Jurnal Sains Nuklear Malaysia, 2024, 36(No. 1): 81 – 98
ISSN: 2232-0946

MODIFICATION OF SILANE-MODIFIED TiO_2 NANOPARTICLES WITH APO-NANOPARTICLES AS AN ANTIMICROBIAL ADDITIVE FOR PALM OIL-BASED SURFACE COATINGS

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ABSTRACT

The resources for palm oil in Malaysia are readily available, renewable, and have lower operating costs than any petrochemical oil resource. In this work, silane-modified anatase titanium dioxide (TiO_2) nanoparticles (NPs) were hybridized with acrylated palm olein (APO) (NPs) synthesized by ionizing acrylic palm oil resin to develop an antimicrobial additive for surface coating applications. The effects of their incorporation on the palm oil film coating's layer as well as the physicochemical characteristics of the hybrid APO and TiO_2 organic-inorganic NPs composites were investigated. The results included compatibility, chemical properties, morphology, roughness, water contact angle, thermal stability, transmittance, hardness, crosslinking and anti-scratch effects on coating surfaces. The test coating sample, POBUA-IPDI, presented a slightly higher adhesion and good crosslinking density, which improved hydrophobicity, thermal stability, and anti-scratch properties. This could be ascribed to a greater surface tension between the molecular forces of an object and the composite resin in the presence of TiO_2-APO NPs compared to other coatings. Antimicrobial features were minimal due to the coating sample's TiO_2 low content of 1%. On the other hand, the microbial inhibition zone can be detected due to the natural hydrophobic nature of palm oil and the chemical cross-linking capabilities of coating products after exposure to UV radiation that limit growth or do not allow microbial attachment surrounding the coating layer's surface. The study's findings demonstrated that a palm oil composite coating product by using TiO_2 as a nanofiller can improve the product's thermal, mechanical, and antimicrobial properties and has the potential to be employed as a surface protective layer.

Keywords: APO nanoparticles, EPOLA, POBUA, radiation curing, TiO_2 nanoparticles

INTRODUCTION

Research studies on the development of palm oil-based materials are being conducted to accommodate the country's varied industrial sectors. Inter-industry nuclear technology that advances palm oil resin research through the use of radiation technology, such as gamma, electron beam (EB), and ultraviolet (UV) for the production of multi-functional products, particularly in the field of surface coating.

Over the last two decades of research, it has been discovered that the effect of irradiation on palm oil materials can improve the physiochemical, thermal, and mechanical properties of these new products in order to meet their specifications and applications in industrial and healthcare demands. Indeed, its value as a renewable material compared petrochemical-based products makes it one of the primary plant oil sources for advanced research (Stavila, 2023). Furthermore, as compared to thermal or other conventional processes, nuclear technology utilized as an advanced material processing technique is more environmentally friendly, resulting in lower greenhouse gas (GHG) emissions.

On the other hand, titanium dioxide (TiO_2) nanoparticles (NPs) also known as titania is one of the nanofillers that are biocides and widely employed in the industrial sector, including the production of nanocomposite materials that guarantee to improve the original physiochemical, thermal, and mechanical properties of the material. Many studies reveal that the presence of TiO_2 NPs in a material can endow it with antimicrobial property. In addition, TiO_2 NPs also has unique features, such as non-toxicity, easy UV-activation, chemical stability, environmental friendliness, inertness, corrosion resistance and, low cost harvesting which has made it one of the choices as an antimicrobial agent.

Medical, food and beverage, building and construction, textile, and other industries have the highest demand for antimicrobial coatings (Zhao, 2011; Mamat Rokhmat, 2017; Abbas, 2018; falco, 2018; Kartini, 2018; Baig, 2020; Tran, 2020; Tudu, 2020; Chuang, 2021; Kumaravel, 2021). Anti-microbial coatings are classified into two types: biocides (which include silver, copper, titania and zinc compounds) and resin (which includes acrylic, polyurethane, epoxy, polyester, and others). Anti-microbial additives or biocides can enhance qualities that includes dimensional stability, heat and chemical resistance, and chemical stability while preventing the growth of microbes in finished products or polymers.

The pitfalls and challenges in this current sector are the potentials for the development of antibiotic resistance, strict regulations, and health concerns with biocide use. The better choice is to use natural polymers with the conjunction with radiation curing technologies. The palm oil-based resins, such as acrylic- and polyurethane-types are actively being developed for surface coatings of wood, paper, and metal applications because they are environmentally friendly and less harmful. Whereas, radiation curing technology is a green technology because it can offer less or zero volatile organic compounds (VOCs) release to the environment as compared to traditional methods (Salih, 2012; Tajau, 2013; Tajau, 2014; Salleh, 2016). Figure 1 represents the various type of resin-coated substrates, such as glass, paper, and wood.

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ISSN: 2232-0946

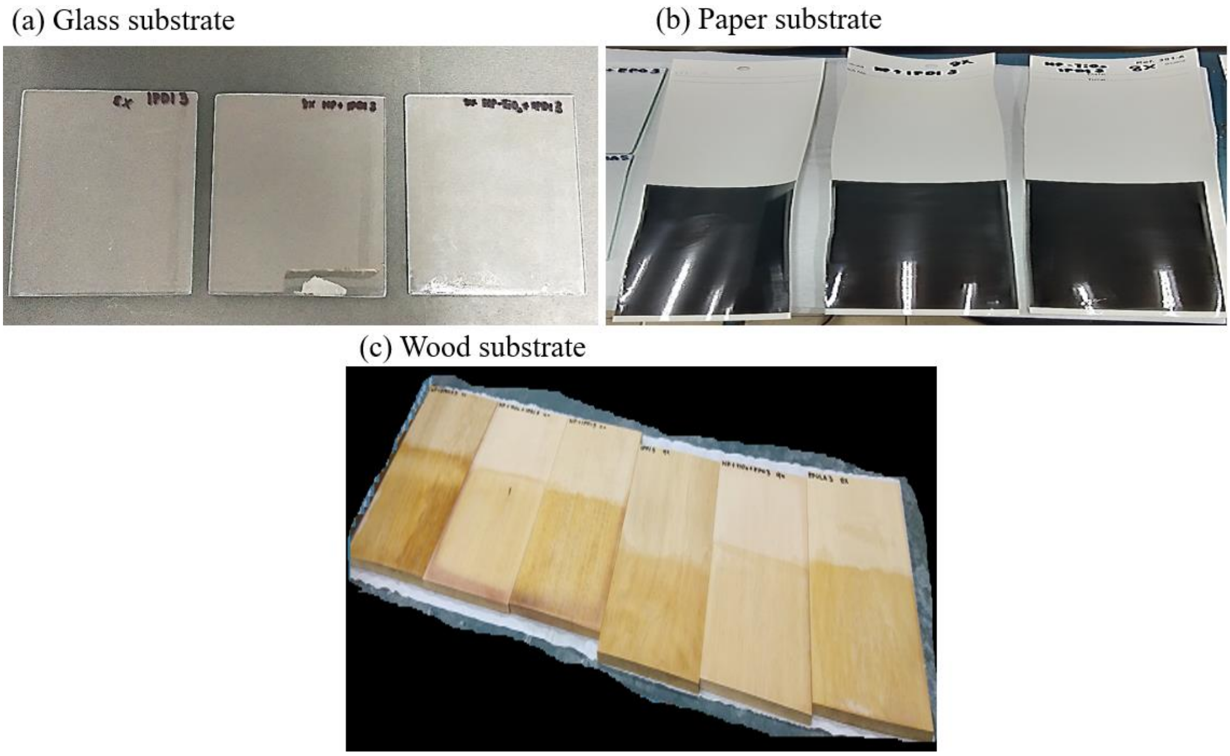

Figure 1 The potential application of coating products on various surfaces: **(a)** glass **(b)** paper and **(c)** wood substrates

The study aimed to develop anti-microbial additives for use in surface coatings. The work focuses on the encapsulation of titanium oxide (TiO_2) with NPs made of acrylated palm oil (APO), which also serves as nanocarriers for anti-microbial agents (Chouirfa, 2019; Tajau, 2021). These NPs will be integrated with palm oil-based resins for use as an antimicrobial additive in surface coatings by using radiation curing technology (Li, 2006; Ingrosso, 2015; Vuong, 2020).

