EFFECTS OF HYBRIDIZATION OF GRAPHENE OXIDE AND HALLOYSITE NANOCLAY ON THE OIL ABSORPTION OF POLYURETHANE NANOCOMPOSITE FOAMS

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effects OF Hybridization of Graphene Oxide And Halloysite Nanoclay On the Oil Absorption Of Polyurethane Nanocomposite Foams**". I also declared that it has not been previously submitted for the award for any degree or diploma of other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

C_e	Concentration of the diesel at equilibrium
C_i	Initial concentration of the diesel
K_1	Pseudo-First-Order rate constant
K_2	Pseudo-First-Order rate constant
O_0	Initial weight of foam
O_A	Weight of absorbed diesel
P_R	Oil absorption percentage
R^2	Correlated coefficient
S_S	Weight of saturated sorbent
S_W	Initial dry weight of sorbent
q_e	sorption capacities at equilibrium
q_t	sorption capacities at specific time
S	Oil sorption capacity
t	Time

LIST OF ABBREVIATIONS

GO	Graphene Oxide
HNC	Halloysite Nanoclay
PFO	Pseudo-First Order
PSO	Pseudo-Second Order
PU	Polyurethane
UTM	Universal Testing Machine
SEM	Scanning Electron Microscope

KESAN-KESAN PENGHIBRIDAN GRAFEN OXIDA DAN HALOISIT TANAH LIAT NANO TERHADAP PENYERAPAN MINYAK BAGI BUSA NANOKOMPOSIT POLIURETANA

ABSTRAK

Kajian ini bertujuan untuk menentukan kesan haloisit tanah liat nano (HNC), grafen oxida (GO) dan hibrid pengisi nano (HNC/GO) terhadap sifat dan kelakuan penyerapan minyak busa nanokomposit poliuretana (PU). Pemuatan pengisi HNC dan GO ialah 0.3, 0.6, 0.9, dan 1.2 phr. Busa nanokomposit PU telah dicirikan menggunakan ujian penyerapan minyak, ujian ketumpatan, ujian mampatan, dan mikroskop elektron pengimbasan (SEM). Imej SEM menunjukkan bahawa saiz liang busa PU menurun apabila HNC atau GO dimasukkan ke dalam formulasi itu. Ketumpatan PU/HNC dan PU/GO meningkat apabila pemuatan pengisi meningkat. Kekuatan mampatan busa nanokomposit PU/HNC meningkat sehingga pemuatan HNC mencapai 0.9 phr, tetapi menurun sedikit pada 1.2 phr. PU/GO pula menunjukkan kekuatan mampatan tertinggi pada 0.3 phr dan menurun dengan penambahan GO yang berlebihan. Penyerapan minyak busa nanokomposit PU telah meningkat dengan penambahan HNC atau GO. Penghibridan HNC dan GO adalah berdasarkan pertimbangan kebolehbusaan, kekuatan mampatan, dan kapasiti penyerapan minyak. PU/HNC-0.3/GO-0.3 mempamerkan kekuatan mampatan yang baik (0.019MPa) dan kapasiti penyerapan minyak (432.4%). Daripada kajian kinetik penyerapan, didapati bahawa penyerapan minyak busa nanokomposit PU sesuai dengan model kinetik pseudo-tertib-kedua, menunjukkan bahawa pengerapan kimia berlaku antara minyak dan busa nanokomposit PU.

EFFECTS OF HYBRIDIZATION OF GRAPHENE OXIDE AND HALLOYSITE NANOCLAY ON THE OIL ABSORPTION OF POLYURETHANE NANOCOMPOSITE FOAMS

ABSTRACT

This present study is aimed at determining the effect of halloysite nanoclay (HNC), graphene oxide (GO) and nanofiller hybrid (HNC/GO) on the properties and oil absorption behaviour of polyurethane (PU) nanocomposite foams. The loading of the HNC and GO is 0.3, 0.6, 0.9, and 1.2 phr. The PU nanocomposite foams were characterised using oil absorption test, density tests, compression tests, and scanning electron microscopy (SEM). The SEM images show that the pore size of the PU foams decreases when HNC or GO are introduced into the formulation. The density of PU/HNC and PU/GO increases as the filler loading increases. PU/HNC nanocomposite foam shows an increment of compressive strength until 0.9 phr and a slight decrease at 1.2 phr, while PU/GO shows the highest compressive stress at 0.3 phr and the compressive stress drops as filler loading increases. The oil adsorption of the PU nanocomposite foam was increased by adding HNC or GO. The hybridization of the HNC and GO is based on the consideration of foamability, compressive strength, and oil absorption capacity. The PU/HNC-0.3/GO-0.3 exhibited good compressive strength (0.019MPa) and oil absorption capacity (432.395%). From the absorption kinetics study, it was found that the oil absorption of the PU nanocomposite foams fit well with the pseudo-second-order kinetic model, indicating that chemisorption happens between the oil and the PU nanocomposite foam.

