Titanium Dioxide-Curcumin Composite Materials from Aceh Curcuma Natural Source and Their Evaluation as Antiradical Agents Through *In Vitro* Study

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Abstract: *The usage of antiradical agents is pivotal for suppressing the negative effects of free radicals on human health. Curcumin, a well-known natural antiradical agent, suffers from its low stability and high price, thus, limiting its potential in real applications. In this work, we carried out the impregnation of encapsulated curcumin from Aceh curcuma source on commercial titanium dioxide. The isolation of curcumin was performed using a simple maceration method, while the encapsulation process was done employing carboxymethylcellulose and maltodextrin to give ethanol-curcumin and triacetin-curcumin powders in 30.35% and 37.21% yield, respectively. The composite materials contained curcumin in a range of 0.016–0.374 mg/g. The characterization data revealed that the curcumin was located on the surface of titanium dioxide through hydrogen bonds. The* in vitro *DPPH assay of the titanium dioxide-curcumin composite material exhibited 39.61 ± 1.36 to 79.70 ± 1.33% antiradical activity which was higher than titanium dioxide (31.78 ± 1.48%). Furthermore, the composite material also gave higher antiradical activity than its curcumin sources, i.e., Aceh curcuma (75.12 ± 1.79%), ethanol-curcumin (56.66 ± 0.25%), and triacetin-curcumin (63.58 ± 0.20%) demonstrating a synergistic antiradical effect of titanium dioxide and curcumin as the antiradical agents. These findings demonstrate the importance of the impregnation and encapsulation of curcumin in composite materials for antiradical applications.*

Keywords: *titanium dioxide; curcumin; Aceh curcuma; antiradical; composite material*

■ INTRODUCTION

Free radicals, including reactive oxygen species, generate serious effects on human health, such as inflammation, cancer, and heart diseases [1]. Unfortunately, these free radicals are spontaneously generated from air pollution, ultraviolet irradiation, and modern lifestyles, i.e., smoking, consuming fast food, and doing less exercise, thus cannot be avoided reaching the human body [2]. Therefore, the use of an antiradical agent is highly required. The antiradical agent is a chemical compound that could convert the free radical to the non-radical species, thus protecting biomolecules and cells from a radical chain reaction [3]. From the molecular point of view, free radical contains at least one unpaired electron; thus, the antiradical agent shall give a hydrogen atom and/or a single electron to deactivate the free radical [4].

Natural sources serve as an abundant source of thousands of chemical compounds that could act as antiradical agents [5]. Among the natural antiradical agents, curcumin is one of the most well-known compounds due to its high antiradical activity, well-established isolation process, and good biocompatibility. The antiradical activity of curcumin is generated from the hydrogen atom donor from its phenolic functional group, in which the formed phenoxy radical is stabilized

through the electron delocalization process [6]. However, curcumin suffers from some serious disadvantages to being applied for commercial purposes, such as low solubility in water, poor stability, and high-cost material [7].

Encapsulation is a useful technique to protect and prevent the degradation of natural compounds. Either carboxymethylcellulose or maltodextrin has been widely employed as the encapsulating agent due to its high efficiency, low toxicity, and low price [8-10]. It was reported by Tomé Constantino and Garcia-Rojas [11] that betanin encapsulation with carboxymethylcellulose could increase the chemical and thermal stabilities of betanin. Furthermore, Negrão-Murakami et al. [12] reported that the encapsulated *Ilex paraguariensis* A St. Hil. extract with maltodextrin increased its physicochemical properties and stability. Furthermore, the antiradical activity of the extract is maintained, as revealed by the *in vitro* 1,1-diphenyl-2-picrylhydrazyl (DPPH) assay.

On the other hand, the encapsulation of curcumin using carboxymethylcellulose and maltodextrin has been reported [13-17]. It was reported that curcumin encapsulation on carboxymethyl cellulose-montmorillonite clay nanocomposite could enhance the stability and solubility of curcumin in water [18]. Taking consideration for antiradical purposes, higher curcumin solubility in water and/or other polar solvents leads to stronger antiradical activity due to less aggregation structure. However, the antiradical activity of encapsulated curcumin is rarely investigated.

Instead of the encapsulation process, the impregnation of natural compounds could suppress the production cost as the expensive natural compounds are homogenously spread on the surface of the substrate [19]. Among the solid substrates, titanium dioxide gives great benefits due to its excellent stability, low cost, and non-toxic properties [20]. Impregnation of natural compounds using titanium dioxide has been massively reported, including curcumin [21-26]. However, the application of titanium dioxide-curcumin material as the antiradical agent has not been comprehensively studied.

In this work, a series of titanium dioxide-curcumin composite materials were prepared through extraction, encapsulation, and impregnation of curcumin on the titanium dioxide substrate. The curcumin was isolated from Aceh curcuma through a maceration technique, while the curcumin encapsulation was carried out utilizing carboxymethyl cellulose and maltodextrin as the encapsulated agents. The impregnation of the encapsulated curcumin on the titanium dioxide substrate was conducted by stirring the mixture in a dark condition at room temperature to yield a series of titanium dioxide-curcumin composite materials. The curcumin content in the extracts and composite materials was quantified using a calibration curve from the UV-vis measurement. The antiradical activities of the composite materials, as well as Aceh curcuma and its extracts, were examined using *in vitro* DPPH assay to study the effect of curcumin isolation, encapsulation, and impregnation on the antiradical activity.

■ EXPERIMENTAL SECTION

Materials

The used materials in this work, i.e., titanium dioxide, carboxymethylcellulose, maltodextrin, methanol, ethanol, triacetin, and DPPH were purchased from Merck and employed without further purification. The curcuma powder from Aceh was kindly donated by PT. Bukit Warna Abadi, West Java, Indonesia while the curcumin standard was obtained from Merck with 84% purity based on HPLC analysis.

