Kwaghe International
Journal of Sciences and Technology

ISSN : 0000-0000
Index: Harvard, Boston, Sydney University, Dimensions, Lens, ResearchGet Scilit, Semantic, Google Scholar, Base etc

https://doi.org/10.58578/KIJST.v1i1.3608

Compounding of Synthesized Monomethylol Urea and Hydroxylated Palm Kernel Oil as Composite Resin for Emulsion Paint Formulation

Archibong C.S[1], Bintu Kime[2], and Fadawa F.G[3]
[1]Federal University Wukari, Taraba State, Nigeria
[2]Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria
[3]Nigerian Police Force Command Headquarters, Bompai Kano. Nigeria
archibong@fuwukari.edu.ng

Article Info:

Submitted:	Revised:	Accepted:	Published:
Jul 1, 2024	Jul 20, 2024	Jul 27, 2024	Jul 31, 2024

Abstract

Palm kernel oil which is a triglyceride was subjected to chemical modification of its structure to add hydroxyl groups. The hydroxylated chemical structure was cross-linked with monomethylol urea, a thermoset resin to produce a composite MMU/HPKO. Fourier transform infrared spectroscopy was used to ascertain the existence of chemical interactions between MMU and HPKO, the reduction of the absorption band around 3360.69cm^{-1} which is due to the presence of hydroxyl groups was an indication of the occurrence of chemical reaction between hydroxylated palm kernel oil and monomethylol urea. The compounded composite was further characterized for the evaluation of physical and mechanical properties. Properties like the elongation at break, viscosity, Gel time, Turbidity and Refractive index increases with percentage inclusion of HPKO until at above 50% where changes were noticed. While parameters like Formaldehyde emission, Moisture uptake, Density and melting point decreases with percentage loading of HPKO. Copolymerization successfully combined the advantages of MMU specie with HPKO while offsetting their shortcomings in a synergetic manner to create a higher performance class of polymer. Therefore, the blending of monomethylol urea with the hydroxylated palm kernel oil in this research work has added flexibility to MMU which hitherto was brittle and hard, improve it water resistance properties because of the hydrophobic nature of the hydroxylated palm kernel oil, and has brought about a reduction in the formaldehyde emission of monomethylol urea due to the percentage's inclusion of hydroxylated palm kernel oil and subsequent deduction of monomethylol urea.

Keywords: Monomethylol Urea, Hydroxylated Palm Kernel Oil, Composite, Emulsion Paint, Compounding, Copolymerization

INTRODUCTION

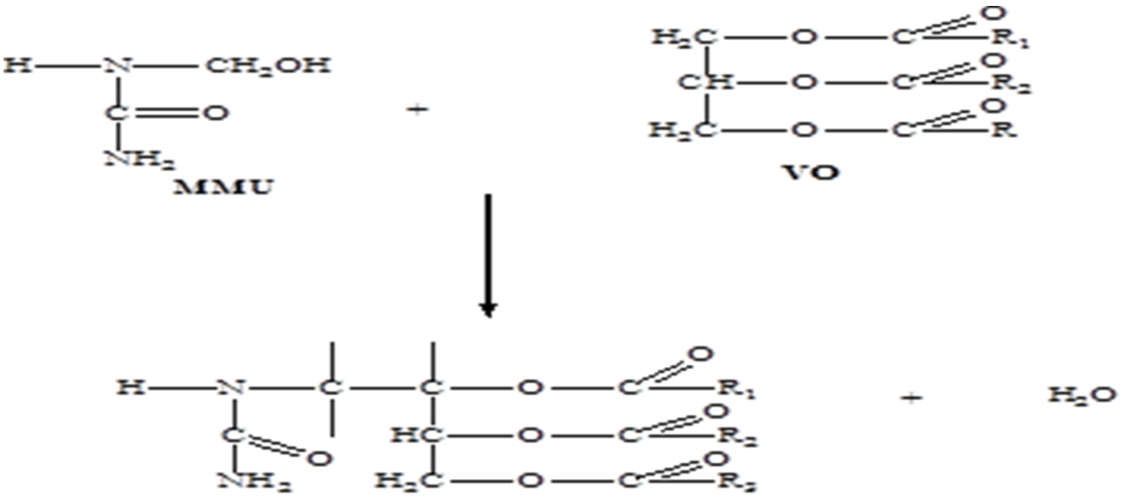
Formaldehyde-based binders are derived from non-renewable petrochemicals and natural gas and hence still have a dangerous chemical problem associated with their manufacture. Unfortunately, there is no method to degrade them at rate comparable to our current rate of consumption. The problem of non-biodegradability is highlighted by overflowing landfills, polluted marine waste and unsightly litter (Huang, 1995). This harmful effect of formaldehyde emission have led to increase effort in research towards developing formaldehyde-free, environmentally-friendly, safer, biodegradable green alternatives, particularly the sustainable ones based on yearly renewable plants (Peijs, 2002).

The coating industry has come under increasing pressure to make production eco-friendlier and efforts to shift the prime resource base of the industry from fossil (non-renewable) to renewable feed stocks. Amongst them, vegetable oils are the most widely used for the industry and still, they are considered to be amidst the most promising raw materials for other purposes, owing to their excellent environmental credentials, which include their ready availability, low cost, inherent biodegradability, low toxicity and their many versatile applications (Roseany *et al.*, 2013).

