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DEWATERING HYDROCARBON BASED ON SMART HYDROPHILIC SPONGE AND HYDROPHILIC GEL

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ABSTRACT

Sponge based on polydimethylsiloxane (PDMS) with a high-capacity, $ZnCl_2$, Polyvinyl alcohol (PVA), and Polyethylene Glycol (PEG) for the dewatering application of hydrocarbon fuel sorbents has been prepared in one-step preparation. The synthesized hydrophilic sponges were named V1 (PDMS: $ZnCl_2$), V2 (PDMS: $ZnCl_2$: PVA), V3 (PDMS: $ZnCl_2$: PEG), V4 (PDMS: $ZnCl_2$: PVA: PEG), V5 (PDMS: $2ZnCl_2$: PVA: PEG) and V6 (PDMS: $3ZnCl_2$: PVA: PEG), respectively. The characteristics of the sponges under the optical microscope and contact angle measurements show the formation of hydrophilic sponge and gel. ATR-FTIR characterization showed peaks at 3100-3500 cm^{-1} and 1750-1735 cm^{-1} identified with the OH stretching vibration and C=O strain vibration, which can be ascribed to the acetate group of the PVA molecule which is responsible for increasing the hydrophilicity. On the addition of PEG, there is an absorption band from the C-H vibration at 941 cm^{-1}, and absorption at 1459, 1351, 1299, and 1256 cm^{-1} is CH, CH_2, and CH_3 bending vibrations. The contact angle measurements showed that the solid hydrophilic sponge V4 has a hydrophilic character (contact angle of 45.5º). And also, the increase in $ZnCl_2$ was proportional to the decrease in contact angle. However, in the composition of V5 and V6, the super hydrophilic character (V5 =38.8º, V6 =14.3º) did not produce a good solid hydrophilic sponge. Characteristics of optical properties show high transmittance of more than 80%.

Keywords: Hydrophilic, Sponges, Hydrocarbon, PDMS, $ZnCl_2$.

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INTRODUCTION

Water-contaminated fuel is dangerous for those with gasoline engines. Due to contamination of water in the fuel tank, the impact caused can interfere with the health of the engine. The effect of water content in gasoline engines can interfere with the combustion process. As a result of the fuel content mixed with water, the main thing that was attacked was the combustion system which had an effect on machine pull and late power, limping spark plugs, until the engine died. The presence of water in the fuel causes the combustion process not to run normally. The functional material with a highly attractive structure is polydimethylsiloxane with open pores (PDMS sponge).[1] The sponges made from it effectively absorb organic compounds in hydrocarbon-based oils due to its hydrophobic properties of PDMS[2,3,4] and also can be used in water purification applications. Furthermore, the composite of PDMS by polymerization or binding through the active silanol group (Si-OH) in PDMS and its chemical properties can be changed to be more hydrophilic by adding or trapping metal cations that have hydrate binding character and some hydrophilic polymers. In certain cases, the presence of water is undesirable, such as in hydrocarbons for fuels and alcohols with water content at a certain level which requires a decrease in the absolute grade. Hydrocarbon drying is needed in the oil reform process and petroleum mining. Another example is a reduction in hydrocarbon-based oils, where the presence of water can cause electrical insulation breakdown or engine damage. Physical adsorption[5,6] on solid materials is one of the most promising approaches to this problem, which is relatively easy to handle and low cost. Several polymeric microparticles[6] or mixtures of ferrous oxide-based magnetic particles have been reported to be used to enrich the hydrophilic properties of materials.[5] The great advantage of the materials is that they can be reusable in many cycles. However, in general, it requires a hydrophilic sorbent filtering process after use.

