Improvement of mechanical-antibacterial performances of AR/PMMA with TiO$_2$ and HPQM treated by N-2(aminoethyl)-3-aminopropyl trimethoxysilane

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Abstract
The mechanical and antibacterial properties of acrylic rubber/poly(methyl methacrylate) (AR/PMMA) blend at 10 to 50 wt% of AR content with non-treated and treated titanium dioxide (TiO$_2$) and 2-Hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) by N-2(aminoethyl)-3-aminopropyl trimethoxysilane were studied. The antibacterial property against Escherichia coli was evaluated. The results found that the mechanical properties of AR$^{t}$-TiO$_2$/PMMA and AR$^{t}$-HPQM/PMMA blend were higher than that of the AR$^{t}$TiO$_2$/PMMA and AR$^{t}$HPQM/PMMA blend. For antibacterial property, the AR$_{HPQM}$/PMMA and AR$_{HPQM}$/PMMA blend could act as the antibacterial material, while the AR$^{t}$TiO$_2$/PMMA blend did not show. However, the AR$_{TiO2}$/PMMA blend could inhibit bacterial cell growth with 10 to 30 wt% of AR content. The recommended compositions of AR$_{TiO2}$/PMMA blend, which improved both mechanical and antibacterial properties, were 10 to 30 wt% of AR and were 10 to 50 wt% of AR for AR$_{HPQM}$/PMMA. Moreover, the UV radiation increased the antibacterial properties by the destruction of the interaction in treated TiO$_2$ and HPQM and improved the antibacterial performance of AR$_{TiO2}$/PMMA and AR$_{HPQM}$/PMMA blend.

Keywords
Acrylic rubber, Antibacterial performance, HPQM, Poly (methyl methacrylate), Silane coupling agent, Titanium dioxide

Introduction
The toughened PMMA was produced by the addition with elastomer, including acrylic rubber$^{1,2}$, acrylonitrile butadiene styrene$^{3}$, epoxidized natural rubber (ENR)$^{4}$, and poly(acrylonitrile-co-styrene) (ASA)$^{5}$. The rubber phase adsorbed the impact energy and generated the plastic deformation in the polymer blend, resulting in the toughness of PMMA$^{6}$. The toughened PMMA can be used more widely than PMMA. The products from toughened PMMA, such as shower cabin, the cover sheet for sanitaryware, are often at risk of the bacteria accumulation on their surface. Therefore, the various additives, including titanium dioxide (TiO$_2$)$^{1,7,8}$, zinc oxide (ZnO)$^{9}$, chitosan$^{10}$, and 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM)$^{11}$, are needed in order to extend this application. HPQM is an inorganic antibacterial agent, which is nontoxic to the human body and non-endocrine disruptor. HPQM could inhibit the cell wall synthesis and the DNA synthesis, resulting in cell...
death.\(^{12}\) Our previous study\(^{13}\) found that the mechanical properties of the AR\(^{TiO2}\)/PMMA blend decreased with increasing TiO\(_2\) content due to the attraction between TiO\(_2\) aggregation by the van der Waals force. Studies have pointed out significant problems, including the reduced mechanical properties of AR/PMMA by the TiO\(_2\) agglomeration. Therefore, the diminished TiO\(_2\) agglomeration by surface treatment with the silane coupling agents was interested.

Silane coupling agents consist of the silica atom and functional group, which could interact with the both organic and inorganic components. Their functional group interacts with the hydroxyl group on the TiO\(_2\) surface.\(^{2,14,15}\) It developed the interaction between the polymer and TiO\(_2\) particles and generated the cross-linked interphase region.\(^{16}\) Work by Xiao et al.\(^{15}\) studied poly (dodecafluoroheptyl methacrylate) (PDFMA) filled with non-treated and treated TiO\(_2\) by 3-(trimethoxysilyl) propylmethacrylate. The results found that the dispersibility of treated TiO\(_2\) in PDFMA was better than that of the non-treated TiO\(_2\) due to the chemical interaction between treated TiO\(_2\) and PDFMA. The chemical interaction between TiO\(_2\) and silane coupling agent was investigated by Zhao et al.\(^{17}\) who claimed that the TiO\(_2\) and silane coupling agent could interact with each other through Ti-O-Si bonding.\(^{18-21}\) Occurrences of the good dispersibility and chemical bonding of treated TiO\(_2\) were claimed to improve the mechanical properties of the matrix. This claim was in good agreement with the findings of Ambrosio et al.\(^2\) who found that the treated TiO\(_2\) increased the mechanical properties of polyamide11 (PA11) due to the improvement of the interfacial adhesion. Regarding the effect of antibacterial property, the non-treated TiO\(_2\) could generate the reactive oxygen species (ROS), producing \(O_2^-\), \(HOO^-\), and \(HO^-\) in the dark environment and \(HO\) in the UV environment.\(^{22}\)

However, the effect of silane coupling agent on the mechanical and antibacterial properties of HPQM in the matrix is still not investigated.

