



Article

Sodium Hydroxide Treatment of Waste Rubber Crumb and Its Effects on Properties of Unsaturated Polyester Composites

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Abstract: This study investigated the optimum NaOH concentration treatment for rubber crumbs that improves adhesion between the polymer matrix and rubber filler in rubber polyester composites. The composite was prepared by mixing rubber crumbs from waste rubber gloves with unsaturated polyester matrix. Rubber crumbs were cryogenically ground from waste gloves and treated with 1%, 4%, 7%, and 10% NaOH (by volume). Treatment with 7% and 10% NaOH provides better wettability and hydrophilicity for rubber as it decreases the surface contact angle by approximately 27%. Higher concentration of NaOH intensively etched the rubber and made the surface rougher with more microcracks, providing a larger surface area for greater polyester coverage and holding the rubber firmly. It also induced more functional groups that increased the rubber surface energy and removed the hydrophobic layer on the rubber. These factors strengthened the interfacial rubber–polyester adhesion, as shown by the SEM micrograph of the tensile fracture which the rubber crumbs adhere well to the polyester matrix. The FTIR analysis of rubber treated with higher NaOH concentration showed a higher peak intensity, which demonstrated more polar groups were generated on the rubber surface. More polar groups created further connections to the polar groups in the polyester matrix, thereby enhancing adhesion between the rubber filler and the matrix.

Keywords: rubber crumbs; waste gloves; sodium hydroxide treatment; surface modification; surface analysis; wettability; interfacial adhesion; recycle rubber

1. Introduction

Rapid growth in the manufacture of rubber products has led to a large number of different types of rubber waste worldwide. Rubber products are non-biodegradable and will have a serious environmental impact if not properly handled [1]. Several works have been published that have used rubber products as part of the effort to ensure that rubber does not end up in landfill. Waste rubber products have been widely used in composite materials that offer better toughness, higher strength, abrasion resistance, and good insulation properties. They are used in a variety of applications such as marine, construction, sports, and recreation [2–15].

However, the use of rubber has an adverse effect on the composites as it weakens the adhesion between the rubber and the matrix and reduces the strength of the composite. Rubber is a hydrophobic material with low surface energy, which prevents the matrix from making a good adhesion to the rubber. Rubber products also contain many additives that over time are diffused to the surface and form a passive layer, which inhibits the matrix adhering well with the rubber [16–23]. For composite materials, adhesion between the filler and matrix is highly reliant on the surface properties that include surface polarity, surface energy, and surface morphology. Therefore, the surface properties of the fillers require modification in order to improve bonding with the matrix [24].

Much research has been conducted to modify the surface properties of rubber to strengthen the adhesion of the rubber with the matrix. Potential methods include alkaline treatment using sodium hydroxide (NaOH); acidic treatments using sulfuric acid, potassium permanganate, or silane; and many more [16,21,25–31]. Surface treatments will oxidize the rubber surface and form more polar groups, which will attach to the polar groups in the matrix. This phenomenon will increase the rubber surface energy thus improving the rubber hydrophilicity and wettability. The surface treatments also etched the rubber surface and it becomes rougher which allows better coverage of the matrix onto the rubber [22,23,26,32].

Treatment with NaOH is common for rubber because it was generally easy, inexpensive, and provides excellent results in improving adhesion between the rubber filler with matrix. NaOH modifies the rubber surface by mechanically etching the surface, resulting in more surface roughness allowing better matrix coverage on the rubber. The rougher the surface of the rubber, the better the rubber wettability properties and adhesion between the matrix and rubber. This indicates that NaOH treatment enhanced the hydrophilic properties of rubber [16,20,33–35]. NaOH also triggered degradation to some of the rubber chains, which creating more functional groups. The more functional groups appeared on the rubber surface the higher rubber surface polarity. The treatment also contributes to the presence of hydrophilic elements such as carboxyl group and increases the functional O–H groups therefore improving the wettability of the rubber surface [27,35–37].

Moreover, NaOH is known as a heavy duty cleaner that helps remove impurities on the rubber surface, such as dirt, oil, or passive layer, which prevents the matrix adhering well to the rubber. For example, insoluble zinc stearate (one of the ingredient in rubber compounds) diffused to the top and formed a passive layer on the rubber surface. NaOH also chemically converted the insoluble element in rubber formulations, such as zinc ion, into water-soluble sodium ions that could easily be washed away. Several works have been published showing that treatment with NaOH provides good rubber surface properties to improve adhesion between rubber and matrix [16,23,35,38–41].

The aim of this paper is to study the effects of different sodium hydroxide concentration treatments on the rubber surface. The goal is to determine the optimum concentration of NaOH, which maximizes the adhesion between rubber and unsaturated polyester in the rubber–unsaturated polyester composites.

2. Materials and Methods

2.1. Materials

Unsaturated polyester (later will be typed as polyester) is used as matrix and supplied by Synthomer Sdn Bhd. Malaysia as Reversol P-9509. It is an orthophthalic and can cure in ambient temperature with an addition of catalyst, methyl ethyl ketone peroxide (MEKP). The properties are viscosity (450–600 cps), thixotropic index (1.8 minimum), specific gravity (1.12 g/cm³), and gel-time at 25 °C with 1% MEKP 25–30 min.

The crumbs were prepared from discarded rubber gloves obtained from the laboratory in Universiti Putra Malaysia. Using cryogenic grinding, the gloves were soaked until frozen in liquid nitrogen and ground into crumbs. The crumbs were sieved and characterized by size; more than 80% were in the

range of 0.85 mm to 1.70 mm. The rubber crumbs were stored for approximate 3 months prior to being subjected to NaOH treatments.

2.2. Rubber Crumbs Surface Treatments

The rubber crumbs were treated using four (4) different NaOH concentrations (1%, 4%, 7%, and 10% by volume). The NaOH was supplied by Evergreen Engineering & Resources, Selangor, Malaysia with concentrations of 99%. The rubber crumbs were first stirred homogenously in each NaOH solution to guaranty a uniform treatment and later soaked for 40 min. Afterwards, the crumbs were rinsed thoroughly with water and final washing was using distilled water. The crumbs were dried for 24 h at 60 °C [22,33,37,40–42] Figure 1 shows the rubber crumb immersed in NaOH solution.

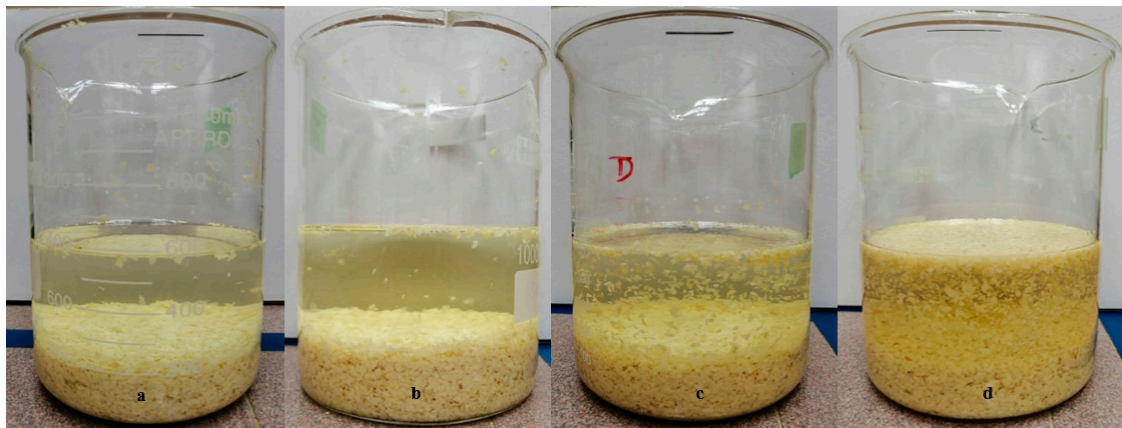


Figure 1. Rubber crumbs surface treatment using NaOH solution: (a) 1%, (b) 4%, (c) 7%, and (d) 10%.

