Assess the Possibility to Substituting Crude Oil-based Film Formers in Automotive Epoxy Metal Primers with Coconut oil-derived Bio-based Polyurethane Film Formers

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ABSTRACT

There is a potential risk that diminishing some islands in the world map within a short time period due to global warming unless people divert into new strategies to use crude oil sustainability or replace with renewable resources. Polyurethane (PU) is one of the most popular film-forming materials in the coating industry because of its better performance. A coconut oil-derived biobased polyol (BBP) was synthesized and acid value, viscosity, reaction water release, oil length, FTIR spectrum, differential scanning calorimetry and Lovibond colourimetric index were assessed during the synthesis. A series of pigmented renewable polyurethane metal primer (RPUMP) wet samples were prepared by using BBP under two categories as direct-to-metal (DTM) primers and undercoat primers (UCP) in two mixing ratios with polyisocyanate hardener as 2:1 and 4:1. All samples were comparatively tested with crude oil born commercially available epoxy metal (CAEMP) primers in Sri Lankan market for apparent viscosity, fineness of grinding, solid content, specific gravity, gloss, drying time, hardness, dry film thickness, adhesion, impact resistance, water resistance, salt spray resistance and cylindrical mandrel bending.

According to the results, it was proven that RPUMP showed overall better performances with the corresponded CAEMP under the DTM category. But under the UCP category RPUMP showed better performances in apparent viscosity, drying time and water resistance but equal magnitude for pencil hardness. CAEMP showed better performances in solid content, specific gravity, dry film thickness, flexibility, impact resistance and salt spray resistance.

Keywords: Coconut oil, bio-based polyol, renewable PU, metal primers.

INTRODUCTION

Polyurethane is one of the most versatile polymers created while reacting polyol and polyisocyanate. They are being used for a wide range of applications such as automotive, furniture, construction, footwear is a major reason for their popularity. But the main raw materials of PU coating systems originate in the crude oil purification process, therefore, it has very low renewability and plant materials can be used to increase the green nature [1]. Paint is a mixture of pigment, binder, solvent and additives that easily applied on a substrate. Normally it dries by loss of solvent after application on a surface and crosslinks may or may not occur to form a film subsequently [2]. Most of the time industrial coatings apply a three-coat system. The bottom coat directly adhere with the substrate is known as primer and different market varieties can be found like zinc phosphate primer, zinc chromate primer and two-pack epoxy primer. The middle coat and topcoat accordingly are base coat paint and top coat lacquer. The corrosion resistance of primers is very important factor that increases the lifespan and reduces the cost of maintenance of metal structures. In 2016 United States invested 3.45% of its GDP to recover metal surfaces from direct damages from corrosion. Corrosion requires moisture, oxygen and metal substrate to react among them as a redox reaction between cathode and anode as follows below,

$2H_2O(l) + O_2(aq) + 4e^- \rightarrow 4OH^-(aq)$ Cathodic reaction

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Anodic reaction

In the early steps, the above ferrous hydroxide oxidized into green hydrated magnetite ($FeO.Fe_2O_3.H_2O$). Because of its instability, it further decomposes into black magnetite ($FeO.Fe_2O_3$). In the presence of oxygen, black magnetite oxidizes to form the well-known red-brown corrosion ($Fe_2O_3.H_2O$).

$$6Fe(s) + 4\frac{1}{2}O_2(aq) + 3H_2O(l) \rightarrow 3Fe_2O_3 \cdot H_2O(s)$$

The above reaction is the overall reaction for corrosion [3].

Seawater accelerates corrosion due to having dissolved chlorine ions which facilitate high conductivity to fast deterioration of metal structures exposed to sea breeze [4]. Metal primers should present with good cohesive properties to promote high bonding with other paint coats and expect to have better adhesion properties with the substrate to make a proper barrier to avoid contacting the environment and the metal surface to avoid corrosion [5]. Temperature, moisture and mechanical stress are the most influencing environmental factors that work on a surface as supportive factors for corrosion. Temperature fluctuation strongly affects to peeling off and cracking of the film due to having different expansion coefficients of both film and substrate. Moisture can dissolve water-soluble impurities in a film to make swell and soften [6].

Corrosion protective mechanisms in metal primers

1. Physical barrier -

i) The paint coat itself appears as an impermeable membrane to moisture and oxygen the main relatives for corrosion [7]. Epoxy coatings are more popular among primers, because of their good mechanical properties, high thermal stability, chemical resistance, corrosion resistance and cheap cost. As an undercoat, adhesion is the most important factor to control corrosion [8]. Corrosion protection increases with the coating thickness, but more thickness increases the cost and reduces adhesion [9]. Nanoscale particles can improve overall barrier properties [10].

ii) The particle size and shape of pigments also play a major role in this case. Especially iron oxide pigments are very common in use in the paint industry to manufacture metal primers. Rhombohedral (needle shape), spheroidal and micaceous are the major iron oxide types represented in primers. Experimental data proved that rhombohedral and spheroidal types work in equal magnitudes [11]. But the micaceous type shows the best performances in corrosion control. The particle morphology of the micaceous type is very thin and oval shape. In a paint film these scales-like particles overlap parallelly similar to a brickwork on a roof to arrange a huge continuous barrier against water, oxygen, salt spray, sulfur dioxide, ammonium salts and all other factors [12]. Being chemically inert, non-toxic and better thermal stability are some plus points in micaceous type [13]. Due to electron transition from t2g to eg in d orbital most iron oxide piments are available in red and yellow colours [14]. According to the experimental results 10% anticorrosive pigment loading showed best anticorrosive properties [8]. Steel surfaces painted by a surface coating without anti-corrosive pigments, tend to shift corrosion region faster [15].

2. Corrosion inhibitors -

Introducing corrosion inhibitors in primer coatings is another method to control corrosion [9]. Zinc phosphate and aluminium tripolyphosphate pigments are most commonly used for this purpose. When the corrosive media penetrates towards the interface through oil-based epoxy film, zinc phosphate partially dissolve to form metal substrate phosphate and stabilizes protective coating containing γ-Fe2O3, α-FeOOH, γ-FeOOH and iron phosphate. Stable iron phosphste block penetrating of corrosive media [16]. The inhibitive action of zinc phosphate is relatively low due to low solubility but later on zinc aluminium phosphate, zinc aluminium polyphosphate, strontium aluminium phosphate developed to enhance the process [17]. Calcium tripolyphosphate also can be used as an inhibitive pigment [18]. Moderate solubility of pigments is considerably important factor. Silicate-based pigments favour to solubilize in high pH values but phosphate-based pigments in low pH values [19].

How do metal primers affect to human health and the environment?

Some lead-based anticorrosive pigments such as red lead, lead suboxide and lead powder alone are harmful to human health [9]. Long term exposure to paint and fumes can cause headaches, trigger allergies, asthmatic reactions, irritations in eye, skin and respiratory tract. According to the World Health Organization, cancer risk in various places specially lungs increased 20% - 40% in people who work in paint-related jobs. Volatile organic compounds (VOC) react with oxygen to produce ozone which attacks to lung tissues [20]. Rapid development of innovations in sustainable materials such as starch, lignin, cellulose, shellac, rosin, wool fiber and plant oils can be used to substitute crude oil-based hazardous plasticizers, adhesives, lubricants in many industries [21].