Based on the literature review, the TiO\(_2\) particles have the hydroxyl group on their surface, which increased the TiO\(_2\) agglomeration. The TiO\(_2\) agglomeration caused stress concentration and reduced the performance of ROS generation, resulting in the reduction of mechanical and antibacterial properties. In the case of HPQM, according to our previous work,\(^11\) the functional group could interfere with the miscibility of the AR and PMMA phase and decreased the mechanical property. Thus, the aim of this present study was to enhance the mechanical and antibacterial properties of the AR/PMMA blend filled with the surface treatment of TiO\(_2\) and HPQM by N-2(2-aminoethyl)-3-aminopropyl trimethoxysilane or KBM603. As recommended by the previous study,\(^{13}\) the non-treated and treated of TiO\(_2\) and HPQM content blend was fixed at 1.5 parts per hundred (pph) in AR/PMMA blend and incorporated with AR phase for 10 to 50 wt%. The tensile properties and impact strength of AR/PMMA blend with non-treated and treated TiO\(_2\) and HPQM were investigated. The antibacterial performance against Escherichia coli (ATCC 25922) was evaluated using the standard method of JIS Z2801:2010. The effect of UV radiation exposure on the antibacterial performance was recognized.

### Materials and methods

#### Chemicals and materials

Acrylic rubber (AR) grade AR 71 and poly (methyl methacrylate) (PMMA) grade MD001 were supplied from Zeon Chemicals (Thailand) Co., Ltd and Mitsubishi Rayon Co., Ltd, respectively. The rutile titanium dioxide (TiO\(_2\)) particles act as a carrier and an antibacterial agent with an average primary particle size of 11.2 \(\mu m\) which was acquired from Chanjao Longevity Co., Ltd. A 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) grade BA 101 as an antibacterial agent was kindly provided from Koventure Co., Ltd (10 wt% of HPQM in solution).\(^{12}\) N-2(aminooethyl)-3-aminopropyl trimethoxysilane (Mw = 222.4) was used as the silane coupling agent for TiO\(_2\) and HPQM, which applied from Shin-Etsu Chemical, Japan. The antibacterial agents were treated by the silane coupling agent called N-2(2-aminoethyl)-3-aminopropyl trimethoxysilane (KBM603), which was supplied by Shin- Etsu Chemical Co., Ltd (Tokyo).

#### Preparation of treated TiO\(_2\) and HPQM by the silane coupling agent

TiO\(_2\) particles were cleaned by sonication in deionized water for an hour to break up any weakly flocculated particles and then dried in a hot-air oven at 60\(^\circ\)C for 24 h. After that, the TiO\(_2\) and HPQM (10 wt% of HPQM in water) were added to a 1 wt% of KBM603 in toluene for 1 h and then dried at 60\(^\circ\)C for 48 h. Then, the solution, as called a treated TiO\(_2\) and treated HPQM was stirred at room temperature for 4 h at 50\(^\circ\)C.

#### Specimen preparation

The blends were prepared by mixing acrylic rubber with non-treated and treated of TiO\(_2\) and HPQM at 1.5 parts per hundred (pph), which was called “modified AR”. The modified AR compounds at loadings from 10 to 50 wt% were then blended with PMMA via a melt blending process using a twin-screw extruder.
at a mixing temperature of 200 to 230°C. The material formulas are given in Table 1. Sheets of the blends for antibacterial performance testing were prepared using a hot compression molding at an operating temperature of 230°C, a holding pressure of 15 N/mm², and an operating time of 15 min. The sheets had a thickness of approximately 2 mm. Sheets of the blends for mechanical properties testing were prepared using an injection molding machine. The samples were a dumbbell shape according to the ISO 527–2:1993 standard.

**UV radiation exposure**

The rectangle samples of the AR–TiO₂/PMMA and AR–HPQM/PMMA blends were exposed to UV radiation for 24 h using a QUV accelerated-weathering tester (Q-LAB, Westlake, USA), in accordance with the ISO 4892–3:2016 standard procedure. The wavelength of UV-A was 320–400 nm with an intensity of 0.77 W/m²/nm at 50°C. These samples were tested the antibacterial performance.

**Mechanical properties**

The mechanical properties, including impact strength, tensile toughness, tensile modulus, tensile strength, and elongation at break of the AR/PMMA blends with non-treated and treated of TiO₂ and HPQM were tested. The notched impact strength was measured using a pendulum impact tester (5 joule) (HIT-5J, ZwickRoell, Germany), following the ISO 179–1:2010 standard test method. Tensile testing was conducted according to the ISO 527–2:1993 standard using a universal testing machine (Model H50kS, Tinius Olsen, UK). The testing conditions were a gauge length of 50 mm and a crosshead speed of 50 mm/min. At least five replicates were averaged for the reported value.

**Qualitative and quantitative determination of antibacterial performance**

The antibacterial performance of non-treated and treated TiO₂ and HPQM of AR/PMMA before and after UV radiation exposure against *Escherichia coli* (ATCC 25922) was evaluated using the standard method of JIS Z2801:2010. The surface-sterilized specimens (2.5 × 2.5 mm) were placed on sterilized Petri dishes. An inoculum of bacterial cell suspension in Nutrient Broth (NB) at a cell turbidity of OD₆₀₀≈0.1 was dropped onto the specimen surface and then covered with sterilized polypropylene film. After incubation at 37°C for 24 h, the bacterial cell suspension on the specimen surface was washed with 10 mL of Soya