2.3. Composites Fabrication

The composites samples were prepared for all 4 treated rubber crumbs including 1 control sample using untreated rubber. The composites were prepared using the hand lay-up technique. Rubber crumbs content for each composite was 5% by weight. The rubber crumbs were gradually added into the polyester followed with Methyl Ethyl Ketone Peroxide (MEKP) using a gentle and homogenous mixing. The mixture was transferred to square stainless steel mould size 300 mm × 300 mm × 4 mm. A 10 kN of load was applied to the mixture and leave 24 h at room temperature for curing.

2.4. Tensile Test

The tensile test was conducted using an INSTRON 5557 Universal Testing Machine, according to ASTM D5083 with crosshead speed at 5 mm/min. The machine capacity is 30 kN load and testing was conducted in the controlled environment with a relative humidity of $50 \pm 10\%$ and temperature 23 ± 2 °C. Test samples were cut as per the dimensions given in Figure 2.

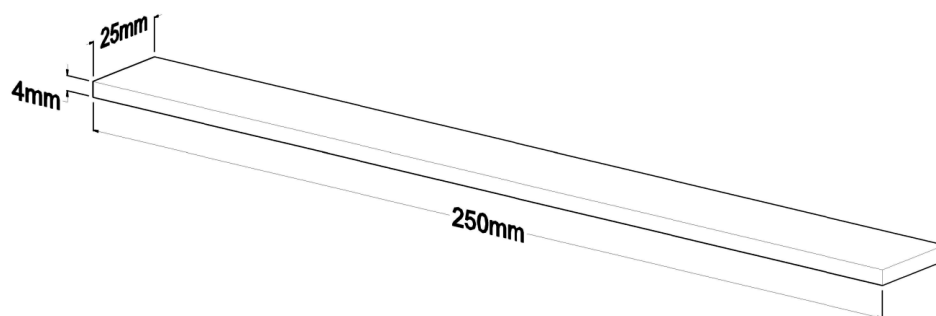


Figure 2. Tensile samples dimensions.

2.5. Scanning Electron Microscope (SEM) Analysis

The SEM analysis was conducted on the fractured surfaces of the tensile samples using Hitachi S-3400N SEM with an accelerating voltage of 10 kV. Samples were cut approximately 5 mm length \times 4 mm height \times 4 mm thickness and were coated with gold to remove the electrostatic charge. The SEM images were obtained using 100 \times and 300 \times magnification.

2.6. Fourier Transform Infrared Spectrometry (FTIR)

FTIR using Perkin Elmer spectrum 100 cc spectrometer with a frequency range of 650 to 4000 cm^{-1} and operated in ATR (attenuated total reflectance) mode.

2.7. Contact Angle Measurement

Contact angle was measured using self-fabricated equipment as shown in Figure 3 [43]. A 5 μL water droplet was put onto the rubber surface using a micrometric syringe and the droplet image was captured by a digital microscope installed inside the equipment as shown in Figure 4a. The contact angle of the droplet was measured using the Image J software. The angle was measured between the tangent to the water at the touch point and the solid rubber surface as shown in Figure 4b. For each sample, the contact angle was measured for six times to ensure measurement accuracy.

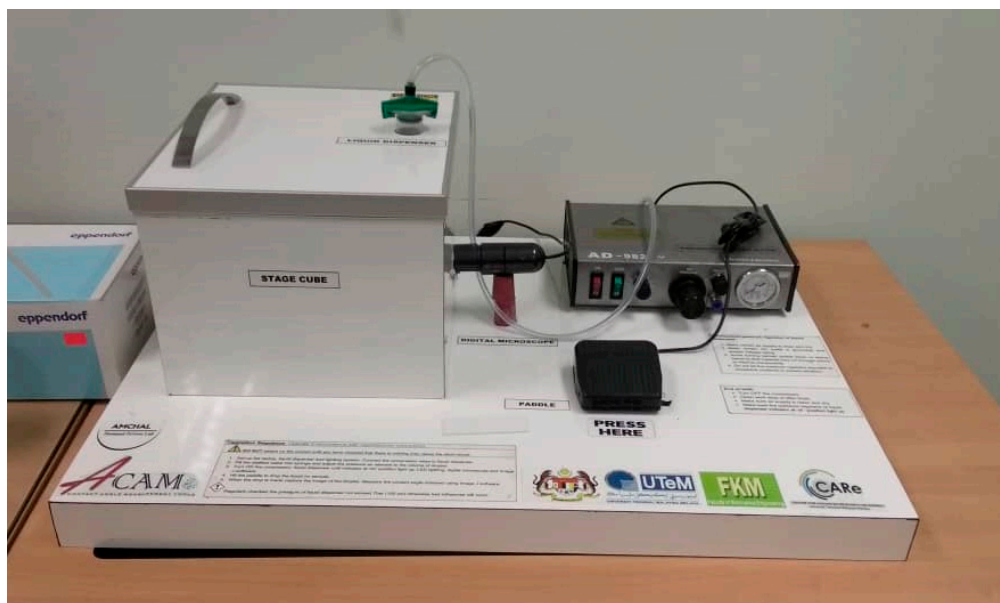


Figure 3. Contact angle measurement equipment.

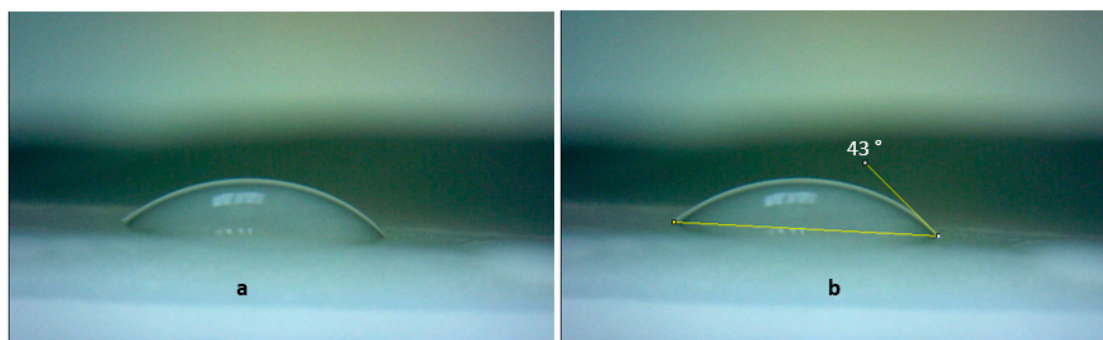


Figure 4. (a) Image of the water droplet and (b) contact angle measurement with Image J software.

