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Coating Properties of Alkyd Resin, Epoxy Resins and Polyurethane Based Nanocomposites: A Review

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ABSTRACT

The uniqueness of alkyd resin, epoxy resin, and polyurethane nanocomposites has brought prominent recognition to the field of heavy-duty coating materials. This is expected due to the collaborative features of nano-sized materials such as the high surface area to volume ratio, great functionality per-unit space, extremely small sizes with high density, and that of alkyd resin, epoxy resin, and polyurethane (biodegradability, great gloss retention, adaptability, flexibility, durability, good drying properties, and weathering resistance). The objective of this review was to analyze the extent and currency of research and the development of alkyd, epoxy, and polyurethane nanocomposites in coating applications. Some of the several types of modifications discussed in this review are the incorporation of varying types of nanoclay and metal nanoparticles materials into alkyd resins, the incorporation of carbon nanotubes, MGel-graphene oxide (GO)/gelatin (MGel), Ni (II) Complex-Zeolite and starch-modified nano-ZnO into epoxy resin and the incorporation of ($Rb_2Co(H_2P_2O_7)_2.2H_2O$), modified nanoparticles of ZnO, diminished graphene oxide (dGO) into polyurethane and their effects on coating applications. The various studied modifications resulted in nanocomposite end-products with much improved properties. However, there are several challenges to the development of nanocomposites that need urgent attention. Some of the challenges discussed are the difficulty involved in transforming fabricated nanocomposites from laboratory to commercialized scale, the capital-intensive nature of synthesizing large nanopowder, etc.

Keywords: Nanoparticles, Coating applications, Modification, Nanocomposites.

1. INTRODUCTION

The applications of polymers to the vast benefit of industries in applications such as construction, aerospace, electrical, electronics, food packaging, coating and automotive could be expanded by the fabrication and advancement of novel types of polymer-based nanocomposites (NC) (Ifijen et al., 2022a; Ifijen et al., 2022b; Ifijen et al., 2018; Ifijen et al., 2019a). The modification of polymer resins with nanomaterials has been shown to improve polymers physical properties, as well as the

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implementation of new features in the polymer matrix (Essien et al., 2016; Hongwei et al., 2007; Haque et al., 2021). The addition of nanomaterials to polymeric material has been used to improve the chemical, drying, physical, magnetic, optical, electronic, and biological properties of polymeric resins (Essien et al., 2016; Ifijen et al., 2020a).

Among the polymer resins utilized in coating application, alkyd resin, epoxy resin and polyurethane are considered among the most abundant bioresources due to their environmental friendliness, low cost, renewability, possible biodegradability, availability, anticorrosive characteristics, quick drying time, and excellent substrate adhesion (Ifijen et al., 2022c; Ifijen et al., 2022d). In addition, they also have outstanding gloss retention, excellent barrier, and thermal properties, good colour retention, good flexibility and strength, ease of application, durability in exterior finishes, moderate resistance to corrosive fumes, good weathering resistance, attractive price and the possibility of synthesing them from renewable resources (Gogoi et al., 2015; Maliki and Ifijen, 2020; Maliki et al., 2020; Santamaria-Echart et al., 2015). Alkyd resin can be synthesized by the polycondensation of polyacids or their anhydride derivatives, plant-based or synthetic oils or polyols and fatty acids. Non-toxic, low cost and eco-friendly vegetable oils such as soybean oil, castor oil, sunflower oil, palm oil, linseeds oil, etc. are usually employed in the synthesis of alkyd resins, for generating biodegradable and renewable coatings that are not dependent on fossil fuels (Alam et al., 2014; Nalawade et al., 2014).

The thermal stability of alkyd resins has been estimated to be about 105 °C (Akintayo and Adebowale, 2004). The properties of the conventional alkyd coatings are acquired principally from the characteristics of drying oils (Nkwor et al., 2020; Nkwor et al., 2021) that were utilised in synthesising the resins (Tiwari et al., 2002; Radoman et al., 2015). The curing of alkyd resins through the auto-oxidation process is made possible due to the presence of unsaturation sites in the oil (Van et al., 2004). They have poor resistance to chemical splash and spillage, particularly in an alkaline medium which can lead to the degradation of the coatings, whenever they come in contact with alkaline (Otabor et al., 2019). Alkyd resins applications are not only limited to decorative paints, but are also applied in air-drying paints, machine tool finishes, inks, matt and semi-matt varnishes of wood furniture, protection of surface from chemical attack, mechanical stress and environmental effect, etc (Saralegi et al., 2013; Otabor et al., 2019; Ifijen and Nkwor, 2020; Ifijen et al., 2020b; Ifijen et al., 2020c).

Epoxy resins are the thermosetting matrix or resin materials, having at least one or more epoxide groups in the molecule (Sun and Yao, 2011). The epoxide, also termed as oxirane or ethoxyline group, is regarded as representative unit of epoxy polymer (Sun and Yao, 2011). Epoxy resin can be applied as binder in cements and mortars, adhesives for general purposes, for non-skid coatings, making rigid foams, industrial paintings and coatings, solidifying sandy surfaces in oil drilling, fiber-reinforced plastics and potting and encapsulating media (Sun and Yao, 2011).