The main intentions of this research are to design, synthesize, characterize bio-based polyol (BBP) using coconut oil and find out the possibility of substituting crude oil-born epoxy in the automotive anticorrosive metal primer while comparing the effectiveness of them using market available metal primers in Sri Lanka. Iron oxide pigments are used as anticorrosive pigments in this research. Comparatively tested and proven coconut oil-based BBP is mentioned in references [21] and [3].

MATERIALS AND METHODS

Refined deodorized bleached coconut oil from Sena mills in Sri Lanka, phthalic anhydride, benzoic acid, pentaerythritol, glycerin, xylene and lithium hydroxide as a catalyst used for BBP synthesis. Raw nitrocellulose RS1/2 sec grade (NC) 70% in isopropyl alcohol was supplied by Sichuan Nitrocell Corporation, China. Ethylacetate, butylacetate, are used as solvents. Iron oxide red pigment 97% Fe_2O_3, iron oxide yellow pigment 86% Fe_2O_3 and iron oxide black were obtained by Elementis-Hong Kong limited as anticorrosive pigments. Titanium dioxide 80-99% pigment was obtained by Millennium Chemicals, Australia used as non-anticorrosive pigment and china clay used as an extender.

A. Designing a formulation of a BBP for RPUMP.

The BBP is a short oil alkyd resin that was synthesized using coconut oil as the main film former in the RPUMP. This was evaluated alongside other CAEMP.

It was done based on an oil analysis of coconut oil.

TABLE I OIL ANALYSIS OF COCONUT OIL

Name of fatty acid	Molecular weight	Weight %	Molecular weight fraction	Moles in 100g of coconut oil.
Caprylic	144	7.0	10.08	0.0486
Capric	172	5.4	9.288	0.0313
Lauric	200	48.9	97.80	0.2445
Myristic	228	20.2	46.056	0.0885
Palmitic	256	8.4	21.504	0.0328
Stearic	284	2.5	7.10	0.0088
Oleic	282	6.2	17.484	0.0219
Linoleic	280	1.4	3.92	0.0050
Total		100	213.232	0.4814

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The BBP containing 20% w/w coconut oil, was prepared with the following raw material by theoretical calculation for the alcoholysis stage.

The average molecular weight of coconut oil = 213.232 g/mol

Total fatty acid moles in 100 g of coconut oil = 0.4814 mol

Total fatty acid moles in 20 g of coconut oil = 0.4814/100 x 20 = 0.0963 mol

Stoichiometric values were considered in the following equation.

$$\underset{1\ mol}{\text{Glycerol}} + \underset{3\ mol}{\text{3 Fatty acids}} \longrightarrow \underset{1\ mol}{\text{Triglyceride}}$$

Total triglyceride moles in 20 g of coconut oil = 0.0963 / 3 = 0.0321 mol

Triglyceride oil was transformed into monoglycerides in the stage of alcoholysis shown in the following equation.

$$\underset{0.0321\ mol}{\text{Triglyceride}} + \underset{0.0642\ mol}{\text{2 Glycerol}} \longrightarrow \underset{0.0963\ mol}{\text{3 monoglyceride}}$$

Required glycerol for alcoholysis = 0.0642 x 92 = 5.906 g

LiOH - 0.01g was added as catalysis.

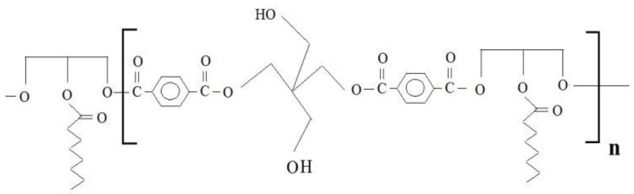

Fig. 1 Expected structure of the BBP

According to the structure, a 2:1 molar ratio was kept between phthalic anhydride and pentaerythritol.

TABLE II THEORETICALLY DESIGNED FORMULATION OF BBP MADE WITH COCONUT OIL

Contents	Quantity %
Coconut oil	20.0
Glycerin	5.906
LiOH	0.014
Xylene	40.0
Phthalic anhydride	23.01
Pentaerythritol	10.57
Benzoic acid	0.5
TOTAL	100.00

B. Synthesis of BBP

The following raw materials were loaded into the five-neck reactor vessel and heated up to 250^0 C while stirring at 100rpm. The mixture kept for 0.5 hour in a nitrogen gas environment. A methanol verification test was conducted, and a clear uniform solution was obtained, confirming the completion of the monoglyceride stage.

Coconut oil - 20.0%

Glyceri - 5.906%

LiOH - 0.014%

Upon cooling of the reaction vessel to 120^0 C temperature, the following raw materials were introduced to the vessel.

Phthalic anhydride - 23.01%

Pentaerythritol - 10.57%

Xylene - 40.0%

Heat the mixture while stirring and 6 samples were taken in 45 min equal intervals to measure viscosity, acid value, and reaction water release. BBPs were synthesized according to the above formulation.

C. Millbase preparation of different RPUMP series

The mill base (pigment dispersion) was prepared by "Dispermat", Type 6DU2-547 (Germany) mill and dispersion blade with 6 cm diameter Teflon were used for dispersion. 1 mm in diameter of zirconium beads were used in 2:1 ratio by weight (mill base: beads) under 4500 rpm, 30^{0}C and 30 min for the preparation. All the other materials were added according to the following tables and stirred at 2500rpm for 10 minutes for completion of the wet primer.

D. Preparation of PU metal primer series

1) 4:1 Low pigment loaded, RPUMP series; (4:1 is metal primer: hardener ratio)

TABLE III FORMULATIONS OF 4:1 LOW PIGMENT LOADED, RPUMP (UCP TYPE)

Ingredients	A	B	C	D	E
Iron oxide yellow	8.0	8.0	8.0	8.0	8.0
Iron oxide red	1.2	1.2	1.2	1.2	1.2
Iron oxide black	0.8	0.8	0.8	0.8	0.8
China clay	5	5	5	5	5
Titanium dioxide	2	2	2	2	2
Bio-based polyol BBP	17.0	17.0	17.0	17.0	17.0
Xylene	10.0	10.0	10.0	10.0	10.0
Bio-based polyol BBP	3.0	5.5	8.0	10.5	13.0
Ethylacetate	31.0	28.5	26.0	23.5	21.0
NC (RS ½ sec)	8.0	8.0	8.0	8.0	8.0
Butylacetate	14.0	14.0	14.0	14.0	14.0
TOTAL	100	100	100	100	100

-Mill base components, - Variables,

2). 4:1, High pigment loaded, RPUMP series (4:1 is metal primer: hardener ratio)

TABLE IV FORMULATIONS OF 4:1 HIGH PIGMENT LOADED RPUMP (UCP TYPE)