Instrumentation

The diffuse-reflectance ultraviolet-visible (DR UV-vis) analysis was carried out using a UV-vis spectrophotometer (Jasco V-760). The X-ray diffraction (XRD) data were measured by an XRD diffractometer (Shimadzu XRD 6000) with Cu Kα (1.54060 Å) as the radiation source at a voltage of 40 kV and current of 30 mA. The Fourier-transform infrared (FTIR) spectra of the samples were recorded by FTIR spectrophotometer (Shimadzu Prestige-21) while the scanning electron microscope (SEM) micrographs of the composite materials were taken by JEOL JSM-6510 LA. On the other hand, the UV-vis analysis was performed on a double-beam spectrophotometer (Shimadzu UV-

1800) for curcumin quantification on its maximum wavelength, as well as, for evaluation of the antioxidant activity of composite materials.

Procedure

Extraction and encapsulation of curcumin

The extraction and encapsulation of curcumin were carried out following the previous report [27]. The curcuma powder (10 g) from the Aceh region was extracted employing ethanol as the solvent (100 mL) with a mass-to-volume ratio at 1:10 m/v through a stirring technique at 750 rpm stirring speed for 3 h at room temperature. The extract (100 mL) was added to distilled water (100 mL) containing carboxymethylcellulose (0.6 g) and maltodextrin (12 g) for the encapsulation process. The mixture was evaporated at 80 °C to eliminate the ethanol and then sprayed at an inlet temperature of 140 °C to obtain ethanol-curcumin sample. The extraction process using triacetin-ethanol-distilled water (1:3:1 v/v/v) solvent mixture was also carried out to yield triacetin-curcumin sample.

Curcumin quantification

The quantification of curcumin was performed according to the standard method employing a UV-vis spectrophotometer [28]. The curcumin standard was dissolved in ethanol and measured from 300–800 nm to find its maximum wavelength. A series of curcumin standards with different concentrations was prepared to make the calibration curve. The absorbance of the sample solution in ethanol was recorded and then the curcumin purity of the samples was calculated using the calibration curve.

Preparation of composite materials

Titanium dioxide (1.00 g) was added to the sample solution containing curcumin (Aceh curcuma, ethanol-curcumin, and triacetin-curcumin) with various concentrations of 5, 25, and 50 mg/L in ethanol (20 mL). The mixture was stirred in a dark condition at room temperature. After 24 h, the mixture was filtered using Whatman filter paper. The solid residue was washed with cold ethanol until the filtrate became colorless. Afterward, the absorbance of the filtrate was measured to quantify the impregnated curcumin on the titanium dioxide materials. The composite materials were characterized using DR UV-vis, XRD, and FTIR analyses.

In vitro *antiradical activity measurement*

The *in vitro* antiradical activity of composite materials was measured following the previous method with slight modification [29]. The composite material (10 mg) was added to methanol (8 mL). Then, DPPH 0.1 mM solution in methanol (2 mL) was added to the mixture. The mixture was shaken in a dark condition for 30 min. The mixture was filtered, and the absorbance of the filtrate was measured using a UV-vis spectrophotometer at 517 nm. The control solution was prepared by mixing methanol (8 mL) and DPPH 0.1 mM solution (2 mL) with the same procedure above. The antiradical activity percentage was determined by calculating the difference between the absorbance of the control and the sample over the absorbance of the control. The antiradical activity of bare titanium dioxide, Aceh curcuma, ethanol-curcumin, and triacetin-curcumin was also measured to evaluate the effect of the impregnation process on the antiradical activity.

■ RESULTS AND DISCUSSION

Extraction and Encapsulation of Curcumin

In this work, the curcumin was isolated from Aceh curcuma powder using a simple maceration method. Ethanol and a mixture of triacetin-ethanol-distilled water were used as the solvent because curcumin is soluble in both media [30]. Carboxymethylcellulose and maltodextrin were employed as the encapsulating agents to enhance the stability of curcumin, as it was known that curcumin could be gradually degraded at room temperature [7]. The curcumin-ethanol sample was obtained as a yellowish orange solid (6.86 g) in 30.35% yield, while curcumin-triacetin was obtained as a yellowish orange solid (8.41 g) in 37.21% yield. The yield of curcumin-triacetin was higher than curcumin-ethanol due to the higher solubility of curcumin in triacetin than in ethanol as previously reported [30]. The curcumin-ethanol sample was checked by thin layer chromatography (TLC) using chloroform:ethanol 97:3 (v/v), yielding retention factor (Rf) values of 0.60, 0.38, and 0.26 for curcumin, demethoxycurcumin, and

bisdemethoxycurcumin, respectively, as reported before [31]. Similar to this, the curcumin-triacetin also yielded three TLC spots at Rf values of 0.60, 0.34, and 0.24 for curcumin, demethoxycurcumin, and bisdemethoxycurcumin, respectively. These results demonstrate the successful isolation and encapsulation of curcumin from Aceh curcuma as the starting material.

Curcumin Quantification

The UV-vis spectrum of the curcumin standard solution at 0.84–8.40 mg/L concentration is shown in Fig. 1. It was found that the maximum wavelength of curcumin in ethanol was observed at 420 nm as previously reported [28]. The absorbance signal at 420 nm originated from π–π* electronic transition of curcumin. The absorbance of curcumin standard solutions at 420 nm was plotted against the curcumin concentration (Fig. 1(a)). The calibration curve with a mathematic formula of "Absorbance = 0.1555 [curcumin concentration] + 0.0077" was obtained with a coefficient of determination (R^2) value of 0.9991, demonstrating the validity of the calibration curve (Fig. 1(b)).