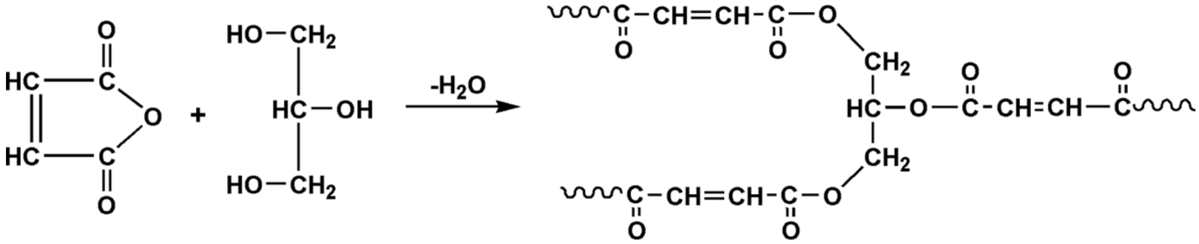
Polyurethanes (PUs) are segmented polymers made up of a soft segment (SS) and a hard segment (HS). The SS, generated by a polyol, inflicts flexibility to the polymer, whereas, the HS, formed by a chain extender and an isocyanate, provides the material with rigidity and strength (Santamaria-Echart et al., 2015). Polyurethane can be utilised in diverse applications such as the generation of foam, seals and gaskets, insulation, suspension components, wheels and tires, surface coatings, adhesives, and biomedical devices (Jing et al., 2015). Nonetheless, like other elastomers, alkyd resin, epoxy resin and polyurethanes (PUs) struggle to attain combinations of features such as high strength, high durability and high elasticity concurrently. As a result, the incorporation of nanomaterials into the aforementioned polymers has emerged as a potential reinforcement approach to alleviate these restrictions, resulting in the enhancement of anticorrosive, chemical resistance, drying, electrical, mechanical, thermal properties and so on (Saralegi et al., 2013). The properties of the aforementioned polymers can be deliberately tuned to possess specific desired properties by incorporating nanosised or other materials during or after their synthesis to achieve specific application. The speedy growth of nanotechnology has led to the notable enhancement of the properties of polymeric materials with a concurrent drop in the cost of the final product. It has been established that nanomaterials maintain chemical and physical characteristics that are precisely different from their bulk counterparts (Kamat, 2002).

Several researchers have investigated the impact of several nano-scale fillers incorporated in alkyd resins, epoxy resin and polyurethane on the properties of their respective nanocomposites. The objective of this review was to analyse the extent and currency of research and development of alkyd, epoxy and polyurethane nanocomposites in coating applications.

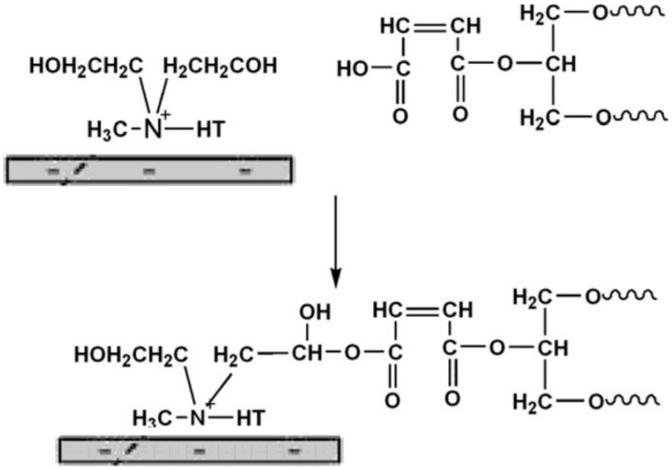
2. ALKYD RESIN CLAY NANOCOMPOSITES COATINGS

Nanoclay materials are optimised nanoparticles of layered mineral silicates, with diverse modification characteristics (Majid et al., 2020). Owing to their high aspect ratio, possibly exfoliation qualities and more reliable mechanical properties, they have become one of the most sought-after reinforcing fillers for composites among other nanoparticles (Rajitha et al., 2020). Nanoclay is made up of about 1 nm thick alumina surface of silicate layer, stacked with around 10 nm in diameter multilayer stacks. Hence, it has a specific surface area of approximately $657 m^2 g^{-1}$ and an exceptional aspect ratio (Majid et al., 2020). The fact that nanoclay filler dramatically facilitates the strengthening and alteration of the mechanical characteristics of fibre reinforced polymer, when nanoclay was completely dispersed in epoxy resin composites has fascinated several researchers (Majid et al., 2020).

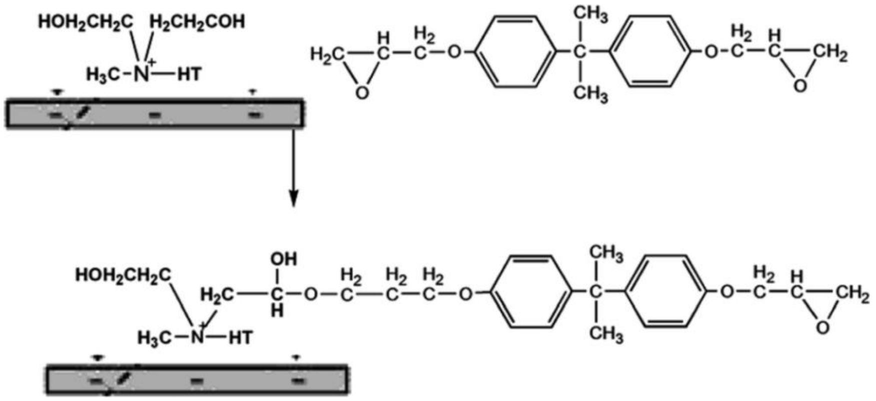
Lin et al. (2008) synthesized biodegradable glycerol-derived alkyd resins from glycerol and maleic anhydride via the polycondensation reactions (Scheme 1). Thereafter, they successfully generated alkyd resin clay nanocomposites by melt blending organo-clays with maleic anhydride-glycerol precursors (Scheme 2). Before usage, the clays were treated with methyl tallow bis-2-hydroxyl ethyl ammonium chloride salt (yielding a nanocomposite designated clay30B), and some samples of the clay30B were further treated with the diglycidyl ether of bisphenol A (DGEBA) (clay30BT) (Scheme 3). For comparison, resin mica and resin talc nanocomposites were fabricated similarly. XRD and SEM analysis revealed that the further treatment of clay30B with the DGEBA led to further delamination of the organoclays, which were mainly exfoliated and well dispersed in both series of alkyd resin nanocomposites leading to a reasonable advancement in thermostabilities (Lin et al., 2008). Lin et al. (2008) were able to establish the comparable nature of the mechanical properties, including tensile modulus, toughness and Young’s modulus to those of the corresponding neat alkyd resin thermoset even at very low loadings. Some issues like the formation of aggregates in the case of talc or mica in the polymer matrix were recorded, even though there were improvements in the mechanical properties of the synthesized glycerol-anhydride alkyd resins.



Scheme 1. Schematic for the preparation of a glycerol-derived alkyd resin made from maleic anhydride and glycerol (Lin et al., 2008).



Scheme 2. Schematic of the reaction of alkyd resin precursor with the 30B clay (Lin et al., 2008).