Ingredients	F	G	H	I	J
Iron oxide yellow	16.0	16.0	16.0	16.0	16.0
Iron oxide red	2.4	2.4	2.4	2.4	2.4
Iron oxide black	1.6	1.6	1.6	1.6	1.6
China clay	10.0	10.0	10.0	10.0	10.0
Titanium dioxide	4.0	4.0	4.0	4.0	4.0
Bio-based polyol BBP	20.0	20.0	20.0	20.0	20.0
Xylene	10.0	10.0	10.0	10.0	10.0
Bio-based polyol BBP	---	2.5	5.0	7.5	10.0
Butylacetate	22.0	19.5	17.0	14.5	12.0
NC (RS ½ sec)	8.0	8.0	8.0	8.0	8.0
Xylene	6.0	6.0	6.0	6.0	6.0
TOTAL	100	100	100	100	100

3). 2:1, High pigment loaded, RPUMP series (2:1 is metal primer: hardener ratio)

TABLE V FORMULATIONS OF 2:1 HIGH PIGMENT LOADED, RPUMP (DTM TYPE)

Ingredients	K	L	M	N	O
Iron oxide yellow	16.0	16.0	16.0	16.0	16.0
Iron oxide red	2.4	2.4	2.4	2.4	2.4
Iron oxide black	1.6	1.6	1.6	1.6	1.6
China clay	10.0	10.0	10.0	10.0	10.0
Titanium dioxide	4.0	4.0	4.0	4.0	4.0
Bio-based polyol BBP	20.0	20.0	20.0	20.0	20.0
Xylene	10.0	10.0	10.0	10.0	10.0
Bio-based polyol BBP	25.0	27.5	30.0	32.5	35.0
Butylacetate	11.0	8.5	6.0	3.5	1
TOTAL	100	100	100	100	100

4). 2:1, Low pigment loaded, RPUMP series (2:1 is metal primer: hardener ratio)

TABLE VI FORMULATIONS OF 2:1 LOW PIGMENT LOADED, RPUMP (DTM TYPE)

Ingredients	P	Q	R	S	T
Iron oxide yellow	8.0	8.0	8.0	8.0	8.0
Iron oxide red	1.2	1.2	1.2	1.2	1.2
Iron oxide black	0.8	0.8	0.8	0.8	0.8
China clay	5	5	5	5	5
Titanium dioxide	2	2	2	2	2
Bio-based polyol BBP	17.0	17.0	17.0	17.0	17.0
Xylene	10.0	10.0	10.0	10.0	10.0
Bio-based polyol BBP	28.0	30.5	33.0	35.5	38.0

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Ethylacetate	15.0	12.5	10.0	7.5	5.0
NC (RS ½ sec)	2.0	2.0	2.0	2.0	2.0
Butylacetate	11.0	11.0	11.0	11.0	11.0
TOTAL	100	100	100	100	100

5). 2:1 and 4:1 RPUMP without iron oxide pigments as controls

TABLE VII FORMULATIONS OF RPUMP WITHOUT ANTICORROSIVE PIGMENTS

Ingredients	WL2	WL4	WH2	WH4
China clay	5.0	5.0	10.0	10.0
Titanium dioxide	12.0	12.0	24.0	24.0
Bio-based polyol BBP	17.0	170	17.0	17.0
Xylene	10.0	10.0	10.0	10.0
Bio-based polyol BBP	33.0	8.0	33.0	8.0
Ethylacetate	10.0	26.0	--	17
NC (RS ½ sec)	2.0	8.0	--	--
Butylacetate	11.0	14.0	6.0	14.0
TOTAL	100	100	100	100

WL4 and WH4 are UCP type but WL2 and WH2 are DTM type.

E. Spray application

Panels applied under 30^0 C, relative humidity 76% environment. Maintained 3.5 bar gun air pressure, a Devilbiss JGA 54 (England) spray gun with a 1.3 mm nozzle diameter was used for spray applications.

Dilution ratio of 4:1 RPUMP series was diluted in 4 volume parts of metal primer and 1 volume part of Sikkens P25 hardener. In 2:1 series same component was kept in 2:1 volume ratio. After adding hardener both series were diluted to get spray viscosity by a solution (thinner) contains 60 pats of xylene and 40 pats of butyl acetate. Thinner was added to all metal primers to satisfy the ratio as metal primer to thinner is 100 parts to 7.5 parts in volumes.

But CAEMP were diluted according to the specifications mentioned in their labels by using recommended hardeners and thinners as following table.

TABLE VIII MIXING RATIOS OF PAINT MATERIALS IN CAEMP

	Metal primer	Chemical nature	Country of origin	Colour	Dilution ratios in volume		
					Metal primer	Hardener	Thinner
1	Market sample – 1 (MS-1)	Epoxy	Indonesia	Pale green	100 parts	50 parts	10-20 parts
2	Market sample – 2 (MS-2)	Epoxy	Indonesia	Grey	100 parts	20 parts	60 parts
3	Market sample – 3 (MS-3)	Epoxy	Sri Lanka	Black	100 parts	100 parts	60 parts

Two single spray paint passes were applied on steel panels with following specifications.

i. Q-panels -150mm x 50mm x 0.6mm.
ii. Bend panels – 150mm x 50mm x 0.6mm (use only for cylindrical mandrel bending test)

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS | Volume IX Issue VII July 2024

Metal surfaces of all panels were prepared according to ASTM 1731-67.

F. Testing

1) Determination of free fatty acid (FFA) content: ASTM D 5555-95 (2001) was followed to measure FFA of coconut oil which is used to synthesize BBP.

2) Determination of acid value: ASTM D 1541-86 was followed to measure acid values of BBP during the synthesis.

3) Methanol verification test: 1.0 ml of the monoglyceride reaction mixture in the reactor was taken out and 1.5 ml of methanol was added to the test tube at room temperature. Uniformity was observed just after stirring and uniform mixture confirmed the completion of monoglyceride stage.

4) Measuring viscosity of BBP samples during the synthesizing process: the synthesizing resin sample was taking out from the reactor and a calculated amount of xylene was added to the nonvolatile mixture to become a resin. The resin was poured into a body tube and a small air gap was kept inside the bodytube. Time taken was measured to travel air bubble from bottom to top in the body tube as the viscosity at 25^0C.

5) Determination of oil length of BBP: Oil length is expressed as weight percentage of glyceride oil in non-volatile in an alkyd resin.

$$\text{Oil length} = \frac{W \times 100}{NV - W_R}$$

W = Weight of glyceride oil

NV = Weight of non-volatile material

W_R = Weight of reaction water

6) Fourier Transform Infrared Spectroscopy (FTIR): Functional groups in BBP samples and coconut oil were determined by NICOLET, Model - 380 FTIR, Thermo electron Corporation. Samples were homogenized with NaCl anhydrous agate. The machine was operated and relevant spectrographs were taken under $400cm^{-1}$ – $4000cm^{-1}$ range.

7) Differential Scanning Calorimetry (DSC): The glass transition temperature of BBP sample was determined by NETZSCH, Model - DSC 204 F1. Nitrogen purge was started under 1 bar pressure. Liquid nitrogen cooling was started until get - 80^0 C. Heating cycle was started at 2^0 C / minute rate.