| Table 1. Material formulas.20ARTiO2/PMMA |
|------------------------------------------|
| **Formula**                | **PMMA (wt%)** | **AR (wt%)** | **TiO₂ (pph)** | **HPQM (pph)** | **KBM603 (%)** |
| 10AR/PMMA                  | 90             | 10           | –              | –              | –              |
| 10AR–TiO₂/PMMA             | –              | 1           | 1.5            | –              | –              |
| 10AR–HPQM/PMMA             | –              | 1.5         | –              | 1.5            | –              |
| 10AR–TiO₂/PMMA             | –              | 1.5         | 1.5            | –              | 1              |
| 10AR–HPQM/PMMA             | 80             | 20          | –              | –              | –              |
| 20AR/PMMA                  | –              | 1           | 1.5            | –              | –              |
| 20AR–TiO₂/PMMA             | –              | 1.5         | –              | 1.5            | –              |
| 20AR–HPQM/PMMA             | –              | 1.5         | –              | –              | 1              |
| 20AR–HPQM/PMMA             | –              | 1.5         | –              | –              | –              |
| 30AR/PMMA                  | 70             | 30          | –              | –              | –              |
| 30AR–TiO₂/PMMA             | –              | 1           | 1.5            | –              | –              |
| 30AR–HPQM/PMMA             | –              | 1.5         | –              | –              | 1              |
| 30AR–HPQM/PMMA             | 1.5            | –           | –              | –              | 1              |
| 30AR–HPQM/PMMA             | –              | 1.5         | –              | –              | –              |
| 40AR/PMMA                  | 60             | 40          | –              | –              | –              |
| 40AR–TiO₂/PMMA             | –              | 1           | 1.5            | –              | –              |
| 40AR–HPQM/PMMA             | –              | 1.5         | –              | –              | 1              |
| 40AR–HPQM/PMMA             | 1.5            | –           | –              | –              | –              |
| 50AR/PMMA                  | 50             | 50          | –              | –              | –              |
| 50AR–TiO₂/PMMA             | –              | 1           | 1.5            | –              | –              |
| 50AR–HPQM/PMMA             | –              | 1.5         | –              | –              | 1              |
| 50AR–HPQM/PMMA             | 1.5            | –           | –              | –              | –              |
Casein Digest Lecithin Polysorbate (SCDLP) broth. Bacterial cell suspension in SCDLP was diluted in 0.85% NaCl and the appropriate dilutions were spread on nutrient agar (NA) plates. After incubation at 37°C for 24 h, the number of bacterial colonies appearing on the NA plates from the specimens with (Ni) and without TiO2 addition (N0) was counted. The values of antibacterial activity (R) of the blends were calculated by the following equation (1).^{23}

\[
\text{Antibacterial activity (R)} = \log \frac{N_0}{N_i}
\]

A value of antibacterial activity (R value) which is equal to or higher than 2.0 indicates greater than 99.9% bacterial reduction and the sample is accepted as an antibacterial material according to the standard of JIS Z2801:2010.

**Results and discussion**

**Mechanical properties of AR/PMMA blends filled with non-treated and treated TiO2 and HPQM**

Figure 1 shows the tensile properties of the AR/PMMA and AR/PMMA blends with non-treated and treated TiO2. Figure 1(a) shows that the addition of non-treated TiO2 decreased the tensile strength of the AR/PMMA blend at 10 and 20 wt% of AR contents and the effect was reverse at 30–50 wt% of AR contents. The explanation of the decreased in tensile strength would be related to the interference of the non-treated TiO2 on the interaction between AR and PMMA phases. PMMA and AR phases could be compatible due to the dipole–dipole interaction between the carbonyl group of PMMA and AR phase.\(^{24}\) Figure 2 shows the FTIR spectrum of PMMA, AR, and 50AR/PMMA blend. Figure 2(a) shows the FTIR spectrum of PMMA. The peaks at 2962, 2951, 2844, 1141, 1190 and 1238 cm\(^{-1}\) can be attributed to the stretching vibration mode of –CH\(_3\), –C–H, –CH\(_2\)–, –O–CH\(_3\), –C–O– and –C–O– (in carboxylic acid), respectively.\(^{25,26}\) The peaks at 1066, 986 and 841 cm\(^{-1}\) are the characteristic absorption vibration of PMMA. The C–H bonded bending of CH\(_3\) group is shown in peak at 1435 cm\(^{-1}\).\(^{25}\) The two peaks at 1387 and 754 cm\(^{-1}\) can be assigned to the methylene group vibration.\(^{25}\) The peak at 1722 cm\(^{-1}\) shows the presence of the acrylate carbonyl group.\(^{26}\) The FTIR spectrum of AR is presented in Figure 2(b). The peak at 2985 cm\(^{-1}\) represents the C–H stretching vibration of OCH\(_2\)CH\(_3\), while peak at 2934 represents the CH\(_2\) stretching vibration of OCH\(_2\)CH\(_3\).\(^{27}\) Two peaks of 1446 and 1378 cm\(^{-1}\) can be attributed to the CH\(_3\) asymmetric deformation vibration.

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**Figure 1.** Tensile properties of AR/PMMA (white) and AR/PMMA blends with non-treated (black) and treated (pattern) of TiO2: tensile strength, (b) percentage of elongation at break, and (c) tensile toughness.
of OCH$_2$CH$_3$ and the peaks at 1247 and 1152 cm$^{-1}$ represent C–O–C asymmetric stretching vibration and R–C–O–R symmetric stretching vibration, respectively. Two peaks of 1096 and 1022 cm$^{-1}$ can be assigned to skeletal vibration of acrylic acid. The peak at 1726 cm$^{-1}$ shows the presence of the carbonyl group. However, the functional groups of 50AR/PMMA blend similar to PMMA and AR, except the peak which represents the carbonyl group. It changed to 1725 cm$^{-1}$ due to the weak bonding between functional group. However, the change of proton of AR and PMMA was examined by the chemical shift positions or $\delta$ values of $^1$H-NMR spectrum.