METHODOLOGY

Preparation of UV Curable Organic/Inorganic Hybrid Coating

The sol-gel method was used to prepare the hybrid coatings. APO NPs of 5 mg with titanium dioxide (TiO_2-APO NPs) were each weighed in a 20 mL flask. Ethanol of 5 mL were added to each flask. The TiO_2-APO NPs solution was sonicated for 2 h. After that, 5 mL of resins respectively from the acrylic, i.e., EPOLA (Mw = approximately 2,000 Dalton) and the polyurethanes (Mw = approximately 5,000 Dalton) i.e., POBUA-IPDI, POBUA-IPDI-PETIA and POBUA-TDI-HEA were prepared in four different flasks. Two set of samples for each resin were prepared. About 1 wt% of TiO_2-APO NPs solution was added to the first set of each resin and the another set of resin was prepared without addition of a nanofiller for comparison purposes. Then, all samples were sonicated for 1 h.

Radiation curing process

The formulated resin was cured by using UV irradiation with a medium pressure mercury vapor lamp of IST-UV Dryer (Switzerland) about 7.0 mA and 10 m/min per pass with 0.72 J/cm^2. The sample was coated on the glass, wood and paper substrate by using 40 µm thickness hand bar coater for product evaluation.

Characterization of UV Curable Organic/Inorganic Hybrid Coating

Physical and chemical properties testing

The coating films performance was tested by using the Byk labotron pendulum hardness tester (Konig Method) in accordance with DN 53157 for hardness test. The coating films underwent scratch resistance test by using Erichsen universal scratch tester (model 413) according to DIN 53799 and the cracking property of the film were analyzed by an optical microscope (Zeiss Primo Star) for examining the surface of the films. The direct tape test method was used in this study for adhesion testing on the paper substrate according to the ASTM D3359-09 Test Method B Cross Cut Tape Test. The optical contact angle (Biolin Scientific, TL 100) was utilized to determine the hydrophobicity of the coating. The transmittance of the coating films was analyzed by using Byk Haze-Gard I Haze Meter according to the ASTM D1003; D1044. An FTIR spectrophotometer (Bruker's Tensor II) was used to analyze the chemical functions. The gel content test also was conducted by using soxhlet extractor method (Salih, 2012). The X-ray diffraction (XRD) spectra were obtained using a PANalytical PW3040/60 X'Pert PRO (Netherlands). The TiO_2 NPs chemical composition was characterized using FESEM equipped with an energy dispersive X-ray (EDX) (Oxford instrument).

Thermal testing

The thermal decomposition property of the designated NPs was analyzed by using the thermogravimetric analysis (TGA) analyzer (model NETZSCH) (German) at a temperature range of 35 °C to 900 °C and heated at a rate of 10 °C/min in a nitrogen gas atmosphere.

Morphology analysis

The FESEM images were captured by using a Zeiss microscope (model Philips XL40) and analyzed at the voltage range of 1 kV. The surface roughness was analyzed by using the atomic force microscopy (Nanowizard II).

Antimicrobial testing

The coating film was contaminated with standard strains of gram-negative bacteria (Escherichia *coli* –code of ATCC 25992) provided. ATCC 25922 is a recommended reference strain for antibiotic susceptibility testing. Inhibition zones were analyzed after 24 h incubation of plates at 37 °C.

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RESULTS AND DISCUSSION

Physicochemical Properties

Chemical interaction

The study's raw materials were EPOLA and POBUA resins, which were later modified to create EPOLA and polyurethane coatings (Figure 2, a-b). The surface of the TiO_2 nanoparticles was altered by using silane precursors via the sol-gel process before being encapsulated by the APO NPs (Horkavcová, 2021; Mahltig, 2018; Cotolan, 2016). Figure 2a shows the reaction mechanism of the sol-gel approach for silane-modified TiO_2 modification and the interactions between organic-inorganic hybrid coatings between those particles and APO nanoparticles (Figure 2, c-d).

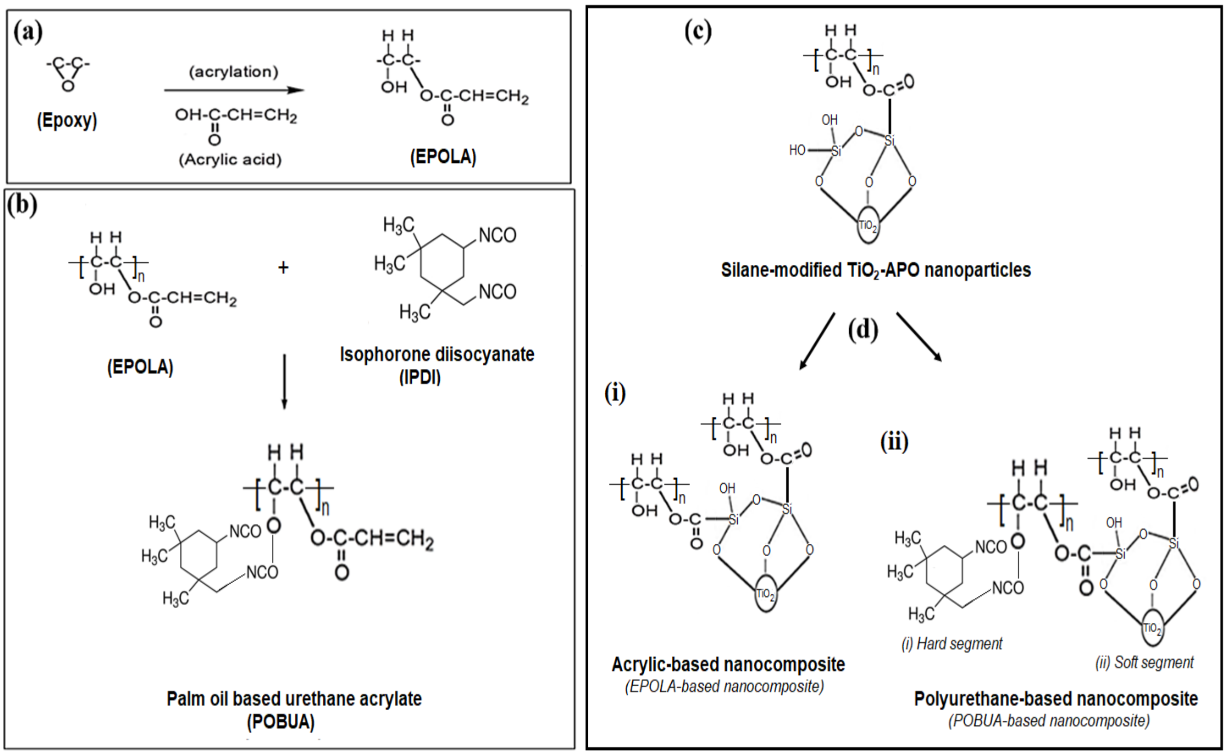
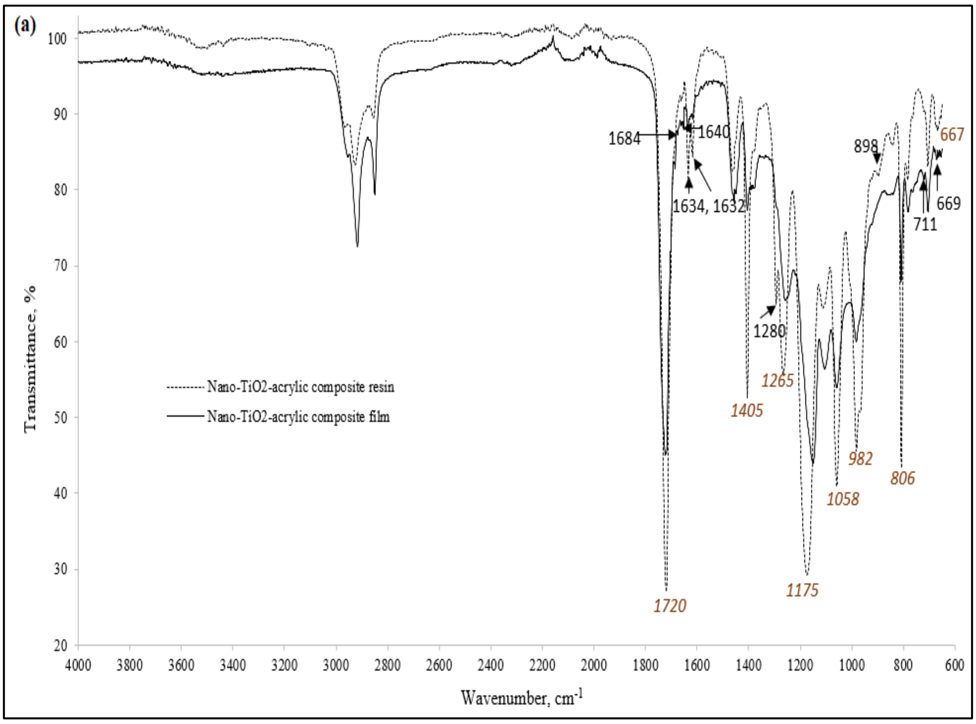