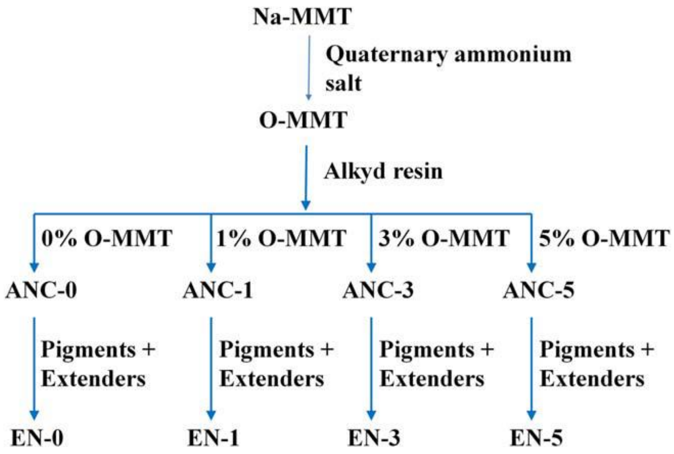


Scheme 3. Schematic of the reaction of DGBEA with the clay30B (Lin et al., 2008).

A few years later, Bal et al. (2010) modified alkyd resins with organoclay. The formulated alkyds were prepared with coconut oil fatty acid (COFA), (PA), glycerine (G), phthalic anhydride, organoclay and dipropylene glycol (DPG). The organoclay (nano clay) used in this study was modified with 15–35wt.% octadecylamine and 0.5–5 wt.% aminopropyltriethoxysilane. However, the chemicals employed in this modification were quite different from pre-treatment chemicals used by Lin et al. (2008). They also went further to subject the modified alkyd resins to a curing process at 140 ^{o}C for 2 hr, using different ratios of melamine-formaldehyde and urea-formaldehyde resins.

Experimental analysis recorded an improvement in the physicochemical characteristics of the cured modified alkyd (Bal et al., 2010)). Properties such as hardness, the drying degree, abrasion resistance, adhesion strength, acid, water, solvent resistance, alkaline and resistance to environmental conditions drastically improved. This study was able to establish that the blending of the urea-formaldehyde resin and organoclay can be depended upon to improve the physical and chemical resistance of the alkyd–amino resins. Tahmaz et al. (2015) studied the effect of blending long oil alkyd resins with different ratios of organoclay towards the formation of the nanocomposite. Investigation of the physical, chemical, and thermal properties of the nanocomposite alkyd resin films shows the following: SEM analysis showed that the organoclay particles have homogeneously dispersed into the resin which was used as the polymer matrix. The hardness values of the synthesized alkyd resin films experience a decrease as the amount of organoclay loading increased. There was an increase in abrasion resistance of the alkyd resin films as the amount of organoclay increased. The incorporation of organoclay to the alkyd resin structure significantly improved the chemical resistance properties of the resins. However, its resistance to alkaline and saltwater was poor. This result differs from the observation of Bal et al. (2010) as the alkaline resistance of the alkyd resins modified with organoclay obtained from their investigation was reported to be very good. The TGA result showed that an increase in the organoclay loading in the alkyd resin structure led to an increase in the thermal stability of the modified alkyd. This result agrees with the studies of Bal et al. (2010); and Tahmaz et al. (2015). However, Tahmaz et al. (2015) establish an optimum organoclay loading capacity of 1%; beyond which the thermal stability of the nanocomposite alkyd resin films would start to decrease. This study, therefore, concluded that long oil alkyd resins containing organoclay are suitable for production surface-coating materials.

Dhirde et al. (2017) investigated the performance of exfoliated organo-modified montmorillonite (O-MMT) clays in improving the mechanical properties and barrier of alkyd resins. The alkyd-clay nanocomposites (NCs) were synthesised using 1, 3 and 5% (on polymer solid) clay loadings of O-MMT with aid of high shear and ultrasonication. The generated alkyd polymer clay nanocomposite was utilised in the formulation of paint (Scheme 4) for the evaluation of their performance in the actual coating formulation. The extent of dispersion of nanoclays in the alkyd matrix was investigated by XRD. Nanoclay layers were exfoliated in alkyd-clay nanocomposites (NCs), up to 3% loading of O-MMT. Mainly intercalated structure was observed at higher loading due to agglomeration of clay platelets. They observed a large number of uniformly dispersed individual clay platelets in exfoliated NCs, which led to improved mechanical and thermal properties. Nanocomposites with 3% clay loading showed the most significant thermal stability, corrosion resistance capability and mechanical property.



Scheme 4. Flow chart of process sequence followed for preparation of nanoclay composites and enamel paints (Dhirde et al. 2017).

3. ALKYD RESIN METAL NANOCOMPOSITES COATINGS

The most promising strategy for ensuring carbon steel pipelines protection is to inhibit corrosion before it happens, and organic based-coatings have long been employed for that purpose (Vakili et al., 2015). Organic coatings have been used in the protection of carbon steel pipelines and other materials against corrosion or degradation by initiating a physical obstacle that stops water, oxygen and corrosive ions from getting to the pipelines surface (Wang et al., 2017).

The two primary disadvantages of organic coatings are weak adhesion and coating permeability (Deyab, 2015). The all-around performance of the coatings is heightened by the adhesion of the organic coating and decreased resin pore channels. This supplementary shielding is commonly accomplished by integrating nanostructured sized pigments, which leads to diminished enhanced coating adhesion and coating permeability (Zhang et al., 2016).