In the use of inorganic oxide or salt hydrophilic sorbents, it is necessary to study the hydration water character of the selected hydrophilic material. Hydrated salt is the preferred hydrophilic sorbent material

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that can bind water into deep/crystal coordination. The stability of solids is a problem, so the manufacture of composites with hydrophobic polymer solids is needed to facilitate the application. The formation of complexes in aqueous solutions is the main step regarding zinc chloride in water for use in dewatering technology. The structure of the concentrated $ZnCl_2$ solution is around Zn^{2+} there is coordination competition between Cl^- and H_2O.[7] The structure of $ZnCl_2.5H_2O$ contains Zn^{2+} both in tetrahedral coordination with Cl^- and in an octahedral environment defined by five water molecules and one Cl^- together with the unit $[ZnCl_4]^{2-}$. Besides it, a gel sponge substrate is made of water-soluble polymer so it has the advantages of high lipophilicity, elasticity, and high porosity. Polymer with excellent properties such as biocompatibility is the most attractive polymer for fabricating three-dimensional matrices used contemplated like poly(vinyl alcohol).[8] In this work, we have designed hydrophilic solid and gel sponge composites from PDMS, $ZnCl_2$, PVA, and PEG at equilibrium with adsorbed H_2O which organic poly(vinyl alcohol) that provided the Microporous structural stability through easy crosslinking and polymerization. Through optimization, the composite formula is required for sponge materials that have hydrophilic characteristics that are able to act as a hydrocarbon dewatering agent. The balance of small lipophilic properties is maintained from the methyl group in PDMS and the addition of PVA and PEG in the composite synthesis process.

EXPERIMENTAL

Synthesis of Gel Sponge-PDMS

The general procedure is PDMS precursor was added with $ZnCl_2$ in a 1:1 (w/w) ratio which had been dispersed in distilled water. The suspension is stirred for 30 minutes and then added PEG as a surfactant. On the other hand, PVA is dissolved in distilled water and stirred for 1 hour at 50 ºC (1:1 w/w). PDMS/$ZnCl_2$ suspension was then added with PVA and stirred for 30 minutes. The prepared hydrophilic sponge was carried out with several precursor compositions as follows: PDMS: $ZnCl_2$ (V1), PDMS: $ZnCl_2$: PVA (V2) composites, PDMS: $ZnCl_2$: PEG (V3), PDMS: $ZnCl_2$: PEG: PVA (V4), PDMS: $2ZnCl_2$: PEG: PVA (V5), and PDMS: $3ZnCl_2$: PEG: PVA (V6). The suspension was dried at 90 ºC for 3 hours, then washed with distilled water to remove a part of $ZnCl_2$ and form a gel sponge. The PDMS-sorbent sponge was then dried at 60 ºC for 1 hour.

Water Contact Angle Measurements

The hydrophilic sponge of PDMS is coated on the glass which has been cleaned using ethanol. The gel-coated glass was dried at 60 ºC for 1 hour. Contact angle as a parameter of hydrophobicity-hydrophilicity measured by dripping water as 10 μL on the surface of the gel sponge of PDMS.

Water Adsorption Capacity Test

Water absorption on the hydrophilic sponges was carried out by inserting the sponges into a container containing 5 mL hydrocarbon fuel (oil bath) with variations of immersion for 5, 15, and 30 minutes. The sample sponge was removed from the oil bath. The hydrocarbon fuel oil after containing sponges was investigated by ATR FTIR.

RESULTS AND DISCUSSION

The sponge gel of PDMS was successfully synthesized by the addition of $ZnCl_2$, PVA, and PEG. When the hydrophilic sponge is immersed in water or a non-water liquid, the pores open due to the presence of water-attracting (hydrophilic) groups, namely OH, OH, C-OH, Zn^{2+}, and also Cl^-. The presence of Zn^{2+}, and Cl^- ion pairs increases the wettability of the polymer. Wettability will decrease the contact angle. The ability of Zn^{2+} to attach to the PDMS matrix due to the interaction of Si-OH with Zn^{2+} in polymeric PDMS.[9] The presence of $ZnCl_2$ acts as a template to form porosity and polar guides, while water as a solvent act as an intermediate medium for the solubility of $ZnCl_2$ in the PDMS matrix.[10] The coordination competition between Cl^- and H_2O around Zn^{2+} affects the structure of $ZnCl_2$.[7] The structure of $ZnCl_2.5H_2O$ has Zn^{2+} both in tetrahedral coordination with Cl- and in an octahedral situation demarcated by five water molecules and one Cl- together with the unit $[ZnCl_4]^{2-}$. O-H···O hydrogen bonding between water molecules as donors and $ZnCl_4$ tetrahedral and water molecules as acceptor groups hints at the structure of a three-dimensional complex in three structures, respectively. Based on the structure, the withdrawal of H_2O in the outer ring is very intensive. In this research, the addition of PVA to achieve long-term hydrophilicity for water absorption by capillary action and has abilities to control the nanoparticle size.[11]