Figure 3(a) to (c) shows the $^1$H-NMR spectrum of PMMA, AR, and 50AR/PMMA, respectively. The assignments of peaks of protons and $^1$H-NMR spectra of PMMA are shown in Figure 3(a). The methyl protons of PMMA (at b region) were observed at chemical shifts around of $\delta$1.022 and $\delta$0.846, whereas protons at c region, the higher chemical shifts at $\delta$3.645 and $\delta$3.597 were found because of the presence of the oxygen atom attached to its neighboring carbon atom. Moreover, the $\delta$ values of protons attached to the carbon atom in the main chain (–CH$_2$–) appeared at 1.732 ppm (at a region). In the case of the AR, the protons which attached to oxygen atom (at f and g region) appeared at $\delta$4.117.
and δ1.249, respectively. A proton opposite with ethoxy group was appeared at δ2.291. However, the δ values of proton attached to the carbon atom in the main chain (–CH2) appeared at 1.548 ppm (at d region), as shown in Figure 3(b). Considering the H1-NMR spectrum of 50AR/PMMA blend (Figure 3(c)), the δ values of proton attached to the carbon atom in the main chain shifted from 1.732 ppm to 1.642 ppm for PMMA, while shifted from 1.548 ppm to 1.621 ppm for AR. According to the literature, the change of FTIR and NMR spectra of AR, PMMA, and 50AR/PMMA blend could indicate the interaction between PMMA and AR phase. Figure 4 shows the possible interactions between AR and PMMA phases. The dipole–dipole interaction between carbonyl group of PMMA and AR could form in 50AR/PMMA blend.

The addition of TiO2 in the AR/PMMA blend could disturb the interaction between AR and PMMA phases. The possible mechanism is shown in Figure 5(a), and the hydroxyl group on the TiO2 could react with the carbonyl group of the AR phase. This claim was in good agreement with the findings of Liu et al. They claimed that TiO2 could interfere with the interaction of poly(ethylene oxide) (PEO) and lithium tetrafluoroborate (LiBF4) by the formation of the hydrogen bonding between ether atom of PEO and a hydroxyl group of TiO2. Moreover, the non-treated TiO2 could form the agglomeration structure and acts as stress concentration, caused the interference of impact force transfer. According to our previous result, the stress concentration was diminished by the uniform distribution of TiO2 particles in the blend with high AR content, resulting in the slight increase in the tensile strength with the addition of 30 to 50 wt% of AR contents. Considering the tensile strength of the AR+TiO2/PMMA blend, it was higher than that of the AR+TiO2/PMMA blend. Because the KBM603 molecules could diminish the hydrophilic properties on the TiO2 surface and form the chemical bonding with the AR phase, as shown in Figure 5(b). The silanol group of KBM603 could interact with the hydroxyl group on non-treated TiO2 particle and the amino group could interact with the chlorine reactive site of the AR chain, resulting in the increase of tensile strength. Many studies have claimed that the rubber–filler interaction was enhanced by the appropriate silane coupling agent.

Figure 1(b) and (c) shows the percentage of elongation at break and tensile toughness of AR/PMMA and AR/PMMA blend with non-treated and treated TiO2, respectively. Similar to the tensile strength in Figure 1(a), the elongation at break and tensile toughness of AR+TiO2/PMMA blend were lower than those of the AR/PMMA blend only at 10 and 20 wt% of AR content, because the dipole–dipole interaction of AR/PMMA blend was interfered by the non-treated TiO2. Moreover, the non-treated TiO2 could form the agglomeration structure and act as stress concentration during the tensile test. However, this interference was diminished in the blend with high AR contents (30–50 wt%), as mentioned earlier. The elongation at break and tensile toughness of the AR+TiO2/PMMA blend were higher than that of the AR+TiO2/PMMA blend. It was associated with the influence of the chemical interaction in AR/PMMA blend by KBM603 molecule. AR and PMMA phase was compatible by the polar interaction. Meanwhile, the macromolecule of the AR/PMMA phase was connected by the treated TiO2. In other words, the treated TiO2 could form the chemical bonding in the AR/PMMA blend, which was stronger than that of the polar bonding. This is probably why the elongation at break and tensile toughness of the AR+TiO2/PMMA blend was higher than that of the AR+TiO2/PMMA blend. Moreover, the KBM603 decreased the agglomeration of TiO2 particle, resulting in decreasing of the stress concentration in AR/PMMA blend.

Figure 6(a) shows the tensile strength of AR/PMMA and AR/PMMA with non-treated and treated HPQM. It was observed that the tensile strength of the AR+HPQM/PMMA blend with 10 and 20 wt% of AR contents was lower than that of the AR/PMMA blend. Considering the chemical structure of the non-treated HPQM molecule, it has an amino group in the structure as shown in Figure 7(a). The amino group could interact with the carbonyl groups of the AR molecule via hydrogen bonding, which interfered the compatibility between AR and PMMA phases. It would be noticed that the tensile strength of AR+HPQM/PMMA blend with 30 to 50 wt% of AR content was higher than that of the AR/PMMA blend, this being associated with the influence of the crosslink structure in AR phase by the reaction between HPQM solution and AR molecules. Regarding the effect of treated HPQM, the tensile strength of AR+HPQM/PMMA blend was
Figure 5. Schematic of the interaction of (a) non-treated and (b) treated TiO₂ particle in AR/PMMA blend.