In modern times, many efforts have been invented to improve the corrosion protection efficiency of organic or polymer coating by assembling novel nano-composite formulas (Deyab et al., 2017a). These measures include the addition of organic and inorganic particles. The performance of epoxy/metallophthalocyanine nanocomposite coating was improved by the application of metal phthalocyanine pigments (Deyab et al., 2017b). Deyaba et al. (2018) generated unique nanocomposite coatings using synthetic lanthanide bis-phthalocyanine complexes, Pc = C32H16N8 denotes the phthalocyanine ligand), $LnPc_2$ (Ln = lanthanide metal to inflict corrosion protection to the underlying carbon steel pipelines. Electrochemical investigations (Potentiodynamic polarization and EIS) demonstrated that the integration of LnPc2 compound ($SmPc_2$, $PrPc_2$ and $HoPc_2$) additives with alkyd coating leads to a considerable boost in the corrosion resistance of carbon steel in 0.5 M HCl solution. In comparison to the neat alkyd coating, the alkyd@LnPc2 nanocomposite coatings absorb lower water volumes. The presence of LnPc2 compounds in the nanocomposites instigated the enhancement of pull-off adhesion of coatings performance from 3.34 MPa to 19.94 MPa. The efficacy of alkyd@$HoPc_2$ coating seems more heightened than that of alkyd@$SmPc_2$ and alkyd@$PrPc_2$ coatings. The shielding features of alkyd@$LnPc_2$ coatings were proven by TGA, SEM, impact resistance, scratch hardness, contact angle analysis and bend test.

Alkyd resin nanocomposite coatings loaded with varying content of titanium oxide (TiO_2) and silicon oxide (SiO_2) nanoparticles (4 and 2 wt/wt%) were generated via the solvent casting technique (Grozdanov et al., 2019). Differential scanning Electron Microscope (SEM) and Scanning Calorimetry (DSC) were employed in the characterization of the synthesized nanocomposite coatings. The nanocomposite coatings were investigated for their mechanical features, chemical stability, abrasion, and impact resistance. DSC examination showed that increase in the nanoparticle content leads to a corresponding shift in the characteristic temperatures (glass transition temperature-Tg, reaction temperature-Tr) towards a lower value. Mechanical analysis exhibited satisfactory elasticity with an impact resistance of 1 kg/cm2 and bending of f=2cm. The wear resistance changed reasonably as the nanoparticle content increased. This study was able to establish a more satisfactory abrasion resistance for nanocomposite coatings with SiO_2 nanoparticles when correlated to nanocomposites containing the same quantity of TiO_2. They fabricated remarkable soy alkyd-based nanocomposites (NCs) using TiO_2 NPs surface adjusted with various gallates and imine acquired from oleylamine (DHBAOA) and 3,4-dihydroxybenzaldehyde. This study is different from the work of Grozdanov et al. (2019) because of the addition of imine to the nanocomposite. The surface-modified and Unmodified anatase TiO_2 NPs were examined using X-ray diffraction (XRD), electron microscopy (TEM), ultraviolet-visible (UV-Vis) spectroscopy and Fourier transform infrared spectroscopy (FTIR), while the adsorbed ligand amounts were estimated from the thermogravimetric analysis (TGA) outcomes. Surface modification of the TiO_2 NPs was confirmed by FTIR and UV-Vis spectra. The impact of the TiO_2 surface modification on the TiO_2 NPs dispersion in the alkyd resin, barrier, thermal, chemical resistance, and mechanical features of alkyd resin/ TiO_2 nanocomposite coatings were also investigated. The glass transition temperature of all the examined composites was seen to be lower than the unadulterated resin. The introduction of TiO_2 NPs to the surface altered with gallates had no meaningful impact on the thermo-oxidative stability of the alkyd resin, while TiO_2-DHBAOA NPs barely enhanced the thermo-oxidative stability of the alkyd resin. Likewise, the TiO_2 NPs modified surface enhanced the barrier features, improved strain and stress at break, chemical resistance, hardness, abrasion resistance and decreased modulus of elasticity of alkyd resin.

Another research concentrated on particles of nano cerium oxide as substitute additives in solvent-based alkyd coatings to enhance anti-anti-ageing and corrosive characteristics (Kızılkonca and Erim, 2019). The authors developed the paint samples with micro and nanoparticles of cerium oxide and thereafter, compared the coating quality properties with coating formulated with commercial UV-aging and anticorrosive agents. The nanocomposite formations were fabricated using 3 wt. % cerium oxide microparticles (CER1), 3 wt. % commercial anticorrosive agent as reference material (RP) and 3 wt. % 1% cerium oxide NPs (CER3 and CER2). The preparations of coatings were achieved using the basket milling approach with zirconium balls and ten characterized using thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), and contact angle measurements. Enhancement in the anticorrosive features was confirmed using accelerated salt spray tests based on ISO 4628 degradation of coatings evaluation and electrochemical impedance spectroscopy (EIS). In addition, mechanical and physical investigations were run in accordance with the standard test strategies for coatings. The outcome of the study revealed that cerium oxide nanoparticles inflict UV defensive, anticorrosive, hand self-cleaning effects and outstanding physical resistance to the generated alkyd coatings. The positive influence of cerium oxide nanoparticles was seen to be more pronounced than those of their microparticles counterparts.

4. COATINGS BASED ON EPOXY RESIN NANOCOMPOSITE

Anti-corrosion coatings have been generated successfully from the epoxy resin in several industries (Deyab et al., 2018; Sumi et al., 2020). In current studies, it was obvious that the exceptional anti-corrosion performance of the epoxy resin was influenced by the functionalisation of carbon nanotubes (CNTs). This assertion was also presented by Deyab and Awadallah (2020). It was demonstrated that the epoxy/f-MWCNTs nanocomposites can preserve steel tanks from corrosion. The reduction in the agglomeration of CNTs inside the epoxy resin is due to the introduction of functional groups on CNTs surfaces and consequently, this enhances the mechanical and anti-corrosion characteristics of the nanocomposites coating.

The covalent link that is generated between the functional groups of the polymeric matrix and the CNT surface, is the principle that explains the precise description of the mechanism of stabilisation of CNTs dispersion inside the polymeric matrix by utilising functional groups. Khodaei et al. (2019) formulated epoxy coatings, with several portions of Ni (II) Complex-Zeolite and discovered that the novel epoxy coating has a reliable anti-corrosion protection impact. Two types of mechanisms were proposed for this behaviour. The first is the dependency on the capacity of the new composite to enhance the cured epoxy coating and to decrease the porosity of the epoxy coating. The second approach is the dependency on the strong attachment between the metal surface and the coating layer.