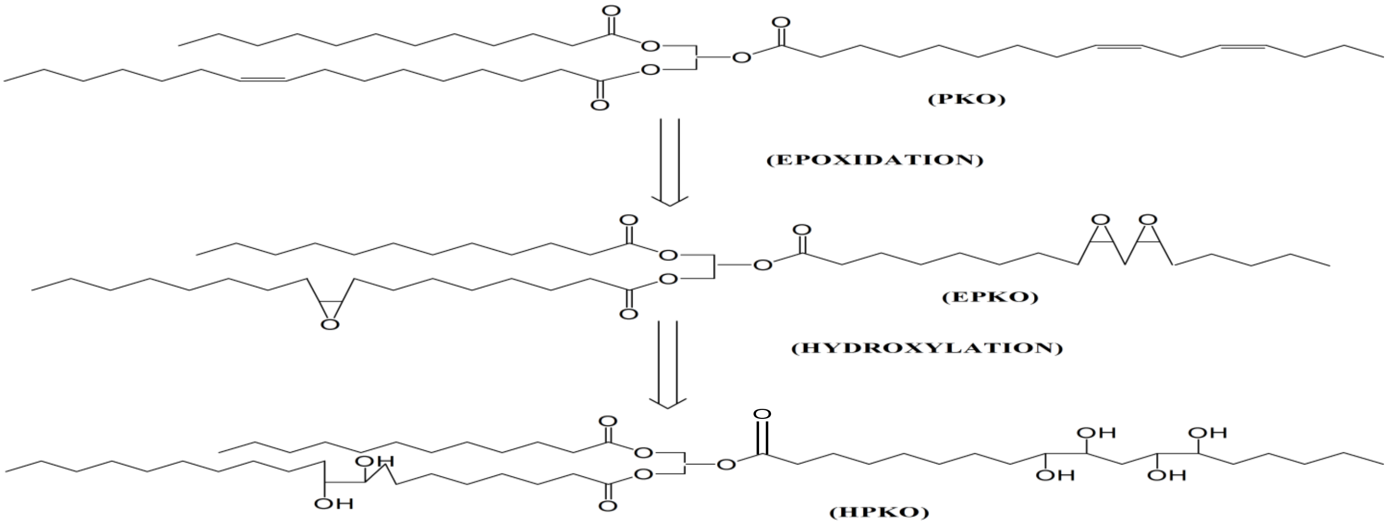
Vegetable oils contain several actives sites amenable to chemical modification. The double bonds in fatty acids chains and the ester groups in the glyceryl part are the most important. These active sites can be used to introduce reactive groups. Hydroxylation of vegetable oil and derivatives are most focused on the modification of fatty acid chain (wang *et al.,* 2013)

Palm kernel oil has a balanced ratio of unsaturated and saturated fatty acids. It has a stable high cooking temperature (high smoking point), longer shelf life, stay longer than other vegetable oils. Zero cholesterol (even though it is high saturated fat), it is relatively low in cost. Thus, the ester linkage and/or COOH group can undergo such reactions as hydrolysis, esterification, saponification, amidation, halogenation etc, while double bonds undergo reactions such as oxidative polymerization, hydrogenation, epoxidation, halogenations, sulphonation and so on (Bashar and Jumat, 2010).

Copolymerization of polymers sums up the advantages of one polymer specie with another while discarding their shortcomings in a manner to create a higher performance class of polymer. Therefore, blending of monomethylol urea with the hydroxylated palm kernel oil which this research seek to achieve will help in introducing flexibility to the hitherto brittle and hard monomethylol urea, improve it water resistance properties because of the hydrophobic nature of the hydroxylated palm kernel oil, and will bring about a reduction in the formaldehyde emission of monomethylol urea due to the percentages inclusion of hydroxylated palm kernel oil and subsequent deduction of monomethylol urea.



Copolymerization of MMU and VO



Route for the Conversion of Palm kernel oil to Hydroxylated palm kernel oil

MATERIALS AND METHODS

Resin Synthesis

MMU was prepared using the one step process (OSP) as reported by Archibong and Osemeahon (2019) with some modifications. One mole of urea (6.0g) was made to react with one moles of formaldehyde (8.11ml) 37-41% (w/v), using 0.02g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 13.0 by using 0.1MH_2SO_4 and 0.5MNaOH solutions. The solution was heated in a thermostatically controlled water bath at 50^0C. The reaction was allowed to proceed for 60min after which the resin was removed and kept at room temperature (30^0C).

Epoxidation Palm Kernel Oil

Epoxidation was carried out using the method describe by Goud *et al.*, (2007). 200cm^3 of oil was introduced in a 1000cm^3 three necked flask equipped with a reflux condenser and a thermocouple. The flask was place on a hot plate with temperature control. Acetic acid and formic acid at a molar ratio of 0.5:1 to the oil and sulphuric acid catalyst 3% weight, hydrogen peroxide as an oxygen carrier was added into the oil. A hydrogen peroxide of a molar ratio 1.5:1 to the oil was added drop wise into the mixture. The feeding strategy is required in order to avoid overheating the system since epoxidation is an exothermic reaction. The reaction was maintained at uniform state by using a magnetic stirrer which runs at about 1600rpm under isothermal condition at 50-60°C. The product was cooled and decanted in order to separate the organic-soluble compounds (epoxide oil) from water-soluble compounds. Warm water was used to wash the epoxidized oil (in small aliquots) in order to remove residual contaminants. This procedure was repeated three times.

Hydroxylation of the Epoxidized Palm Kernel Oil

Hydroxylation of the palm kernel oil was carried out using procedure described by Patrovic *et al.,* (2003). The reaction was performed in a 1000cm^3 three necked flask equipped with a reflux condenser and a thermocouple. The flask was placed on a hot plate with temperature control. 150cm^3 of the epoxidized oil was hydroxylated using alcohol (methanol and isopropanol) with molar ratio of 4:1 to the oil and water at a molar ratio of 2:1 was mixed with the epoxidized oil and sulphuric acid catalyst in the reactor. The reaction was performed at fix temperature of 60°C for 5 hours. Uniformity was maintained by using a magnetic stirrer which runs at about 1600rpm. The product (polyol) was cooled and decanted in order to separate the organic-soluble compounds from water-soluble compounds. Warm water was used to wash the polyol (in small aliquots) in order to remove residual contaminants. This procedure was repeated three times.

Compounding

This was carried out by blending different concentrations (10-70%) of HPKO with MMU.

Determination of Density, Turbidity, Melting Point and Refractive Index

The density of the resins was determined by taking the weight of a known volume of resin inside a density bottle using Pioneer (Model PA64) weighing balance. Three readings was taken for each sample and average value calculated. The turbidity of the samples was determined by using Supertek digital turbidity meter (Model 033G). To determine the effect of melting point on monomethylol urea (MMU), a melting point differential macrophase separation technique was developed. In this technique, MMU was introduced into a porcelain dish. The dish with it content was transferred into an oven set at 120ºC for curing. The mixture was removed periodically from the oven and stirred until the mixture gelled and finally solidified. The temperature was then raised to 150ºC and left for 5min after which the sample was removed and cooled for observation. The experiment was repeated three times

Determination of Gel Time and Viscosity

Gel time was determined by gel-time meter. The temperature was set for 121°C in gel time meter and filled with liquid paraffin till the brim of the container. The heating system and stirrer were switched on. 10 gms of the sample was weighed and it was taken in a test tube and placed vertically in hot paraffin bath using wooden holder. Resin level in the tube was taken such that it was well within hot bath. A glass rod was placed in test tube and it was locked to the spindle drive with magnetic couple. The spindle was now rotated. When the top spindle rotates, magnetic coupling and bottom fin also started rotating along with glass rod. When the resin started solidifying, rotation of glass rod was resisted, which in turn stop rotation of bottom fin. Upper fin, still rotating freely, come into contact with static one, and the time was noted from the stopwatch. The gel-time was found out.