3. Results and Discussion

3.1. FTIR Analysis

FTIR provides information about the chemical functional groups present in the sample and allows us to monitor any changes due to the treatment. Treatment with NaOH generally caused degradation of the rubber chain, which resulted in some modifications towards the rubber chemical structure and generated more polar groups. NaOH surface treatment caused oxidation and aging of the rubber resulting in more functional groups that contains oxygen as carbonyl, carboxyl, and hydroxyl. These functional groups improve rubber polarity hence improves rubber hydrophilicity that helps enhancing the rubber polymer adhesion [11,17]. Figure 5 shows the main absorbance peaks for the all treated and untreated rubber crumbs. The FTIR spectra of the treated rubbers shows changes in peak intensity, in which the peaks become more prominent as the treatment concentration increases.

It can be observed that the spectra for both the untreated and treated rubber display peaks at 3400 cm^{-1} , which reflect O–H stretching hydroxyl group vibrations. The O–H peak intensity of treated rubber is higher than the untreated rubber, which shows the presence of more O–H groups and intermolecular hydrogen bonding [28,44]. The O–H peak intensity gets higher for the 7% and 10% NaOH as it represents, the increased number of O–H groups caused by the extensive oxidation due stronger alkaline on the rubber.

Notable peaks were also observed at wavenumbers of 2853 cm^{-1} and 2924 cm^{-1} for all treated and untreated rubber crumbs resulting from the alkyl stretch of C–H bond vibration. For these peaks, it can be observed that it has higher intensity for 7% and 10% NaOH treated rubber when compared to 1% and 4% NaOH because more intensive alkaline treatment further oxidized the rubber and induces the formation of more functional groups on the rubber surface [45–47].

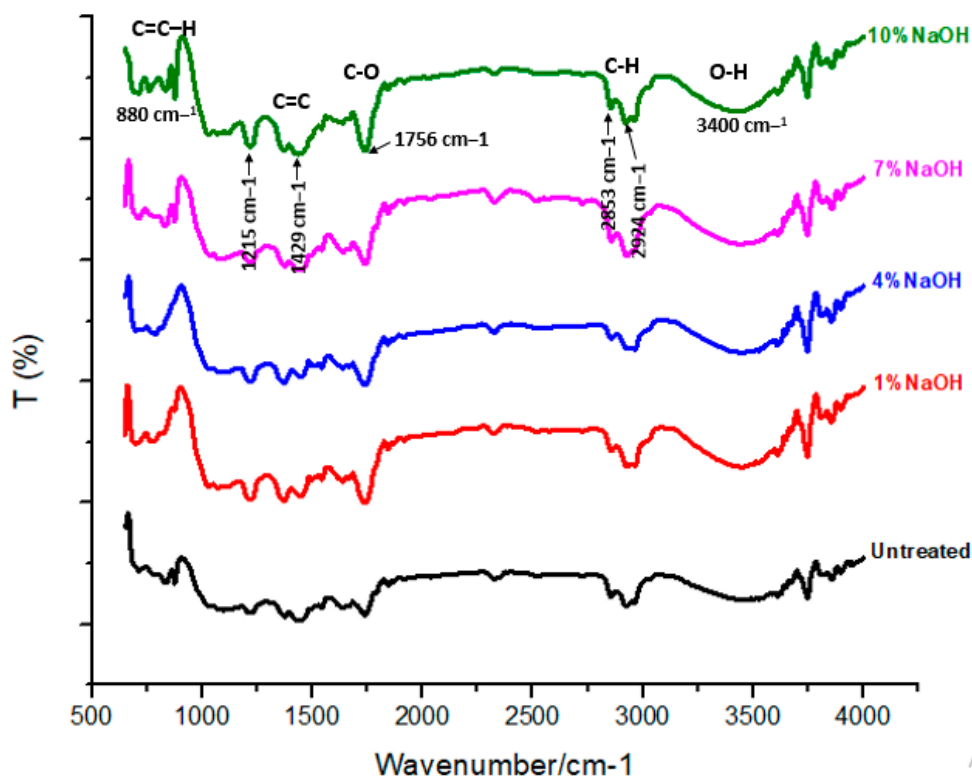


Figure 5. FTIR spectra for untreated rubber crumbs and treated rubber crumbs with different NaOH concentrations.

Note that in the spectra of the untreated rubber a weak band at 1756 cm^{-1} appeared; however, with the NaOH treatment the peaks were more pronounced. The intensity of this carbonyl C=O stretch become slightly higher for 7% and 10% NaOH, which represents an increase in the amount of carbonyl groups due to more extensive surface oxidation by stronger alkaline [28,30]. The carbonyl groups which are more hydrophilic had improved the hydrophilicity of the rubber surface which enhanced the adhesion between rubber and the polyester.

A noticeable peak between 660 cm^{-1} and 880 cm^{-1} in the spectra can be observed for the rubber treated with 7% and 10% NaOH if compared to 1% and 4% NaOH, which signified the presence of more C–H bond stretching connecting to carbon–carbon double bond. The spectra also show that there are obvious multiple bands in between 1450 cm^{-1} and 1750 cm^{-1} , indicating the existence of more C=C bonds [11]. Apparent peaks can be observed for 7% and 10% NaOH treated crumbs at 1429 cm^{-1} that represent the decrement of the double bond C=C due to partial degradation of some constituents because of the because stronger alkaline treatment. The degradation of these elements due to physical changes in the rubber surface such as the formation of more micro-cracks and rougher surfaces.

At 1215 cm^{-1} a quite noticeable peak can be observed for 10% NaOH treated rubber, which is caused by the vibration of S=O stretching indicating the appearance of more sulphonic groups. The appearance of more sulphonic groups may be due to the effect of breaking of some of the sulfur cross-links due to the high concentration NaOH treatment [11,28,45,46,48].

Apparently, NaOH treatment caused oxidation of the rubber, thus creating more polar groups, such as carbonyl and hydroxyl groups on the rubber surface, creating a large number of functional groups to attach to the polar group on the polyester. Higher polarity increased the surface energy of the rubber and increased the wettability and hydrophilicity of the rubber, consequently improving the adhesive strength of the rubber and polyester matrix and thus the mechanical properties of the composites [11]. Hydrophilic improvement of the rubber surface treated with a higher concentration of NaOH was demonstrated by the water droplet profile, which will be discussed later in the contact angle section.

3.2. Tensile Strength

The mechanical performance of the composite is highly dependent on the ability of the matrix and the filler to adhere well to each other. In general, the incorporation of waste rubber crumbs into composites resulted in a decrease in tensile strength caused by poor interfacial adhesion between rubber and matrix. Rubber is hydrophobic in nature and has low surface energy, which prevents the matrix from coating well on the rubber surface, therefore adhesion between the matrix is not [23,48]. However, the rubber surface treatment is expected to improve the interfacial bonding of rubber crumbs to the polyester matrix. Figure 6 shows the rubber–polyester composite's tensile strength and elongation at break of composite with untreated rubber crumbs and composite with rubber treated with different NaOH treatment concentrations. From the graph it can be observed that treatment of NaOH to the rubber caused a decrease in tensile strength towards the composite; however, the tensile strength improved when the concentration of the NaOH increased. Treatment with NaOH provides excellent roughness to the surface, induces more functional groups, and removes the hydrophilic layer, which collectively enhance adhesion between rubber and the polyester. However, NaOH also caused damaged to the rubber structure and thus degrades the mechanical properties [23]. The increasing trend of tensile strength with the increase of NaOH concentration is because the higher concentration mechanically etched the rubber surface to a greater extent, producing numerous micro-cracks and forming much smaller cracks, making the rubber surface rougher. A rougher rubber surface provides a larger surface area for polyester to adhere on the rubber. This ensures maximum adhesion between rubber and polyester, enhanced the interfacial bonding, and improved the tensile strength of the composites [23,35,36,48,49]. From the tensile strength result, it can be noticed that composite tensile strength with 10% NaOH treated rubber is relatively comparable with composites of 7% NaOH.