8) Pencil hardness test of a dried paint film: ASTM D 3363-74 was followed and measured resistance to scratch of metal primer coatings. Erichsen pencil hardness tester was used.

9) Cylindrical mandrel bending test for dried paint film: ASTM D 1737-62 test method was followed. 2mm spindle is used to assess the bending of metal primer coatings.

10) Impact resistance test for a dried paint film: ASTM D 2794-84 test method was followed. 500g weight was fallen down from 3feet height and number of cracks were observed on dried metal primer paint films.

11) Density of paint: The ASTM D 1475 test method was followed for wet metal primer paints.

12) Colourimetric value of a varnish by Lovibond Tintometer: BS 684 test method was followed to determine colour values of BBP and coconut oil.

13) Apparent viscosity: The BSA15 flow cup was used. The time taken to fill up a 50cc cup through the BSA15 by wet metal primer paints were measured.

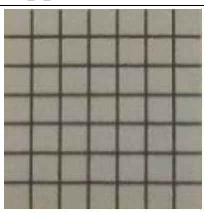
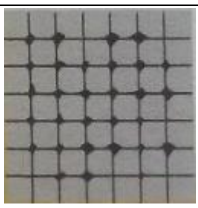
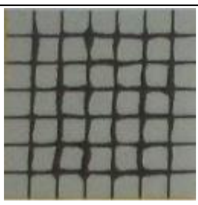
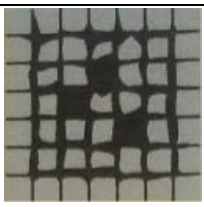
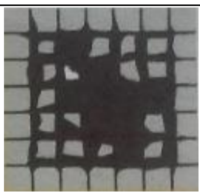
14) Dried film gloss: ASTM D523-80 test method was followed. The gloss value was measured after 48 hours of drying period by 60^0 angle.

15) Touch drying time of a paint film: Time taken to obtain no permanent finger marks at a light touch on applied metal primer paint films.

16) Hard drying time of a paint film: Time taken to obtain no permanent finger marks at heavy touch on applied on metal primer paint films.

17) Crosshatch test: The ASTM D 3359-83 test method was followed to assess dried metal primer coatings and the below ratings were given.

TABLE IX EVALUATION CRITERIA OF CROSSHATCH TEST.

Rating	Appearance	Description
5B		The edges are very smooth. No detaches of squares in the lattice
4B		Small flakes of the coating are detached at intersections. Affected area is less than 5%.
3B		Small flakes of the coating are detached along edges and intersections. Affected area is 5-15%
2B		Coating flakes are detached along the edges and parts of squares. Affected area is 15-35%.
1B		Ribbons and whole squares are detached. Affected area is 35-65%.
0B		Detached area is worse than 1B

18) Dry film thickness of a paint film: ASTM D 1186-81 test method was followed to measure the thickness of dried metal primer coatings.

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19) Water immersion test of organic coatings on steel: ASTM D 870-54 test method was followed. Painted panels were kept for 7 days and submerged in distilled water for 18 hrs. The appearance of the submerged and the rest of the panel was compared for wrinkles, chalking, blisters or any specified.

20) Fineness of grinding: The ASTM D 1210 test method was followed to assess the mill-base of metal primer coatings to maintain particle size 5-20µm.

21) Solid content: SLS 489: 1980 test method was followed.

22) Salt spray test: ASTM D 117-11 test was followed to assist corrosion resistance of dried and seven days cured metal primer coatings. 5% concentrated salt solution was used for 200 hours under 30^0C temperature. Panels were selected based on their performances and at least one panel representing a one category.

RESULTS

A. Characterization of coconut oil

1. Free fatty acid content (FFA): 0.242 mgKOH/g(oil)

2. Colourimetric value in Lovibond tintometer: 4

3. Specific gravity of coconut oil: 0.914

4. FTIR spectrum:

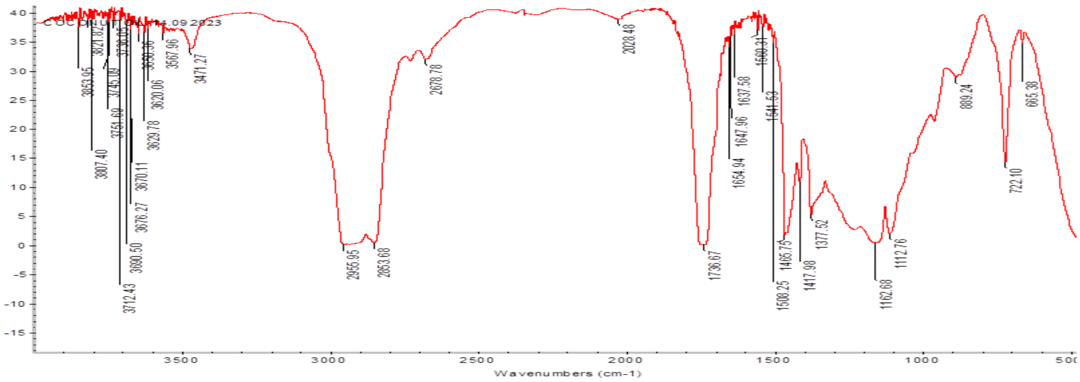

Fig 2. FT-IR of coconut oil

B. Characterization of BBP

1.. FTIR spectrum:

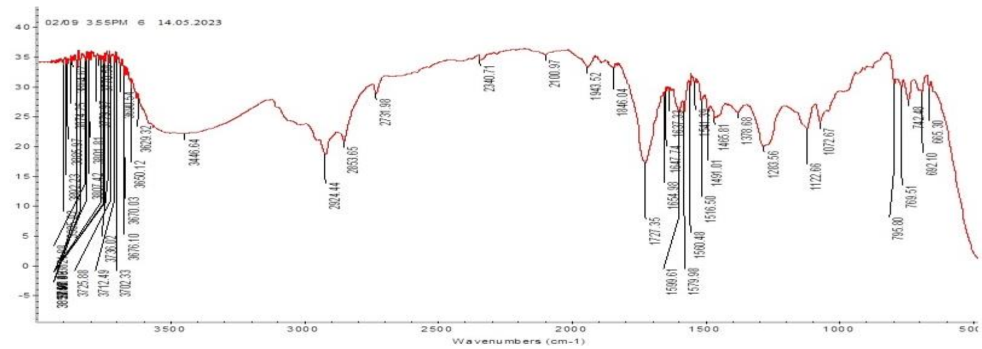

Fig 3. FT-IR of synthesized BBP-1 at the 6^{th} sample

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2. Differential scanning calorimetry of BBP:

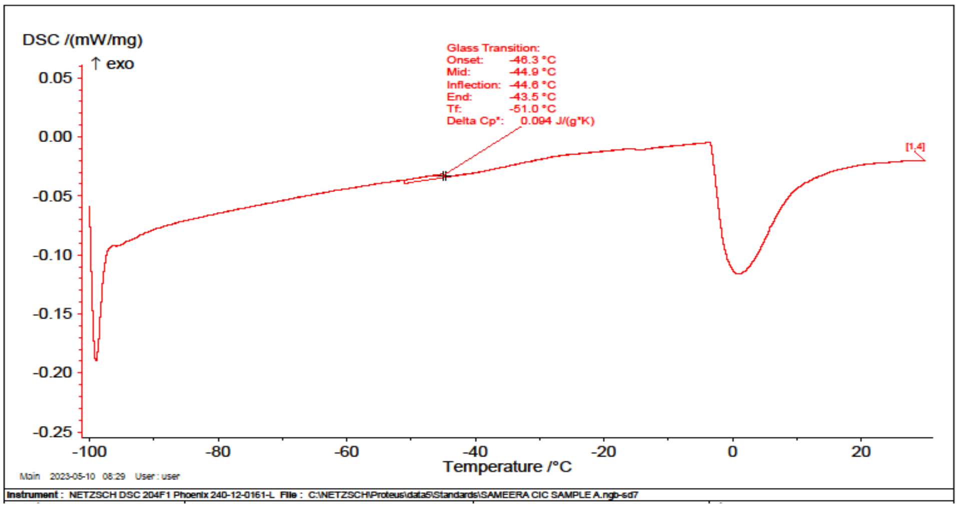

Fig 4. DSC of BBP.

3. Viscosity of BBP by the bodytube during the synthesis: The first sample was drawn after 30 minutes of reflux begun. Continuously 6 samples were drawn while keeping 45 minutes intervals.

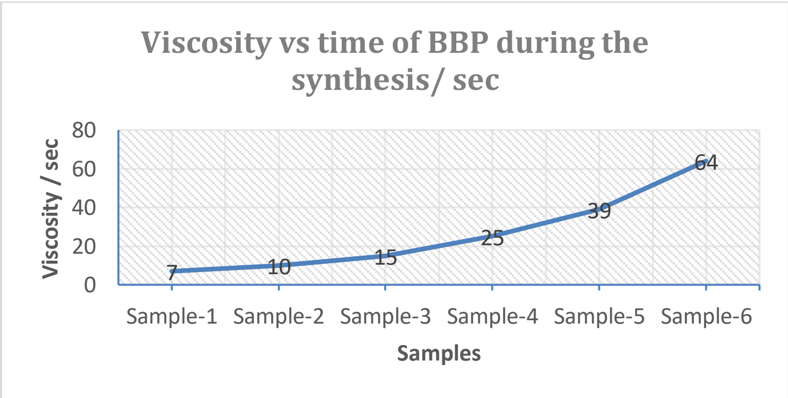

Fig 5. Viscosity changes during synthesis of BBP.

4. Reaction water collection of BBP during the synthesis: The first sample was drawn after 45 minutes of reflux. Continuously 6 samples were drawn while keeping 45 minute intervals.

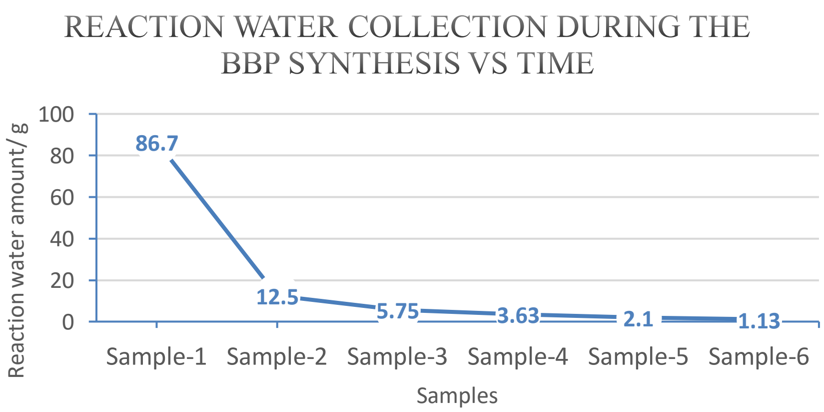

Fig 6. Collected reaction water of BBP in 45 minute intervals.

5. Acid values of BBP during the synthesis: The first sample was drawn after 45 minutes of reflux. Continuously 6 samples were drawn while keeping 45 minute intervals.

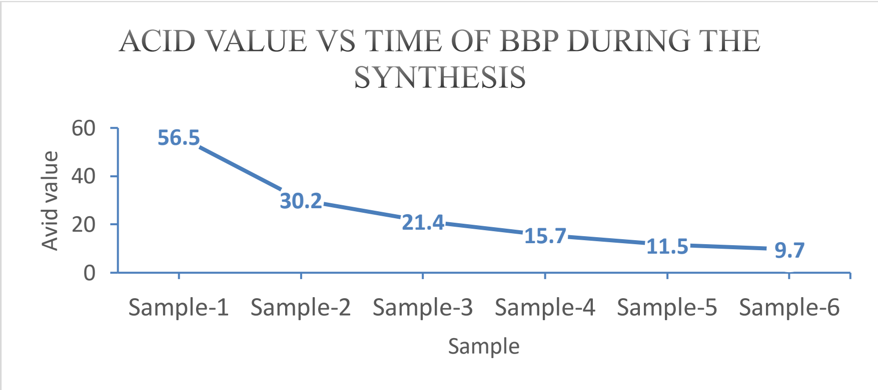

Fig 7. Variation of acid value in BBP mixture in 45 minute intervals during the synthesis.

6. Properties of BBP

TABLE X Property comparison of BBP

	Property	Value
1	Viscosity by Bodytube / sec	64
2	Acid value / mgKOH/ g	9.7
3	Oil length %	35.54
4	Colourimetry by Lovibond tintometer	8
5	Solid content %	61.35