Figure 2. Chemical synthesis route for the production of palm oil-based resins based on the patent innovation registration number: **(a)** EPOLA production (PI2016704907) and **(b)** POBUA production (MY-142814-A), and schematic diagram of chemical structure interaction for development of TiO_2-APO NPs and the acrylic-type composite resin: **(c)** Silane-modified TiO_2-APO nanoparticles and **(d)** organic-inorganic hybrid composite of the TiO_2-APO NPs with the coatings: **(i)** acrylic-based nanocomposite and **(ii)** polyurethane-based nanocomposite

FTIR analysis and Nano-TiO_2 content evaluation

The chemical functional group of carbonyl and ester (C=O), carbon double bond (C=C), ester (-C-O), hydrocarbon (-C-H), and TEOS are the key indicators used to evaluate the curing process in coatings. The infrared tests results showed the resolution of ATR FTIR of the resins and films/ coatings as displayed in Figure 3, and the results are summarized in Table 1. The reaction between the -OH group of silane-modified TiO_2-APO NPs with the acrylic and urethane ester groups respectively showed a decrease in peak intensity at carbonyl 1,720 cm^{-1} and 1,722 cm^{-1} (Figure 2d, i-ii and Figure 3, a-b). Furthermore, as demonstrated in Table 1, the occurrence of cross-linking reactions has resulted in a decrease in the peak intensity of the active functional groups.

Meanwhile, the FTIR spectra showed the presence of anatase TiO_2 NPs in the coating films. The functional group spectra of Ti-O and Ti-O-Ti were at 669 cm^{-1} and 806 cm^{-1} for the acrylic film, and at 656 cm^{-1} and 808 cm^{-1} for the polyurethane composite film (Figure 3, a-b). A comparable analysis of the FTIR spectrum of anatase TiO_2 NPs revealed these relative functional groups, as reported by Praveen et al. (2014). The TiO_2 NPs characterization of anatase type was also proven using XRD as shown in Figure 4.



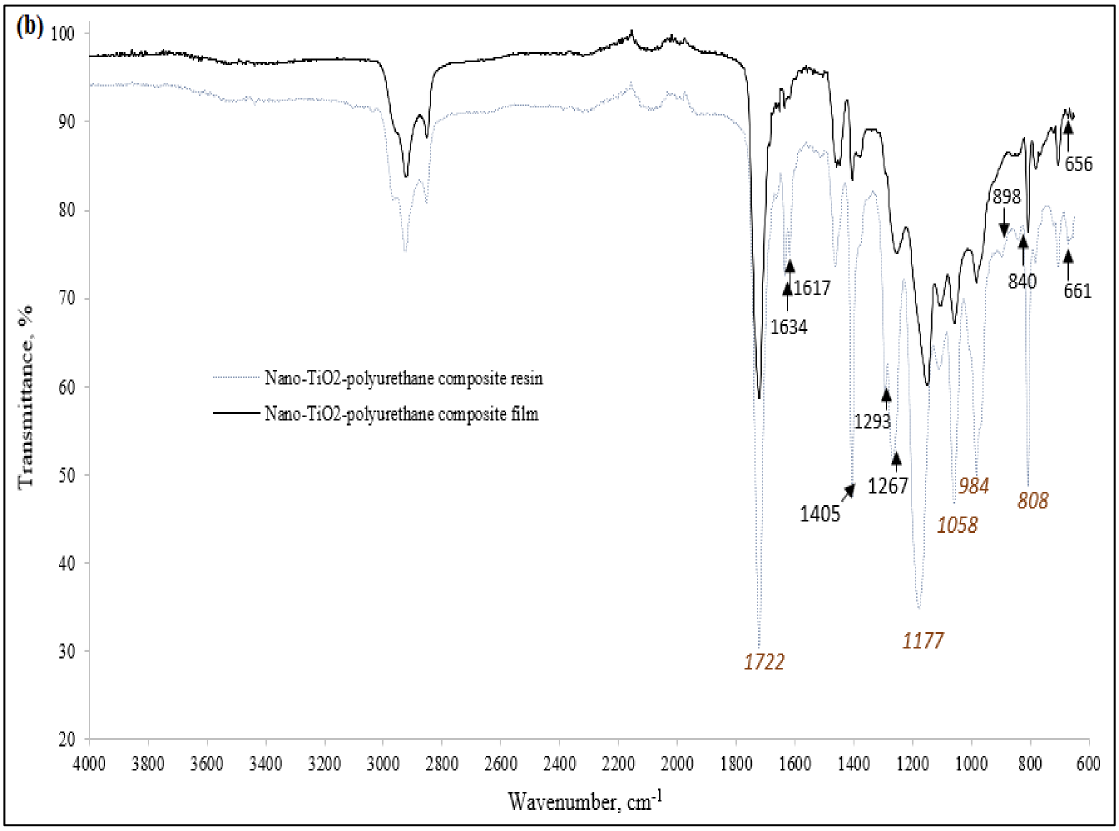


Figure 3 FTIR spectra of the resin composites after curing: **(a)** nano-TiO_2-acrylic composite film; **(b)** nano-TiO_2-IPDI-polyurethane composite film

Table 1 FTIR frequency range and functional groups in the sample after curing process

Wavenumber, cm^{-1}	Decreases of peak after curing	
	(a) Acrylic	(b) Polyurethane
C=O carbonyl	1720	1722
C=O ester	1684, 1640	-
-C=C-	1634, 1632	1634, 1617
-C-O	1280	1267, 1293
-C-H	898	898
TEOS	711	840
Ti-O, Ti-O-Ti	669, 806	656, 808