CHAPTER 1

INTRODUCTION

1.1 Overview

This chapter covers the research background, problem statement, research objectives, research approach, research scope, and thesis outline of this study. The background of Polyurethane (PU) provides an overview on this research work. Problem statement has pointed out the problem faced in this field of research study. There are two research objectives that need to be achieved in this study. The research approach and research scope are used to ensure that the research objectives are achieved. Finally, the overall thesis outline of this study is summarized.

1.2 Background

PU was invented by Otto Bayer and Colleagues from Germany in 1937. PU is a thermoset polymer that exhibit with good mechanical and physical properties, excellent elastomeric properties, and high durability (Li et al., 2021). PU is a thermoset polymer which is composed of urethane links, and it is a versatile polymer which can be used in many types of application (Lanaro et al., 2018). These polymers exhibit interesting properties that arise from their block copolymer structure and the resulting phase separation (Health et al., 2020). PU can be obtained through the reaction between diisocyanate with the presence of (R-N=C=O) and polyol which is an organic compound that containing multiple hydroxyl group and after the reaction there is carbamate group (–$NHCO_2$) exist in the molecular backbone of the PU (Laad, 2020).

Nanocomposite is a class of the nanomaterials where in one or more phases at nano-sized dimension which is zero, one and two dimension and it can be embedded in ceramic, metal or polymer materials (Malhotra et al., 2018). Polymer nanocomposites (PNCs) can be defined as polymeric matrices with the addition of nanofillers with at least a dimension within the range of 100 nm (Idumah et al. , 2021). Polymer nanocomposites is a composite material which is consists of a polymer matrix and an inorganic dispersive phase that has at least one dimension is in nanometric scale (Passador et al., 2017). Conventional wet and dry processing techniques are used to produce the nanocomposites (NCs). PNCs have been widely reported in the scientific literature due to its vast applications like sensors, material science, dielectrics, semiconductors, biomedical field, biotechnology, ballistic and aerospace materials, food packaging, coating and cosmetics. Researchers found out that the addition of organic/ inorganic nanofillers in polymer helps to improve the mechanical properties and thermal properties of PNCs (Vidya et. al., 2020).

Foams are defined as materials containing gaseous voids surrounded by a denser matrix, which is usually a liquid or solid. Foams have been widely used in a variety of applications: e.g., insulation, cushion, filtration, absorbents and weight-bearing structures. Foams of high porosity with interconnected pores have also been used as tissue engineering scaffolds for cell attachment and growth. Various polymers have been used for foam applications, e.g., PU, polystyrene (PS), polyolefin (polyethylene (PE) and polypropylene (PP)), poly (vinyl chloride) (PVC), polycarbonate (PC) and others. Depending on the composition, cell morphology and physical properties, polymer foams can be categorized as rigid or flexible foams. Rigid foams are widely used in applications such as building insulation, appliances, transportation, packaging, furniture, flotation and cushion, and food and drink containers, whereas flexible foams are used as furniture, transportation, bedding, carpet underlay, textile, gaskets, sports applications, shock and sound attenuation, and shoes.

In order to remove oil contaminant from water, different techniques have been developed in the past centuries and there 3 methods to remove oil from water which are chemical, biological and physical methods. All of those 3 methods were done with the usage on different type of filters, chemical dosing, reverse osmosis, gravity separation, ultra-filtration, microfiltration, biological processes, air floatation, membrane bioreactor, chemical coagulation, electrocoagulation and also electroflotation. Among all the methods that had been used for removal of oil contaminants, absorption is the most profitable methods to do it as it can easily remove or recover the oil from the water. There are 3 basic types of oil sorbent which are natural organic, natural inorganic and synthetic adsorbents. In the case of natural sorbents, sugar can bagasse and vegetable fibers were the popular natural sorbents to be use for the adsorption of oil. Synthetic sorbents that used for the adsorption of the oil contaminants were rubber powder, expanded perlite, polymeric material based on butyl rubber and oleophilic polyurethane foams (Nikkhah et. al., 2015).

Oil sorption mechanism is just an uptake of oil by the absorbent which the process involves multiple kind of mechanism such as adsorption, absorption and capillary uptake into the sorbent matrix. There are 2 major factor that will act as the limiting factor that determine the oil sorption capacity which are structural parameter such as foam pore size and surface area-to-volume ratio, and wetting properties of the materials such as hydrophobicity. In recent year, 3-Dimensional (3D) porous material have been widely explored by the industries for the oil sorbent application due to their high porosity, large specific surface are, low density, and flexibility for the material system design. (Hwang et. al., 2020).