This suggests that the 7% NaOH treatment offers the ultimate modification to the rubber surface in order to achieve the desired surface properties.

Rubber naturally has very high elasticity; however, treatment with NaOH may cause a slight decrease in elasticity. This can be observed as the elongation at break of the composite with 1% NaOH treated rubber declined when compared to the composite with untreated rubber. However, elongation at break of the composite with treated rubber shows a slight increase as the NaOH concentration increased, which is a similar trend to the composite tensile strength as discussed earlier. The higher NaOH concentration modified the rubber surface for better adhesion with polyester thus reflecting an increase of elongation at break for the composite.

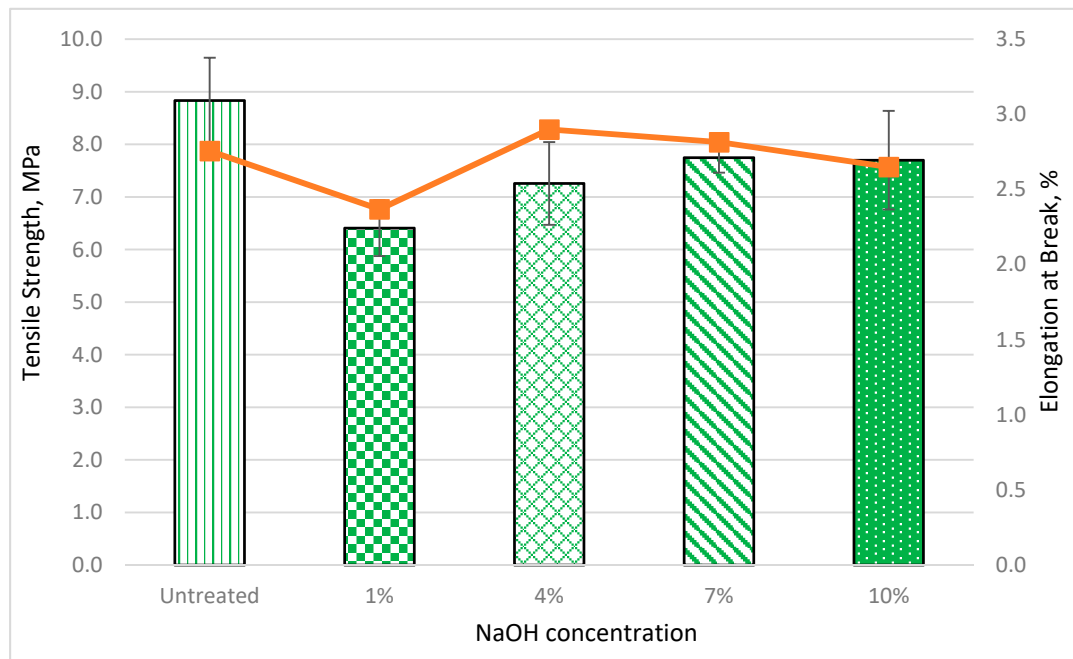


Figure 6. Tensile strength and elongation at break of the composites with different NaOH concentration.

Figures 7–10 displayed the SEM rubber surface morphology, in which a significant effect of the different treatment concentration on the roughness of the rubber surface can be observed. Figures 7 and 8 showed that the rubber surface with 7% and 10% NaOH treatment were rougher with many microcracks and the cracks are much smaller, these attributes lead to a larger rubber surface area. While Figures 9 and 10 revealed that the rubber crumbs treated with lower NaOH concentration, 1% and 4% NaOH, respectively, which had a smoother surface with less micro-cracks and cracks are larger. A smooth surface inhibits the good coating of polyester on the rubber, and consequently the bonding is weaker, leading to lower tensile strength. A smoother surface typically has a higher contact angle with poor wettability properties; therefore, the polyester could not be well wetted on the rubber and did not have a sufficient physical bonding system to strengthen the adhesion. As a consequence, rubber and polyester will experience poor interfacial adhesion resulting in lower tensile strength.

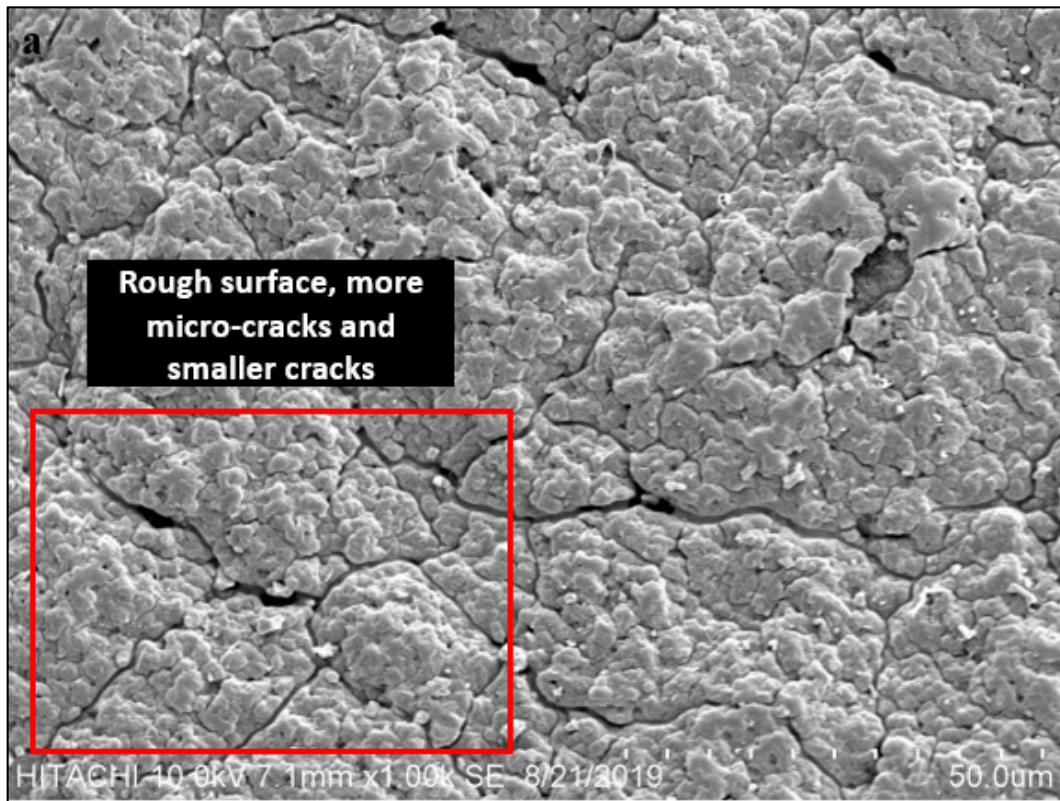


Figure 7. SEM of 7% NaOH treated rubber surface morphology.