C. Physical properties of wet RPUMP

1. Fineness of grinding by Hagman gauge: All metal primers were maintained 0-10µm particle size.

2. Solid content (%) of all metal primers:

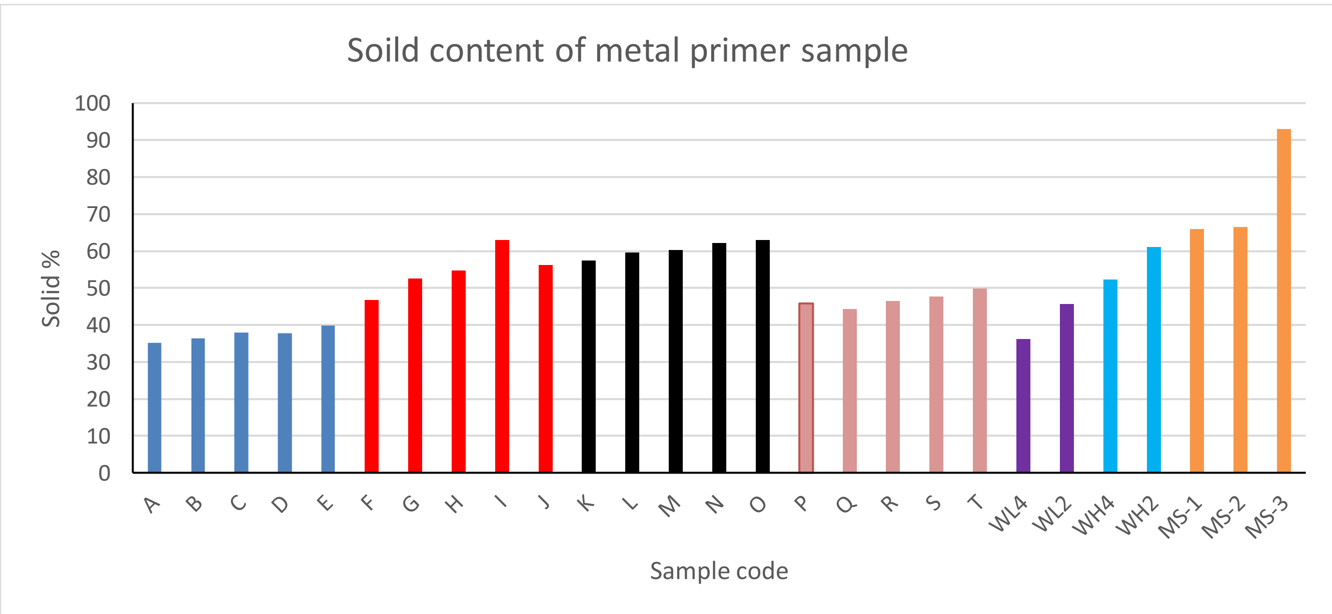

Fig 8. Variation of the solid content of RPUMP and CAEMP

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS | Volume IX Issue VII July 2024

3. Density (Specific gravity) of all metal primers:

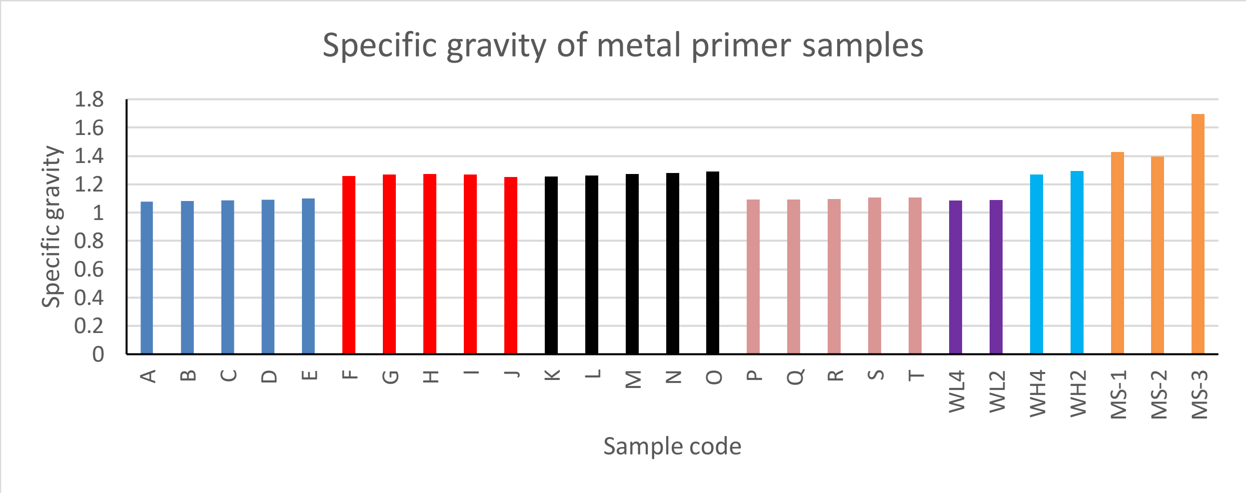

Fig 9. Variation of specific gravity of RPUMP and CAEMP

4. Apparent viscosity of all metal primers:

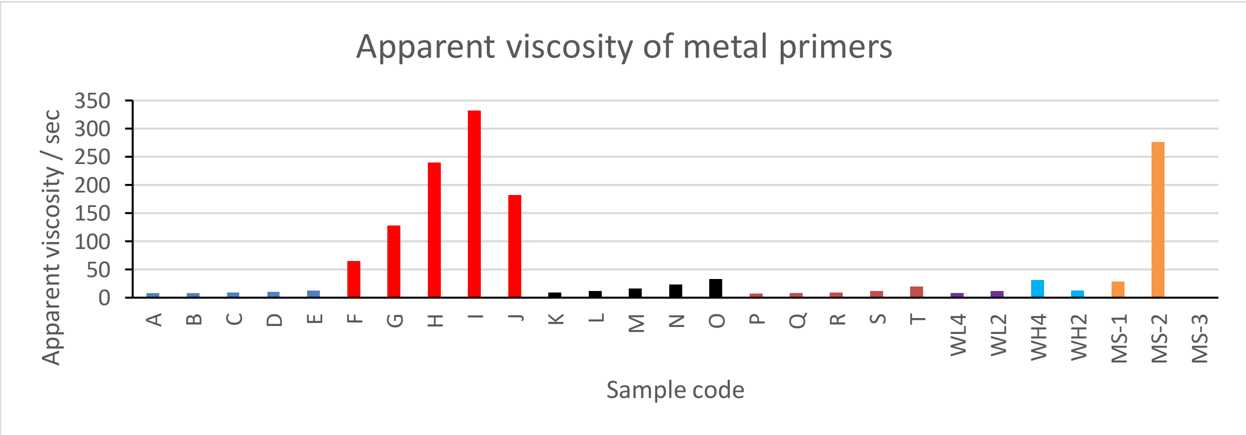

Fig 10. Variation of the apparent viscosity of RPUMP and CAEMP

The viscosity of MS-3 was very high and it was impractical to measure in viscosity cups.