By using the equation, it was found that Aceh curcuma contained 4.24% curcumin. On the other hand, curcumin-ethanol and curcumin-triacetin contained 2.43% and 2.56% curcumin, respectively, which were lower than originated Aceh curcuma (4.24%) due to the presence of maltodextrin and carboxymethylcellulose as the encapsulating agents. Compared to the curcumin-ethanol, the curcumin content in curcumin-triacetin sample was higher than curcumin-ethanol due to the higher solubility of curcumin in triacetin as reported before [30].

Preparation of Composite Materials

The titanium dioxide-curcumin composite materials were prepared to evaluate the effect of encapsulation of curcumin on the antiradical activity. The composite materials were obtained in 91–99% yield based on the initial mass of titanium dioxide (1 g). Fig. 2 shows the photographed image of the composite materials with different curcumin sources and concentrations. The presence of curcumin generated yellow color in the composite material as curcumin powder existed in yellowish orange color [32]. The color intensity was stronger when the initial concentration of curcumin was higher.

The titanium dioxide-Aceh curcuma composite materials were obtained as orange solid, while the titanium dioxide-ethanol-curcumin and titanium dioxide-triacetin-curcumin composite materials were obtained as yellowish color solid. This phenomenon might be caused by the presence of other components besides curcumin in the Aceh curcuma sample. It was reported that crude curcumin powder contains α-phellandrene, β-caryophyllene, turmerone, bisabolone, and sesquiphellandrene [33]. These compounds might be eliminated during the extraction and encapsulation process; thus, the color of titanium dioxide-ethanol-curcumin and titanium dioxide-triacetin-curcumin composite materials originated mainly due to the curcumin color.

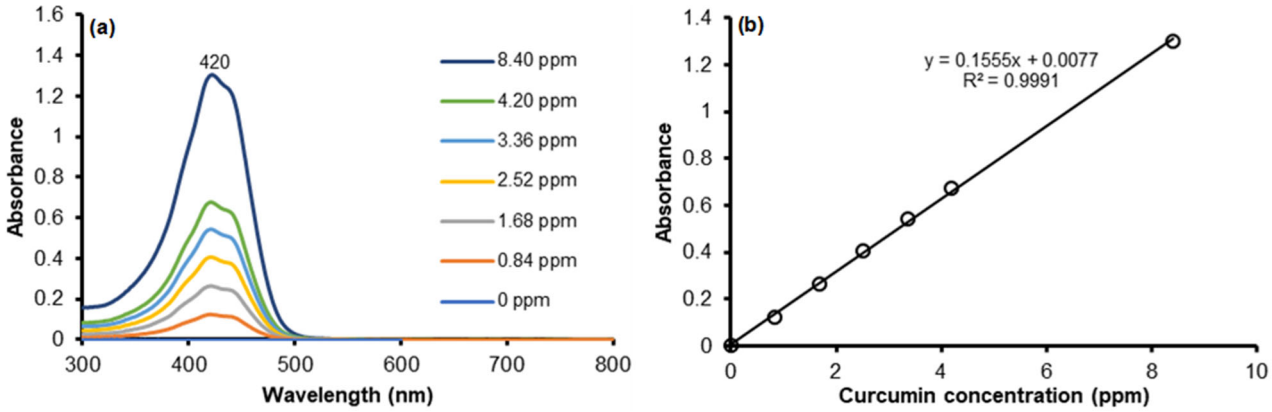

Fig 1. The (a) UV-vis spectra and (b) calibration curve of standard curcumin solution