Viscosity was determined by adopting Ganeshram *et al.,* 2013 method, using Brookfield viscometer. Spindle number was selected and the speed of motor was set. The temperature of the solution was measured using temperature probe. The spring cap was removed and the spindle was fixed. It was immersed up to the mark in the resin and the motor switched on. Spindle rotates inside the solution and produces shear, which gives value of viscosity. It was carried out at a temperature of 25°C.

Determination of Moisture Uptake

The moisture uptake of the resin films was determined gravimetrically, according to method described by Archibong *et al.,* 2018. Known weights of the samples was introduced into desiccators containing a saturated solution of sodium chloride. The increase in weight (wet weight) of the sample was monitored until a constant weight was obtained. The difference between the wet weight and dry weight of the sample was recorded as the moisture uptake by the resin. Triplicate determinations was made for each sample and the average value recorded.

Determination of Elongation at Break

The elongation at break was determined using Inston Tensile Testing Machine (Model 1026). Resin films of dimension 50mm long, 10mm wide and 0.15mm thick was brought to rupture at a clamp rate of 20mm/min and a full load of 20kg. Three runs were carried for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Determination of formaldehyde emission using UV-Spectrophotometer

To determine any possible absorbance by formaldehyde, deionized water was used as the blank. The cuvette was rinsed several times with tap water followed by deionized water, it was then filled with deionized water, and placed in the holder, and the spectrophotometer was blanked at 563 nm. The sample was then put into another cuvette and the absorbance was noted at the same wavelength of 563 nm, with concentration recorded

Determination of Water Solubility

The solubility of MMU was determined by mixing 1ml of the resin with 5ml of distilled water at room temperature (30^0C). The degree of solubility was evaluated visually and the result recorded.

RESULTS AND DISCUSSION

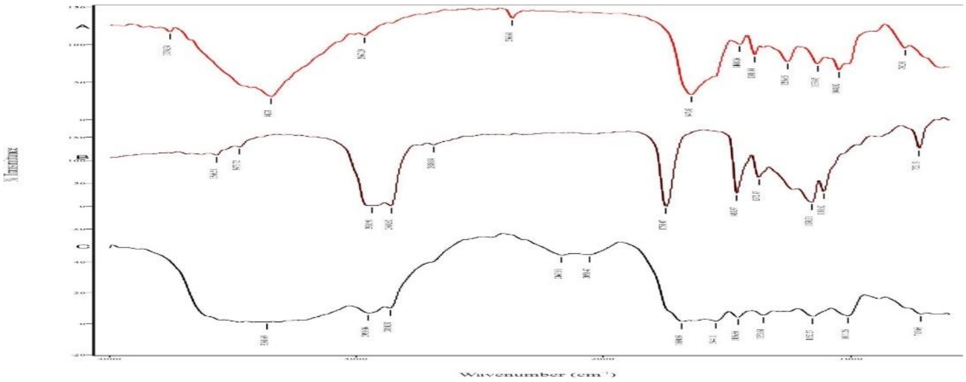


Fig.1 FTIR Spectra of A=MMU, B=HPKO, C=MMU/HPKO

Fig.1 shows the spectra of A (MMU), B (HPKO). C (MMU/HPKO). The FT-IR spectra of A (MMU) shows the appearance of a sharp band in the region 3754.34 cm^{-1} and another broad band at 3344.73cm^{-1} frequency indicating the presence (OH) on the monomethylol urea. The appearance of stretching bands at 2967.29 cm^{-1} and 2369.61 cm^{-1} indicates the presence N-H, the peak at 1647.43 cm^{-1} is due to C=O of urea, the bands at 1448.06 cm^{-1}

and 1388.84 cm^{-1} is due to C-H of methylene bridge and the bands at 1256.55 cm^{-1} through 1048.02 cm^{-1} was due to characteristic C-O-C ether linkage stretching (Abbas *et al* 2014).

In the FT-IR spectrum of B (HPKO), the broad band stretching at 3566.51cm^{-1} and 3473.72 cm^{-1} are due to – OH group present in the HPKO. The dual band sharp transmitted at 2936.91 cm^{-1} and 2850.82cm^{-1} produced by stretching of the C-H group of alkanes in the spectrum of HPKO can be remarkably distinguished. The peak at 1750.07 cm^{-1} indicates C=O stretching vibrations of the saturated ester present in the oil (Yelwa *et al.,* 2017). In addition, the region of 1460.97cm^{-1} and 1372.87 cm^{-1} of the IR spectrum show two bands that correspond to the bending vibration of C-H of alkane. The peak at 1158.31 cm^{-1} is due to C-O stretching mode of carboxylic acid (Patrick et al., 2009).

In the MMU/HPKO spectra the O-H peak at 3754.34cm^{-1} in MMU now appeared a lower frequency band of 3360.69cm^{-1}, this may be due to the hydrogen bonded hydroxyl groups that contribute to the complex vibrational stretches associated with free inter- and intra-molecular bound hydroxyl groups (Shashidhara and Jayaram, 2010). Also the frequency bands of C=O, N-H, CH_2, C=C, C-O-C, C-H in MMU and HPKO all shifted to a different bands in the MMU/HPKO composite, thus indicating chemical reaction actually took place between MMU and HPKO.

Effect of HPKO concentration on the Viscosity of MMU/HPKO

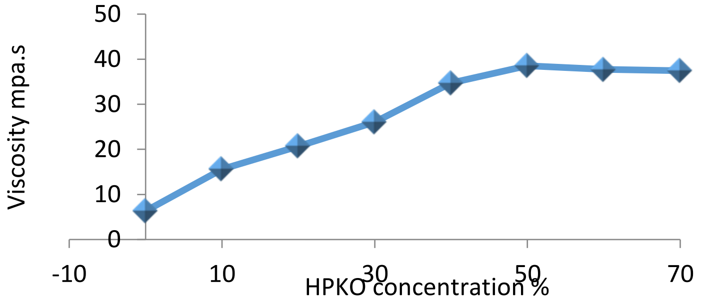


Fig.2 Effect of HPKO concentration on the Viscosity of MMU/HPKO

Fig. 2 is a plot of the effect of HPKO concentration on the viscosity of MMU/HPKO. The viscosity is observed to increase with increasing percentage concentration of HPKO until at above 50% addition of HPKO, the viscosity then decline. The increasing viscosity could be a reflection of increased intermolecular interactions in the MMU monomer and the palm kernel oil fatty acids because they contain groups that can induce the formation of abundant hydrogen bonds between hydroxyl and ester group. Hydrogen bond and the entanglements within the system could have been destroyed at higher HPKO concentration, thus the reduction in the viscosity at above 50% inclusion (Kiran and Sigit, 2018). This apparent increase in the viscosity may also have been contributed by the formation of higher crosslinking density of the polymeric matrix due to increasing curing of MMU and HPKO. The free volume might have contributed to the little decrease. The free-volume of a material is the summation of the spaces or holes that exist between molecules of a material resulting from the impact of one molecule or molecular segment striking another.

