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Enhanced Efficiency of Protective Coatings with Graphene-based Nanosheets

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Abstract

A protective coating is applied on the material surface to enhance the wear resistance, corrosion resistance, and aesthetics and are imperative for the industries, automobiles, and domestic appliances. Recently, researchers are interested in graphene-based nanosheets (GNS) as an additive to coatings owing to their exceptional mechanical, chemical, and catalytic properties, in turn ensuing variety of valuable applications. Here, in the present investigation we have synthesized the graphene oxide (GO) and graphene and blended with our optimized formulation (coating), comprises Alkyd, BUF resin, butyl cellulose, butanol, xylene, para-toluene sulphonic acid, and graphene-based nanosheets. Experiments are carried out by coating the blend on the wood panels and are characterized for various properties such as viscosity, density, surface drying time, tack free drying time, gloss, cross cut, alkaline, and acid test. The experimental results have demonstrated that the desirable properties of coatings are enhanced upon incorporating graphene-based nanosheets. This work implies the potential of the nano thick graphene-based material and its adaptability can be effectively used in numerous technological applications.

Keywords: *Graphene; BUF resin; Amino resins; Cross linking agents*

1.0 Introduction

Coatings are thin layer of material that are applied as covering to the surface of an object as a functional, decorative, or both[1,2]. The most common criteria in choosing a coating are the life expectancy, cost, substrate material compatibility, and environment[3]. Paints are the commonly used coatings that serves as both functional and decorative materials; and when applied to the substrate it totally changes the surface properties, such as corrosion resistance, wear resistance, adhesion, and wettability[4]. The amino resins that are added to paints acts as crosslinking agent and in turn brings about improved mechanical properties of the coatings. The most commonly used amino resins in industries are butylated urea formaldehyde (BUF) resins, butylated melamine formaldehyde resins, and methylated melamine formaldehyde resins[5]. Owing to low cost and fast curing rate, the BUF is the most preferred commercial resin, which is produced by using urea, formaldehyde, and butanol, in the presence of acid etherification[6].

Researchers are successful in formulating the variety of conventional coating techniques to augment the life of the base object/material. For example, the usage of hexavalent chromium (Cr(VI)) and tributyltin (TBT) as metal protective coating is prohibited because of their carcinogenic risk and biocidal nature[7]. The adoption of TBT as antifouling coating has been banned to protect the marine ecosystem. Other commonly used coating elements such as cadmium (Cd),

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cobalt (Co) and copper (Cu) have also been recognized as toxic for the eco-system and carcinogenic to humans[8]. Therefore, the primary objective of the coating industry is to add the ecofriendly substitutes without compromising in its characteristics[9].

In the present investigation we have optimized the base formulation of the coating by tailoring the alkyd to amino ratio and keeping the other parameters unchanged[10]. The resin properties are likely to change with different extent of alkylation. For instance, highly alkylated BUF resins impart very good water resistance and impact resistance compared to low amino type alkylated resins[11]. Also, we have incorporated graphene-based nanosheets into the formulation to enhance the desirable characteristics of the final coating such as scratch proof, acid resistance, pot life, and gloss etc.

The objective of our present research work is to vary the composition of the cross-linking agent and primary film former, to study and measure the various film coating properties, and enhance the mechanical properties of the coating by incorporating graphene-based nanosheets.

2.0 Materials and Methods

2.1 Materials

Short Soya Coconut Alkyd (70 per cent solids content Angel Coatings), Butylated U-F resin (60 per cent solids content Angel Coatings), Xylene (Angel Coatings, Bakrol GIDC), Normal Butanol (Angel Coatings, Bakrol GIDC), Butyl Cellulose (Angel Coatings, Bakrol GIDC), Silicon Additive (Angel Coatings, Bakrol GIDC), Para-Toluene Sulphonic Acid (Angel Coatings, Bakrol GIDC). All the raw materials were used without further treatment.

2.2 Preparation of Base Formulations

The formulations for the coatings are made as per Table 1 and all are in weight percentage.

Table 1: The components required for the formulations in weight percentage

Alkyd/Amino	60/40	55/45	40/60
Alkyd 70%	42.857	39.29	28.571
Urea 60%	33.333	37.5	50
Silicon Additive	0.5	0.5	0.5
Butanol	1.65	1.608	1.481
Butyl Cellosolve	1.498	1.46	1.345
Xylene	20.162	19.65	18.102
	100.00	100.00	100.00

2.3 Estimation of Physical Properties

Physical properties of the Alkyd and BUF resin were determined by the following methods:

Viscosity: The viscosities of the two resins were determined at 30°C by recording the time (in sec) required by the sample to flow through the standard Ford Cup ISMO-3994 B4 cup.

Per cent solids or non-volatile content: This was determined by heating 2g sample at 120°C for 2h and weighing the left residue.

Acid-value: The acid value was measured by dissolving 4 to 5g of the sample in xylene-methanol mixture and titrating against standard alcoholic KOH solution using phenolphthalein as indicator.