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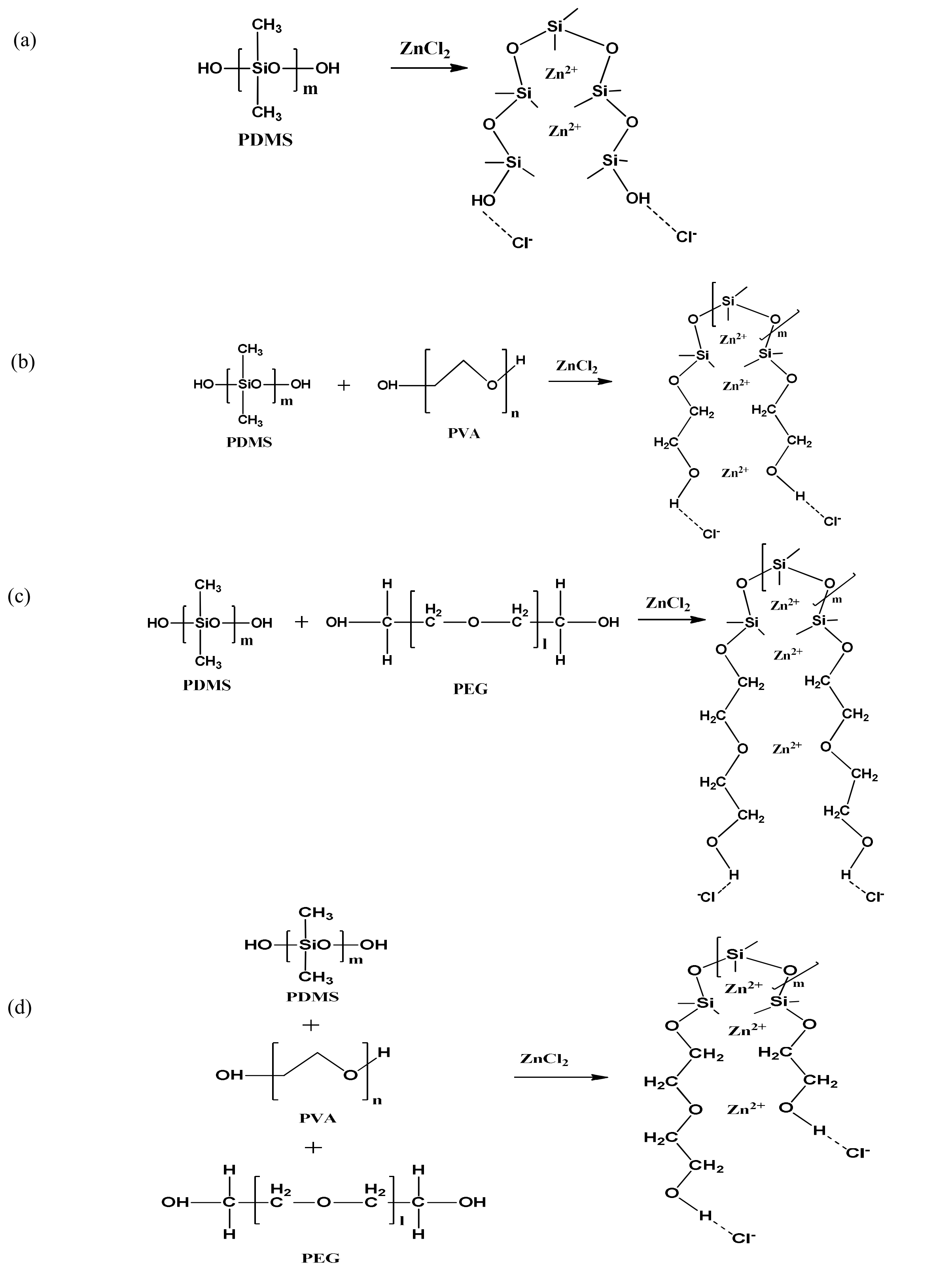