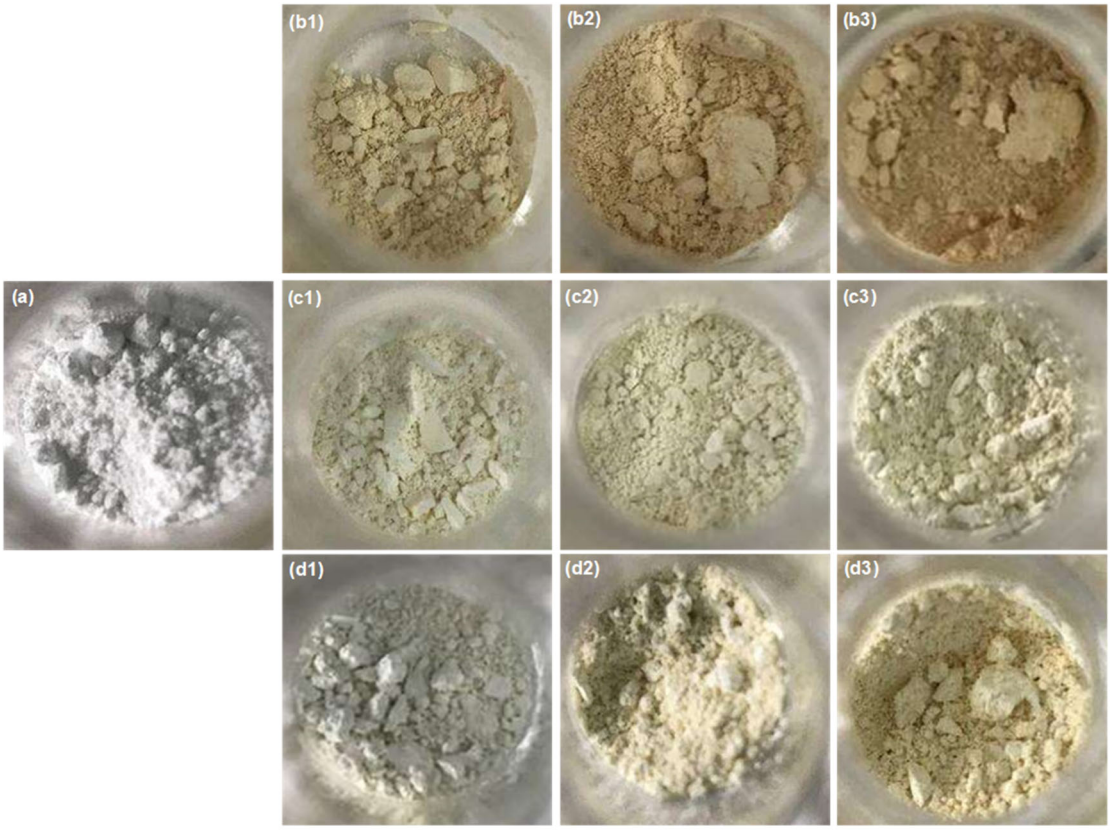

Fig 2. The photographed image of (a) titanium dioxide, (b1–b3) titanium dioxide-Aceh curcuma, (c1–c3) titanium dioxide-ethanol-curcumin, and (d1–d3) titanium dioxide-triacetin-curcumin composite materials. Terms (1), (2), and (3) stand for the initial concentration of curcumin solution of 5, 25, and 50 mg/L, respectively

The composite materials were then characterized using DR UV-vis, XRD, and FTIR instruments. The DR UV-vis spectra of the composite materials are shown in Fig. 3. In accordance with the photographed image of the curcumin samples, Aceh curcuma, curcumin-ethanol, and curcumin-triacetin showed broad absorption signal at 400–550 nm, which corresponded to its orange-yellowish color as previously reported [21]. Meanwhile, bare titanium dioxide had no absorption signal at the visible region (400–800 nm). Consequently, the impregnation of curcumin on the titanium dioxide material showed a weak absorption band at 420 nm. The titanium dioxide-curcumin sample showed the strongest absorption signal at 420 nm among the composite materials, as indicated by its orange color. Meanwhile, the absorption signals of titanium dioxide at 200–380 nm were not significantly influenced, indicating that the curcumins were located on the surface of titanium dioxide as the preparation was

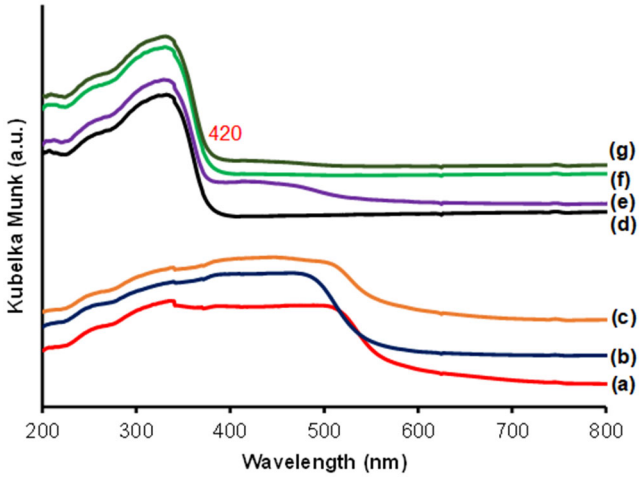

Fig 3. The DR UV-vis spectra of (a) Aceh curcuma, (b) ethanol-curcumin, (c) triacetin-curcumin, (d) titanium dioxide, (e) titanium dioxide-Aceh curcuma 50 mg/L, (f) titanium dioxide-ethanol-curcumin 50 mg/L, and (g) titanium dioxide-triacetin-curcumin 50 mg/L composite materials

performed using a stirring method at room temperature. This phenomenon was also reported for the impregnation of betalain and chlorophyll pigments on the titanium dioxide substrate [22,26].

Fig. 4 shows the XRD data of the titanium dioxide, Aceh curcuma, curcumin-ethanol, curcumin-triacetin, and the titanium dioxide-curcumin composite materials. The Aceh curcuma, curcumin-ethanol and curcumin-triacetin existed as amorphous phases. On the other hand, the unmodified titanium dioxide existed in the anatase crystalline phase of (101), (004), (200), (105), (211), (204), (116), (220), (215), and (224) according to JCPDS No 00-021-1272. Therefore, the XRD data of the composite materials were very similar to the unmodified titanium dioxide. This result strengthened the DR UV-vis data that curcumin was located on the surface of titanium dioxide as no observed changes in the crystalline phase of the titanium dioxide after the impregnation process. A similar result was observed for the *in-situ* synthesis of polyaniline on anatase TiO_2 nanorod [34]. The incorporation of the amorphous phase into the crystalline structure did not change the anatase crystalline structure.

The FTIR spectra of the composite materials are shown in Fig. 5. The FTIR spectrum of Aceh curcuma showed the absorption signals at 3487, 2924, 1627, 1504, 1273, and 1018 cm^{-1} for ArO–H, C_{sp3}–H, C=O, C=C, C–O–C, and C–O vibrations, respectively, on its FTIR spectrum. This result agreed with other curcuma samples [35-37]. After the encapsulation process, the vibration signals of curcumin-ethanol were shifted from the Aceh curcuma one. The ArO–H signal was shifted from 3487 to 3364 cm^{-1} due to the encapsulation of curcumin with carboxymethylcellulose and maltodextrin. Meanwhile, the other functional groups of curcumin-ethanol remain, i.e., C_{sp3}–H (2924 cm^{-1}), C=O (1627 cm^{-1}), C=C (1504 cm^{-1}), and C–O (1018 cm^{-1}) vibrations. On the other hand, the FTIR spectrum of curcumin-triacetin showed an additional C=O ester signal of triacetin at 1743 cm^{-1}, while the other signals were not significantly different from the Aceh curcuma sample.