The viscosity of a binder is an important factor to the coating industry. This is because the viscosity of the binder controls many of the processing and application properties such as flow rates, leveling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to the substrate (Archibong and Osemeahon, 2019). Because of the presence of functional groups in the polymeric backbone, inter-polymeric specific interactions have long been known to result in unusual behaviour and material properties that are dramatically different from those of the nonfunctional polymers (Qi et al., 2002). These interactions include ion-ion coulumbic interaction, hydrogen bonding and transition metal complexation. Specific interaction between polymers causes aggregation or complexation of the component polymer chains, resulting in solution viscosity variation (Qi et al., 2002).

Effect of HPKO concentration on the Turbidity of MMU/HPKO

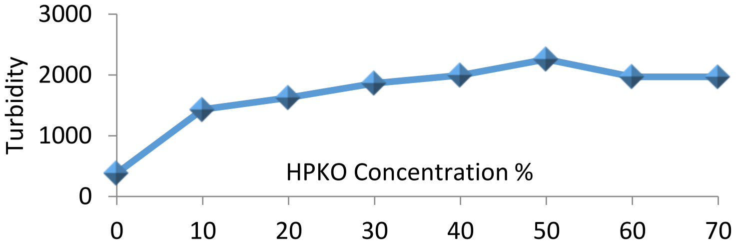


Fig.3 Effect of HPKO concentration on the Turbidity of MMU/HPKO

Fig 3. Is a graph of the effect of HPKO concentration on the turbidity of MMU/HPKO. The turbidity of MMU is observed to rise initially with increase in HPKO concentration and later after at about 50% HPKO inclusion it begins to decrease. The initial increase may be due to the growth of large inter-polymer aggregate, and tendency towards sedimentation with HPKO increase (Sahad, 2015). The polymer chains might have experienced a strong frustration in chain packing in the interfacial region due to the formation of large loops at high HPKO addition and inability of the longest chains to be incorporated in the crystalline structure, resulting in the decreasing turbidity (Bin *et al.*, 2016).

Turbidity actually derived its principle from light scattering, when we have homogeneity and few particles, there will be less scattering; hence, higher scattering is observed when we have a non-homogenous system with a lot of particles. The measurement of turbidity of the binder is usually performed in order to characterize the optical properties of the binder as related to gloss property. The refractive index gives an indication of the turbidity. Light interaction with a colloidal system is its turbidity. Turbidity of the system can be used as an indication of the level of interchain cross-linking (Al-Marnasir, 2009).

Effect of HPKO concentration on the Formaldehyde emission of MMU/HPKO

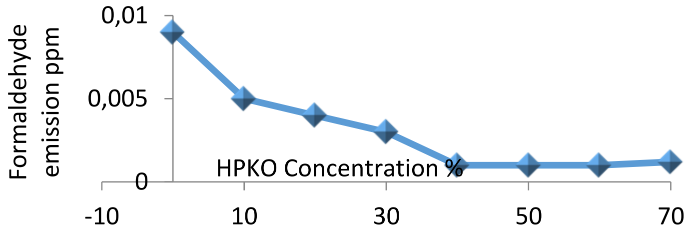


Fig.4 Effect of HPKO concentration on the Formaldehyde emission of MMU/HPKO

Fig. 4 is a graph representing the effect of HPKO concentration on the formaldehyde emission of MMU/HPKO. The formaldehyde emission shows decreasing tendency with increasing concentration of HPKO concentration, which was more pronounce at 40% inclusion. This occurrence could be due to the deceleration of curing process which influence change of methylene-ether bridges and various active sites in triglyceride structures like the double bond, the ester group, the allylic carbons, and the carbons α to the ester group, in consequence, the decreasing of methylene-ether bridges causes the reduction of formaldehyde emission (Garnier, 2002). It could also be due to the reduction in stress during cure which reduces emission as a result of improve flexibility brought about by the introduction of HPKO to MMU, since a reduce density results in high flexibility and increased ability to absorbed but less ability dissipate energy (Stefana *etal.,* 2005).

Hydrolysis of cured urea resins has been known to be responsible for formaldehyde emission leading to sick building syndrome (Park *et al.*, 2010). Formaldehyde is higher indoors than outdoors. High emissions of formaldehyde from latex paint have been reported by Salthalmmer *et al.* (2010). Because of the health challenge formaldehyde emission possess to human and environ it is necessary to determine it emission during MMU synthesis. The present result shows that formaldehyde emission is within acceptable level of (0.10ppm).

Effect of HPKO concentration on the Moisture uptake of MMU/HPKO

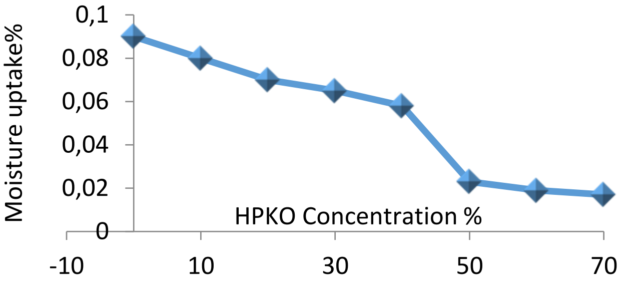


Fig.5 Effect of HPKO concentration on the Moisture uptake of MMU/HPKO

Fig.5 is a graph of the effect of percentage concentration of HPKO on the moisture uptake of MMU/HPKO. The moisture uptake decline gradually with the continued inclusion of HPKO. This can be attributed to the addition of a large soft/flexible and hydrophobic hydroxylated palm kernel oil component to decrease the rigid, compact structure of MMU polymer as well as introducing water proof resistance to the composite. Increase in percentage concentration of HPKO content also leads to a lower composite swelling ratio, which could indicate not only high crosslinking density but also a lower absorbability of the network in the solvent in this case water (Unar *etal.*, 2010). The low moisture uptake recorded in the MMU/HPKO composites could also be explained in terms of the reduction of MMU loading in the presence of the hydrophobic palm kernel oil. Generally, these MMU polymers are highly hydrophilic, but when HPKO are typically included, they added to hydrophobic polymer matrices, enhancing reinforcement and matrix adhesion and thus decreases the hydrophilicity.