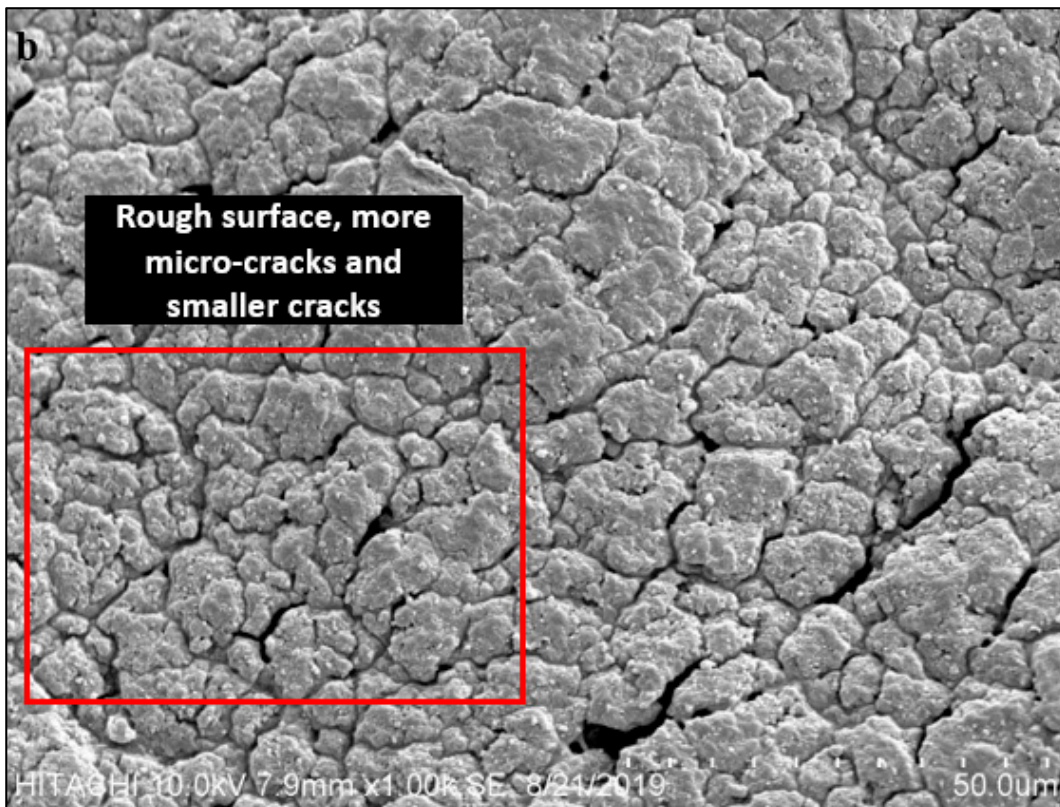


Figure 8. SEM of 10% NaOH treated rubber surface morphology.

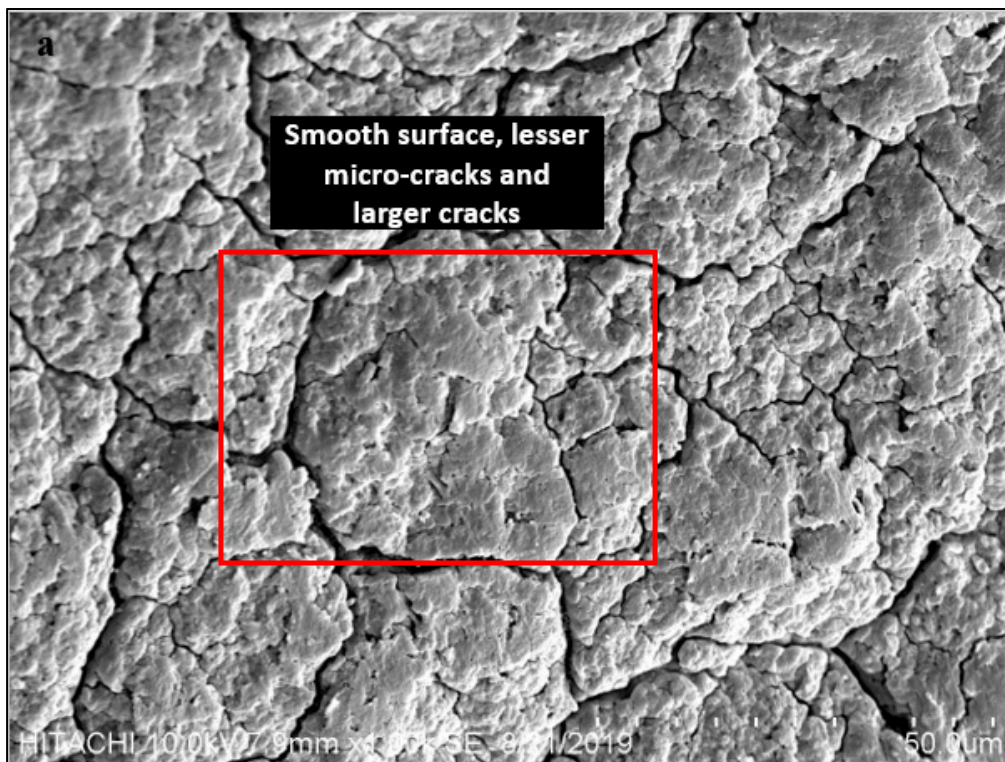


Figure 9. SEM of 1% NaOH treated rubber surface morphology.

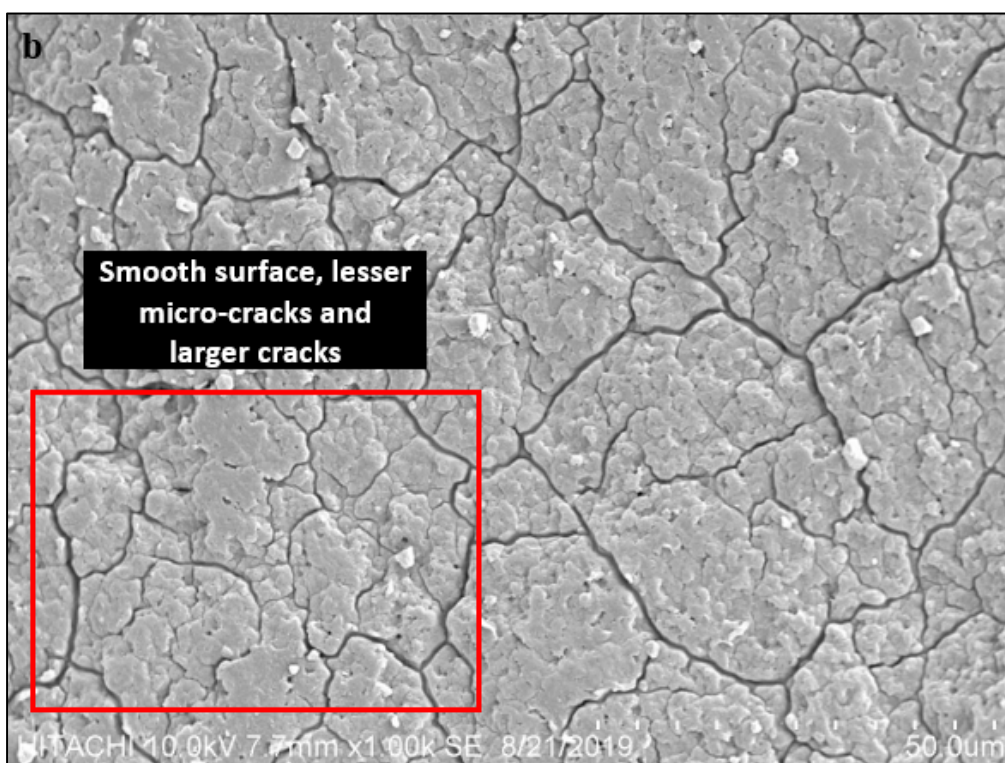


Figure 10. SEM of 4% NaOH treated rubber surface morphology.

