

Table 3.2 shows the data generated using design expert; two factors were studied: Solvent (A) and Binder (B) in relation to drying and coverage time response and a total number of 13 experimental runs were required from the RSM. The influence of the chosen key factors was studied experimentally with a central composite design (CCD). These variables at two levels, low and high: A (10g – 70g), B (10g – 160g) were selected and inputted respectively on the design of experiment interface tool. The use of the design expert 12.0.3 version in planning of the experiment to optimize the process parameters was advantageous as it gave values beyond the low and high ranges.

Table 3.2: Design of experiment data

Std	Runs	Factor 1 g	Factor 2 g	Response 1 Time(min)	Response2 (m)
4	1	70	160	-	-
10	2	40	85	-	-

ISSN: 1213-4406

8	3	40	190	-	-
7	4	40	-20	-	-
1	5	10	10	-	-
11	6	40	85	-	-
13	7	40	85	-	-
9	8	40	85	-	-
12	9	40	85	-	-
6	10	82	85	-	-
5	11	0	85	-	-
3	12	10	160	-	-
2	13	70	10	-	-

Analysis of formulated paints

Table 3.3 indicates the auto base formulated paint's viscosity, pH values, density and specific gravity for each run. The pH values of the formulated paints as shown on the table above falls within 6.8 to 7.1, which are slightly acidic and neutral for all 13 runs. Unlike water base paint where its pH value is expected to fall between 8.5 and 9.0 (Oragwu, 2013) due to the alkaline nature of the applied substrates, there is no reported literature on pH specification for car paint (oil base paint). The viscosity of paint is one of the quality control test that is required as part of product delivery specification. Thus, the viscosity for 13-runs of experiments with varied formulations were tested and presented in Table 3.3. According to Peugeot Automobile Nigeria, PAN (2013) auto base standard specification, the viscosity of an auto base paint is expected to be (30±05) cP. As presented in Table 4.1, runs 1, 3, 7, 8 and 13 fall within the range, which is an indication that the viscosity of the runs were balanced (neither too thick nor too thin). The five runs fall in semi-viscous ranges which can easily be adjusted by car manufacturers to suit their ranges of applications so as to maintain a right applicable viscosity.

Table 3.3: Results of the formulated paint

Run	Density (g/cm3)	Specific gravity	Viscosity (mPa.s)	pH
1	0.888	0.897	127.9	6.8
2	1.063	1.074	187.0	6.9
3	0.654	0.661	154.0	7.1
4	0.736	0.743	9.99	6.9
5	0.823	0.831	266.0	6.8

6	0.892	0.901	190.0	7.0
7	0.890	0.899	185.0	6.8
8	0.892	0.901	187.0	6.9
9	0.895	0.904	170.5	6.9
10	0.801	0.809	76.0	7.0
11	0.893	0.902	655.0	6.8
12	0.862	0.871	184.0	6.9
13	0.837	0.845	153.0	7.0

Performance parameters such as coating film build, colour match, voids and chemical resistance are all linked directly to the viscosity of the liquid coating at the point of application. Very low-end viscous paints (below 100 cP) are likely to cause turbulence (bad for spray guns and nozzles), fine, overspray and possibly contribute to sagging. The upper end (above 180cP) tends to give poor atomization, possibly gun spits or cobwebs and unacceptable appearance (ASTM D1200), (ASTM D7395). Generally, these viscosities can be adjusted by car manufacturers or auto painters to suit the ranges of application to maintain the right applicable viscosity. Table 3.3 also presents the densities of the formulated paints. The density of each run was determined using Equation 2.1 from the raw data showed in the appendix. The significance of the weight oil-water relationship in paint formulation is that low density favors large volume production, which is a positive gain for the manufacturers/formulators. Thus, as it can be seen from the Table 3.3, run 3 has the lowest density, followed by run 4, 10, and then 5 as compared to other runs. Specific Gravity relates to the actual coverage rate (ACR), everything else being equal, lower specific gravity is better (powder Technology Inc.).

Drying Time and Coverage Responses

Table 3.4 shows clearly the drying time and coverage which were the two responses studied from the two factors varied at two levels (i.e. low and high). A and B are the variable factors while drying time and coverage are the two responses studied. Where A = Solvent, B = Binder.