It has been shown that oil-based polymers do not form uniform blends due to the variable fatty acid composition within each oil, which can result in a micro-phase separation of the matrix, thereby compromising the mechanical properties of the final polymeric material. Hydrophobicity and flexibility of vegetable oil-based polymers can be tuned by monomer composition and by the selection of the specific oil to be used as a monomer.

Polymeric binders play a major role in moisture transport properties of paint, because it is one of the major constituents. Waterborne coatings are susceptible to durability issues pertaining poor water resistance. The functional groups on polymers or copolymer resins that are used can undergo hydrogen or ionic bonding, unless the hydrophilic character is balanced with that of the hydrophobic, the coating will either be water sensitive or the formulation will not have colloidal stability. Hydrophobic components in the binder give the best combination of improving water resistance of water-borne coating. A detailed knowledge of moisture transport is also essential for understanding the resistance of a material against attacks from its environment (Emile, 2003; Bharath and Swamy, 2009).

Effect of HPKO concentration on the Density of MMU/HPKO

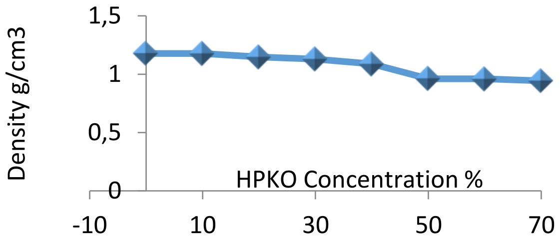


Fig.6 Effect of HPKO concentration on the Density of MMU/HPKO

The effect of HPKO concentration on the density of MMU/HPKO is shown in fig.6. The density is observed to decrease with increasing addition of HPKO. This result may be due to the inherently flexible structure of fatty acid chain, which is prone to form a less compact crosslinked structure compared to the stiffer MMU repeat units (Unar *etal.*, 2010). It can also be as a result of differences in the molecular features and morphology which influenced the packing nature of resin molecules as the concentration of HPKO increases. Physical properties of polymer depend on chain length and content of soft and hard segments. The decrease observed from 0 to 70% HPKO loading could be due to increasing amount of soft segment (Mavani *et al.,* 2007).

In general, an increase in HPKO content decreased crosslink density compared to a neat anhydride cured MMU. Unreactive saturated components like cryptic acid and lauric acid pendant chains in HPKO enhance the flexibility and degree of freedom for movements of the molecular chains in the monomethylol urea network and hence a reduction in the degree of crystallinity and molecular weight. Crosslinking density increasing with oxirane value has also been observed within various vegetable oils but palm kernel has less of these oxirane value and therefore manifest in the formation of less crosslinking density.

The density of a paint binder in the coating industry has an important influence on factors such as pigment dispersion, brush-ability of paint, flow, levelling and sagging. Density measurements are very useful for the identification and characterization of different substances and a significant factor that affects the production cost and profitability of the manufacturing process (Kazys and Rekuviene, 2011).

Effect of HPKO concentration on the Elongation at break of MMU/HPKO

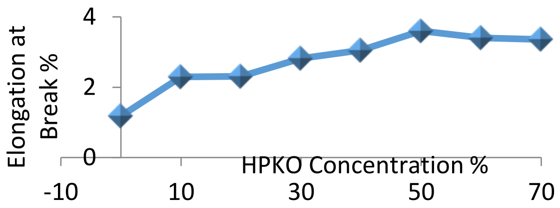


Fig.7 Effect of HPKO concentration on the Elongation at break of MMU/HPKO

The plot of the effect of percentage concentration of HPKO on the elongation at break of MMU/HPKO is depicted in fig.7. The elongation is seen to steadily increase with increasing inclusion of HPKO. Elongation at break is a measure of ductility of the material. It has been reported that plasticizers lower tensile strength of film but increase % elongation as it is observed here where the incorporation of HPKO introduces depressions of tensile strengths because of this plasticizing effects and increases the elongation at break (Madufor *etal.,* 2013). In as much as a high concentration of HPKO often permits a fast crosslinking process in the composite, it can also bring about the formation of many structural defects in the composite network such as dangling chains that are not elastic active, perhaps the reason for the decline noticed after about 50% HPKO inclusion. The increase in elongation at break with increasing concentration could be due to increase in molecular mobility emanating from the specific interactions between MMU and the oil. In addition, the liberated saturated fatty acid esters behave as plasticizers in the matrix to increase the chain segment mobility and decrease crosslink density. The decrease in cross-link density induces increase in elongation at break with increase in HPKO content not beyond 50%.

Elongation gives a picture about how much the material will be stretched before it breaks. The structure of thermosetting resins also leads to some unwanted mechanical properties that limit their structural applications. They are relatively brittle. Elongation at break can be a propel tool to determine the adhesion between phases, because of its sensitivity for load transfer between phases (Cakir *et al.,* 2012).

Effect of HPKO concentration on the Gel time of MMU/HPKO

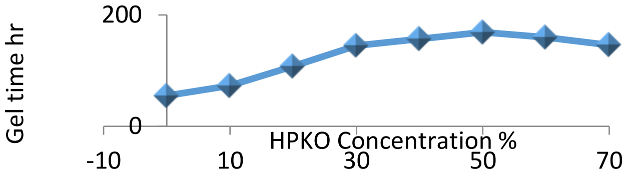


Fig.8 Effect of HPKO concentration on the Gel time of MMU/HPKO

Fig.8 represent the graph of HPKO concentration on the gel time of MMU/HPKO. The gel time rises with increase in HPKO addition. This could be due the fact that oils contain fatty acids with carbon–carbon double bonds that can act as reactive sites for crosslinking, and creating a stronger polymer network. This behaviour could also be attributed to increase in molecular weight and cross-linking density which led to increase in viscosity and reached a stage where nucleation process begins producing microgel particles which enhanced increase in viscosity build up (Menkiti and Onukwli, 2011). At above 50% inclusion phase inversion and dissociation sets in and this explains the slight decrease in the gel time.