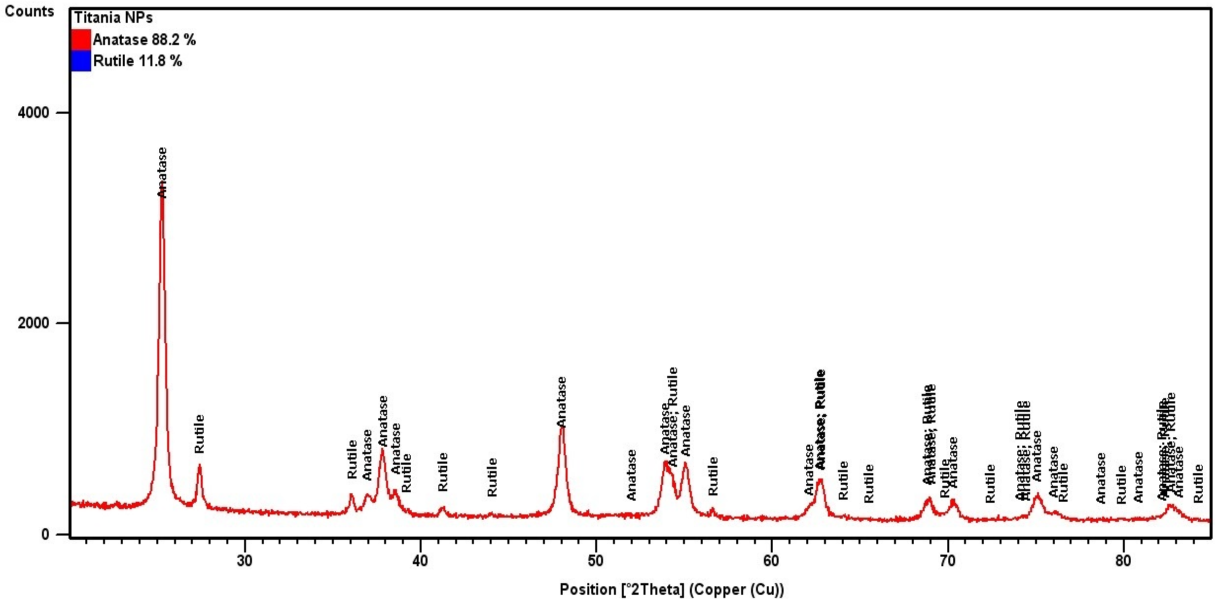
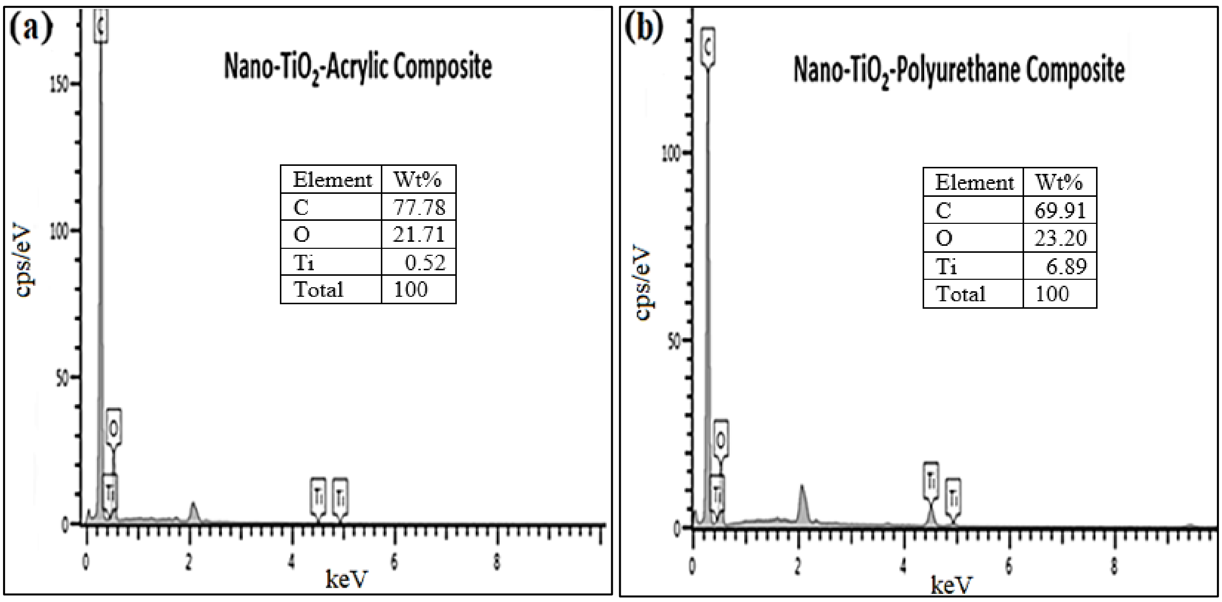


Figure 4 XRD spectrum of anatase TiO_2 NPs

Furthermore, the EDX analysis of composite films was depicted in Figure 5a and Figure 5b. The findings revealed the presence of nano-TiO_2 chemical elements in nano-TiO_2-acrylic composite film and nano-TiO_2-IPDI-polyurethane composite film were 0.52% and 6.89%, respectively. Furthermore, the addition of nano-TiO_2 in acrylic composite film and polyurethane composite film calculated by using UV-Vis spectrophotometer were 6.42 mg/L and 6.98 mg/L, respectively (Figure 5c), whereby the percentage value is corresponding to the EDX's element percentage, especially the nano-TiO_2-IPDI-polyurethane composite film.

Therefore, the effects of key reaction parameters, such as type of soft and hard segments of the polymer bonds influence the physical properties of coatings. The soft segment of polymer is responsible for facilitating the incorporation of the nanofiller mixture into the polymer chain (Figure 2d). Similarly, a higher molecular weight (Mw) of polyurethane allows for a greater uptake of nanofiller volume than the smaller size Mw of acrylic.



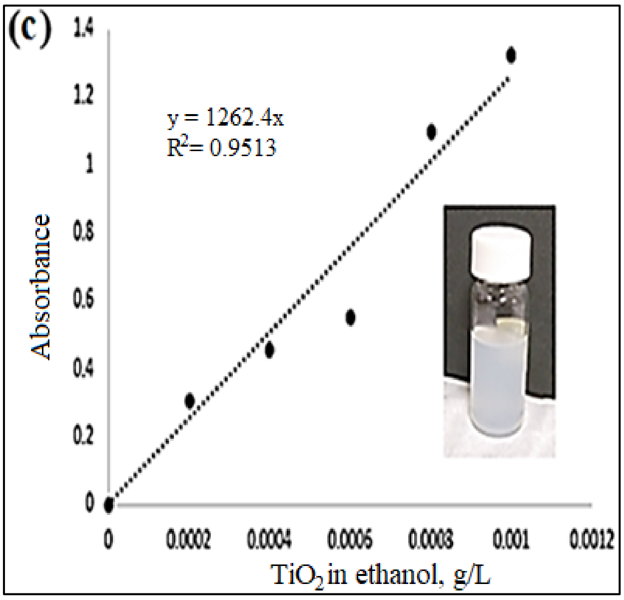


Figure 5 EDX elemental mapping of the nano-TiO_2: **(a)** nano-TiO_2 acrylic composite and **(b)** nano TiO_2-IPDI polyurethane composite, **(c)** Calibration curve of TiO_2 in ethanol solution by using UV-Vis spectrophotometer

Surface characterization and hydrophobicity

The FESEM images showed that the TiO_2-APO NPs were less than 150 nm in size and were spherical shape (Figure 6). Vuong (2020) also found a similar result with TiO_2 NPs in the acrylate urethane coating. Nanocoatings that containing the TiO_2-APO NPs produced a high-water contact angle. The present findings demonstrated the hydrophobic behavior by showing that the inclusion of TiO_2 NPs raised the contact angle for both acrylic- and polyurethane-type composite coatings, with a value greater than 90^o (Figure 6e). The addition of NPs such as graphite to the palm oil-based coating produced a similar effect, as reported by Alias in 2022(b).

The polyurethane- and acrylic-based films that showed hydrophilic properties had turned to hydrophobic by the presence of TiO_2 NPs as a composite film (Figure 6e). Furthermore, a small roughness surface of acrylic composite coating at 77.83 nm was proposed to be the reason for the higher hydrophobicity rate (Figure 6 d-e). The composite coating film of acrylic-type exhibited substantially higher rate of water contact angle although the polyurethane-IPDI composite coating resulted a higher value of water contact angle (Figure 6e ii, iv).