Density: This was determined at 30°C by using SG cup.

Drying time: For determining the drying time, the coating formulations were applied on well-prepared solid wood panels. The solid wood was placed with 180 – grit emery paper and then with 320 – grit emery paper along the grain, surface being wiped clean in between. Further the wood stain was applied using muslin cloth. The stain was then allowed to air-dry for 15 to 30 min. The first coat of wood base sealer was applied using spray gun at 30-40 Psi and was allowed to dry for 5 to 6 hours. The solid wood panel was placed with 180 – grit emery paper and then with 320 – grit emery paper along the grain, surface being wiped clean in between. Again, second coat of wood base sealer was applied by spray gun and 320 – grit emery paper was placed along the grain. The topcoat was applied by spray gun using 20 per cent thinner and allowed to dry. 'Surface dry time' was tested by rolling finger over the finish gently, and the absence of tackiness was checked. The 'tack free dry time' was tested by pressing and rotating thumb over the coating, checking for absence of tackiness.

Gloss: The base formulation was applied by spray gun at pressure 30-40 Psi, it was allowed to air-dry till tack free dry time is achieved. The gloss was measured at 60°C by using single angle gloss meter. Three readings of a single panel were taken at top, middle and bottom respectively and then the average was noted.

Pot-life: The pot-life was tested by measuring the time required for gelation of the liquid finish after mixing the base formulation with the hardener that is the catalyst.

Hot and cold test: This test was carried out after 10 day of curing or drying of the panel at room temperature. The panel is kept for 1 hour in freezer at 0°C, half an hour at room temperature, 1 hour at 120°C in oven. This completes one cycle of hot and cold test. Cycles were completed till the cracking was observed on the panel.

Adhesion test: This test was carried out after 10 day of curing or drying of the panel at room temperature. Select area free of blemishes, make parallel vertical and horizontal cuts one mm apart at 90°. Place the canter of the tape over the grid and in the area of the grid smooth into place by a finger to ensure good contact with the film rub the tape firmly with the eraser, pull the tape at 45°. The result was reported on a relative scale of four.

MEK rub test: This test was carried out after 10 day of curing or drying of the panel at room temperature. 50 rubs of methyl ethyl ketone on wood panel was done by taking MEK through cotton. The result was reported on a relative scale of four.

Butyl acetate rub test: This test was carried out after 10 day of curing or drying of the panel at room temperature. 50 rubs of Butyl Acetate on wood panel was done by taking MEK through cotton. The result was reported on a relative scale of four.

Resistance to alkaline: This test was carried out after 10 day of curing or drying of the panel at room temperature. 5 per cent solution of KOH was prepared, panels were immersed into the solution and observed at time interval of one hour until coating/gloss disappear or fade away. The result was reported on a relative scale of four.

Resistance to acid: This test was carried out after 10 day of curing or drying of the panel at room temperature. 20 per cent solution of Acid was prepared, panels were immersed into the solution and observed at time interval of one hour until coating/gloss disappear or fade away. The result was reported on a relative scale of four.

2.3 Synthesis of Graphene oxide

Graphene oxide was synthesized from natural graphite powder by the Hummers method.[23,24] In this method, the graphite powder was oxidized using sodium nitrate, sulphuric acid, and potassium permanganate. The resulting mixture, i.e., graphitic oxide washed several times with four weight per cent aqueous HCL solution and ultrapure deionized water to remove residual salts and acids. The graphitic oxide was suspended into deionized water and exfoliated into an individual graphene oxide sheet using a probe sonicator. Thus, the obtained graphene oxide was dialyzed in ultrapure deionized water to remove remaining salts.

3.0 Results and Discussions

The synthesized nanosheets were characterized for their structure and properties. The characterization involves like UV-visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

Our characterization reveals thin sheet like structures and these nanosheets were incorporated in the coatings and was applied over the panels and tested for the physical properties of the coating with the above said methods mentioned in the section 2.