Gelation is characterized by the incipient formation of a material of an infinite molecular weight and indicates the conditions of the process-ability of the material. Prior to gelation, the system is soluble, but after gelation, both soluble and insoluble materials are present. As gelation is approached, viscosity increased dramatically and the molecular weight goes to infinite. The reaction between monomers leads to the formation of network, hence gelation. Both molecular weight and poly-dispersity increase until one single macromolecule is formed. At this point, the behavior of the system changes from liquid-like to rubber- like thus the reactive system becomes a gel (Gonzalez *et al.,* 2012).

Effect of HPKO concentration on the Melting point of MMU/HPKO

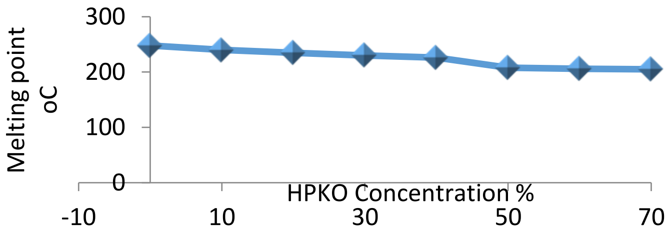


Fig.9 Effect of HPKO concentration on the Melting point of MMU/HPKO

Fig 9 stands for the graph of the effect of HPKO concentration on the melting point of MMU/HPKO. The melting point decrease as the HPKO concentration increases. The decrease in melting point of the compound below the optimum level of vegetable indicates domination of plasticising action of vegetable oil over its coupling effect. This specific interaction led to the formation of a gel-like intermolecular complex structure which gave rise to an increase in molecular mobility; hence a reduction in melting point (Qi et al., 2002). With increase in HPKO at a varied loading of MMU the decrease in melting point is not continuous as is evident from contour plots. It is observed that up to a certain dose of HPKO in the compound, melting point shows an increasing trend, the increase in the melting point of the compound might be a manifestation of increasing cross-link density, thus, confirming the findings by Kukreja *etal.* (2002) that vegetable oil acts as a coupling agent causing increase in cross-link density and it also involves in the physicochemical bonding with the MMU interfaces.

Thermal property, molecular weight, degree of cross linking and the level of rigidity of the polymer is related to its melting point. The melting point of a compound increases with its molar mass, intermolecular Van der Waals interactions and also the intrinsic structures that affect the rigidity. In the case of coating industry, the melting point of a binder is related to its thermal resistance as well as to the brittlity.

Table 1. Effect of HPKO concentration on the solubility in water of MMU/HPKO resin

HPKO concentration (%)	Solubility
0	Soluble
10	Soluble
20	Soluble
30	Soluble
40	Soluble
50	Soluble
60	Insoluble
70	Insoluble

The effect HPKO concentration on the solubility in water of MMU/HPKO copolymer is presented in table1. As seen from the table (0 -50) % HPKO concentration, the composite is soluble in water because the hydrophilic nature of MMU appears to dominate, the copolymer is in a hydrophilic state, with hydrophilic MMU dominating. This allows it to stay in aqueous solution, When HPKO concentration became higher it leads to the formation of globule-like conformation that most often becomes insoluble in pure water (Unar *etal.*, 2010). Also, the effect of interchain repulsions due to increasing HPKO inclusion may allow hydrophobes to take part at least to some extent in intramolecular associations.

Effect of HPKO concentration on the Refractive index of MMU/HPKO

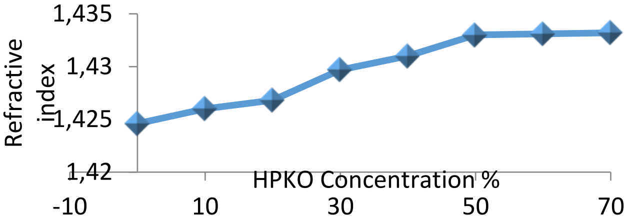


Fig.10 Effect of HPKO concentration on the Refractive index of MMU/HPKO

Fig.10 represents a plot of the effect of HPKO loading on the Refractive index of MMU/HPKO. The refractive index increases with increasing HPKO addition until it got to a point where the continuous inclusion appeared to have no effect on the refractive index. It is apparent from the results that, as the polymer molecular weight increases due to the coupling effect of the HPKO which resulted in increasing crosslinking density, the refractive index increases towards a limiting value characteristic of the infinite molecular weight polymer. By inspection, it is clear that in the low molecular weight region these values show an unmistakeable upward trend with increasing molecular weight. It is seen that the influence of molecular weight on refractive index may entirely be an end group effect because as the proportion of repeat units to end groups increases, so the refractive index increment approaches its limiting value (Khot *etal.*, 2001). The point where inclusion of HPKO appeared to be of no effect in the refractive index may also be attributed to a possible fall in crosslinking density as the HPKO concentration increases.

Gloss is a measure of the ability of coated surface to reflect light. Reflection of light from surfaces can be classified according to the diffuse component or the specular component. The diffuse component results from light penetration to the surface, undergoing multiple reflections and refractions, and then re-emerging again at the surface.

Table 2: Comparison of Some Physical Properties of MMU/HPKO Film with Films from other paint Binders

Physical properties							
Type of Resin	**Visc (mpa.s)**	**RI**	**Density (G/cm^3)**	**MP (%)**	**MU (%)**	**EB (%)**	**Literature**
MMU/HPKO	**38.5**	**1.4331**	**0.96113**	**208**	**0.023**	**72**	**Present work**
MMU/NR composite	**220**	**1.3501**	**0.5708**	**260**	**1.95**	**340**	**Archibong and Osemeahon 2019**
Epoxy-based divinyl Ester	**38.0**	**ND**	**1.04**	**197**	**ND**	**ND**	**Gawdzik and Matynia, 2001**
Styrene Modified Epoxy	**ND**	**ND**	**ND**	**200**	**ND**	**ND**	**Yoon and Mc Grath 2001**
Epoxy Fumerate resin	**45.0**	**ND**	**1.07**	**110**	**ND**	**ND**	**Gawdzik etal., 2001**
Whey protein isolate biopolymer	**ND**	**1.4838**	**ND**	**ND**	**ND**	**ND**	**Trezza and Kroctia, 2001**
Styrene butadiene latex	**ND**	**ND**	**ND**	**ND**	**ND**	**220**	**Azanam and Siew, 2007**
Aromatic amines-modified polyethylene	**ND**	**ND**	**0.96**	**133**	**ND**	**ND**	**Archibong and Osemeahon 2019**
Aqueous-based polyurethane	**ND**	**ND**	**ND**	**ND**	**25**	**713**	**Huang et al., 2012**
Rubber seed oil modified alkyd resins	**3.11**	**ND**	**0.95**	**ND**	**ND**	**ND**	**Alakrach et al., 2018**
Glacidyl methacrylate and piparazin	**ND**	**ND**	**ND**	**ND**	**ND**	**1700**	**Hwang et al., 2012**
Epoxy resins	**ND**	**ND**	**ND**	**101**	**0.04**	**ND**	**Hu et al., 2001**
Innovative UF	**ND**	**ND**	**ND**	**ND**	**0.25**	**ND**	**Zorba et al., 2008**
DMU/PS composite	**35.60**	**1.4295**	**1.1953**	**181**	**0.26**	**144**	**Osemeahon et al., 2015**