Figure 6. Tensile properties of AR/PMMA (white) and AR/PMMA blends with non-treated (black) and treated (pattern) of HPQM; (a) tensile strength, (b) percentage of elongation at break, and (c) tensile toughness.
higher than that of the AR$^{\text{HPQM}}$/PMMA blend because the silanol group of the KBM603 molecule could interact with the carboxylic salt of non-treated HPQM molecule, as shown in Figure 7(b). Moreover, the amino group of KBM603 could interact with the chlorine reactive site of AR chain, as expected, caused the enhancement of tensile strength. The percentage of elongation at break and tensile toughness of AR/PMMA and AR/PMMA blend with non-treated and treated HPQM is shown in Figure 6(b) and (c), respectively. This suggests that the elongation at break and tensile toughness of AR$^{\text{HPQM}}$/PMMA blend with 10 and 20 wt% of AR content were lower than those of the AR/PMMA blend due to the interference of HPQM molecules. According to our previous work, this interference was diminished by the crosslink structure in AR phase by the reaction between HPQM and AR molecules. Moreover, the addition of treated HPQM in AR/PMMA blend enhanced the elongation at break and tensile toughness, due to the chemical interaction in AR/PMMA blend by KBM603 molecule, as discussed earlier. Thus, it could be claimed that the KBM603 molecule acts as the silane coupling agent for TiO$_2$ particle and HPQM molecules and the crosslinker for AR/PMMA blend.

However, it was noticeable that the AR/PMMA blend with 10 and 20 wt% of AR content with non-treated and treated TiO$_2$ and HPQM shows the high tensile strength, but the elongation at break and tensile toughness were low. Meanwhile, the tensile strength of AR/PMMA blend with 30 to 50 wt% of AR content was low, but the elongation at break and tensile toughness were high. The explanation of these results would be related to phase reversion, which affected the properties of the AR/PMMA blend. The morphology of AR/PMMA blend with low AR content was the AR dispersed in PMMA matrix phase. Therefore, the properties of the AR/PMMA blend were controlled by the PMMA phase (high tensile strength, low elongation at break, and tensile toughness). However, the AR/PMMA blend with high AR content (30 to 50 wt% of AR content) in AR/PMMA blend changed the morphology to the co-continuous phase between AR and PMMA. If so, it can be postulated that the properties...
of AR/PMMA blend with high AR content were controlled by the AR phase. In other words, they were a rubber-like material, resulting in the low tensile strength and the high elongation at break and tensile toughness. The study of Amoabeng et al. observed the morphology of polyisobutylene (PIB) and polyethylene oxide (PEO) blend. They found that the co-continuous phase of the PEO/PIB blend has occurred when adding equal or higher than 30 wt% of PEO content. Moreover, the decreasing of the tensile properties of AR\textsuperscript{TiO2}/PMMA and AR\textsuperscript{HPQM}/PMMA blend as compared with AR/PMMA blend did not pronounce with 30 to 50 wt% of AR content. The explanation for the AR\textsuperscript{TiO2}/PMMA blend relates to the uniform force transfer. According to our previous work, the distribution of TiO\textsubscript{2} particle in AR/PMMA blend at high AR content was more uniform than that of the low content, which could regularly distribute force during the tensile test. In the case of the AR\textsuperscript{HPQM}/PMMA blend, this would probably be caused by the chemical interaction of the HPQM and AR phase. The amino group of HPQM molecule could interact with the chlorine reactive site of AR phase and form the chemical interaction with the AR phase, resulting in the increase of tensile properties.

Figure 8(a) and (b) shows the impact strength of AR/PMMA and AR/PMMA blends with non-treated and treated TiO\textsubscript{2} and HPQM, respectively. The impact strength depends on the energy consumption for damage PMMA and AR phase,\textsuperscript{48,49} which differs from the tensile toughness. It was seen that the impact strength of AR\textsuperscript{TiO2}/PMMA was lower than that of the AR/PMMA blend because non-treated TiO\textsubscript{2} particle was not compatible with the AR phase, caused the interference of the impact force transfer.\textsuperscript{13}

For the impact strength of the AR\textsuperscript{TiO2}/PMMA blend, it was higher than that of the AR\textsuperscript{TiO2}/PMMA. It could be associated with the crosslinked structure in the AR phase from treated-TiO\textsubscript{2} which could adsorb the impact force during the test. In the case of AR\textsuperscript{HPQM}/PMMA, the impact strength tended to be higher than that of AR/PMMA. According to the earlier discussion, the amino group of the HPQM molecule could form the crosslinked structure by the interaction with the chlorine reactive site group of the AR phase. If so, it can be postulated that the impact force was adsorbed by their crosslink structure. However, the impact strength of the AR\textsuperscript{HPQM}/PMMA blend tends to be higher than that of the AR\textsuperscript{HPQM}/PMMA blend. According to the scheme, as shown in Figure 7(b), the KBM603 molecule could interact with chlorine reactive site of AR phase and form the crosslinked structure, which adsorbed the impact force.\textsuperscript{5,50–52} The evidence, which investigated the interference of TiO\textsubscript{2} and HPQM, was the FTIR spectrum at the carbonyl group position. Figure 9 shows the FTIR spectrum of the 50AR/PMMA, 50AR\textsuperscript{TiO2}/PMMA, and 50AR\textsuperscript{HPQM}/PMMA. The results show that the FTIR spectra of the carbonyl group of the 50AR/PMMA phase shift from 1723 cm\textsuperscript{-1} to 1725 cm\textsuperscript{-1} of the 50AR\textsuperscript{TiO2}/PMMA, and AR\textsuperscript{HPQM}/PMMA, which supported the occurrence of the weak interaction between AR phase and the antibacterial agents (TiO\textsubscript{2} and HPQM). It could be concluded that the interference of the antibacterial agent decreased the compatibility between PMMA and AR phases, and this resulted in the discontinuous force transfer during the impact test.