5. Touch drying time:

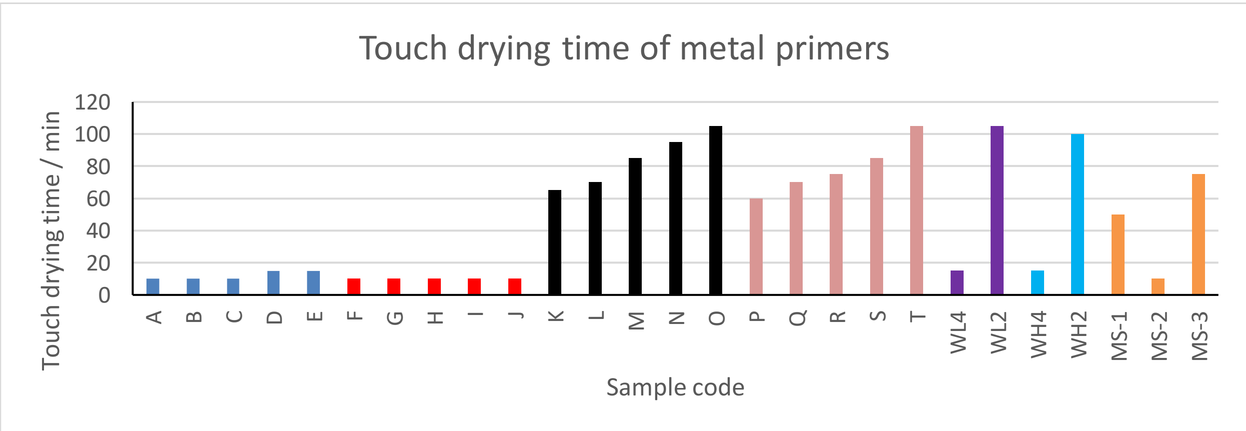

Fig 11. Variation of touch drying time of RPUMP and CAEMP

7. Hard drying time:

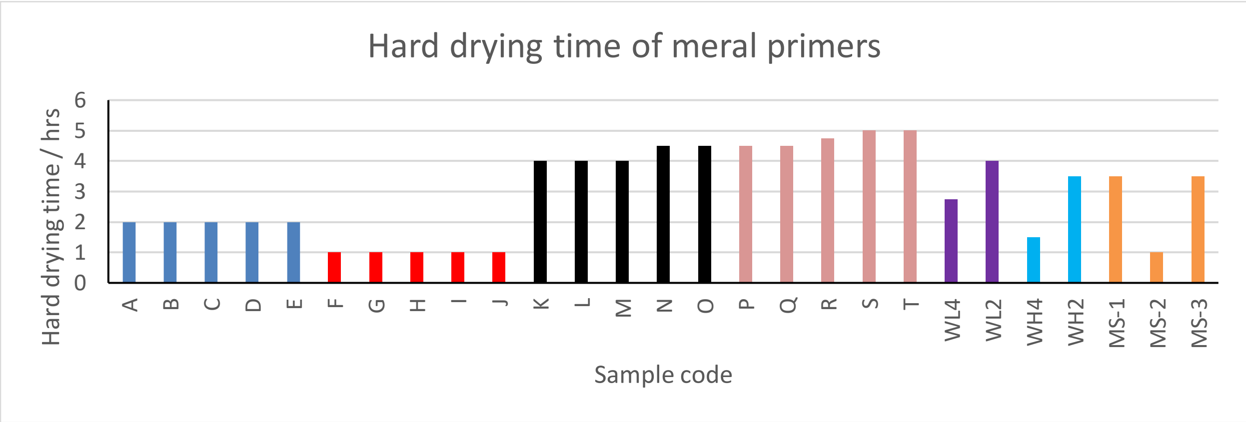

Fig 12. Variation of hard drying time of RPUMP and CAEMP

D. Physical properties of dried metal primer coatings on steel panels (Q panels)

1. Dry film thickness (DFT):

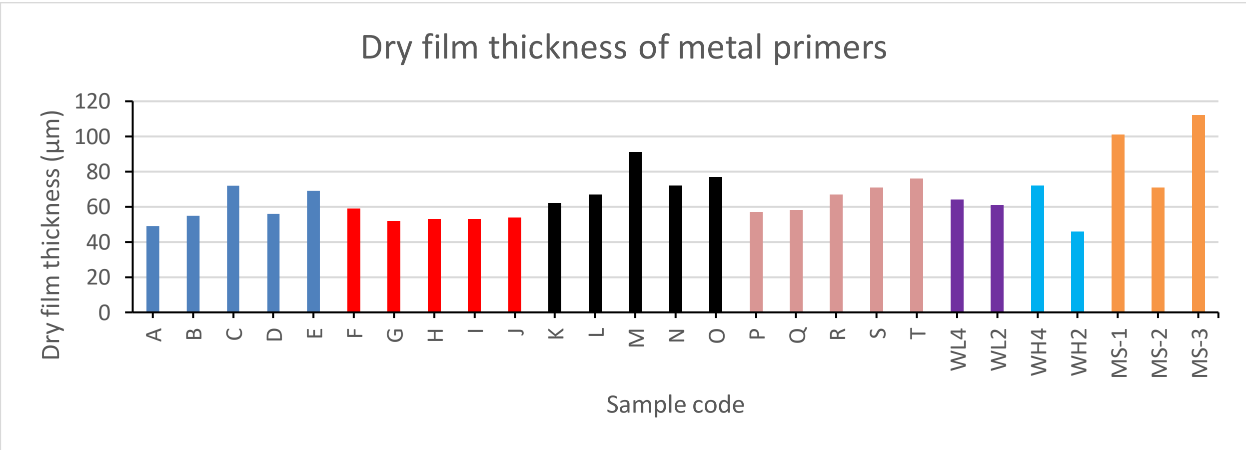

Fig 13. Variation dry film thickness of RPUMP and CAEMP

2. Gloss 60^0

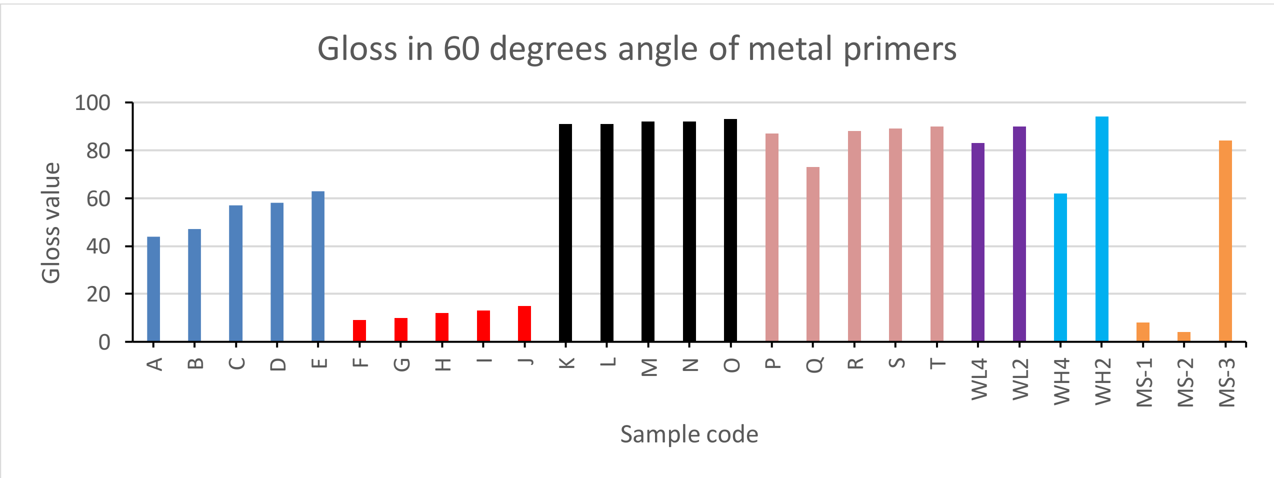

Fig 14. Variation of gloss 60^0 of RPUMP and CAEMP

3. Pencil Hardness Test: All specimens were satisfied with 4H pencil hardness.

4. Crosshatch test results:

TABLE XI Results of cross hatch test

5B states achieved specimens	4B states achieved specimens
A,B,C,D,E, K,L,M,N,O, P,Q,R,S,T,WL2, WH2, WH4, MS-1, MS-2, MS-3,	WL4, F, G, H, I. J

5. Water immersion test:

TABLE XII Results of water immersion test

No changes found in immersed area in water	A permanent chalky patch occurred in an immersed area in water
A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S, T WL2, WL4, WH2, WH4, MS-1,	MS-2, MS-3