Diverse studies have described the modification of graphene oxide with epoxy resin for applications on anticorrosion. Rajitha et al. (2020) reported the anti-corrosion action of epoxy nanocomposites, comprising modified MGel-graphene oxide (GO) and gelatin (MGel), against steel. They showed that the excellent distribution of GO into epoxy resin matrix develops the cross-linking and strength of epoxy resin, leading to a development in the protection efficiency of newly generated nanocomposites by 59%, compared to the unmodified coating. The thermal stability of MGel-GO/epoxy composite was observed to be higher than GO without modification. It was attributed to the conversion of unstable OH groups of GO into a stable structure by interacting with MGel. The exceptional physical and chemical characteristics of nano-ZnO have made its utilisation as a second phase in the composites coating more attractive for numerous researchers (Ng et al., 2017).

The isothermal cure kinetics of epoxy/ZnO nanocomposite was reported by Karasinski et al. (2013). They suggested that the addition of ZnO nanoparticles hindered the curing activation energy, and this develops of resin cross-linking degree. This implies that the ZnO nanoparticles penetrate the epoxy resin polymer network, inducing the cross-linking of the polymer and expedition in the solidification of an epoxy resin. Likewise, Sari et al. (2018) reported a unique nanocomposite based on starch-modified nano-ZnO (ZnO-St) and epoxy. An extremely cross-linkable transparent coating was obtained by this group, by the addition of ZnO-St nanoparticles to the resin composites.

Lately, the need to develop the performance of epoxy resin with phosphate compounds to shield the metal structures from corrosion is very pressing. As a result, Deyab et al. (2021) developed epoxy nanocomposite coatings (P-M/epoxy composites). The metal vanadium oxyphosphate M0.5VOPO4 (where M=Mg, Ni, and Zn) determines the P-M/epoxy composites. Mechanical and electrochemical examinations were used to investigate the function of P-M/epoxy composites as anticorrosion coatings. Electrochemical impedance spectroscopy (EIS) showed higher polarization and pore resistance of the P-M/epoxy composites when compared to the neat epoxy. The highest impact on the cathodic dis-bonded area and water absorption was induced by the presence of P-M/epoxy composites. Besides, P-M/epoxy composites exhibited a heightened mechanical feature. Additionally, the greatest effect on the anti-corrosion properties of epoxy coating was observed to be in the order: $Mg_{0.5}VOPO_4$ $Zn_{0.5}VOPO_4$ $Ni_{0.5}VOPO_4$. The net outcome from this investigation is promising for prospect works on the anti-corrosion coating.

5. COATINGS BASED ON POLYURETHANE NANOCOMPOSITE

Polyurethane coatings have several excellent characteristics, such as not being flammable, high wear resistance, high abrasion resistance and waterproof. The protection of metal from corrosion using nanocomposite coatings based on polyurethane has been attempted by several researchers (Huang et al., 2017). Usually, polyurethane polymer-supported with nanoparticles, manifest outstanding characteristics like barrier properties, high resistance to impact and anti-corrosion properties (Li et al., 2014).

The inclusion of nanoparticles in the polyurethane matrix, revealed the current tendencies for generating anti-corrosion nanocomposite coatings. For example, Deyab et al. (2017c) generated waterborne polyurethane (WBPU) coatings by incorporating nanoparticles ($Rb_2Co(H_2P_2O_7)_2 . 2H_2O$) into its matrix. Analytical investigations revealed that the incorporation of pyrophosphate nanoparticles leads to the enhancement in the pull-off adhesion features and the reduction of the permeability of O_2 gas of WBPU. They ascribed the behaviour to the presence of pyrophosphate nanoparticles that can create a tortuous track inside WBPU and this inhibited the movement of the corrosive ions *via* the polymer matrix. In a similar manner, an innovative nanocomposite based on modified nanoparticles of ZnO and waterborne polyurethane (WBPU) was described by Christopher et al. (2016). The fabricated nanocomposite is employed in protecting steel from corroding. They concluded that the increment in the content of modified ZnO in WBPU enhances the anti-corrosion capability of WBPU.

To fabricate anti-corrosion coating, Li et al. (2014) introduced a functionalised diminished graphene oxide (dGO) into WBPU. In this instance, when the dGO was 0.2 wt.%, the 3-dimensional random distribution of dGO was observed in the WBPU nanocomposite coatings, which generates a long zig-zag path for the motion of corrosive solution inside the coating matrix. This promotes the anti-corrosion characteristics of WBPU nanocomposite.

The regular use of polyurethane (PU) coatings with exceptional wear and corrosion resistance in metal corrosion protection, furniture coating, electronic device protection and other fields have been reported by several studies (Das and Mahanwar, 2020). The regular use of polyurethane (PU) coatings with exceptional wear and corrosion resistance in metal corrosion protection, furniture coating, electronic device protection and other fields have been reported by several studies (Okieimen and Bakare, 2007; Obazee et al., 2020). Nevertheless, PU coatings are normally restricted to the fabrication of breathable and waterproof material, owing to the drawbacks caused by low thermal stability and hydrophobicity (Liang et al., 2020). Hong et al. (2012) solved this issue by generating polyurethane enhanced with silica carbide (SiC) NPs and perfluorooctyltriethoxysilane (PFOTS) via a spraying approach (Figure 1) (Hong et al., 2012). They observed a considerable enhancement in the dispersion of SiC after the chemical grafting amendment of PFOTS in PU. The incorporation of hard SiC nanoparticles into the PU coating delivered a remarkable micro-nano structure on its surface, changing the coating wettability from hydrophilic to superhydrophobic. The most promising superhydrophobic features which rely on the even dispersion of SiC with increased thermal conductivity and hardness in the PU coating were observed by the 125 wt% F-SiC/PU composite coating. The anti-stripping capacity, wear resistance, salt spray resistance, thermal stability and acid/base resistance improved considerably. The 125 wt% F-SiC/PU composite coating can offer superhydrophobic characteristics on varying substrates, such as ceramic, aluminium alloy, filter paper and plastic sheet. It was also shown to have anti-fouling features. The authors concluded that a novel approach for the fabrication of anti-fouling and wear-resistant PU superhydrophobic coatings can be achieved by employing this simple technique.