Antibacterial performance of AR/PMMA blends filled with non-treated and treated TiO\textsubscript{2} and HPQM

The quantitative antibacterial activities using R value of AR/PMMA blend with non-treated and treated
TiO$_2$ and HPQM against the growth of *E. coli* using JIS Z2801 specifications are given in Figure 10. If the R value is equal to or higher than 2.0, bacterial reduction approaches 99.9%, and the sample is accepted as an antibacterial material. It was seen that the AR$^{\text{TiO}_2}$/PMMA blend did not act as the antibacterial material. However, the R-value of the AR$^{\text{t-TiO}_2}$/PMMA blend was higher than 2.0, as shown in Figure 10(a). Because the chemical reaction of the AR phase and treated TiO$_2$ particle established the large free volume between the AR-PMMA molecule, which increases the flexibility in AR/PMMA blend. Work by Gali et al. claimed that TiO$_2$ could generate O$_2^•$, HO$_2$ and HO$^•$ in the dark due to dissolved oxygen. Thus, it can be speculated that the oxygen from the environment and bacterial suspension could support the ROS generation from TiO$_2$. Therefore, the ROS could move to contact with bacteria cell by the free volume of the AR/PMMA blend. However, the R value of AR$^{\text{t-TiO}_2}$/PMMA blend at 40 and 50 wt% of AR content slightly decreased. According to this result, the TiO$_2$ particles were embedded under the sample surface. Considering the morphology of AR/PMMA blend with low AR contents, 10 to 30 wt% in this case, the AR was a dispersed phase in PMMA matrix. The treated TiO$_2$ particles in the AR dispersed phase could interact with dissolved oxygen and generate ROS to inhibit bacteria cell growth. Meanwhile, the co-continuous morphology demonstrated the AR/PMMA blend with high AR contents (40 and 50 wt%). Some of the treated TiO$_2$ particles were embedded underneath the sample, which reduced the interaction between TiO$_2$ particles and dissolved oxygen. Therefore, the inhibition of bacteria cell growth by ROS decreased. Nevertheless, it was noted that the R value of AR$^{\text{t-TiO}_2}$/PMMA blend after exposure to UV radiation was higher than 2.0 and was higher than that of the AR$^{\text{TiO}_2}$/PMMA, because the excess ROS was increased by the photocatalysis process from TiO$_2$ particle.

Figure 10(b) shows the antibacterial activities of AR/PMMA blend with non-treated and treated HPQM against the growth of *E. coli*. It was observed that the R value of AR$^{\text{HPQM}}$/PMMA and AR$^{\text{t-HPQM}}$/PMMA blend was higher than 2.0. HPQM molecules are the organic material which solutes in the water, and they could penetrate throughout the specimen to contact with bacteria cell wall by the stress concentration gradient theory. In the case of the effect of UV radiation, the R value of AR$^{\text{t-HPQM}}$/PMMA blend was still higher than 2.0, because the HPQM and KBM603 molecule could form the weak polar interaction. After exposure to UV radiation, the polar interaction of treated HPQM was destroyed, which supported the generation of HPQM molecule throughout the specimen. It could be concluded that KBM603 was recommended for the treatment of TiO$_2$ and HPQM to improve the mechanical properties for all
AR/PMMA content. Considering the antibacterial performance of AR/PMMA blend, the treated TiO₂ and HPQM by KBM603 recommended for the hygiene products which were exposed to UV radiation.

Conclusions

The addition of non-treated TiO₂ and HPQM decreased the mechanical properties of AR/PMMA blend, whereas the treated of TiO₂ and HPQM by KBM603 in AR/PMMA blend increased. The treatment of TiO₂ and HPQM increased the free volume and flexibility in AR/PMMA blend due to the chemical reaction. The interaction between PMMA and AR phase was provided by FTIR and 1H-NMR. Considering the antibacterial performance, the AR/PMMA blend with non-treated and treated HPQM could act as the antibacterial material. Therefore, the AR₃HPQM/PMMA blend with 10 and 20 wt% of AR content was recommended for the sanitarywears, which demand the high tensile strength and toughness, such as the shower cabin. Meanwhile, the AR₁HPQM/ PMMA blend with 30 to 50 wt% of AR content was recommended for the cover sheet of the shower bath, which needs high elongation during the processing. Meanwhile, the AR₁TiO₂/PMMA blend did not show the antibacterial performance, but the AR₁TiO₂/ PMMA blend could inhibit bacterial cell growth with 10 to 30 wt% of AR content. Therefore, the AR₁TiO₂/ PMMA blend with 10 to 30 wt% of AR content was recommended for the sanitarywears, which demand the high tensile strength and toughness. Moreover, the treated TiO₂ and HPQM by KBM603 recommended for the hygiene products were exposed to UV radiation for all AR/PMMA content.