On the other hand, titanium dioxide showed three major peaks at 3433, 678, and 517 cm^{-1} for the vibration of TiO–H, Ti–O–Ti, and Ti–O functional groups, respectively [38]. Therefore, the FTIR spectra of titanium dioxide-curcumin composite materials were similar to the FTIR spectrum of bare titanium dioxide sample except for the slight shift of the O–H functional group from 3433 to 3425–3387 cm^{-1} and the addition of very weak absorption signals at 1627–1018 cm^{-1} region

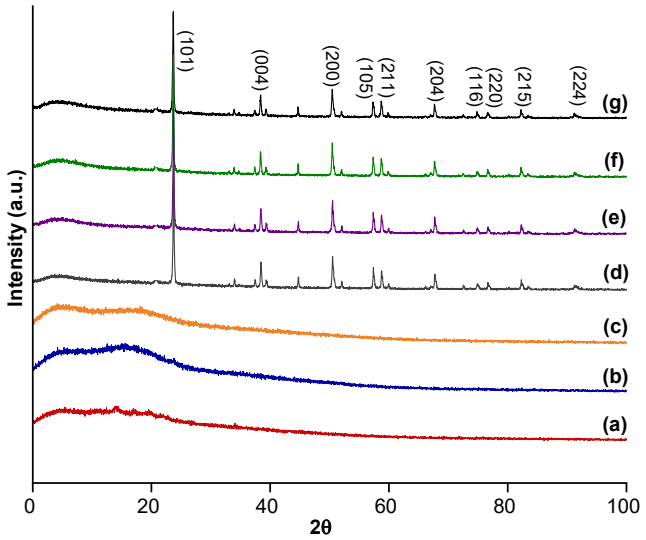

Fig 4. The XRD patterns of (a) Aceh curcuma, (b) ethanol-curcumin, (c) triacetin-curcumin, (d) titanium dioxide, (e) titanium dioxide-Aceh curcuma 50 mg/L, (f) titanium dioxide-ethanol-curcumin 50 mg/L, and (g) titanium dioxide-triacetin-curcumin 50 mg/L composite materials

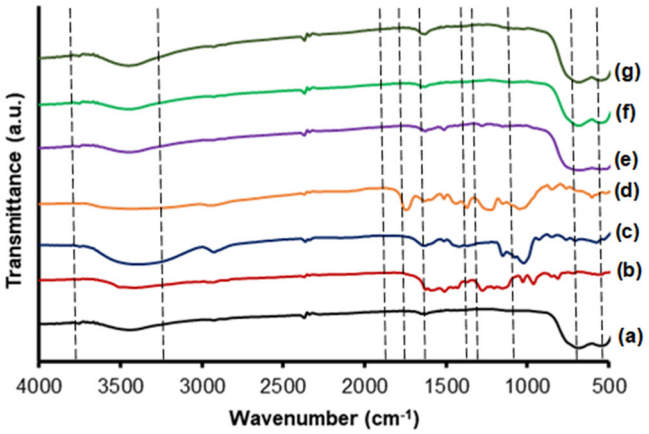

Fig 5. The FTIR spectra of (a) titanium dioxide, (b) Aceh curcuma, (c) ethanol-curcumin, (d) triacetin-curcumin, (e) titanium dioxide-Aceh curcuma 50 mg/L, (f) titanium dioxide-ethanol-curcumin 50 mg/L, and (g) titanium dioxide-triacetin-curcumin 50 mg/L composite materials

due to the presence of impregnated curcumin on the composite materials. In the previous reports, these weak absorption signals indicated the presence of natural compounds in the titanium dioxide [22,26]. Besides, the titanium dioxide signals, i.e., TiO–H, Ti–O–Ti, and Ti–O, were not significantly influenced by the presence of curcumin. This result agreed with the DR UV-vis and XRD data indicating that curcumin was impregnated on the surface of titanium dioxide.

The SEM micrographs of titanium dioxide and its composite materials are shown in Fig. 6. It was found that the impregnation of curcumin either from Aceh curcuma or ethanol-curcumin or triacetin-curcumin did not significantly change the surface morphology of the titanium dioxide. This result agreed with the DR UV-vis, XRD, and FTIR data. The distribution of the impregnated curcumin on titanium dioxide was evaluated through the elemental mapping of titanium dioxide and its composite materials shown in Fig. 7. The carbon (C) atoms (red color) appear clustered in several spots for TiO_2-curcuma samples and tend to be more evenly distributed in the composite materials for curcumin (Fig. 7(c) and 7(d)). This indicates a better particle distribution for curcumin compared to curcuma on TiO_2 surfaces. The better solubility of curcumin in the solvent system also resulted in better curcumin distribution (Fig. 7(d)). This is in line with the previous quantitative fact that the amount of curcumin in the triacetin-curcumin sample (2.56%) is higher than that in the ethanol-curcumin sample (2.43%).

The EDX analysis (Table 1) shows the presence of carbon atoms in the composite materials which come from the impregnated curcumin on the titanium dioxide's surface. The carbon atom percentages in the titanium dioxide-Aceh curcuma-50 mg/L composite material were much higher than titanium dioxide-ethanol-curcumin-50 mg/L and titanium dioxide-triacetin-curcumin-50 mg/L composite materials. This result was reasonable as Aceh curcuma contained not only curcumin but also other organic compounds, such as