Table 3.4: Optimized Results Generated from Design Expert

Std	Runs	Factor 1 A: Solvent g	Factor 2 B: Binder g	Response 1 Drying time Time (min)	Response 2 Coverage (m)
4	1	70	160	62	0.92
10	2	40	85	58	0.84
8	3	40	190	40	1.12
7	4	40	-20	75	0.76
1	5	10	10	81	0.96
11	6	40	85	61	0.78
13	7	40	85	59	0.81
9	8	40	85	60	0.79
12	9	40	85	57	0.80
6	10	82	85	55	0.64
5	11	0	85	66	0.76
3	12	10	160	113	0.68
2	13	70	10	65	0.92

The drying time and coverage responses were obtained using ASTM D1640 and D4417 standard specification methods respectively. As presented in the table, run 3 has the lowest and best drying time and coverage respectively among others. This may be attributed to the right combination of paint raw materials during the formulation process which is attributed to the significance nature of design of experiment. The optimum drying time obtained in this study was 40 minutes for run 3 which is lower than the ASTM standard specifications.

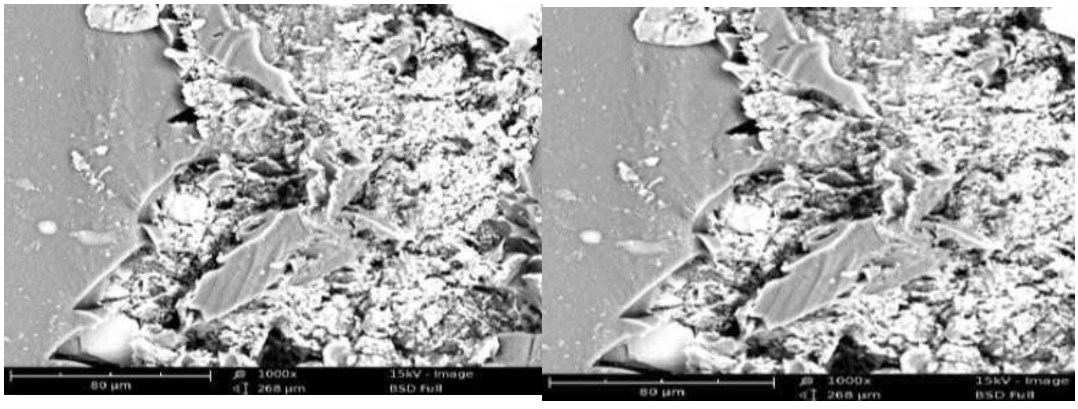
Self-Healing Property of Chitosan Investigation on the Formulated Paint

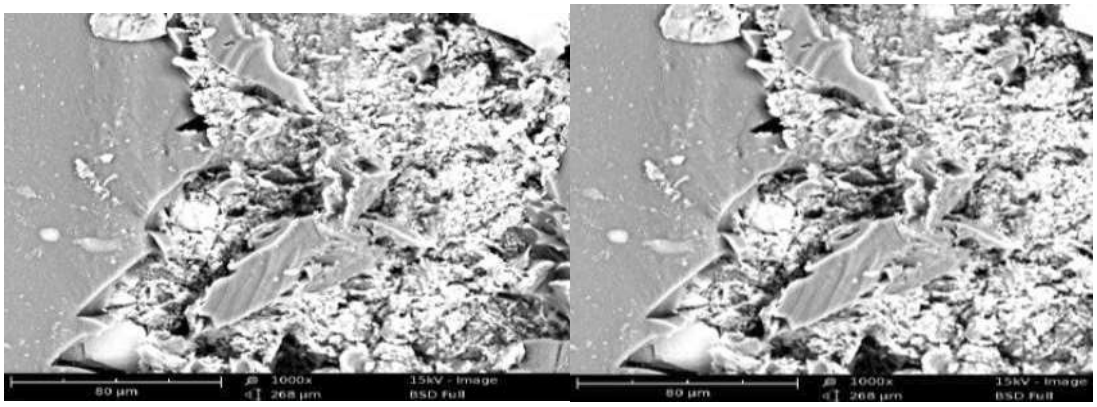
This test was conducted using four samples labelled as 0.0g (control sample), 5.0g, 7.5g and 10.0g chitosan concentrations. The self-healing property of chitosan on the scratched metal surface painted with the formulated self-healing car paint was analyzed using scanning electron microscope (SEM). The condition of the various scratched surfaces was noted in their 0 minute

immediately after the surface is scratched and 90 minutes after exposing to sunlight.