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References

1. Alrahlah A, Fouad H, Hashem M, et al. Titanium oxide (TiO₂)/polymethylmethacrylate (PMMA) denture base nanocomposites: mechanical, viscoelastic and antibacterial behavior. Materials 2018; 11: 1–15.
2. Ambrósio JD, Balarim CVM and De-Cardvalho GB. Preparation, characterization, and mechanical/tribological properties of polyamide 11/titanium dioxide nanocomposites. Polym Compos 2016; 37: 1415–1424.
3. Haddadi E, Choupani N and Abbasi F. Experimental investigation on the mixed-mode fracture of rubber-toughened PMMA using essential work of fracture method. Eng Fract Mech 2016; 162: 112–120. 10.1016/j.engfracmech.2016.05.011
4. Nakason C, Pankieng Y and Kaesaman A. Rheological and thermal properties of thermoplastic naturak rubbers based on PMMA/EPDM blends. J Appl Polym Sci 2004; 92: 3561–3572.
5. Asaletha R, Kumarana MG and Thoma S. Thermoplastic elastomers from blends of polystyrene and natural rubber morphology and mechanical properties. Eur Polym J 1999; 35: 253–271.
6. Association JS JIS Z2801 antibacterial products in test for antibacterial activity and efficacy. Japan: Japanese Standards Association, 2010, p.27.
7. Shen SC, Letchmanan K, Chow PS, et al. Antibiotic elution and mechanical property of TiO₂ nanotubes functionalized PMMA-based bone cements. J Mech Behav Biomed Mater 2019; 91: 91–98.
8. Sodagar A, Khalil S, Kassaei MZ, et al. Antimicrobial properties of poly (methyl methacrylate) acrylic resins incorporated with silicon dioxide and titanium dioxide nanoparticles on cariogenic bacteria. J Orthodont Sci 2016; 5: 7–13.
9. Sathy S, Murthy PS, Devi VG, et al. Antibacterial and cytotoxic assessment of poly(methyl methacrylate) based hybrid nanocomposites. Mater Sci Eng C Mater Biol Appl 2019; 100: 886–896.
10. Tan H, Peng Z, Li Q, et al. The use of quaternised chitosan-loaded PMMA to inhibit biofilm formation and downregulate the virulence-associated gene expression of antibiotic-resistant Staphylococcus. Biomater 2012; 33: 365–377.
11. Tangudom P, Wimolmala E, Prapagdee B, et al. Mechanical properties and antibacterial performance of PMMA toughened with acrylic rubber containing 2-hydroxypropyl-3-piperazinyl-quinoline carboxylic acid methacrylate (HPQM) and HPQM absorbed on TiO₂ particles. Polym Test 2019; 79: 106023.
12. Microsciencetech. *Technical data sheet: BCA101A0*. www.mst21.com (accessed 29 May 2000).
13. Tangudom P, Wimolmala E, Prapagdee B, et al. Material formulations for AR/PMMA and AR-TiO$_2$/PMMA blends and effects of UV radiation and TiO$_2$ loading on mechanical and antibacterial performances. *Polymer* 2018; 57: 1963–1976.
14. Wang L, Jiang X, Wang C, et al. Titanium dioxide grafted with silicone coupling agents and its use in blue light curing ink. *Color Technol* 2019; 1: 1–8.
15. Xiao Z, Guo P and Sun N. Preparation, thermostability, and hydrophobic properties of TiO$_2$/poly(dodecafluorohexyl methacrylate) nanocomposites. *J Appl Polym Sci* 2017; 134: 44377.
16. Sombatsompop N and Chaochanchaikul K. Average mixing torque, tensile and impact properties, and thermal stability of poly(vinyl chloride)/sawdust composites with different silicone coupling agents. *J Appl Polym Sci* 2005; 96: 213–221.
17. Zhao J, Milanova M, Warmoeskerken MMC et al. Surface modification of TiO$_2$ nanoparticles with silicone coupling agents. *Colloids Surf A* 2012; 413: 273–279.
18. An J, Kang BH, Choi BH, et al. Observation and evaluation of scratch characteristics of injection-molded poly (methyl methacrylate) toughened by acrylic rubbers. *Tribol Int* 2014; 77: 32–42.
19. Lee BH, Chang YW and Lim HM. Preparation and characterization of poly(methylmethacrylate) (PMMA)/acyr- late rubber (ACM) blend for light diffuser applications. *Elastom Compos* 2015; 50: 49–54.
20. Haddadi E, Choupani N and Abbasi F. Experimental investigation on the mixed-mode fracture of rubber-toughened PMMA using essential work of fracture method. *Eng Fract Mech* 2016; 162: 112–120.
21. Cocco DR, De Carvalho FP and Felisberti MI. Structures and morphologies olefin situ-polymerized blends of PMMA and ASA. *J Appl Polym Sci* 2013; 130: 654–664.
22. Gali NK, Ning Z, Daoud W, et al. Investigation on the mechanism of non-photocatalytically TiO$_2$-induced reactive oxygen species and its significance on cell cycle and morphology. *J Appl Toxicol* 2016; 36: 1355–1363.
23. Chung CJ, Lin HI and He JL. Antimicrobial efficacy of photocatalytic TiO$_2$ coatings prepared by arc ion plating. *Surf Coat Technol* 2007; 202: 1302–1307.
24. Lommerse JPM, Pricce SL and Taylor R. Hydrogen bonding of carbonyl, ether, and ester oxygen atoms with alkanol hydroxyl groups. *J Comput Chem* 1998; 18: 757–774.
25. Duan G, Zhang C, Li A, et al. Preparation and characterization of mesoporous zirconia made by using a poly (methyl methacrylate) template. *Nanoscale Res Lett* 2008; 3: 118–122.
26. Ramesh S, Leen KH, Kumutha K, et al. FTIR studies of PVC/PMMA blend based polymer electrolytes. *Spectrochim Acta A Mol Biomol Spectrosc* 2007; 66: 1237–1242.
27. Tangboriboon N, Sirivat A and Wongkasemjit S. Electrotherochemistry and characterization of acrylic rubber and lead titanate composite materials. *Appl Organometal Chem* 2008; 22: 262–269.
28. Tangboriboon N, Sirivat A, Kunanuruksapong R, et al. Electrotherochemical properties of novel piezoelectric lead zirconate titanate Pb(Zr$_{0.5}$,Ti$_{0.5}$)O$_3$-acrylic rubber composite. *Mater Sci Eng* 2009; 29: 1913–1918.
29. Kader MA and Bhowmick AK. New miscible elastomer blend from acrylate rubber. *Rubber Chem Technol* 2000; 73: 889–901.
30. Wootthikanokhan J, Burford RP and Chaplin RP. Effect of acrylic diblock copolymer upon interfacial adhesion. *J Appl Polym Sci* 1996; 62: 835–844.
31. Fujiu N, Miyauchi T, Oda T, et al. Influence of fluoroacrylate cure site monomer on the thermal and mechanical properties of the polyacrylic ester elastomer. *Rubber Chem Technol* 2020; 93: 395–413.
32. Rachellowe. *NMR of PMMA – tacticity and its determination through NMR*. Impact Solution, www.impact-solutions.co.uk/nmr-of-pmma/s (accessed 11 August 2017).
33. Green RD. The nature of C–H hydrogen bonding. In: Green RD (ed) *Hydrogen bonding by C–H groups*. Hoboken, NJ: Wiley, 1974, pp.158–167.
34. Somann VV and Kelkar DS. FTIR studies of doped PMMA – PVC blend system. *Macromol Symp* 2009; 277: 152–161.
35. Liu Y, Lee JY and Hong L. Morphology, crystallinity, and electrochemical properties of in situ formed poly(ethylene oxide)/TiO$_2$ nanocomposite polymer electrolytes. *J Appl Polym Sci* 2003; 89: 2815–2822.
36. Elsaka SE, Hamouda IM and Swain MV. Titanium dioxide nanoparticles addition to a conventional glass-ionomer restorative: influence on physical and antibacterial properties. *J Dent* 2011; 39: 589–598.
37. Tanumiharja M, Burrow MF and Tyas MJ. Microtensile bond strengths of glass ionomer (polyalkenoate) cements to dentine using four conditioners. *J Dentistry Children* 2000; 28: 6.
38. Huang L, Chen K, Lin C, et al. Fabrication and characterization of superhydrophobic high opacity paper with titanium dioxide nanoparticles. *J Mater Sci* 2010; 46: 2600–2605.
39. Bansod ND, Kapgate BP, Das C, et al. Controlled growth of in situ silica in a NR/CR blend by a solution sol–gel method and the studies of its composite properties. *RSC Adv* 2015; 5: 53559–53568.
40. Kapgate BP, Das C, Basu D, et al. Effect of silane integrated sol-gel derived in situ silica on the properties of nitrile rubber. *J Appl Polym Sci* 2014; 131: 40054.
41. Scotti R, Wahba L, Crippa M, et al. Rubber–silica nanocomposites obtained by in situ sol–gel method: particle shape influence on the filler–filler and filler–rubber interactions. *Soft Matter* 2012; 8: 2131–2143.
42. Wahba L, D’Arienzo M, Donetti R, et al. In situ sol–gel obtained silica-rubber nanocomposites: influence of the filler precursors on the improvement of the mechanical properties. *RSC Adv* 2013; 3: 5832–5844.
43. Wang J, Zhang X, Jiang L, et al. Advances in toughened polymer materials by structured rubber particles. *Prog Polym Sci* 2019; 98: 101160.
44. Carballeira P and Haupert F. Toughening effects of titanium dioxide nanoparticles on TiO₂/epoxy resin nanocomposites. *Polym Compos* 2010; 31: 1241–1246.