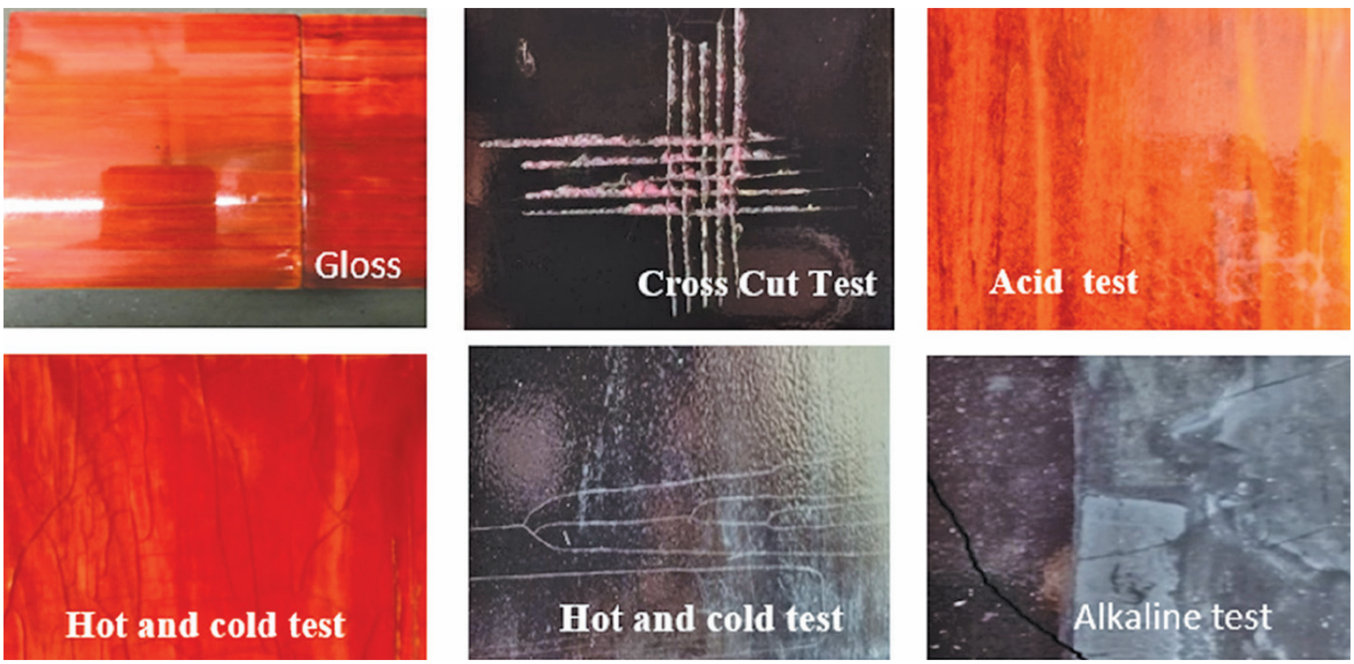

Figure 1: Gloss test, cross cut test, acid test, hot and cold test, and alkaline test for the resin without graphen-oxide

Table 2: Demonstrating the characterization of coatings of the various formulations

Selection Criteria	Alkyd/BUF Ratio	59/41	58/42	57/43
	Parameters			
1	Initial Viscosity @ 30°C (sec)	52	52	49
	Initial Density (gm/cc)	1.01	1.01	1.01
	After 10 Days Viscosity @ 30°C (sec)	83	64	63
	After 10 Days Density (gm/cc)	1.01	1.01	1.01
2	SD on Solid Wood Panel (min)	18	18	18
	TF on Solid Wood Panel (min)	38	40	42
3	Pot Life (hrs)	16	16	16
4	Gloss @ 60 °	93.4	90.7	88.4
	After 10 Days Gloss @ 60°	81.2	81.2	81.3
5	Hot-Cold Cycle	4/4	4/4	4/4
	Alkaline Test	3	2	1
	Acid Test	1	2	3
	Cross Cut Test	1	2	3
	MEK Rub Test	no effect	no effect	3
	Butyl Acetate Rub Test	no effect	no effect	3

With our formulations the coatings were made over the panels and tested for various tests such as gloss test, cross cut test, acid test, hot and cold test, and alkaline test for the resin without graphene-oxide and is shown in Figure 1.

The characteristics of the formulations are summarized in the Table 2. The results demonstrate that the formulation with 59/41 alkyd/BUF ratio yields good characteristics of the coating.

Upon addition of the graphene-oxide, the desirable coating characteristics has been enhanced and is shown in the table.

Criteria for selection	Alkyd to BUF Ratio	JPS'-3	JPS-7	Standard
	Parameters			
1	initial Viscosity @ 30°C (sec)	94	96	52
	initial Density (gm/cc)	0.100	0.995	1.010
	After 10 days Viscosity @ 30°C (sec)	90	92	64
	After 10 days Density (gm/cc)	0.100	0.995	1.010
2	SD on Solid Wood Pannel (min)	12	10	18
	TF on Solid Wood Pannel (min)	32	33	59
3	Pot Life (hrs)	6	6.5	16
4	Gloss @ 60 °	89	82.5	96.85
	After 10 days Gloss @ 60°	87	74.6	96
5	Hot-Cold Cycle (Cold/ Hot)	6/6	6/6	4/4
	Alkaline Test (rated among 3)	3	2	1
	Acid Test (rated among 3)	3	2	1
	Cross Cut test (rated among 3)	2	3	1
	MEK Rub (rated among 3)	1	2	3
	Butyl acetate Rub (rated among 3)	1	2	3

4.0 Conclusions

In the present work we have optimized the optimized best coating formulations: Alkyd/BUF proportion, % paint solids, % catalyst concentration. Also developed GO and graphene based BUF alkyd coating formulation and measured various properties of the GO and graphene based wood finish such as Hot and cold cycle, cross cut test, pot life, MEK rub test, butyl acetate rub test, alkaline and acid test etc. Obtained coating with fast drying, good initial gloss and better chemical resistance.

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