In the tensile fracture micrograph in Figure 11, stronger rubber–polyester adhesion for rubber that treated with 7% NaOH can be observed. The strong rubber–polyester adhesion provide composite with higher tensile strength. The SEM showed the rubber crumb was strongly embedded in the matrix

even after fracture, and it is evident that the crumb was firmly adhered to the matrix. Figure 12 showed the rubber pull-out from the matrix, which demonstrated a poor interfacial adhesion between the rubber treated with 4% NaOH and the polyester matrix.

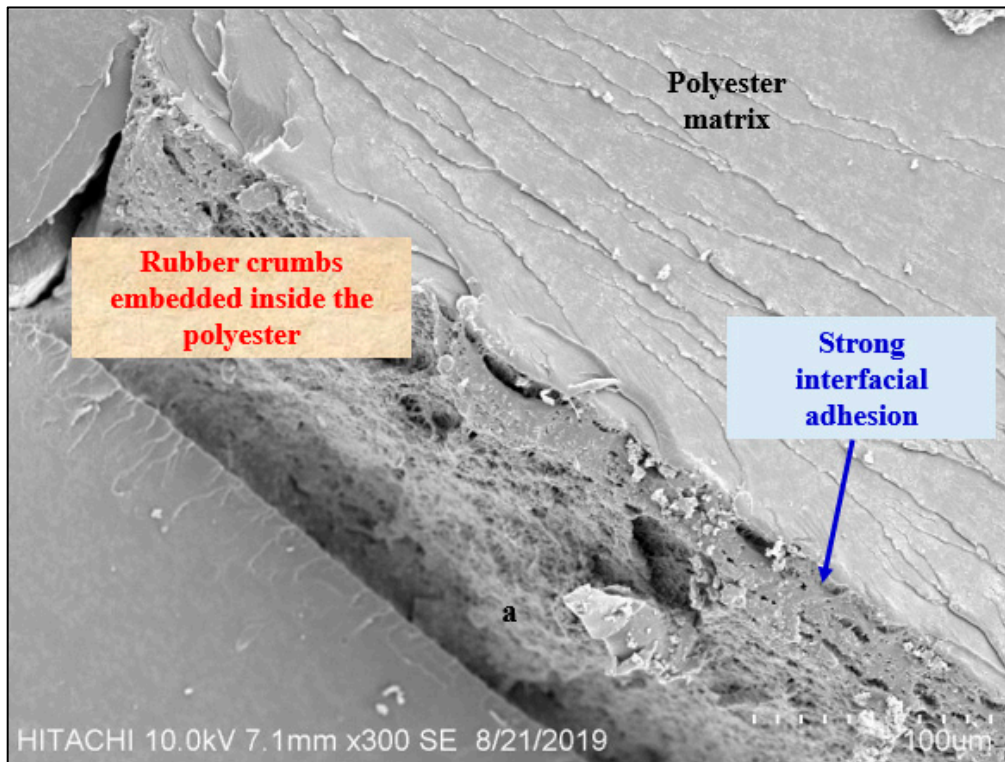


Figure 11. Tensile fracture micrograph of composites with 7% NaOH treated rubber crumbs.

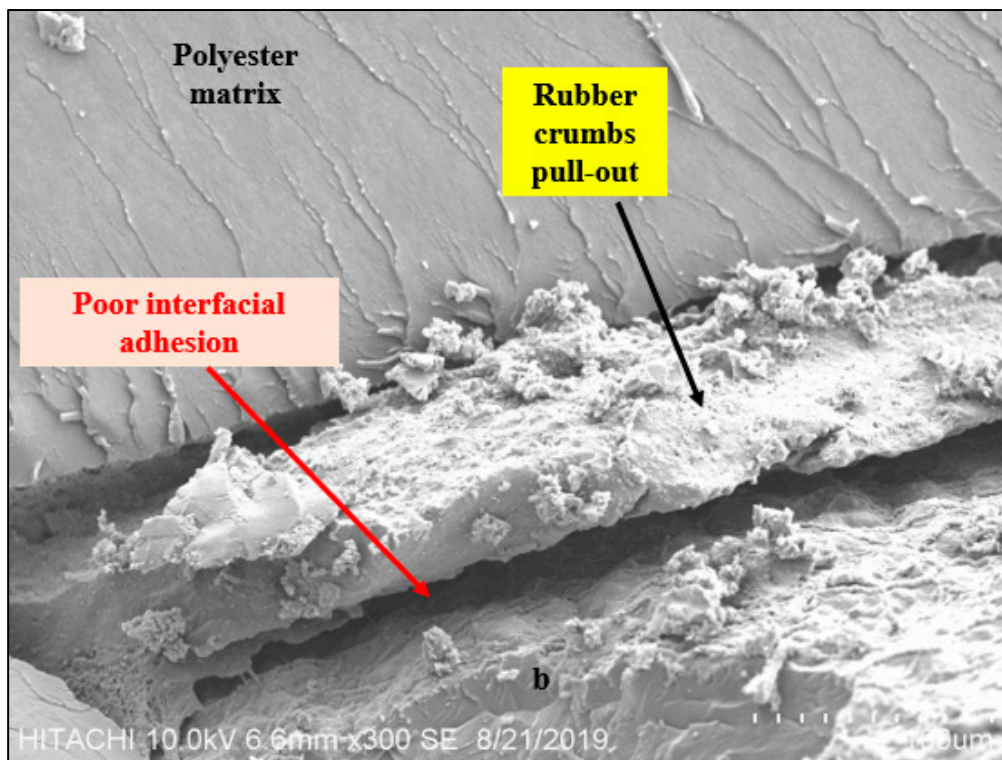


Figure 12. Tensile fracture micrograph of composites with 4% NaOH treated rubber crumbs.

Apart from tensile strength, the modulus of elasticity of the composite also increased with an increased concentration of NaOH treatment, as shown in Figure 13. The improved bonding between the rubber matrix and the polyester matrix has a positive effect on their interfacial adhesion and prevents the failure of the composite from accelerating [23]. Furthermore, the ability of the rubber crumbs to adhere well in the composites enabled rubber to transfer the applied load evenly throughout the composites. It preventing from composite failure, thus providing the composite with better elastic modulus [41,50]. However, treatment with NaOH, to a certain extent, caused damaged to the rubber structure and elasticity, which decreases the composite modulus elasticity.