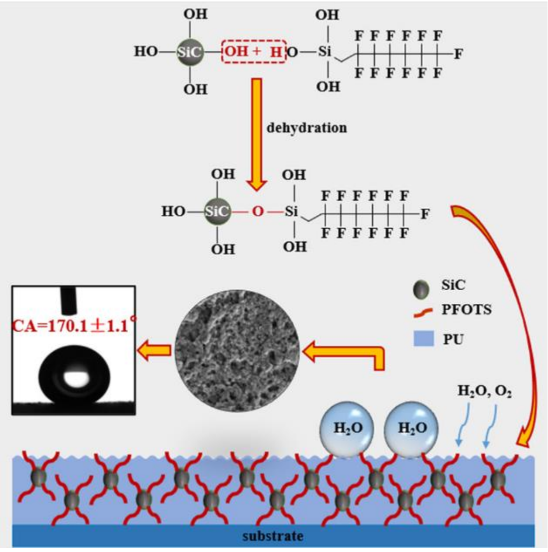


Figure 1. SiC-enhanced PU composite coatings modified by perfluorooctyltriethoxysilane (PFOTS) (Hong et al., 2012).

The incorporation of coating material into fertilizer has gained increased prominence in agriculture because it reduces air and groundwater contamination, and increases nutrient utilization efficiency (Liang et al., 2019). An assertive reliance on the utilized coating material has been indicated by its nutrient release pattern (Bortoletto-Santosa et al., 2020). Polyurethane (PU) produced by the reaction of isocyanate and polyol is a type of block copolymer that comprises of a hard chain segment and chain segment. The microstructure of PU can be altered with an improvement in distinct features by adjusting the proportion and composition of the two existing phases, consequently, presently, manufacturers of non-solvent in-situ reaction coated fertilizers and researchers have preferred the use of polyurethane coatings (Sun et al., 2019; Zhang et al., 2019; Wang et al., 2020). The preparation of bio-based PU coatings from natural sources such as lignin, ostarch, vegetable oil and cellulose are considered to be sustainable, green, and low-cost (Li et al., 2021). Therefore, they have displayed tremendous prospect as an alternative to traditional synthetic polymer coatings. The generation of castor oil-based polyurethane-coated fertilizer was successfully achieved by Bortoletto-Santos et al. (2020). The authors observed that the prepared fertilizer had a 40 days remarkable nitrogen discharge duration with a coating rate of about 4 wt%. Several studies developed a sequence of coated fertilizers by curing liquefaction products of wheat straw, starch and wastepaper on the surface of the fertilizer, resulting in coatings that had satisfactory biodegradability in soil. The investigations of the impact of coating microstructure on the performance of fertilizer, specifically for the ultrathin coating have been investigated by several scientists (Tian et al., 2019; Lu et al., 2016; Zhang et al., 2018). They optimize the microstructure via blending and fabrication of nanocomposite (Wang et al., 2019). Bio-based polyurethane coating material was modified by employing polyester or epoxy resin to form an interpenetrating network structure, which improved the sluggish-discharge characteristics of coated fertilizers (Ma et al., 2018; Ahghari et al., 2020). In-situ polymerization was used by Zhao et al. (2017) to create a variety of modified bentonite (MBT)/polyurethane (PU) composites from MBT, isocyanate, and soybean oil-based polyols to coat urea granules and delay the release of nitrogen (N). By intercalating polyethylene glycol inside the interlayer gap of bentonite (BT), the layer spacing of BT was increased, and the performance of composites was enhanced. The structure, thermal stability, mechanical strength, surface wettability, and urea slow-release performance of the MBT and MBT/PU composites were all evaluated. Tensile strength is 13.53

MPa with 5.0 wt percent MBT added, which is an increase of 27.52 percent and 67.97 percent, respectively, over pure PU. Breaking elongation is 20.66 percent. The PU-5 percent -MBT composites coated urea had a 74-day release period. According to the finding's, modified films are suitable for use with slow-release fertilizers. They observed a nutrient discharge period of coated urea of 74 day with 5 wt% addition content of polyethylene glycol-intercalated bentonite.

For so many years, a nutrient release period of more than 30 days has never been achieved for a fertilizer coating rate lower than 2.5 wt%. An uncomplicated and efficient technique for designing microstructures and tuning release properties of fertilizers with ultrathin bio-based polyurethane coatings was very challenging. However, nanomaterial offer a choice for the microstructure optimization of coatings. For instance, the development of polyhedral oligomeric silsesquioxanes (POSS), a cage-like molecule retaining RSiO3/2 units, is an eco-friendly nanostructured material that combines the benefit of both inorganic and organic components, and novel features induced by its synergistic outcome (Behera et al., 2018; Ghermezcheshme et al., 2015). POSS containing eight PEG groups connected to a cage (POSS-PEG) was exploited in modifying MDI-PTMG-based polyurethane. The POSS-PEG distributed satisfactorily on the molecular level and functioned as a diluent to plasticize the molecular dynamics (Ghermezcheshme et al., 2015). In another study, an eco-friendly polyurethane nanocomposite with POSS as a chain extender was generated by Huang et al. (2016). Its surface hydrophobicity was remarkably enhanced in correlation with the PU that is free from POSS. The controllability of polyurethane coating degradation for the controlled release of drugs has also been reported to be improved by the integration of POSS (Ayandele et al., 2012). The impact of POSS on the discharge behaviour of fertilizer from polymer-coated fertilizer was investigated by a previous study. It is necessary to especially achieve an in-depth investigation of the solvent-free in-situ polymerization of bio-based PU coating on the surface of the fertilizer owing to the effect of the combination model of polymer matrix with nanoparticles and the topology of nanocomposite caused by the raw material type and production approach (Kamkar et al., 2020). Li et al. (2021) formulated and incorporate two similar polyhedral oligomeric silsesquioxanes (POSS), with eight octaphenyl and poly (ethylene glycol) (PEG) groups connected to the cage, respectively, into thin castor oil-based polyurethane coatings through in-situ polymerization on the surface of the urea (Figs 2 and 3) (Li et al., 2021).