Fig.-1: Inorganic-Organic Gel Sponge Synthesis Scheme (a) PDMS: $ZnCl_2$ (V1), (b) PDMS: $ZnCl_2$: PVA (V2) composites, (c) PDMS: $ZnCl_2$: PEG (V3), (d) PDMS: $ZnCl_2$: PEG: PVA (V4), PDMS: $2ZnCl_2$: PEG: PVA (V5), and PDMS: $3ZnCl_2$: PEG: PVA (V6)

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Adsorbed PVA on the surface of the PDMS immobilized by heat at a temperature of 100 ºC. Fig.-1 shows the scheme hydrophilic sponge of PDMS preparation with long chains of OH groups. PVA interacts very slowly with alcohols and solubility increases with the addition of water and undergoes gelation overnight. Hydrophilic sponges were synthesized according to Table-1. The hydrophilic sponge results were shown in Fig.-2. The composition of the synthesis of sponge-based PDMS, $ZnCl_2$, PVA, and PEG produces intermediate gels with different viscosity.

Table-1: Composition of the Synthesis of Sponge-Based PDMS, $ZnCl_2$, PVA, and PEG

Sample name	Composition (w/w)
V1	PDMS:$ZnCl_2$ (1:1)
V2	PDMS:$ZnCl_2$:PVA (1:1:1)
V3	PDMS:$ZnCl_2$:PEG (1:1:1)
V4	PDMS:$ZnCl_2$:PVA:PEG (1:1:1:1)
V5	PDMS:$ZnCl_2$:PVA:PEG (1:2:1:1)
V6	PDMS:$ZnCl_2$:PVA:PEG (1:3:1:1)

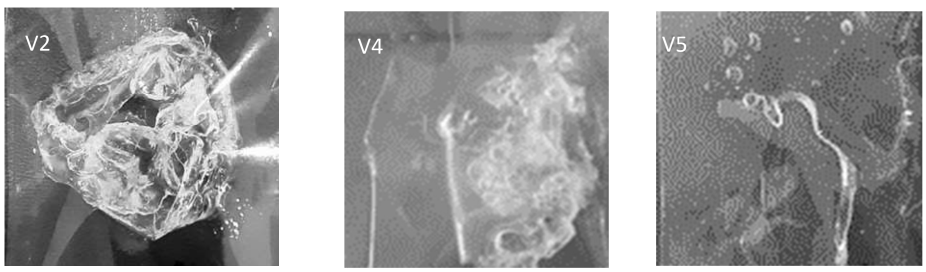

Fig.-2: Image of Hydrophilic Sponge

Characteristics by optical microscopy are shown in Fig.-3 with 4X magnification. In V1, it is difficult to form a solid sponge, only a PDMS gel is formed which holds $ZnCl_2$ bound to water. A bit difficult to see on an optical microscope. In PDMS: $ZnCl_2$ (V1) tends to be more liquid than composites added with PVA. Also in V3, a very high degree of hydrolysis results in gelation and is difficult to form a solid sponge product. V2 is the best hydrophilic solid sponge, which is formed from the composition of PDMS, $ZnCl_2$, and PVA. In V4, sponge solids were formed due to the influence of the presence of PEG increasing the density of the sponge, and in V5 with a higher $ZnCl_2$ composition which attracted water, the sponge formed was more jelly-like. When PVA is added, a hydrophilic solid sponge is formed because PVA is able to interact with water solvent through hydrolysis reaction although it is slow, then during further gelation process, the water will evaporate and form a solid hydrophilic sponge of PDMS: $ZnCl_2$: PVA (V2, V4, V5). Through the addition of PEG (V3), the hydrophilic nature of PEG will greatly increase the binding of water through the hydrolysis process while the condensation reaction is so suppressed that the material is retained as a gel form. Theoretically, the cross-linked sponge (PEG) has a higher water absorption ability which is related to the larger pore size in which water can be stored after immersion. In other conditions, through the addition of PEG and PVA, namely at V4, V5, and V6, they can form sponges, respectively. It was observed that with the same composition of PVA and PEG, while $ZnCl_2$ was increased, it showed an increased degree of gelation and the sponge became jelly-like.