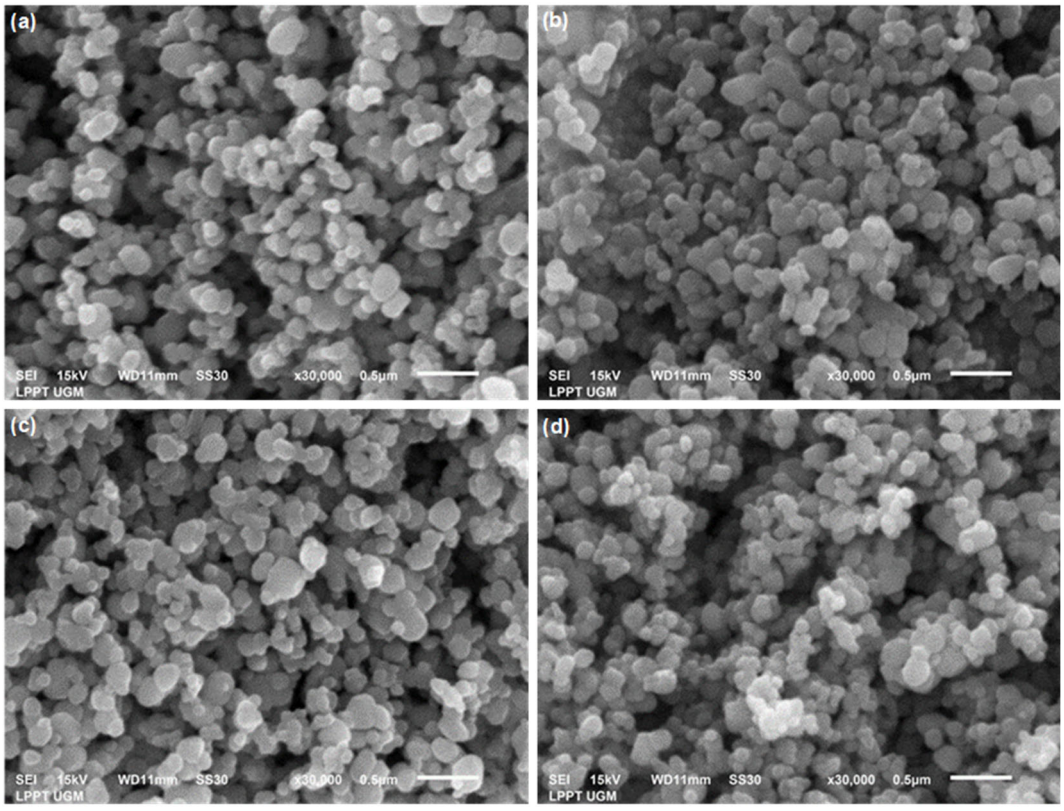

Fig 6. The SEM micrographs of (a) titanium dioxide, (b) titanium dioxide-Aceh curcuma 50 mg/L, (c) titanium dioxide-ethanol-curcumin 50 mg/L, and (d) titanium dioxide-triacetin-curcumin 50 mg/L composite materials

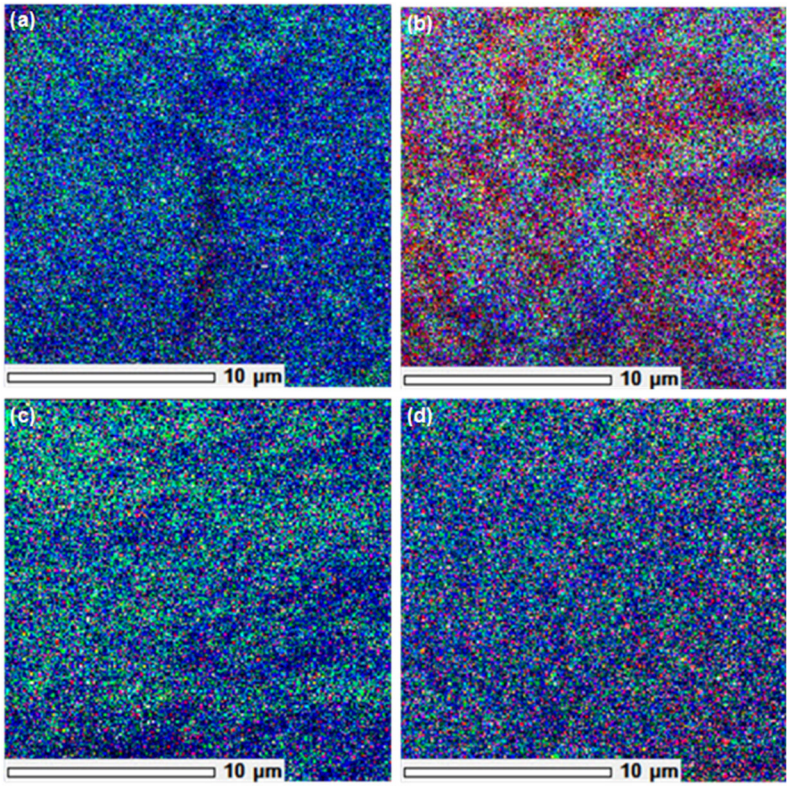

Fig 7. Elemental mapping of (a) titanium dioxide, (b) titanium dioxide-Aceh curcuma 50 mg/L, (c) titanium dioxide-ethanol-curcumin 50 mg/L, and (d) titanium dioxide-triacetin-curcumin 50 mg/L composite materials. Blue, green, and red colors represent titanium, oxygen, and carbon atoms

Table 1. The EDX results of titanium dioxide and its composite materials

Sample	%Atom		
	Ti	O	C
Titanium dioxide	27.16	72.84	-
Titanium dioxide-Aceh curcuma-50 mg/L	12.37	47.20	40.43
Titanium dioxide-ethanol-curcumin-50 mg/L	29.80	63.80	6.41
Titanium dioxide-triacetin-curcumin-50 mg/L	27.46	66.09	6.45

α-phellandrene, β-caryophyllene, turmerone, bisabolone, and sesquiphellandrene, that may be adsorbed on the surface of titanium dioxide. These compounds may result in clustering on the surface of titanium dioxide, as observed in the SEM mapping images.