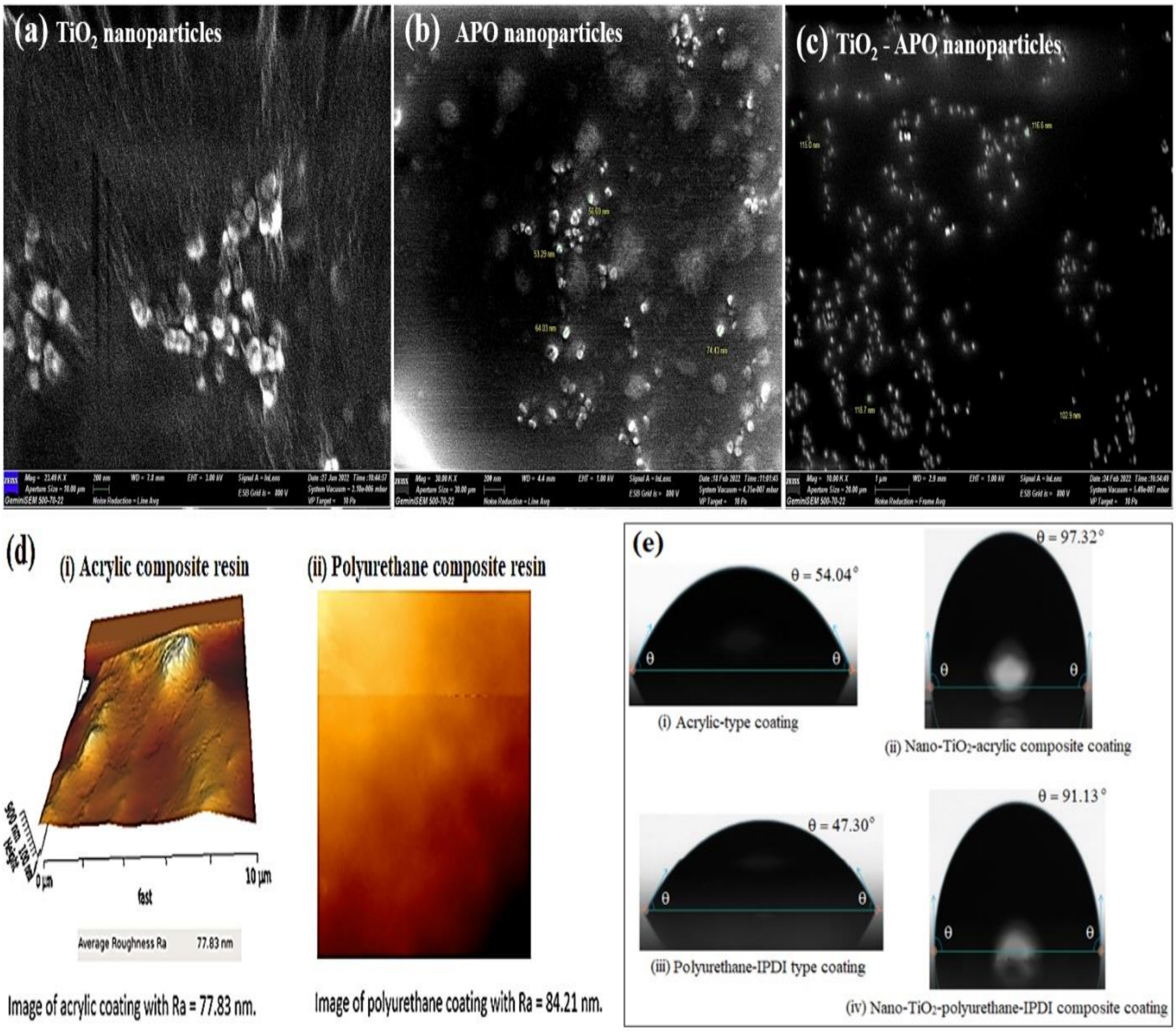


Figure 6 FESEM image of nanoparticles: **(a)** TiO_2 NPS, **(b)** APO NPs, **(c)** TiO_2-APO NPs, **(d)** AFM image of acrylic- and polyurethane composite coatings comprising TiO_2-APO NPs and **(e)** Water contact angle measurement of acrylic- and polyurethane-type coatings

Thermal and Mechanical Properties

Plots of the thermogravimetric (TG) reduction rate versus the temperature measured under a N_2 atmosphere are displayed in Figure 7, and the results are summarized in Table 2. The acrylic and polyurethane films underwent a three-step thermal degradation profile while the composites bond underwent a four-step thermal degradation profile (Figure 7).

In the present work, synthesis revealed the influence of TiO_2-APO NPs on the thermal performance of composite coatings. The thermal stability of the polymer composite coatings doped with TiO_2-APO NPs increases. TGA results showed that the presence of TiO_2 NPs practically decelerated the decomposition of composites backbone by means of a significant improvement in thermal property for surface coating applications. A comparable result was produced using TiO_2 NPs in the thermoplastic polypropylene nanocomposites coating, as studied by Bendaoued et al. (2022).

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The polyurethane-IPDI type coating containing TiO_2-APO NPs demonstrated superior thermal properties as compared to the acrylic-based type coatings and common polyurethane film, with degradation profile started at peak temperatures of 197 ^oC (Li, 2006). The degradation of the acrylic and polyurethane films started at 130 ^oC and 157 ^oC, respectively while the acrylic-composite bond started at peak temperature of 133 ^oC. Figure 2d (ii) shows that the presence of a hard segment network and TiO_2-APO NPs made polyurethane-IPDI-based coating films more stable.