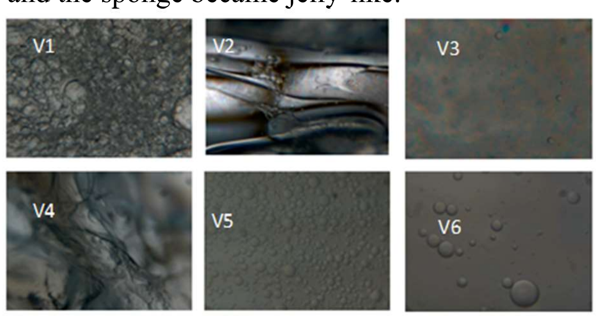

Fig.-3: Morphological Characteristics by Optical Microscope

The ATR-FTIR characteristic of hydrophilic a sponge is shown in Fig.-4. Each composite shows the presence of OH absorption at the wave number ~ 3300 cm^{-1}. On the addition of PVA, at the wavenumber 1000-1400 cm^{-1}, there are several bands observed at 1420, 1381, 1261, 1092, and 1028 cm^{-1} which can be identified as the presence of a CH_2, CO-C, and from C stretching.[8] The composites were added with PVA characteristic peaks at 3100-3500 and 1750-1735 cm^{-1} associated with –OH stretching and C=O vibrations, which can be attributed to the acetate group of the PVA molecule. The ATR-FTIR of the PVA spectrum shows a broad and strong band between 3550-3200 cm^{-1}, which corresponds to the O-H stretching vibration. On the addition of PEG (V3), there is an absorption band from the C-H vibration at 941 cm^{-1}. Absorption at 1459, 1351, 1299 and 1256 cm^{-1} is CH, CH_2, and CH_3 bending vibrations. The absorption peak at 1638 cm^{-1} is OH bending, while the absorption at ~1100 cm^{-1} shows the Si-O-Si group which indicates condensation of silicon alkoxide. In the variation of PDMS: $ZnCl_2$: PVA: PEG, C-H stretching vibrations are associated with long alkyl chains.

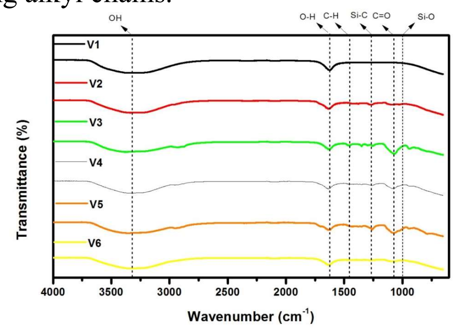

Fig.-4: ATR-FTIR Spectra of Hydrophilic Sponge

The contact angle characteristics of the hydrophilic sponge are shown in Fig.-5. The glass as a control substrate showed hydrophilic properties with a contact angle of 59.45º. Whereas in a sponge gel of V1 the contact angle is 44.6º because Zn^{2+} ions were successfully attracting water molecules, as well as the Si-O group of PDMS. At V2, the contact angle was 26.1º due to the presence of the OH group from PVA can increase the hydrophilicity of PDMS: $ZnCl_2$.