From the micrographs of the SEM analysis done on the formulated car paint incorporated with chitosan at different grams composition as clearly indicated in figure 3.1(i –viii), the paint with chitosan incorporated formed composite coatings which exhibit self-healing property. This is evidence from the SEM micrograph of sample that contains 0.0g (control sample), 5.0g, 7.5g and 10g chitosan composition. As shown in figure 3.1 (i) and (ii), there is no clear difference between the micrograph in Figure 3.1 (i) and 3.1 (ii) respectively (i.e., at 0 minute and after been exposed to sunlight for 90 minutes). Even though the dimensions scratched damaged area in figure 3.1 (iii) and (iv) with 5.0g chitosan composition are not measured or scaled, there is still a clear difference of the scratched surfaces. The damaged area in Figure 3.1 (iii) is wider than the one in Figure 3.1 (iv). This can be attributed to the presence of chitosan (which has the tendency to initiate self-healing) on the surface coated sample, which occurred after 90mins of being exposed to sunlight. Similar trend was observed for figure 3.1 (v) and (vi) and 3.1 (vii) and (viii) with 7.5g and 10.0g compositions respectively. Consequently, from the observations of the SEM micrographs shown in the Figures 3.1(i – viii), it can be said that the presence of chitosan in the incorporated paint samples exhibit self-healing characteristic as seen clearly from the micrograph image difference between Figure 3.1 (iii), (iv), (v), (vi) and 3.1 (vii), (viii) compared to the control sample shown in Figure 3.1(i) and (ii).

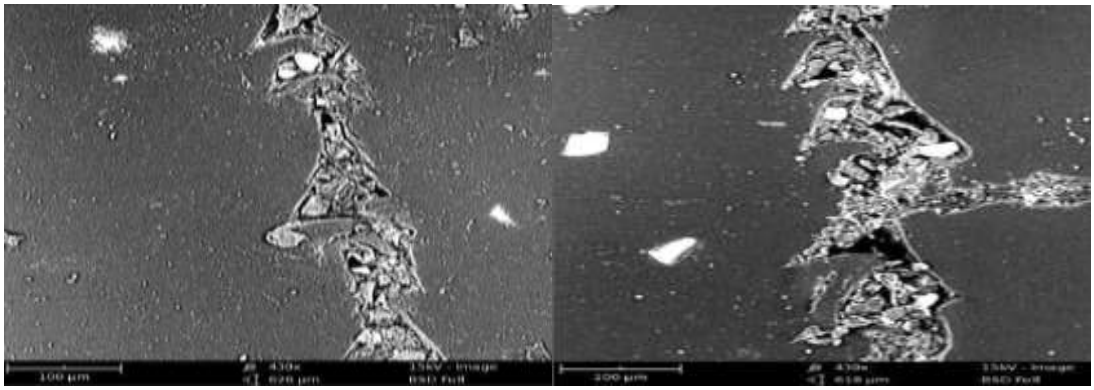
Figure 3.1: SEM analysis of the four samples





(i) (ii)

Figure 3.1(i) and (ii): 0% chitosan-paint (control sample) at 0 minute and 90minutes respectively



(iii) (iv)

Figure 3.1 (iii) and (iv): 5.0g chitosan-paint incorporation at 0 minute and 90minutes respectively

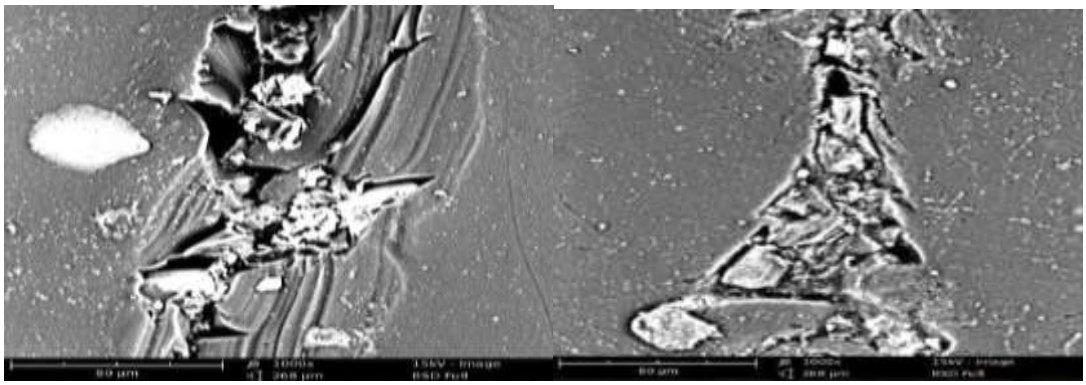


Figure 3.1 (v) and (vi): 7.5g chitosan-paint incorporation at 0 minute and 90 minutes respectively