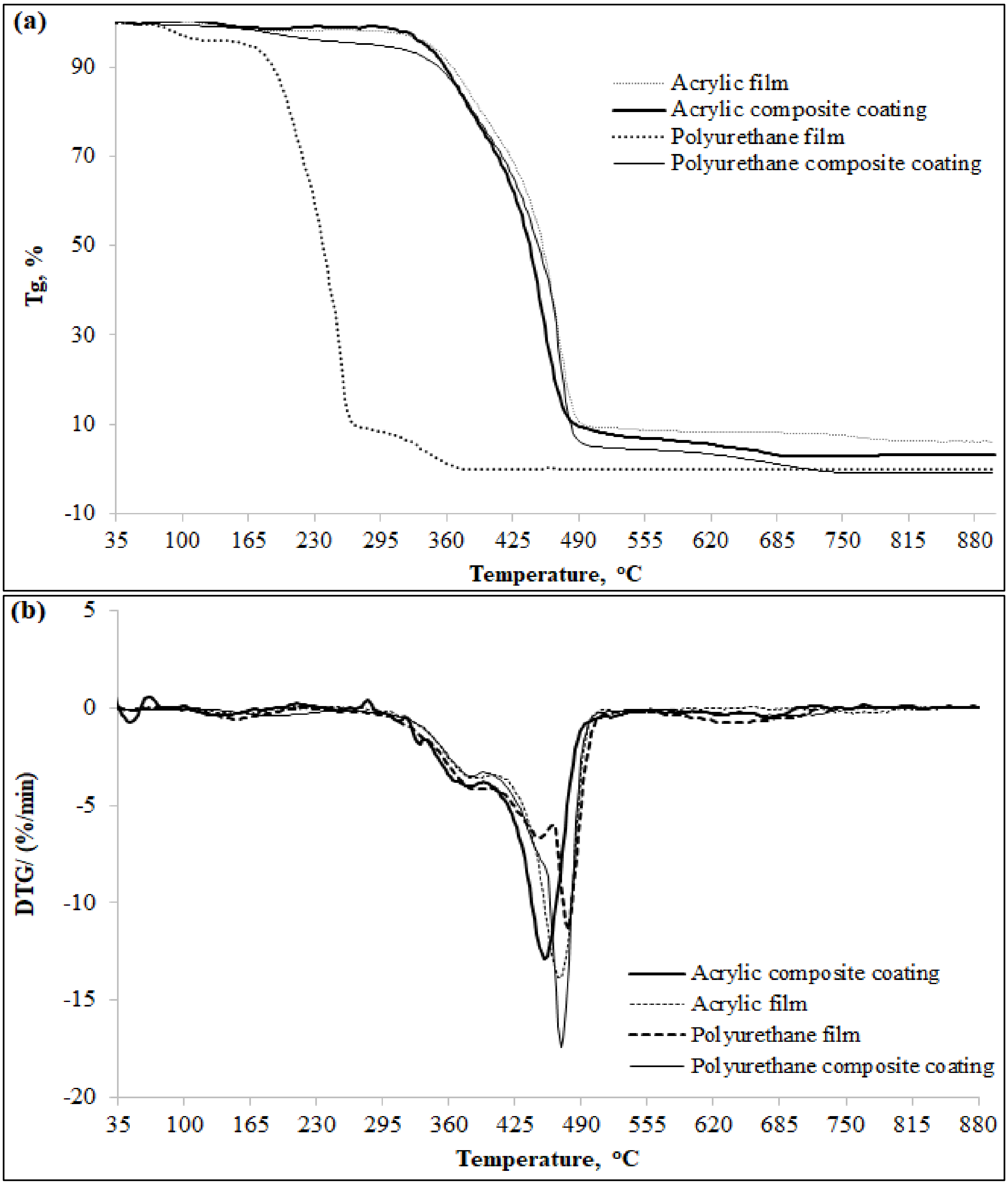


Figure 7 TGA curves of the polymer coatings: **(a)** TG curve and **(b)** Derivative thermogravimetry (DTG) curve

Table 2 Thermal degradation temperatures of coatings obtained with thermogravimetric analysis (TGA) (N_2)

Coatings	First-step thermal temperature (°C)	Second-step thermal temperature (°C)	Three-step thermal temperature (°C)	Four-step thermal temperature (°C)
Acrylic film	130	382	469	-
Acrylic composite coating	133	384	454	673
Polyurethane film	157	387	477	-
Polyurethane composite coating	197	385	470	672

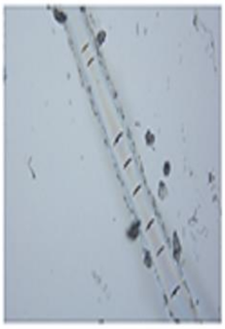
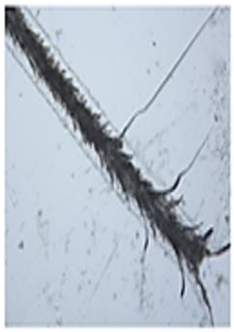
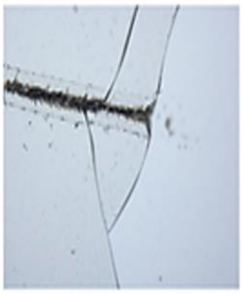
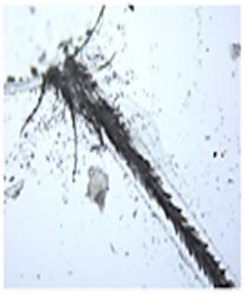
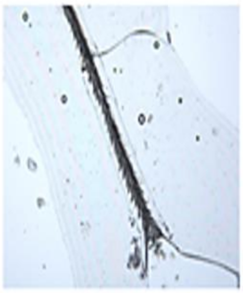
Table 3 reveals the mechanical properties of coatings under various testing conditions. The incorporation of TiO_2-APO NPs into the coatings increased the gel content property. Increased gel content means increased crosslinking, thermal and several mechanical strengths, as evidenced by the polyurethane-IPDI type coating, which has improved thermal, anti-scratch, and adhesion properties (Shahnooshi, 2019)

Table 3 Mechanical property of coatings at different preparation conditions

Coatings	Acrylic-based resin		Polyurethane-based resins					
	EPOLA		POBUA-IPDI		POBUA-IPDI-PETIA		POBUA-TDI-HEA	
	Control	With NPs	Control	With NPs	Control	With NPs	Control	With NPs
Gel content (%)	66.75	96.31	90.66	97.88	85.58	97.69	72.92	100
Scratch test, N	2.0	3.0	1.0	4.0	3.0	2.5	5.0	4.0
Adhesion, Percent area remained, % (on white paper surface)	72	92	84	100	92	52	98	100
Hardness, %	92.67	8.77	90.66	27.98	93	42.72	89.67	59.88
Transmittance, %	85.70	86.3	89.4	86.3	88.80	86.4	85.83	86.5

The addition of TiO_2-APO NPs to the coatings resulted in increased anti-scratch properties (Table 3). For polyurethane, the anti-scratch property of IPDI-based aliphatic diisocyanate increased while the end-capped type, such as the IPDI-PETIA-aliphatic diisocyanate and the TDI-HEA-aromatic isocyanate decreased, respectively (Table 4). Figure 8 shows the diisocyanates and monomers commonly used for polyurethane synthesis. Type of diisocyanate and monomer influenced the polyurethane property. The anti-scratch property of acrylic and polyurethane-IPDI type composites increased due to its rigid crosslinking network as compared to the other coatings (Page, 2007; Ingrosso, 2015; Verma, 2018; Alias, 2022 a,b) (Table 2). According to the findings of a study conducted by Alias et al. (2022, a,b) cross-linked polyurethane (POBUA) surfaces have the ability to function as a barrier coating that protects mild steel surfaces from corrosive substances.

Table 4 Scratch test of coatings at different preparation conditions

Coatings	EPOLA	POBUA-IPDI	POBUA-IPDI-PETIA	POBUA-TDI-HEA
Control	2.0 N 	1.0 N 	3.0 N 	5.0 N 
Composite films with TiO_2- APO NPs	3.0 N 	4.0 N 	2.5 N 	4.0 N 

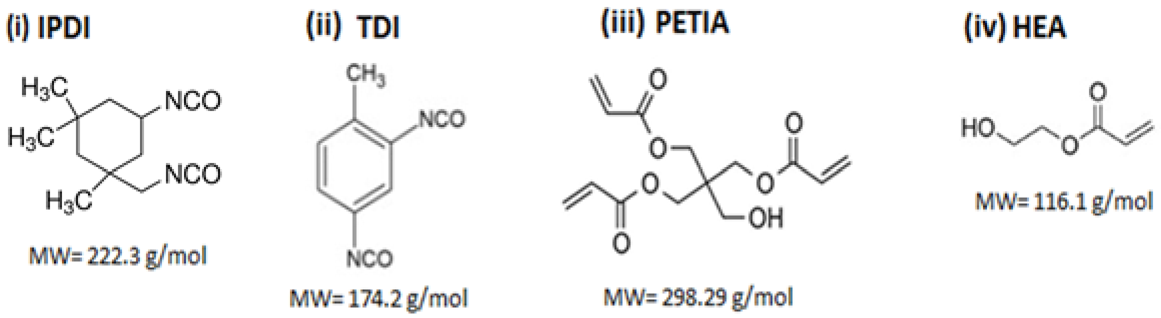


Figure 8 The diisocyanates: (i) IPDI (Isophorone diisocyanate), (ii) TDI (Toluene diisocyanate) and the monomers: (iii) PETIA (Pentaerythritol triacrylate), (iv) HEA (2-Hydroxyethyl acrylate) used in polyurethanes synthesis

The coating sample exhibited an increased adhesion property after the addition of TiO_2-APO NPs, which attributed to improved surface tension between the molecular forces of the object and the composite resin (Winnicki, 2021) (Table 3). However, hardness did not increase indefinitely with increasing crosslink density. The TiO_2-APO NPs had a larger influence on hardness because the coating hardness had decreased with addition of 1wt% of NP-TiO_2 content in the blend. The result presented that as the soft and hard segments of the polymer chain gets irregular by TiO_2-APO NPs, the hardness property of the coating decreases (Figure 2, d2). Previous studies have shown that TiO_2 NPs is distributed on the soft segment of the polyurethane which involves the interaction of -OH groups of TiO_2 NPs and the ester groups of polymers (Salahshoori, 2023). A high crosslinking density but a low hardness feature may arise from the typical termination processes of free radical polymerization on the dead polymers/ monomers, given the needless side reactions that lead to non-active polymers/ monomers (Yamago & Nakamura, 2013). Similarly, the transmittance results showed almost no significant progress in the transmittance properties of the coatings (Table 3).