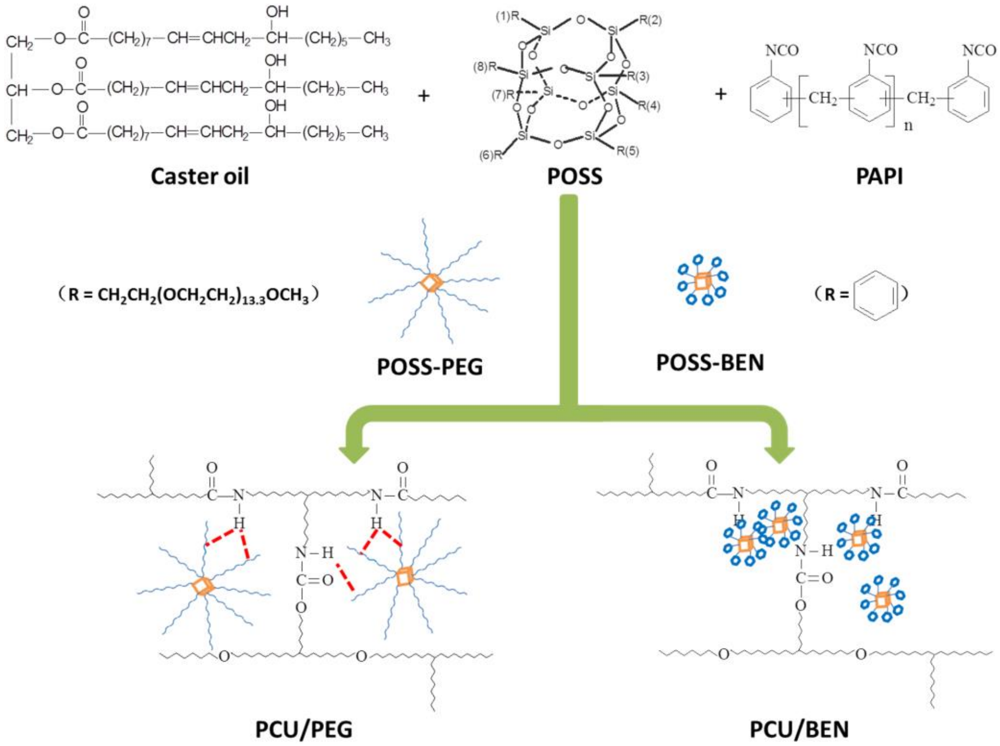


Figure 2. Formation illustration of nanocomposite coatings (Li et al., 2021).

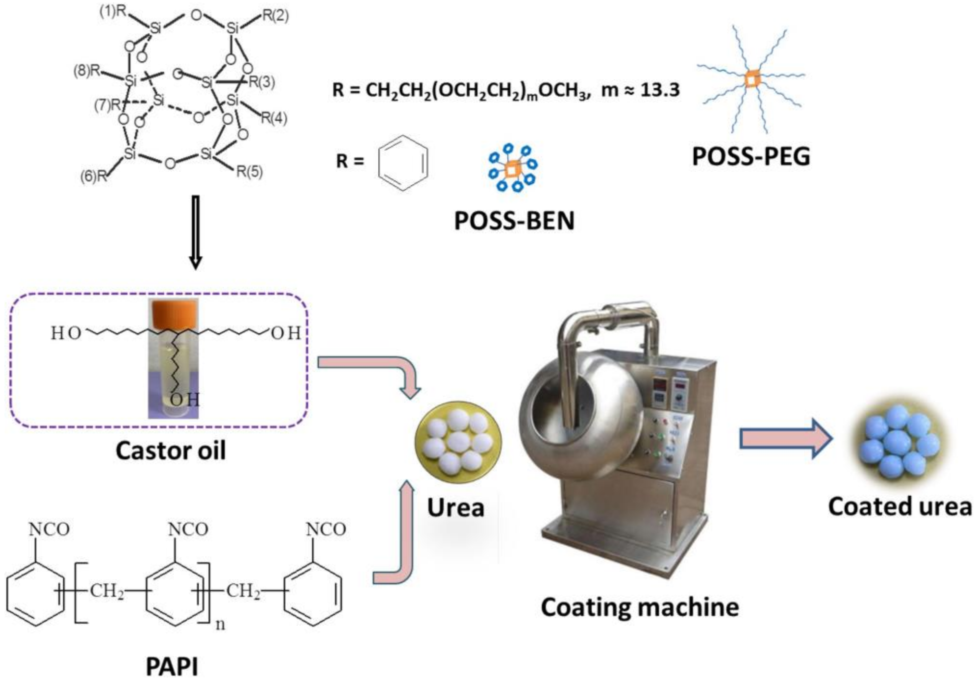


Figure 3. The preparation process of nanocomposite coated urea (Li et al., 2021).