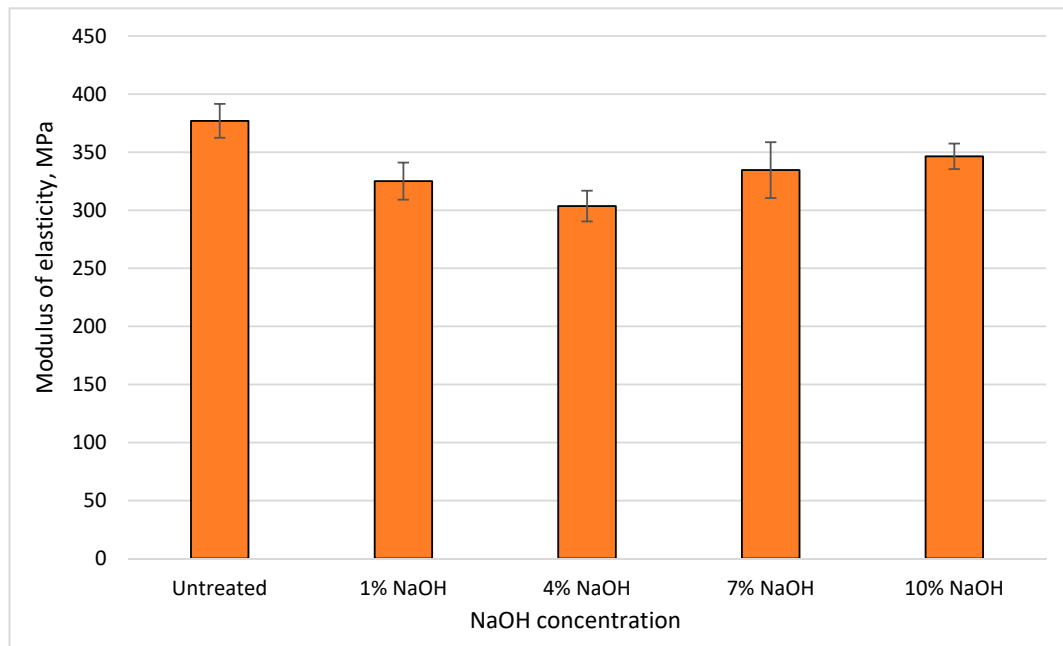


Figure 13. Modulus of elasticity of the rubber polyester composites.

3.3. Contact Angle Measurement

The strength of the composites depends so much on the capacity of the filler to distribute the load evenly throughout the composites. It is therefore highly dependent on the well-dispersed fillers in the composites and the good interfacial interaction between the fillers and the matrix [51,52]. Good interfacial adhesion of the filler–matrix is strongly influenced by the surface properties of the filler, such as surface energy, polarity, surface morphology, and surface hydrophilicity. The surface of the fillers must be cleared from any obstructions and impurities that prevent it from being well coated by the matrix. Stronger adhesion requires the fillers to have lower surface energy so that the well matrix coverage on the rubber can be achieved [24]. The surface of the rubber gloves is generally hydrophobic due to the vulcanization process and the surface coating. These properties help to minimize cross-contamination during use. Therefore, surface modification is essential to alter the surface properties to improve the wettability of the rubber surface to facilitate strong interfacial adhesion between the rubber fillers and the polyester matrix. The effect of surface modification towards surface properties can be assessed by measuring the contact angle; it measured the angle between the tangent to the water droplet at the touch point and the rubber surface. Smaller contact angle means the surface is hydrophilic because the water droplet can simply wet or easily occupy the surface of the rubber [37]. This mechanism provides better matrix wetting on the rubber surface, enhances adhesiveness between rubber and matrix and strengthens the composites.

Different NaOH concentration treatment for rubber crumbs altered the rubber surface differently. Figure 14 shows the degree of contact angle decreased as the NaOH concentration increased. The 1% and 4% NaOH treated rubber have a high contact angle of at 62.27° and 59.39° , respectively, and a

noticeable decrease in contact angle from the 4% NaOH to 7% NaOH treatment can be observed. An approximately 27% decrease in contact angle degree for the 7% NaOH treated rubber compared to the 4% treated rubber was observed. It is worth to note that contact angle of 7% and 10% NaOH treated rubber provides almost similar degree of contact angle. This result showed that 7% is the optimal concentration of NaOH which adequately altered the rubber surface. The rubber surface treated with 7% NaOH obtained the best surface properties that provide better interfacial adhesion between rubber and polyester, resulting in maximum improvement for the composites of rubber–polyester.

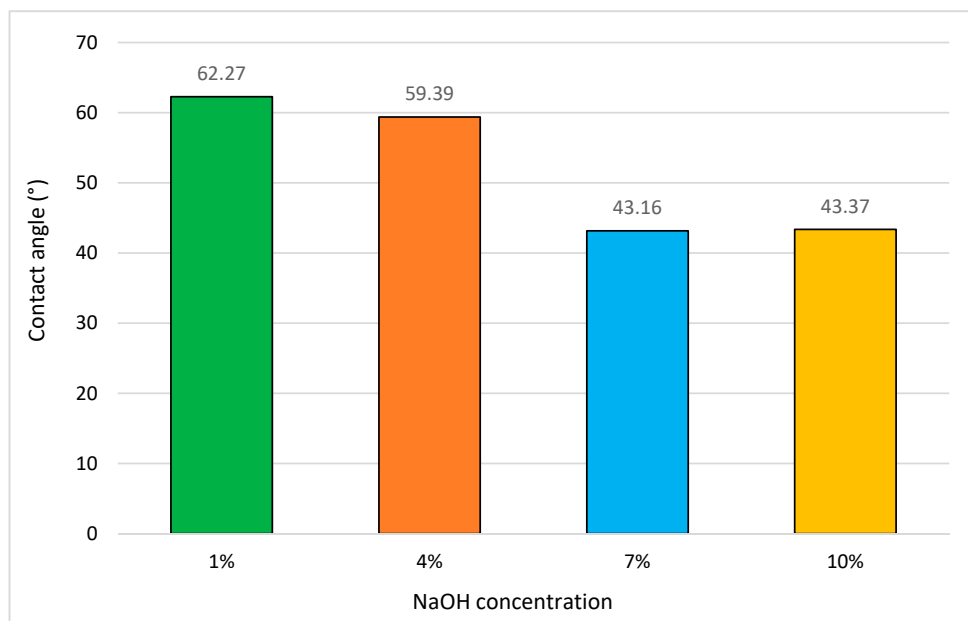


Figure 14. Contact angles of treated rubber crumbs.

The decrease in the contact angle due to the increased concentration of NaOH indicated the wettability of rubber surface was increased [17], which clearly demonstrated in Figure 15. Water droplets on the surface of 7% and 10% of NaOH treated rubber tend to occupy a larger surface, which showed an improvement in surface wettability. However, the water droplet on the 1% and 4% NaOH treated rubber are more spherical, which covers less of the rubber surface [11,27,28,37,46,47,53,54].

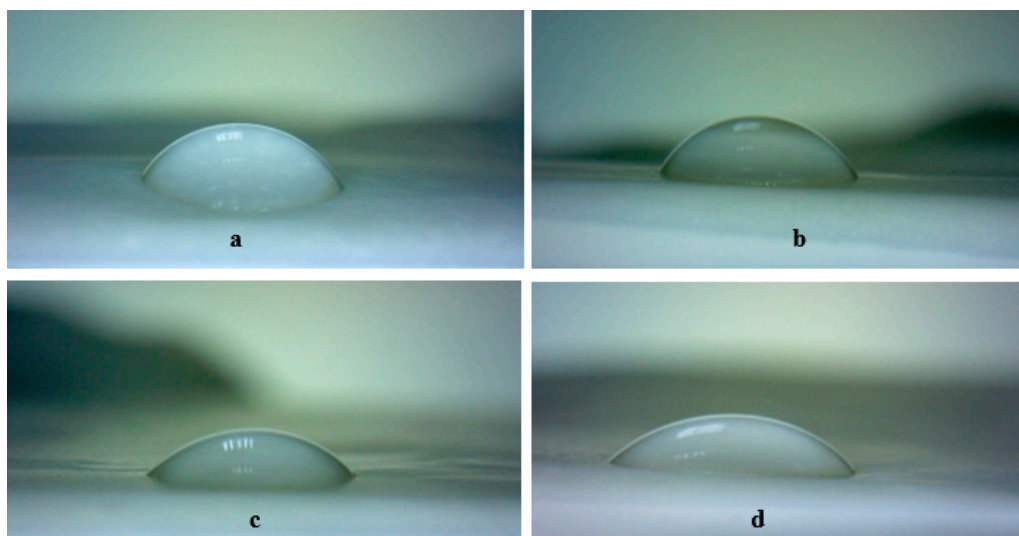


Figure 15. Water droplet profiles on NaOH treated rubber crumbs surface: (a) 1%, (b) 4%, (c) 7%, and (d) 10%.