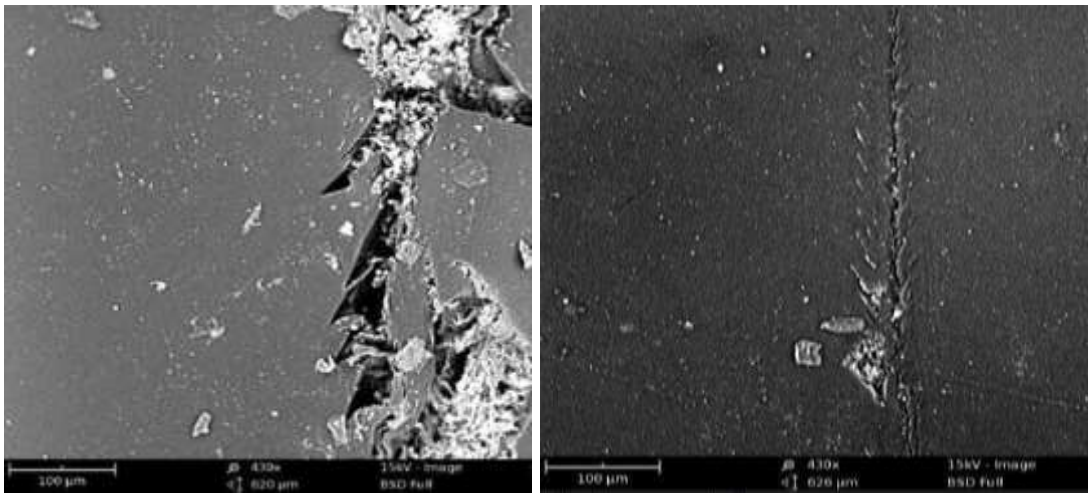


Figure 3.1 (vii) and (viii): 10.0g chitosan-paint incorporation at 0 minute and 90 minutes respectively

FTIR Analysis

Figure 3.2a and 3.2b shows the FTIR graph of the raw chitosan used in this work, the formulated paint and the self-healing car paint respectively. The analysis was used to determine the functional groups present with and without the incorporation of the chitosan. From figure 3.2a, a strong band was observed in the region 3257 – 444 cm^{-1} corresponding to N-H and O-H stretching, as well as the intermolecular hydrogen bonds. The absorption bands at around 2922.23 cm^{-1} and 2877.51 cm^{-1} can be attributed to C-H symmetric and asymmetric stretching respectively. The presence of residual N-acetyl groups was confirmed by the bands at around 1625.12 cm^{-1} (C=O stretching of amide I) and 1416.39 cm^{-1} (C-N stretching of amide III) respectively. All bands observed are in agreement with reports by (Geoge, 2011; Subhashree *et al.*, 2011). NH_2 also occurs in a band peak position of 3389.04cm^{-1} while CH_2 occurs close to peak position of 2944.44cm^{-1}. Also, the OH group was found in a peak position of 2844.13cm^{-1}. The OH groups depicted in Figure 3.2a and 3.2b have IR absorbance value of 2952.15$cm^{-1}$and 2844.13cm^{-1} respectively. This shows that, the OH group present in the chitosan used and the self-healing formulated paint that contains chitosan as

(self-healing agent) occur in different IR peak position, this may be due to other additives present in the formulated paint. However, the NH_2 functional group present in both cases were found in the same IR peak position which is an evidence that, chitosan (the self-healing agent) is present in the self-healing formulated paint and it is not present in the formulated paint without chitosan as depicted in Figure 3.2a and 3.2b respectively. Also, the increased intensity of the aldehydes/ketones band from the IR of chitosan formulated paint depicted an improved self-healing ability of the final sample. These changes could be attributed to the presence of high carboxylic groups present in the chitosan as presented in section 3.2a. Furthermore, the presence of primary hydroxyl group (O-H) which exists in the paint samples corresponding to band 1259.84 cm^{-1} to 1118.20 cm^{-1} on the spectra indicates the ability of the paint having free crosslinking OH bonds which aids the self-healing ability of the formulated paint product.