Polymeric coatings with antimicrobial activity

The antimicrobial assessment showed that no antimicrobial zone had formed (Figure 9). The slight presence of 1wt% of NP-TiO_2 seemed had no influence on the antimicrobial activity detected on top and bottom surfaces of the film. However, the center zone potentially revealed a clear zone that was unoccupied by E-coli in comparison to the surrounding area that was occupied by E. coli (Figure 9). The composite coatings and polyurethane film, displayed antimicrobial effect on the central zone as compared to the control acrylic film. The composite coatings and polyurethane film in this study showed a qualitative inhibitory effect.

On the other hand, the hydrophobic nature of the coating due to the chemical cross-linking effect could improve its antimicrobial properties on both surfaces, which can potentially be explained by the lack of adhesion and microbial growth (Arango-Santander, 2018). The coating's internal cross-linking features most likely cause no pores to exist between the polymer network due to the durable three-dimensional network that potentially prevents microbes or dirt from growing on the surface.

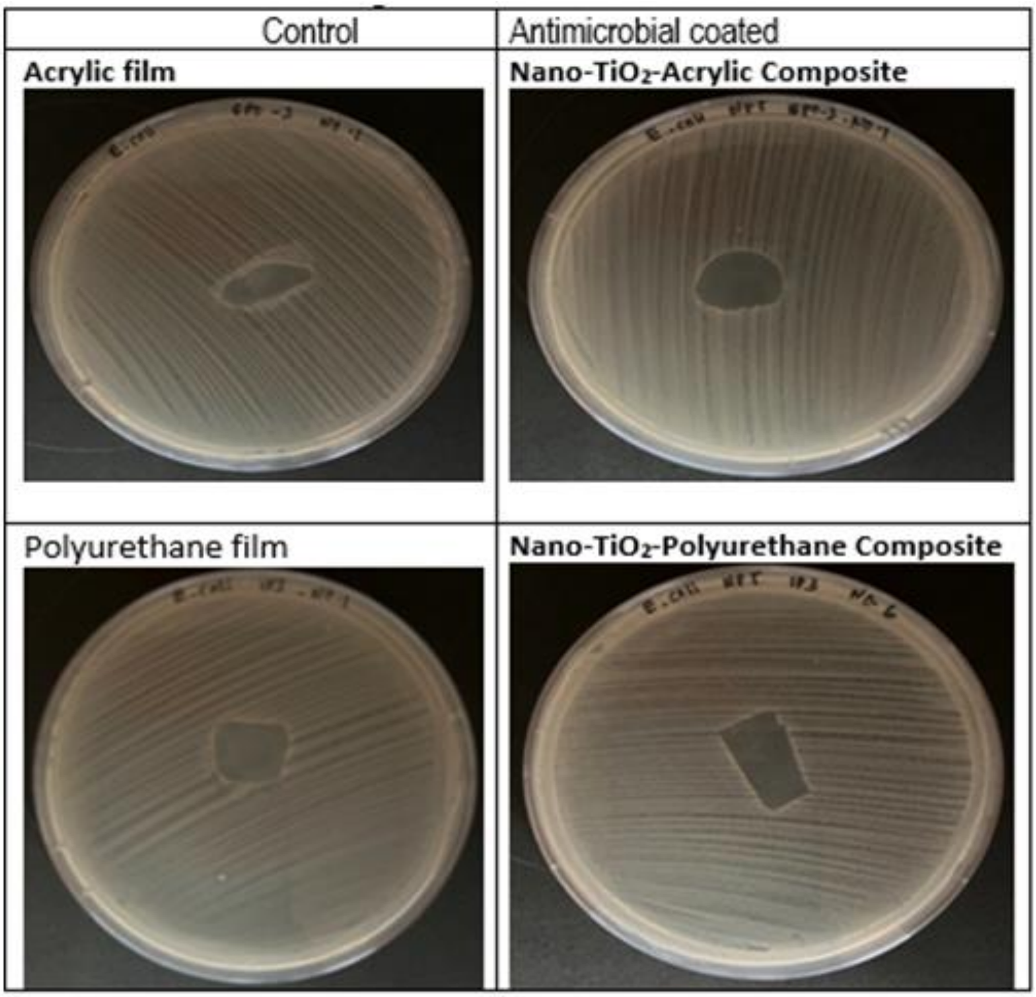


Figure 9 Comparative assessment of antimicrobial activity of palm oil-based coatings against E. coli (Gram-negative bacteria)

CONCLUSION

A variety of unique materials can be functionalized by using the sol-gel technique, which is notably useful for creating inorganic-organic coating materials. The presence of TiO_2-APO improves the properties of the gel content and anti-microbes. Acrylic and polyurethane composite films containing nano-TiO_2 have a high potential for antimicrobial coating applications, such as improving the safety of coated surfaces against microbes by increasing the volume of TiO_2 NPs above 1%. The study also demonstrated that polyurethane-IPDI composite has better thermal, anti-scratch, and several mechanical properties for surface coating applications than acrylic-based and common polyurethane coatings.

ACKNOWLEDGEMENTS

Acknowledgments were attributed to those who directly and continuously contribute to and promote this research, including all of the Synthesis and Radiation Curing Group (KSPS) staff at the Malaysian Nuclear Agency's Radiation Processing Technology Division (BTS). The authors would like to thank the Malaysian Nuclear Agency for the research support (NM-R&D-20-52).

REFERENCES

Abbas, M.; Iftikhar, H.; Malik, M.H.; Nazir, A. (2018). Surface Coatings of TiO_2 Nanoparticles onto the Designed Fabrics for Enhanced Self-Cleaning Properties. *Coatings*, *8*: 35.

Alias, M.S, Othman N., Kamarudin S., Harun M.H., Mohamed M., Mohamad S.F., Saidin N., Tajau R., and Abdul Halim K.A. (2022a). Green corrosion coating using palm oil based urethane acrylate (POBUA) on mild steels in 3.5 NaCl solution, *Materials Today: Proceedings*. 66.

Alias, M.S, Othman N., Kamarudin S., Harun M.H., Mohamed M., Mohamad S.F., Samsu, Z. (2022b). Influence of graphite particles in UV-curable corrosion protection coating from palm oil based urethane acrylate (POBUA), Industrial Crops and Products, 187(B): 115436.

Arango-Santander, S., Pelaez-Vargas, A., Freitas, S.C. and García, C. (2018). A novel approach to create an antibacterial surface using titanium dioxide and a combination of dippen nanolithography and soft lithography. Scientific Reports, 8:15818.

Baig, U., Uddin, M.K., Sajid, M. (2020). Surface Modification of TiO2 nanoparticles using Conducting Polymer Coating: Spectroscopic, Structural, Morphological Characterization and Interaction with Dye Molecules, Materials Today Communications, ISSN 2352-4928, 25: 101534.

Bendaoued, A., Messaoud, M., Harzallah, O., Bistac,S. and Salhi, R. (2022). Nano-TiO2 effect on thermal, rheological and structural properties of thermoplastic polypropylene nanocomposites, *Journal of Materials Research and Technology*, 17: 2313-2325.

Chouirfa, H., Bouloussa, H., Migonney, V., Falentin-Daudré, C. (2019). Review of titanium surface modification techniques and coatings for antibacterial applications. Acta Biomaterialia, Elsevier, 83: 37- 54

Chuang, Y., Wang, L., Feng, K., Subramanian, A., Chang, C., Simon, M., Nam, C. and Rafailovich, M. (2021), The Role of Titania Surface Coating by Atomic Layer Deposition in Improving Osteogenic Differentiation and Hard Tissue Formation of Dental Pulp Stem Cells. Adv. Eng. Mater., 23: 2100097.