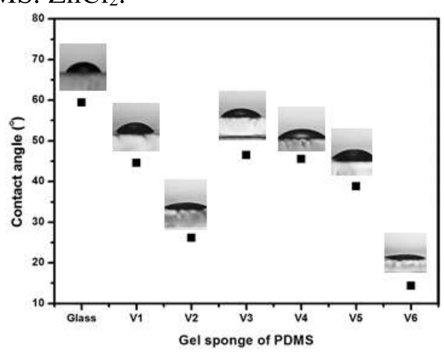

Fig.-5: The Contact Angle of Hydrophilic Sponge PDMS

At V3 the contact angle was 46.5º, the material seems like a gel. Besides that, V4 shows a contact angle of 45.5º. The addition of higher $ZnCl_2$ (V5 and V6) shows a decrease in the contact angle to 38.8 and 14.3º. This is due to the presence of PVA and PEG, and the increased $ZnCl_2$ greatly enhances the hydrophilic properties. In comparison, V4 succeeded in forming a hydrophilic solid sponge, while V5 and V6 formed a hydrophilic sponge, but with a jelly-like shape. The increase in hydrophilicity is indicated by the widening of the absorption band at 3400 cm^{-1} as the OH absorption band binds water. Optical characteristics (transmittance) were conducted to determine the intensity of light passing through the hydrophilic sponge (Fig.-6). Each composite shows a transmittance > 80% so that it can be applied to glass prototypes for dewatering

The hydrophilic sponge of V4 test for dewatering fuel oil shows that the hydrophilic sponge's ability to absorb water is very good (Fig.-7). Water is added intentionally to the oil as much as 2% (v/v). The V2 is unable to absorb water in fuel oil because the super hydrophilic of V2 is soluble in them. Observations show that due to the hydrophobic nature of the oil, there is no hydrogen bonding between the CH hydrocarbon and OH (water) dispersant in water. Then there is no OH-bound stretching absorption at around 3400 cm^{-1} and OH-bound deformation/scissors bending at around 1600 cm^{-1}. The IR spectra show that the uptake of dispersant water in the oil is rapidly absorbed as shown by the loss of hindered water in the vibration bending region 700-1250 cm^{-1}.

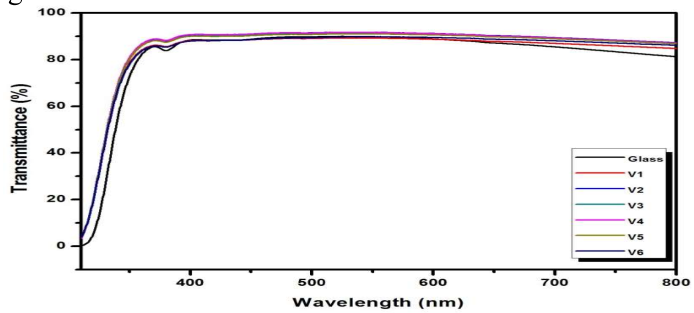

Fig.-6: The Transmittance of Gel Sponge PDMS

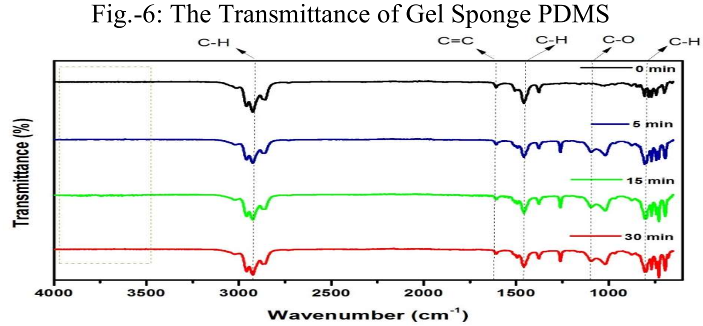

Fig.-7: ATR FTIR Hydrocarbon Fuel Oil after Dewatering with Hydrophilic Sponge V4 in Various Dipping Times

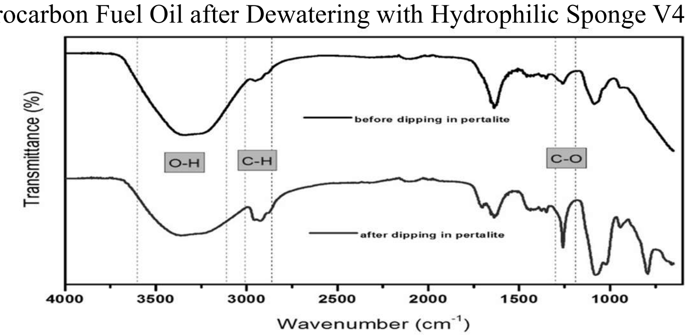

Fig.-8: Peaks of the ATR-FTIR Spectrum of V4 Hydrophilic Sponge Observed after 30 min Dipping On Hydrocarbon Fuel Oil