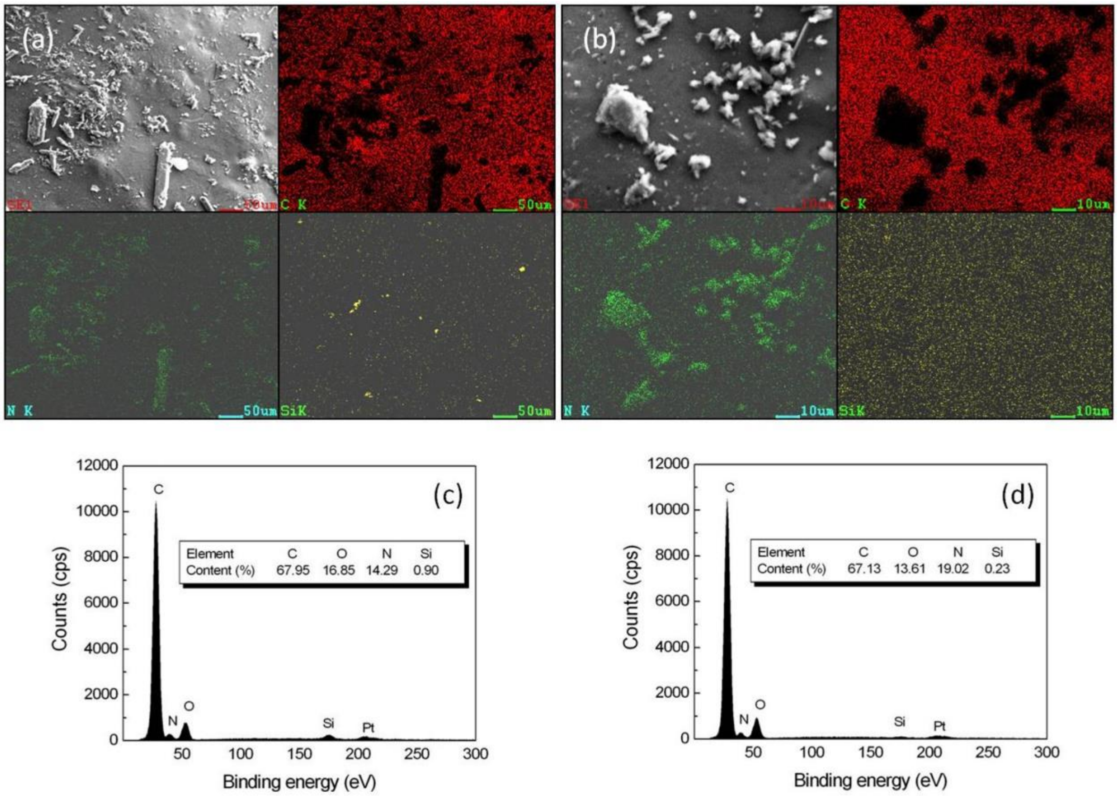


Figure 4. SEM images of surface morphologies and corresponding EDS mappings of C, N, Si of coatings, PU/2 wt% POSS-BEN nanocomposite PCU/BEN2 (a) and PU/2 wt% POSS-PEG nanocomposite (PCU/PEG2) (b) at × 1000 magnification, and EDS spectra of PCU/BEN2 (c) and PCU/PEG2 (d) (Li et al., 2021)

The obtained nanostructure coatings are simple to design, eco-friendly, and property tunable. The outcome of their study reveals that the vertex group of POSS had a prominent impact on the interaction degree and level of dispersion between POSS and polyurethane that satisfactorily adjusted the discharge routine and duration of coated urea, even when the coating rate was as low as 2 wt.%. The liquid POSS with flexible and long PEG groups had more suitable dispersibility and compatibility in polyurethane matrix than the solid POSS with tough octaphenyl groups, as confirmed by SEM/EDS (Fig 4). The observed outstanding features were ascribed to the various degrees of physical crosslinking. The authors, therefore, concluded that the modification of bio-based polyurethane coating with POSS offers an alternative route to controlling and regulating the features of coated fertilizer.

6. MAJOR CHALLENGES TO DEVELOPMENTS OF NANOCOMPOSITES

6.1. Transforming Fabricated Nanocomposites from Laboratory to Commercialized Scale

At the commercial level, the huge-scale fabrication of polymer nanocomposites is a problem due to the difficulty in their generation (Viswanathan et al., 2006; Ifijen and Ikhuoria, 2019). In addition to the fabrication difficulty, suitable selection of fabrication techniques and operating conditions should also be put into consideration by research scientist. As a result of this, various parameters must be defined such as interactions between the nanofiller and polymer matrix, the dispersion and stability of nanofiller in the polymer matrix, polymer chain flexibility, surface charge, the crystallisation ability of the nanofiller and surface chemistry.

6.2. Generation of Nanopowders

The feedstock materials of most nanocomposite fabrication techniques make use of nanopowders. Despite the development of nanopowders over the last decade, it is yet to reach the maturity to generate a hefty quantity of nanopowders at an inexpensive price for their successful consolidation into nanocomposite (Rivas et al., 2018). There is an urgent need to create techniques which are cost-effective and also able to produce large amount of nanoparticles.

6.3. Handling of Nanopowders

The ultrafine powders have high surface activity due to their high surface area, and thus are vulnerable to contamination (Viswanathan et al., 2006; Ifijen et al., 2018; Ifijen et al., 2019a; Ifijen et al., 2019b; Ifijen et al., 2019c). The physical, chemical, and mechanical properties of the end-products are easily compromised by the existence of such surface contaminants. As a result, better ways of storing and handling nanopowders should be investigated to prevent any contamination so that the advantages that comes with generating 'nanoscale materials''' can be harnessed to the maximum level.

6.4. Fabrication/Consolidation Techniques

The focal point of nanotechnology is dependent on the possibility of creating nanostructured materials that bring into being properties with novel characteristics in the 'macroscale' (Ifijen et al., 2020a; Ifijen and Ikhuoria, 2020; Ifijen et al., 2022e). Preserving the nanostructure nature of the final product using the traditional consolidation techniques can be very challenging because of the issue of excessive grain growth (Ifijen et al., 2022f; Ifijen et al., 2020a; Ifijen et al., 2020b;

Ifijen et al., 2018). Hence, there is a pressing call for scrutinizing the existing powder consolidation techniques and also to find out some innovative means of nanopowders densification.

6.5. Interdisciplinary Effort

The well-known function of nanotechnology for societal gain is stoutly based on the dynamic involvement of all disciplines of science and technology at all levels (Viswanathan et al., 2006; Omorogbe et al., 2019; Omorogbe et al., 2020). To fully comprehend this astonishing, but inadequately explained technology, the expansion of a cross-functional scientific workforce that transcends the predictable limits of a variety of disciplines is necessary. The development and implementation of new paradigms for training students and researchers of a new breed, who are not scared to cross-domains of several scientific disciplines needs to be carried out by academicians and administrators in the universities. .

7. CONCLUSIONS

This review has divulged current advances in the utilization of alkyd -clay-based nanocomposites, nanocomposite coatings based on epoxy resin and nanocomposite coatings based on polyurethane coatings applications. The alteration made on alkyd resins, epoxy resins and polyurethane over the years has helped to reduce the limitations of the aforementioned resins. Physical-chemical properties like drying properties, coating performances, anticorrosive properties, resistance to chemicals and thermal stability of the studied resins have experienced drastic developments in current times. This review has confirmed that the potential of nanotechnology in coating applications is boundless and encouraging. Further research on alkyd resin, epoxy resin and polyurethane nanocomposites is recommended to further enhance properties such as adhesion, drying time, gloss retention, resistance to scratch, chemical resistance capability in various corrosive environments, thermal stability, flexibility, roughness, hardness, abrasion resistance and mechanical strength, etc.

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9. CONFLICT OF INTEREST

Authors declare that there is no conflict of interest.

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