6. Cylindrical mandrel bending test:

TABLE XIII Results of cylindrical mandrel bending test

Passed specimens (No cracks)	Failed specimens
K, L, M, N, O, P, Q, R, S, T, WL2, WH2, WH4, MS-1, MS-2	A, B, C, D, E, F, G, H, I, J, WL4, MS-3

7. Impact resistance test:

TABLE XIV Results of impact resistance test

Passed specimens	Failed specimens
A, K, L, M, N, O P, Q, R, S, T, WL2, WL4, WH2, WH4, MS-1, MS-2, MS-3	B, C, D, E, F, G, H, I, J,

8. Salt spray test:

			
C	H	M	P

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS | Volume IX Issue VII July 2024

			
R	T	WL2	WL4

				
WH2	WH4	MS-1	MS-2	MS-3

TABLE XIII Results of salt spray test

Sample code	Corrosion performance according to ASTM D1654-08	Evaluating blisters according to ASTM D714-02
C	Passed (Corrosion was controlled)	Medium
H	Passed (Corrosion was controlled)	Dense
M	Passed (Corrosion was controlled)	Few
P	Passed (Corrosion was controlled)	Dense
R	Passed (Corrosion was controlled)	Medium dense
T	Passed (Corrosion was controlled)	Medium
WL2	Passed (Corrosion was controlled)	Few
WL4	Passed (Corrosion was controlled)	Few
WH2	Passed (Corrosion was controlled)	Medium dense
WH4	Passed (Corrosion was controlled)	Medium dense
MS-1	Passed (Corrosion was controlled)	No blisters
MS-2	Passed (Corrosion was controlled)	Dense
MS-3	Failed – the film was peeled off.	Few

ISSN No. 2454-6194 | DOI: 10.51584/IJRIAS | Volume IX Issue VII July 2024

DISCUSSION

A) Discussion on BBP synthesis

i. FT-IR: During the condensation reaction of BBP (Fig 3) has shown a prominent peak at 1731 cm^{-1} which corresponds to aromatic ring ester. It confirms the condensation reaction during the synthesis of phthalic anhydride and benzoic with monoglyceride and pentaerythritol in the reaction mixture. During the condensation reaction BBP has shown a remarkable peak at 1122 cm^{-1} which is corresponding of $-C(=O)-O-C-$ ester group. In the IR spectra a particular peak at 2678 cm^{-1} which corresponds to cis distribution of –C=C– is gradually disappeared. Cis distributed double bonds are only present in unsaturated fatty acids in coconut oil monoglycerides. During the synthesis of BBP, those double bonds have used in any other bond formation. Mainly in crosslink formation between polymer chains.

ii. DSC: As shown in Fig 4, there was no considerable changes of Tg in BBP, DSC thermograms recorded was not clearly show any difference in Tg values of the same. Therefore, it is not possible to predict the thermal behavior of the BBP using DSC results, however it has shown considerably low Tg value which will provide some flexibility of structure at room temperature.

iii. The acid value, reaction water and viscosity: According to Fig-7, the acid value decreased over time as the acid groups in the mixture replaced with OH groups to form polyester through condensation reaction. The viscosity increased as shown in Figure 5, due to formation of polymer molecules. Figure 6 indicated that at the start of the reaction, there was a high release of water due to the high probability of reaction acid base groups, but this decreased over time.

iv. Oil length: The polyol was confirmed to be a short oil alkyd resin with a fairly low drying time.

v. Colorimetric value by Lovibond tintometer: As shown in Table X, the Lovibond tintometer value of the BBP was 8, but the coconut oil was 4. This excessive yellow tone has no effect because the metal primer is an undercoat and it always covers with at least one topcoat.

B) Discussion on RPUMP and CAEMP

i. Solid content, specific gravity and dry film thickness: The specific gravity provides an indication of the amount of solid materials present in a wet sample. In practice, there appears to be a relatively equal relationship when comparing Figure 8 and Figure 9. However, the dry film thickness (DFT) indicates the amount of solids that retain after the application of spray and this is dependent on the presence of added thinner and hardener contents.

ii. Touch drying time and hard drying time: In RPUMPs 4:1 shows very low drying time relative to 2:1 samples. In 2:1 samples contain more hardener and more polyols therefore, they required longer time period to cure.

iii. Apparent viscosity: The MS-3 sample had the highest viscosity compared to the other, and it could not be measured by the flow cup. The viscosity is dependent on the solvents used in the paint mixture. This is the only parameter that influences people to accept or reject the paint in the market without opening the can.

iv. Gloss 60^0 angle: Gloss value depends on the resin solid content in a wet paint sample. 2:1 RPUMP samples have relative high gloss value than 4:1 samples. 2:1 PUs considerably high in resin solids. Then samples from K to T can use as DTM type just like MS-3. But samples from A to J can use as UCP type.

v. Water immersion: All RPUMPs and MS-1 were showed better water resistance but MS-2 and MS-3 were turned into chalky appearance of submerged area. Therefore MS-2 and MS-3 have poor water resistance.

vi. Pencil hardness: All samples exceeded the 2H hardness value. Therefore, all specimens are resistant to scratches and can withstand friction.

vii. Crosshatch test: All panels were exceeded 4B states. Therefore, all are having good surface adhesion.

viii. Cylindrical mandrel bending test: All 4:1 RPUMP samples were failed but all 2:1 RPUMP samples were passed in the test. In 2:1 RPUMPs resin content is high and hardener addition also 50% higher than 4:1 RPUMPs. Therefore, 2:1 RPUMPs are more flexible than 4:1 RPUMPs.

ix. Impact resistance test: Results of impact resistance are nearly identical to the rest of cylindrical mandrel bending. High flexibility films show positive results, but brittle films are prone to damage and failure against impacts.

x. Salt spray test: During the salt spray test, two responses were observed: blisters and spreading corrosion along gash area. Only MS-1 showed resistance to both defects and had exact resistance to the salt. All the other panels had more or less blisters. Only MS-3 failed for both defects, and its corrosion spread due to the paint film disbanding from the substrate.

CONCLUSIONS

The research aims to synthesizing and characterization BBP to explore its potential as a replacement for crude oil-based film formers in automotive metal primers.

1. When considering water resistance all RPUMPs exceeded 2 of 3 CAEMP. Therefore, RPUMPs performed better than CAEMP in water resistance.

2. According to salt spray results, which represent anticorrosive properties, all RPUMPs equally performed with MS-2 and MS-3 in CAEMP. MS-3 was worst and disbanded in salt spray test. Therefore, RPUMPs can compete successfully with crude oil-based CAEMP.

3. MS-3 is a DTM type epoxy coating and renewable PUs represent this category is from sample K to T. MS-3 failed in the mandrel bending test, water immersion test and salt spray test but corresponded all RPUMPs were passed. Therefore, RPUMPs performed better than CAEMP.

4. P,R, and T are low pigment loaded, DTM type RPUMPs were shown equality in properties of adhesion, water resistance, flexibility and surface hardness but dry film thickness was increased accordingly. Their result for anticorrosive properties in blisters evaluating was dense, medium dense and medium. Therefore, it clearly shows anticorrosive property increases with dry film thickness.

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