45. Eksirinimitr A, Wimolmala E, Taptim K, et al. Effects of simulation conditions on antibacterial performance of polypropylene and polystyrene doped with HPQM antibacterial agent. *Polym Test* 2016; 55: 123–134.

46. Habekost LV, Camacho GB, Lima GS, et al. Properties of particulate resin-luting agents with phosphate and carboxylic functional methacrylates as coupling agents. *J Appl Polym Sci* 2013; 127: 3467–3473.

47. Amoabeng D, Roell D, Clouse KM, et al. A composition-morphology map for particle-filled blends of immiscible thermoplastic polymers. *Polymer* 2017; 119: 212–223.

48. Collyer AA. *Rubber toughened engineering plastics*. Dordrecht: Springer Science+Business Media

49. Thankappan Nair S, Vijayan PP, Xavier P, et al. Selective localisation of multi walled carbon nanotubes in polypropylene/natural rubber blends to reduce the percolation threshold. *Compos Sci Technol* 2015; 116: 9–17.

50. Hesami M and Jalali-Arani A. Morphology development via static crosslinking of (polylactic acid/acrylic rubber) as an immiscible polymer blend. *Macromol Mater Eng* 2018; 303: 1700446.

51. Jiang X, Xu C, Wang Y, et al. Polyvinylidene fluoride/acrylonitrile butadiene rubber blends prepared via dynamic vulcanization. *J Macromol Sci Part B Phys* 2014; 54: 58–70.

52. Lee JK and Han CD. Evolution of polymer blend morphology during compounding in an internal mixer. *Polymer* 1999; 40: 6277–6296.