The water content in the hydrophilic sponge was identified using ATR FTIR spectra (Fig.-8). The peaks with intensities at 1055 and 1210 cm^{-1} superficially increase upon dehydration, the peak of H_2O rocking modes at 1036 cm^{-1}, the peak of H_2O hindered rotation at 1052 cm^{-1} and the peak of H_2O wagging at around 874 cm^{-1}. The shoulder peak at around 3229, 3399 is attributed as O−H stretching in H_2O, while in the region 1506, 1643, 1685, 1692, 1695, 1700, 1717, 1728, 1786, and 1808 cm^{-1} attributed as H_2O scissoring.[12] The morphology of V4 after dipping in hydrocarbon fuel oil is shown in Fig.-9 (a,b).

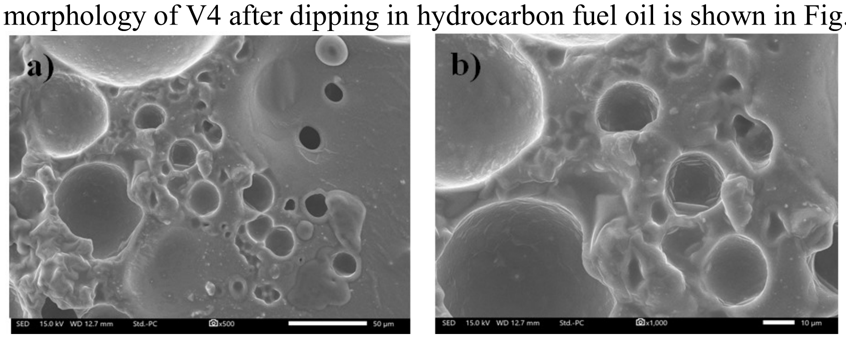

Fig.-9: SEM images of V4 Hydrophilic Sponge after Dipping on Hydrocarbon Fuel Oil a) 5000X and b) 10.000X Magnification

It is evident that sponges with macropores show an interaction with water. In a porous sponge (V4), when immersed in a hydrocarbon fuel oil containing water, the pores will open wide due to the ionic affinity of the polar layer for water molecules.[9]

CONCLUSION

The synthesis of hydrophilic sponge material has been carried out and has been successfully optimized through the composition of materials, namely PDMS, $ZnCl_2$, PVA, and PEG. It is difficult to form a solid sponge if only PDMS and $ZnCl_2$ are mixed. In PDMS: $ZnCl_2$ (V1) tends to be more liquid than composites added with PVA. A very high degree of hydrolysis results in gelation and is difficult to form a solid sponge product as in PDMS: $ZnCl_2$: PEG (V3). In PDMS: $ZnCl_2$: PVA (V2) is a superhydrophilic solid sponge, which is formed from the composition of PDMS, $ZnCl_2$, and PVA but can be soluble in water in fuel oil. The presence of PEG increased the density of the sponge, and also a higher $ZnCl_2$ composition which attracted water, the sponge formed was more jelly-like. While, when PVA is added, the hydrophilic solid sponge is formed because PVA is able to interact with water solvent through slowly hydrolysis reaction. In other conditions, through the addition of PEG and PVA, namely PDMS: $ZnCl_2$: PVA: PEG (V4), PDMS: $2ZnCl_2$: PVA: PEG (V5), and PDMS: $3ZnCl_2$: PVA: PEG (V6), they can form sponges, respectively. It was observed that with the same composition of PVA and PEG, while $ZnCl_2$ was increased, it showed an increased degree of gelation and the sponge became jelly-like. The sample is capable of absorbing water in fuel oil and is a hydrophilic and solid sponge, and there is PDMS: $ZnCl_2$: PVA: PEG (V4).

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