From the quantitative analysis, it was found that titanium dioxide-Aceh curcuma contains 0.016–0.040 mg curcumin/g composite material. The titanium dioxide-ethanol-curcumin composite materials contain higher curcumin content of 0.093–0.218 mg/g composite material while the titanium dioxide-triacetin-curcumin composite materials contain a much higher curcumin content of 0.059–0.374 mg/g composite material. The highest content of curcumin in the titanium dioxide-triacetin-curcumin composite materials supports the deduction drawn from the SEM mapping data. Even though both ethanol-curcumin (2.43%) and triacetin-curcumin (2.56%) samples contain lower curcumin content compared to the Aceh curcuma sample (4.24%), the impregnated curcumin on titanium dioxide-ethanol-curcumin and titanium dioxide-triacetin-curcumin composite materials is higher due to the encapsulation process. The encapsulation of curcumin with carboxymethylcellulose and maltodextrin changes

the hydrophilicity of curcumin through host-guest complexation. Therefore, the curcumin complex could be impregnated onto the titanium dioxide surface through hydrogen bonds. The presence of hydrogen bond interactions was supported by the shift O–H signal at the FTIR data of the composite materials (3425–3387 cm^{-1}) compared to the bare titanium dioxide (3433 cm^{-1}). The plausible interaction of curcumin complex with carboxymethylcellulose and maltodextrin on the surface of titanium dioxide is displayed in Fig. 8.

In Vitro Antiradical Activity Measurement

The antiradical activity of the composite material was evaluated through an *in vitro* assay using DPPH as the artificial free radical. The antiradical activity of titanium dioxide, Aceh curcuma, curcumin-ethanol, curcumin-triacetin, and the composite materials is listed in Table 2. When the DPPH radical attracts a hydrogen atom and/or receives an electron from the antiradical agent, the color change occurs from purple to yellow. Because of that, DPPH has become the most common artificial free radical used in the *in vitro* antiradical activity assay due to its simple colorimetric quantification using a spectrophotometer [29]. The qualitative observation of the DPPH assay for the determination of the antiradical activity of the composite materials is shown in Fig. 9.

Aceh curcuma, ethanol-curcumin, and triacetin-curcumin gave antiradical activity of 75.12 ± 1.79%, 56.66 ± 0.25%, and 63.58 ± 0.20%, respectively. Aceh curcuma, ethanol-curcumin, and triacetin-curcumin

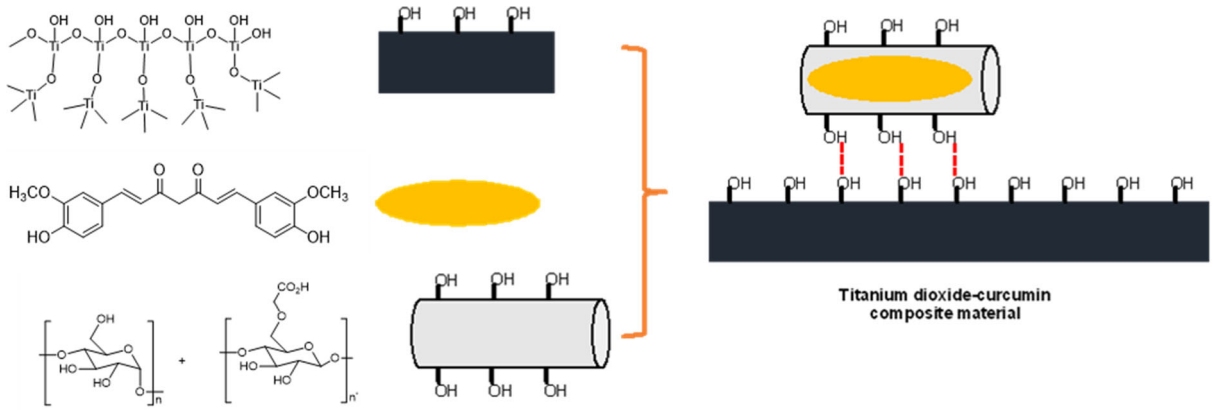

Fig 8. Plausible interaction of curcumin on the surface of titanium dioxide

Table 2. Antiradical activity of titanium dioxide, Aceh curcuma, curcumin-ethanol, curcumin-triacetin, and the composite materials against DPPH radicals

Sample	%Antiradical activity
Aceh curcuma	75.12 ± 1.79
Ethanol-curcumin	56.66 ± 0.25
Triacetin-curcumin	63.58 ± 0.20
Titanium dioxide	31.78 ± 1.48
Titanium dioxide-Aceh curcuma-5 mg/L	55.31 ± 0.63
Titanium dioxide-Aceh curcuma-25 mg/L	58.45 ± 2.03
Titanium dioxide-Aceh curcuma-50 mg/L	76.80 ± 0.65
Titanium dioxide-ethanol-curcumin-5 mg/L	49.66 ± 2.35
Titanium dioxide-ethanol-curcumin-25 mg/L	57.05 ± 2.43
Titanium dioxide-ethanol-curcumin-50 mg/L	73.74 ± 0.20
Titanium dioxide-triacetin-curcumin-5 mg/L	39.61 ± 1.36
Titanium dioxide-triacetin-curcumin-25 mg/L	62.03 ± 1.46
Titanium dioxide-triacetin-curcumin-50 mg/L	79.70 ± 1.33