ND: Not Determined

CONCLUSION

The modification of monomethylol urea with different contents of hydroxylated palm kernel oil was studied, analyzing their morphology and mechanical properties. Also, the viability of using these modified monomethylol urea resins as a paint binder was evaluated.

All studied monomethylol urea blends presented enhanced mechanical properties comparing with the pure thermosetting resin. At 50% content, the blends presented enhanced viscosity, gel time moisture uptake, elongation at break, refractive index and melting point etc. justifying an an overall improvement on the methylol resin. The enhancement of mechanical properties of modified monomethylol urea resins together with their micro structured morphology caused a dramatic increase of their paint binder's properties. These important enhancements are very significant for future applications taking into account the relative low cost and availability of the hydroxylated palm kernel oil added and the simplicity and speed of manufacturing process of monomethylol urea resin modified with hydroxylated palm kernel oil.

REFERENCES

Abbas Kazaure Adamu, Muhammed Kabir Yakubu, and Olufemi Kassim Sunmonu (2014) International Conference on Biological, Chemical and Environmental Sciences (BCES-2014) Penang (Malaysia Characterization of Emulsion Paints Formulated using Reactive – Dyed Starch as a Pigment)

Afsoon F, Laleh R, Faramarz A (2011). DSC analysis of thermosetting polyimide based on three bismaleimide resin eutectic mixtures. Iranian Polym. J. 20(2):161-171

Alakrach, A.M., Hamzah, R., Noriman, N. Z., Omar S Dahham1, Z Shayfull, S Z Syed Idrus , S Sudin (2018). Recycled Natural Rubber Latex Gloves Filled Chloroprene Rubber: Effects of Compatibilizers J. Phys.: Conf. Ser. 1st International Conference on Green and Sustainable Computing.

Al-Manasir, N. (2009). Preparation and Characterization of crosslinked polymeric nanoparticles for enhanced oil recovery applications. University of Oslo, Norway. Pp.12-85

Archibong C. and Osemeahon S (2019). Development of monomethylol urea for coating application: effect of time on synthesis. *Current trends biomedical engineering & biosciences,* 2019; 18(2):1-6 issn:2572-1151

Archibong, C.S., Osemeahon S.A., Ushie O.A., and Ugwuja, D.I., (2018). Trimethylol urea and polyethylene waste composite as Binder for emulsion paint Formulation. *International Journal of modern Chemistry*, 10(1):1-13

Astarloa-Aierbe, J.M., Echewerria, Vazquez, A. I. Mondragon (2000). Influence of the amount of Catalyst and pH on the Phenolic Resol Resin Formation. *Journal polymer* 41:3311-3315

Azanam, S.H., and Siew, K (2007). Natural rubber and its derivatives, elastomers, Nevin Cankaya, intechopen, DOI: 10.5772/intechopen.69661.

Bharath, N.K., and Swamy, P.R (2009). Adhesive tensile and moisture absorption characteristics of natural fibers' reinforced urea formaldehyde composites. *International Journal of recent trends in Engineering,* 1(5):60-62

Bin, F., Xiang, F., Huai-Xi, W., Wen, D and Yu-Chun, L(2016). The effect of Crystallinity on the compressive Properyies of A-PTFE. Journal of Polymers, 8(10):356-362.

Cakir, M.S., Ivana, S.R., Vladislav, M.J., Radmilaz, R., Olivera, Z.I., and Jao, K.B (2012). Investigation of the curing kinetics of alkyd-melamine-epoxy resinsystem. *Progress in organic coatings,* 73(4):415-424.

Emile, M (2015). Moisture transfer properties of coated gypsum. Eindhoven University Press, Eindhoven, Netherlands. 15(7):2-6

Fahad AlObaidi, Zhibin Ye, Shiping Zhu (2004). Ethylene Polymerization with Homogeneous Nickel-Diimine Catalyst: Effect of catalyst structure and polymerization conditions on catalysts activity and polymer properties. *Jounal of polymer,* 45:6823-6829

Garnier, S., Pizzi, A., Vorster, O.C., Halasz, L. (2002). Rheology of polyflavonoid tannin. Formaldehyde reactions before and after gelling. I: Methods. Journal of Applied polymer Science, 86(4):852-863.

Gawdzik, B and Matynia, T (2001). Synthesis and modification of epoxybased divinyl ester resin. *Journal of Applied Polymer Science*, 81(4):2062-2067

Gonzalez GM, Cabanelas JC, Baselga J (2012). Application of FTIR on epoxy resins-Identification, monitoring the curing process, phase separation and water uptake. Infrared Spectrosc. – *Mater. Sci. Eng. Technol.* 261-283.

Goud, V., Patwardhan, A.V., Dinda, S. and Praddhan, N.C (2007). Epoxidation of karanja (pongamia glabra) oil catalyzed by acidic ion exchangers. *European journal of lipid Science and Technology,* 109:575-584

Hamad, K., Kaseem, M., and Deri, F. (2010) Effect of recycling on rheological and mechanical properties of poly (lactic acid)/ polystyrene polymer blend, Springerlink.

Hu, X., Fan, J., Yue, C.Y (2001). Rheological study of crosslinkingand gelation in bismaleimide/cyanate ester interpenetrating polymer network. *Journal of Applied Polymer Science,* 80(5):2437-2445.

Hwang, Y., Sangmook, L., Youngjae, Y., Kwangho, J., and Lee, W (2012). Reactive extrusion of polypropylene/polystyrene blends with supercritical carbon dioxide. *Journal of Macromolecular Res. 20(6):559-567.*

Jain W (2008). Evaluation of second generation indirect composite resins. A thesis submitted to the faculty of the University Graduate School in partial fulfilment of the requirements for the degree, Master of Science in the Department of Dental Materials, Indian University, Idianapolis. Pp. 1-94.