Cotolan, N., Rak, M., Bele, M., Cör, A., Muresan, L.M. and Milošev, I. (2016). Sol-gel synthesis, characterization and properties of TiO2 and Ag-TiO2 coatings on titanium substrate, Surface and Coatings Technology, ISSN 0257-8972, 307 (A):790-799.

Falco, G.D., Ciardiello, R., Commodo, M., Gaudio, P.D., Minutolo, P., Porta, A., D'Anna, A. (2018). TIO2 nanoparticle coatings with advanced antibacterial and hydrophilic properties prepared by flame aerosol synthesis and thermophoretic deposition, Surface and Coatings Technology, ISSN 0257-8972, 349: 830-837.

Horkavcová, D.; Doubet, Q.; Lecomte-Nana, G.L.; Jablonská, E.; Helebrant, A. (2021). Development of Adhesive, Bioactive and Antibacterial Titania Sol-Gel Coating on Titanium Substrate by Dip-Coating Technique. Coatings, 11: 243. https://doi. org/10.3390/coatings11020243

Ingrosso, C., Ca Corcione, C.E., Striani, R., Comparelli, R., Striccoli, M., Agostiano, A., Lucia Curri, M. and Frigione, M. (2015). UV-Curable Nanocomposite Based on Methacrylic-Siloxane Resin and Surface-Modified TiO_2 Nanocrystals. *ACS Applied Materials & Interfaces*, *7*(28):15494-15505.

Kartini, I., Khairani, I. Y. , Chotimah, C., & Wahyuni, K. T. S. (2018). Nanostructured Titanium Dioxide for Functional Coatings. In (Ed.), Titanium Dioxide - Material for a Sustainable Environment. IntechOpen.

Kumaravel, V., Nair, K.M., Mathew, S., Bartlett, J., Kennedy, J.E., Manning, H.G., Whelan, B.J., Leyland, N.S., Pillai, S.C. (2021). Antimicrobial TiO2 nanocomposite coatings for surfaces, dental and orthopaedic implants, Chemical Engineering Journal, ISSN 1385-8947, 416: 129071.

Li, F., Zhou, S., Gu, G., and Wu, L. (2006). UV-curable coatings with nano-TiO_2. Polymer Engineering and Science - POLYM ENG SCI. 46. 1402-1410.

Mahltig, B., Grethe, T., Haase, H. (2018). Antimicrobial Coatings Obtained by Sol-Gel Method. In: Klein, L., Aparicio, M., Jitianu, A. (eds) Handbook of Sol-Gel Science and Technology. Springer, Cham.

Mamat Rokhmat, S., Wibowo, E. and Mikrajuddin Abdullah, K. (2017). Coating TiO2 nanoparticles on the surface of transparent plastic granules using combined electrostatic and heating methods for the photocatalytic degradation of organic pollutants in water, Environmental Nanotechnology, Monitoring & Management, ISSN 2215-1532, 8:1-10.

Page, K., Palgrave, R.G., Parkin, I.P., Wilson, M., Savin, S.L.P. and Chadwick, A.V. (2007). Titania and silver–titania composite films on glass—potent antimicrobial coatings. *J. Mater. Chem.*, 17: 95-104.

Praveen, P., G. Viruthagiri G., Mugundan, S., and Shanmugam, N. (2014). Structural, optical and morphological analyses of pristine titanium di-oxide nanoparticles – Synthesized via sol–gel route. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 117: 622–629.

Salahshoori, I., Asghari, M., Jorabchi, M.N., Wohlrab, S., Rabiei, M., Raji, M., Afsari, M. (2023). Methylene diisocyanate - aided tailoring of nanotitania for dispersion engineering through polyurethane mixed matrix membranes: Experimental investigations, *Arabian Journal of Chemistry*, 16(6): 104792.

Salih, A.M., Wan Yunus, W.M.Z., Mohd Dahlan, K.Z. and Ahmad, M. (2012). UV-Curable Palm Oil Based-Urethane Acrylate/Clay Nanocomposites, *Pertanika J. Sci. & Technol.*, 20(2), 435-444.

Salleh, M.Z., Tajau, R. and Mudri, N.H. (2016). The evolution of palm oil acrylates within 20 years in Nuclear Malaysia, Nuclear Malaysia R&D Seminar 2016, IAEA, Vienna, 1-6.

Shahnooshi, M., Eshaghi, A. and Aghaei, A.A. (2019). Transparent anti-fogging and anti-scratch $SiO_2/SiO_2–TiO_2$ thin film on polycarbonate substrate, *Mater. Res. Express* 6 086447.

Stavila, E., Yuliati, F., Adharis, A., Laksmono, J.A. and Iqbal, M. (2023). Recent advances in synthesis of polymers based on palm oil and its fatty acids, RSC Adv., 13: 14747-14775.

Tajau, R., Hilmi, M.H., Salleh, M.Z., Mohd Dahlan, K.Z., M.D. Che Ismail, R., Muhammad Faisal, S., Sheikh Abdul Rahman, S.M.Z. (2013). Production of uv-curable palm oil resins/oligomers using laboratory scale and pilot scale systems, Sains Malaysiana, 42: 459-467.

Tajau, R., Ibrahim, M.I., Mohd Yunus, N., Mahmood, M.H., Salleh, M.Z. and Nik Salleh, N.G. (2014). Development of palm oil-based UV-curable epoxy acrylate and urethane acrylate resins for wood coating application, AIP Conference Proceedings 1584, 164. Doi: 10.1063/1.4866125.

Tajau, R.; Rohani, R.; Alias, M.S.; Mudri, N.H.; Abdul Halim, K.A.; Harun, M.H.; Mat Isa, N.; Che Ismail, R.; Muhammad Faisal, S.; Talib, M.; Rawi Mohamed Zin, M.; Izni Yusoff, I.; Khairul Zaman, N.; Asyila Ilias, I. (2021). Emergence of Polymeric Material Utilising Sustainable Radiation Curable Palm Oil-Based Products for Advanced Technology Applications. *Polymers*, *13*, 1865

Tran, M.L., Fu, C.C., Wei, T.H., Hsieh, C.T., Juang, R.S. (2020). Surface coating of titania and graphene oxide onto plasma-activated polymer membranes as efficient photocatalysts for organics removal from water, Journal of Water Process Engineering, ISSN 2214-7144, 37:101488.

Tudu, B.K., Sinhamahapatra, A. and Kumar, A. (2020). Surface Modification of Cotton Fabric Using TiO_2 Nanoparticles for Self-Cleaning, Oil–Water Separation, Anti-stain, Anti-Water Absorption, and Anti-bacterial Properties, *ACS Omega*, *5*(14): 7850-7860.

Verma, J., Nigam, S., Sinha, S. and Bhattacharya, A. (2018). Development of polyurethane based anti-scratch and anti-algal coating formulation with silica-titania core-shell nanoparticles,Vacuum 153: 24-34,ISSN 0042-207X.

Vuong, N.T. (2020), The role of rutile TiO_2 nanoparticles on weathering resistance of photocurable acrylate urethane coating. Vietnam Journal of Chemistry, 58: 314-320.

Winnicki, M., Łatka, L. Jasiorski, M., Baszczuk, A. (2021). Mechanical properties of TiO2 coatings deposited by low pressure cold spraying, Surface and Coatings Technology, ISSN 0257-8972, 405, 126516.

Yamago, S., and Nakamura, Y. (2013). Recent progress in the use of photoirradiation in living radical polymerization, Polymer, 54(3): 981-994.

Zhao, L., Wang, H., Huo, K., Cui, L., Zhang, W., Ni, H., Zhang, Y., Wu, Z., and Chu, P. (2011). Antibacterial nano-structured titania coating incorporated with silver nanoparticles. Biomaterials. 32, 5706-16.