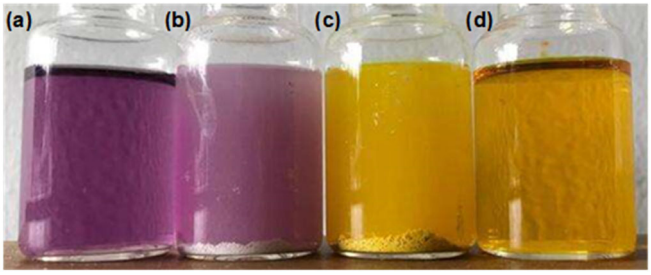

Fig 9. Photographed observation of DPPH solution (a) before and after the addition of (b) titanium dioxide, (c) titanium dioxide-curcumin composite material, and (d) Aceh curcuma as the antiradical agent

contained ArO–H functional group that could also donate its hydrogen atom to scavenge the DPPH radical. High antiradical activity of Aceh curcuma was indicated from the orange color solution composed of yellow color of DPPH and orange color of Aceh curcuma extract as shown in Fig. 9. The antiradical activity of Aceh curcuma was higher than triacetin-curcumin and much higher than ethanol-curcumin. This result was caused by the higher curcumin content in Aceh curcuma (4.24%) than curcumin-triacetin (2.56%) and curcumin-ethanol (2.43%). Furthermore, other bioactive compounds in the Aceh curcuma samples may act as antiradical agents. Even though Aceh curcuma contains curcumin in 1.74–1.66 times higher than the curcumin-ethanol and curcumin triacetin, the antiradical activity of curcumin-ethanol and curcumin triacetin was only 1.18–1.33 times lower than Aceh curcuma. This phenomenon could be caused by the prevention of curcumin aggregation in curcumin-ethanol and curcumin triacetin due to the encapsulation process thus, each impregnated curcumin molecule could serve as a hydrogen atom donor to the DPPH radical as previously reported [39]. A high aggregation tendency for curcuma impregnated onto titanium dioxide has also been detected in SEM mapping results (Fig. 7(b)).

On the other hand, the antiradical activity of unmodified titanium dioxide was 31.78 ± 1.48%. From the FTIR data, titanium dioxide had TiO–H functional groups, which could donate the hydrogen atom to deactivate the DPPH radical. However, since the antiradical activity was low, the color of the DPPH solution remained purple after 30 min incubation period. The antiradical activity of the composite material was in a range of 39.61 ± 1.36% to 79.70 ± 1.33%. Fig. 8(d) shows the DPPH solution color after the addition of titanium dioxide-Aceh curcuma-50 mg/L with an incubation period of 30 min. High antiradical activity of the composite material was shown from the disappearance of the purple color of DPPH chemicals. The antiradical activity is enhanced by increasing impregnated curcumin content. Titanium dioxide-Aceh curcuma, titanium dioxide-ethanol-curcumin and titanium dioxide-triacetin-curcumin composite materials contain 0.016–0.040, 0.093–0.218 and 0.059–0.374 mg curcumin/g composite material, respectively. Therefore, it is reasonable if titanium dioxide-Aceh curcuma (55.31 ± 0.63% to 76.80 ± 0.65%) and titanium dioxide-ethanol-curcumin (49.66 ± 2.35% to 73.74 ± 0.20%) exhibited lower antiradical activity than the titanium dioxide-triacetin-curcumin (39.61 ± 1.36% to 79.70 ± 1.33%).

It was also interesting to note that the antiradical activity of the composite material was higher than the antiradical activity of the titanium dioxide and curcumin samples. For example, the antiradical activity of titanium dioxide-Aceh curcuma-50 mg/L (76.80 ± 0.65%) was higher than titanium dioxide (31.78 ± 1.48%) and Aceh curcuma (75.12 ± 1.79%). Additionally, the antiradical activity of titanium dioxide-ethanol-curcumin-50 mg/L (73.74 ± 0.20%) was higher than titanium dioxide (31.78 ± 1.48%) and ethanol-curcumin (56.66 ± 0.25%). The antiradical activity of titanium dioxide-triacetin-curcumin-50 mg/L (79.70 ± 1.33%) was also higher than titanium dioxide (31.78 ± 1.48%) and triacetin-curcumin (63.58 ± 0.20%). These results indicated the synergistic effect of titanium dioxide and curcumin as the antiradical agent. Furthermore, the difference in the antiradical activity of titanium dioxide-ethanol-curcumin-50 mg/L with ethanol-curcumin (Δ = 17.08%) and titanium dioxide-triacetin-curcumin-50 mg/L with triacetin-curcumin (Δ = 16.22%) was higher than of titanium dioxide-Aceh curcuma-50 mg/L with Aceh curcuma (Δ = 1.68%) indicating that encapsulation process is crucial on the stability of curcumin on the composite material on its application as the antiradical agent.

■ CONCLUSION

Titanium dioxide-curcumin composite materials derived from Aceh curcuma and its extracts have been successfully prepared. The isolation and encapsulation of curcumin using ethanol and triacetin-ethanol-distilled water yielded orange-yellowish solids in 30.35% and 37.21% yield, respectively. TLC analysis revealed that the extracts contained curcumin, demethoxycurcumin, and bisdemethoxycurcumin. The curcumin content was quantified using a calibration method employing a UV-vis spectrophotometer at a fixed maximum wavelength of 420 nm. The Aceh curcuma contains 4.24% curcumin while the curcumin-ethanol and curcumin-triacetin contains 2.43% and 2.56% curcumin, respectively. These materials were further employed for the preparation of titanium dioxide-curcumin composite materials in 91–99% yield with curcumin content in a range of 0.016–0.374 mg/g composite material. The composite materials have been characterized by DR UV-vis, XRD, FTIR, and SEM-EDX-mapping analyses, which indicated that the curcumin complex with carboxymethylcellulose and maltodextrin was impregnated on the surface of titanium dioxide through hydrogen bonds. The *in vitro* antiradical activity assay of the composite material exhibited 39.61 ± 1.36% to 79.70 ± 1.33%, which could be higher than that of titanium dioxide (31.78 ± 1.48%), Aceh curcuma (75.12 ± 1.79%), ethanol-curcumin (56.66 ± 0.25%), and triacetin-curcumin (63.58 ± 0.20%) due to the synergistic effect of titanium dioxide and curcumin as the antiradical agents. It meant that both impregnation and encapsulation processes are critical for the antiradical activity and stability of curcumin on the surface of titanium dioxide.

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