The wettability of the rubber surface increases due to many factors, such as the removal of hydrophobic elements such as zinc stearate, which diffused onto the rubber surface and formed a passive hydrophobic layer. Sodium hydroxide converted zinc stearate into sodium stearate, which is water-soluble and easy to rinse-off. This removal of sodium stearate leads to significant changes in the surface properties of the treated rubber. It increased the area for contact surface between the rubber and the matrix and strengthening the bond between them [20,21,23,39,42,53,55].

Surface roughness is also important in determining the surface wettability. The wettability of the surface increases as the contact angle decreases [11,23,39,41,49,56]. Rough surface substrate has smaller contact angle, meaning that the water droplet was thinner, indicating the surface is hydrophilic [17]. As discussed in the previous section, the rubber of 7% and 10% NaOH treatment has a rougher surface compared to 1% and 4% NaOH treated rubber (Figures 7 and 8), which contributed to the lower contact angle measured in this work.

The surface energy of the rubber is equally important in affecting the surface wettability. Surface energy increases with increasing surface roughness, the surface with higher surface energy has a smaller contact angle, thus the surface can be wet well by the liquid [49]. The surface with more functional groups has higher polarity, which also provides the rubber with higher surface energy. As referred to the FTIR analysis in the previous section, treatment with higher NaOH concentrations facilitated oxidation on the rubber surface which generated more functional groups [11,22–24,31,49,50,55,57].

Figure 16 clearly demonstrated the correlation between the composite tensile strength and the contact angle of the rubber surface. Higher concentration NaOH sufficiently altered the rubber surface and obtained the maximized surface properties. Thus, it increased surface wettability which allowed better matrix coating on the rubber, enhanced the rubber–polyester interface bonding and improved the composites tensile strength.

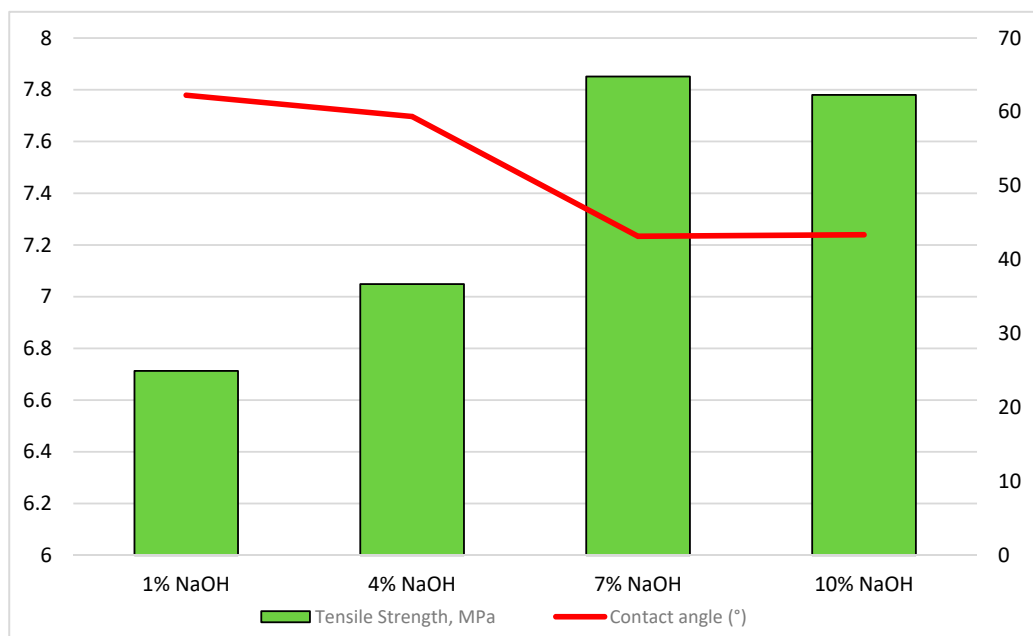


Figure 16. Effect of rubber contact angle on tensile strengths.

4. Conclusions

Rubber crumbs have been treated with 1%, 4%, 7%, and 10% NaOH concentrations to determine the optimum NaOH concentration that can provide strong adhesion between the polyester matrix and the rubber filler in the rubber polyester composites. The treatment is to modify the rubber surface by mechanically etching the surface and to provide the rubber with a rougher surface, induced more

functional groups, and removed a passive hydrophilic layer, which prevents a good polyester adhesion to the rubber. Tensile testing, FTIR analysis, contact angle measurement, and a microscopic surface texture study were conducted to evaluate the effects of the treatments. The following conclusions are drawn from the analysis of this work.

1. NaOH treatment provides the rubber with a good roughness surface, induced more functional groups that increase the polarity of the rubber, removed the passive hydrophilic layer and insoluble ions from the rubber surface, and enhanced the hydrophilicity and wettability of the rubber.
2. However, NaOH treatment causes some degree of damage to the rubber structure, which decreased the mechanical properties of the composites.
3. The optimum concentration of NaOH for the rubber crumbs treatment is 7%, which has sufficiently etched the rubber surface, producing numerous micro cracks which give rubber a rougher surface, thus providing a larger surface area for polyester to adhere to the rubber. The 10% NaOH treatment showed comparable surface properties as seen in 7% of treatment.
4. Rubber that has been treated with 7% and 10% NaOH has a lower contact angle measurement which indicates a better wettability of the rubber surface.
5. Rubber treatment with a higher NaOH concentration further modified the rubber surface, intensively oxidized the rubber, generated more polar groups and provided better rubber surface morphology, which improved the rubber wettability and hydrophilicity.
6. Higher concentration of NaOH treatment has altered the rubber to some degree which increases the rubber surface energy that makes the rubber surface has a lower contact angle.
7. Increased rubber surface energy is the result of higher polarity of the rubber surface, rougher rubber surface, as well as the removal of the passive hydrophobic zinc stearate layer from the rubber surface and the present of soluble sodium ions which has been converted from the insoluble zinc ions.
8. Therefore, as the rubber has better wettability and hydrophilicity, the polyester is capable of adhering well to the rubber surface, ensuring maximum bond and resulting in stronger interfacial adhesion between the two surfaces.
9. On the other hand, rubber that has been treated with a lower concentration of NaOH; 1% and 4% treatments have a higher surface contact angle due to insufficient surface modification. Weaker alkaline treatment is not capable of sufficiently etching the rubber surface and cannot effectively disrupt the rubber chains, and therefore generates fewer polar groups. As a consequence, the rubber surface has poor wettability and hydrophilicity.

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