Jon won Kang and yun-kyoo Han (1997). Polymerization of Tetrahydrofuran with new transition metal catalyst and its mechanism: (p-methylbenzyl)-o-cyanopyridium Hexafluoroantimonate. Bull Koren Chem. Soc.18(4):1-16

Kaniappan K, Latha S (2011). Certain Investigations on the formulation and characterization of polystyrene/poly (methylmethacrylate) blends. *Int. J. Chem. Res.* 3(2):708-717.

Kazys, R., and Rekuviene, R (2011). Viscosity and density measurement methods for polymer melts. *Ultragarsas "Ultrasound"* 66(4):20-25.

Khot, S.N., Lascala, J.J., Erde, C., Williams, I.G (2001). Development and application of triglyride-based polymers and composites. *Journal applied Polymer Science*, 82(2):213-224

Kim, M.G., Kanatzidis, M.G., Facchetti A., Marks T.J (2011). Low-Temperature Fabrication of high Performance Metal Oxide Thin-Film electronics via combustion Processing. *US Nat. Lib. Of Med. Natural inststitute of Health.* 10(5):382-8

kirana, suswato, and sigit T. Nicaksmo (2018). Effect of thermoset plastic addition in physical and mechanical properties of plastics waste composite for construction material application. *AIP conference proceedings*, 34(2):1-20

Lee J., Jeon. H., Kim S. (2011). Green adhesives using tannin and Cashew nut shell liquid for environmental-friendly furniture materials. J. Korean Furniture society. 22(3):219-229

Liem, H., Etchegoin, P., Whitehead, K.S., and Bradley, D.DC (2002). Raman Scattering as a probe of morphology in conjugated polymer thin films. Journal of Applied Physics. 92(2):1154-1161.

Luis Alexandro, Francisco J.E., Horlesian M.T., Florentino S.C., Hector R.C., Claude S.T., Francisco H.G., Jose L.C., Ramon E.D. (2016). The Influence of co-catalyst in the polymerization of 1,3-butadiene catalyzed by Neodynium chloride Tripentanoate. J.*Mex. Chem. Soc.* 60(3):56-62

Madufor, I., Eze, O., Marthin, U. (2013). The effect of bamboo powder on some mechanical properties recycled low density polyethylene (RLDP) composite. Journal of Natural and Applied Sciences, 4(1):409-419

Mavani. I.S., Mehta, M.N., Parsania, H.P (2007). Synthesis and physico-chemical study of polyester resin of 1,1-bis (3-methyl-4- hydroxyl phenyl) cyclohexane and rininoleic acid and its polyurethanes with polyethylene glycol. *Journal of Science and and industrial research,* 66(6):377-384

Menkiti M.C., Onukwuli O.D (2011). Utilization potentials of rubber seed oil for the production of alkyd resin using variable base oil lengths. New York Sci. J. 4(2):51-59.

Ming Cao, Taohong Li, Jiankun Liang and Guanben D.U. (2017). The influence of pH on Melanine-Dimthylurea-Formaldehyde Co-condensations: A Quantitative 13C-NMR Study. MDPI J. of Polymer 10(9): 1-12

Ming Liu, Rooban Venkatesh K.G. Thirumalai Yiqiang Wu and Hui Wan (2017). Characterization of the Crystalline Region of Cured Urea Formaldehyde Resin. R.S.C. 7:49536-49541

Nooijen, G.A., Amsterdam B.V., (2001). Ziegler/Natta catalysts in particle form ethylene polymeriza- tion: The effect of polymerization start-up on catalyst activity and morphology of the produced polymer. Elsevier Science Publishers (11):35-46

Park, B.D., Jeong, H.W and Lee, S,m (2010). Morphology and chemical elements detection of cured urea formaldehyde resins. Journal of applied science, 120(3): 1475-1482.

Patrick, T.W., Rita, K.W., Thomas A.C., Thomas A.G.,and Basil G. (2009). Infrared spectroscopy of exfoliated human cervical cells: evidence of extensive structural change duringcarcinogenesis. *Progress of national Academics of science*, 88(7):10988-10992

Patrovic Z.S., Zlatanic A., Lava C.C., and Sinasinovic-fise S. (2003). Epoxidation of soyabean oil in toluene with peroxoacetic acid and peroxoformi acids-kinetics and side reactions. *European journal of Lipid Science and Technology*, 104(5): 293-299

Qi, G.R., Wang Y.H., Li, X.X., Peng, H.Y., and Yang S. L (2002). Viscometric study of on the specific interaction between proton-donating polymersand proton-accepting polymers. *Journal of Applied Sciences,* 85:415-421

Sahad, N., Som, A., Baharuddin, A., Mokhtar, M., Buzu Z.,and Sulaiman, a (2015). Physicochemical characterization of Oil palm Decanter Cake (OPDC) for Residual Oil Recovery. Bioresources, 9(8):6361-6372.

Salthammer T, Mentese S, Marutzky R (2010). Formaldehyde in the indoor environment. *Chem. Rev.* 110(4):2536-2572.

Sancheza, E.M., Zavagliaa, C.A., Felisbertib, M.I (2000). Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties. Journal of Polymer 41:765-769.

Shashidhara, Y and Jayaram, S. (2010). Vegetable oils as a potential cutting fluid-an evolution. T*ribology international,* 43(5):1073-1081.

Stefena Acierno, Peter Van Puyvelde (2005). Effect of short chain branching upon crystallization of model polyamides-11. *Journal of Polymer*, 46:10331-10338.

Trezza, T ant Krochta, J. (2001). Specular reflection, gloss, roughness and surface heterogeneity of biopolymer coatings. *Journal of Applied Polymer Science*, 79(6):2221-2229

Unar, I.N., Soomro, S.A., Aziz, S (2010). Effects of various additives on the physical properties of polyvinyl chloride Resins. *Journal of Analytical and Environmental Chemistry*, 11(2):44-50

Yelwa, J.M., Osemeahon, S.A., Nkafamiya, I.I. and Abdullahi, S. (2017). Synthesis and Characterization of Hydroxylated Sunflower Seed Oil/Poly Vinyl Acetate Copolymer as a Binder for Possible Application in the Coating Industry, 4(7): *International Journal of Science,* 4(7):39-43

Zorba, T., Papadopoulou E., Hatjiissaak A., Paraskevopoulos K.M and Chrissafis K (2008). Urea-formaldehyde resins characterized by thermal analysis and FTIR method. *Journal thermal Analysis and Calorimetry* 92:29-33.