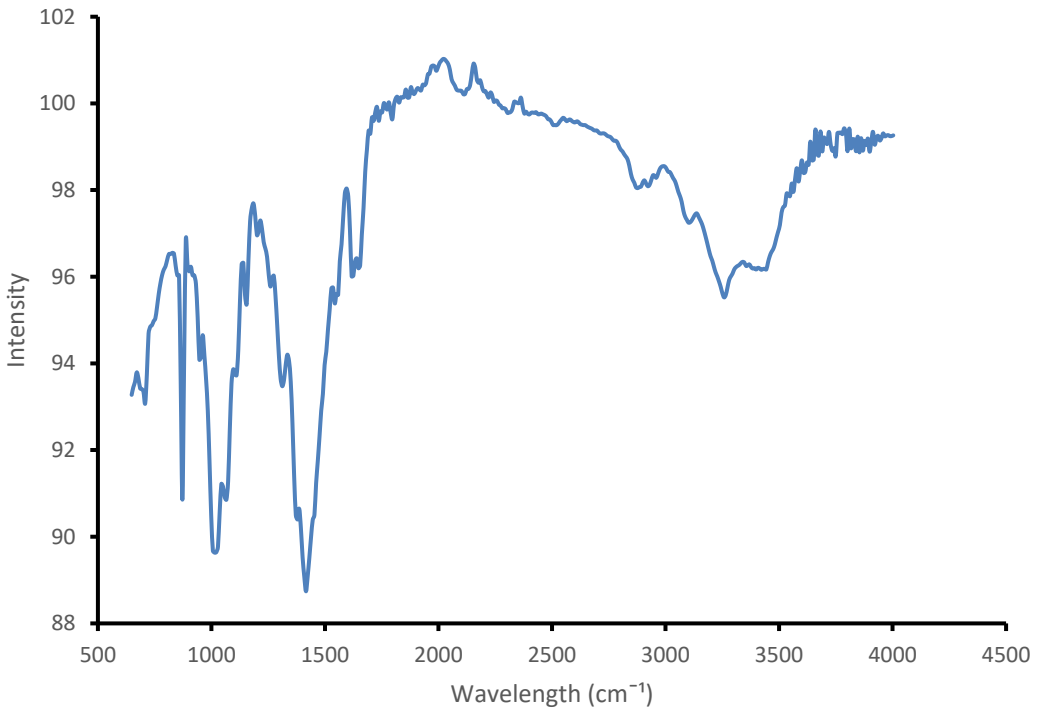


Fig. 3.2a FTIR spectra of Chitosan

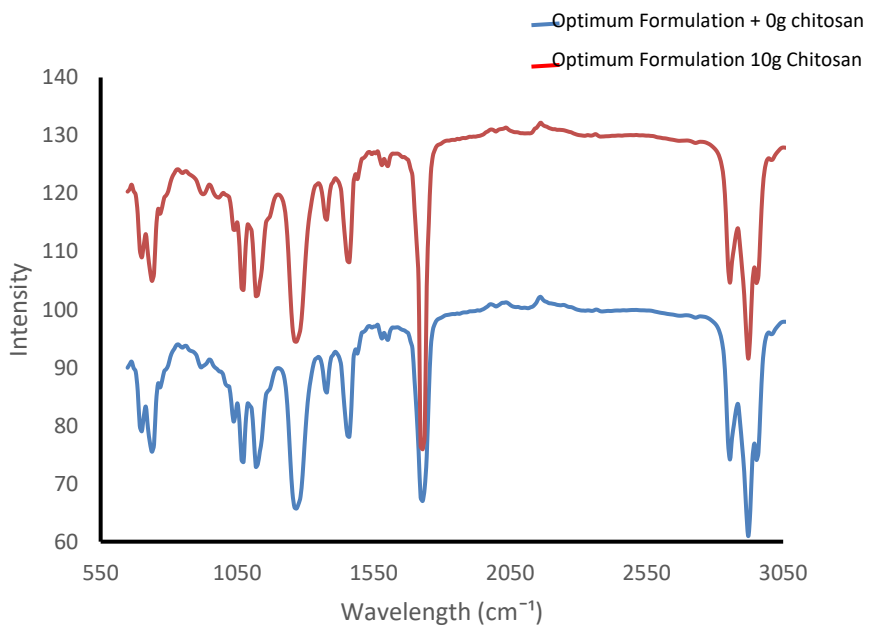


Fig. 3.2b FTIR Spectra of Paint Samples

CONCLUSION

The present study, formulation and characterization of self-healing car paint using chitosan was carried out by developing a model for the car paint using RSM where optimum values were obtained. It was observed that the interactions between the varying independent parameters (solvent and binder) had significant effects on the drying time and coverage responses. From the 13 runs generated by RSM, it was observed that run 3 had the best physio-chemical properties as it falls in the range of ASTM standards. The addition of chitosan in the optimum paint formulation showed self-healing property as seen from the SEM analysis. It was observed that the optimum self-healing analysis is dependent on the incorporation of chitosan in the right proportion; however, from this research work, 10g chitosan composition of run 3 of the paint formulation had the best self-healing performance. The FTIR analysis of the raw chitosan, the formulated paint without chitosan and the self-healing formulated paint revealed that the predicted functional groups in the raw material and the formulated paint products were actually present. The study findings have suggested that it is possible to produce self-healing car paint by incorporating chitosan. Further characterization studies such as

Transmission electron microscope (TEM) should be carried out on chitosan for better analysis of damaged surfaces and recovery extents.

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