In current reported studies about porous adsorbent, there are roughly 3 categories which are natural absorbents, 2-Dimensional and 3-Dimensional synthetic porous materials. Natural absorbents such as straw, cotton/wool fibrils, corn cobs, cellulose/kapok fibrils, and milkweed floss (Payne et al., 2012), are the materials used for oil spill cleanup in the early days due to their high degradability under natural weathering. However, due to their limitation such as low oil/water selectivity, poor absorption capability, low rate of reusability which are the reason limit their effectiveness when using them during the oily wastewater treatment process. (Xu et al., 2015). 2-Dimensional materials such as membranes and mesh (Zhang et al., 2013), have lower and easier production cost and process and possess of high separation efficiency helps them to play a significant role in the real-life industrial separation of oil/water mixtures (Oliveira et al., 2021). However, in order to carry out oil/water separation mechanism for 2-Dimensional porous material, it need to collect all the oil-contaminated water before the oil removal process which increase the difficulty to undergoes removal of oil spillage at the outside environment (Feng et al., 2015). However, the 3D porous materials, mainly including sponges (Chen et al., 2019), aerogels (Zhang et al., 2021), and foams (Rizvi et al., 2014) had overcome the difficulty to carry out oil removal process in the outside environment with just put the materials in the oil contaminated area without any requirement of specific equipment unlike 2-Dimensional material have to undergo some specific process (Lu et al., 2014). In the future, there are possibilities that 3-Dimensional porous material to develop into more environmentally friendly, recyclable, facile and also can perform high efficiency in purifying or removing the oil/water mixture with a better flux rate.

Among the 3-Dimensional porous material that mentioned in previous paragraph, carbon sponges and aerogels had shown superhigh oil-solvent/water separation capabilities with an oil absorption capacity of more than 130 g/g and a separation efficiency of up to 98.8% but the performance of the porous material all come from very complex synthesis process and expensive materials. In some cases, the high-performance materials possess very poor mechanical properties which are challenging for worldwide application. In this context, the low material and manufacturing costs, outstanding mechanical performance and reusability, and pronounced separation capability of oily wastewater mixture that possessed by the polymer-based material become a promising candidate for the widely usage application (Zhao et al., 2021).

Among all the porous materials that available in the market, polyurethane (PU) foam can be a promising candidate for the oil sorption application due to it good oil swelling properties, excellent mechanical properties ang also facile mass production. However, the hydrophilic and hydrophobic functional groups that exist on the surface of the PU foam will encourage the absorption of water as well as oil. Therefore, addition of the additives and filler had become an option in order to improve the oil/water selectivity. In some studies that been conducted in the past few decades, some researchers found out that the incorporation of fillers such as nanoclay, carbon nanotube, graphene oxide and silica can help to enhance the sorption capability the foam (Hwang et. al, 2020).

In the year of 2014, Wang et al. prepared superoleophilic and superhydrophobic polyurethane sponge by coating with the usage of carbon nanotubes embedded in poly(dimethylsiloxane)and the results shows that higher efficiency of separating oil from water was obtained. Oribayo et. al (2017) said that polyurethane foam with the incorporation of the graphene oxide in the matrix was identified as unique oil sorbent for the oil removal application. Pan et al. (2013) had done a research on depositing chitosan and TiO_2 nanotubes alternatively using layer by layer self-assembly technique in flexible PUF and the results shows that the sorption capacity was 29 times, and this sorption ability was maintained even after 50 absorption cycles. Tai et al. (2014) introduced carbon-silica nanofibrous membrane with improved mechanical strength, thermal insulation, toughness and flexibility via electrospun technique. Liu et al. (2019) prepared super hydrophobic and super oleophilic graphene-melamine foam (rGO-MF) via simply soaking and chemical reduction method. The prepared foam showed excellent oil absorbing capacity with very good performance even after 10 cycles of experiment (Liu et al., 2019). Bifunctional MoS2 coated melamine-formaldehyde sponges for efficient oil–water separation and water-soluble dye removal was explored (Wan et al., 2017). The nanoclay that introduce to the PU foam is used as the novel oil sorbent and with the presence of the nanoclay in the PU formulation, the efficiency and removal capacity were improved compared to PU foam without nanoclay (Nikkhah et al., 2015).

1.3 Problem Statement

According to Rahmani et al. (2017), in order to remove and collect oil in oil-water system, porous absorbent materials such as organoclays, straw and activated carbon were used as the desired choice for the oil removal application due to their low operational and manufacturing cost. However, there are limitation existed in the absorbent materials such as environmental incompatibilities, low absorption capacity, low absorption rate and poor reusability always the challenge the industry facing. According to Satria (2022), PU foams has become a promising absorbent material in recent year due to it being excellent in mechanical properties, existence of the porous structure, low density and also high surface area-to-volume contact ratio have made PU foam a good porous structure to be use in the oil removal applications. However, the oil selectivity of the PU foam on oil was decrease when the oil is in an oil-water system. The poor selectivity of the PU foam will also absorb water which lower the efficiency of the oil absorption capacity and efficiency. The incorporation of nanofiller into the matrix of PU can be done in order to increase the oil absorption efficiency of the nanomaterial PU foam. There some researchers incorporate nanoclay with PU foam to increase the oil absorption efficiency and the result shows that the capacity of oil uptake was increased 18% and the efficiency of oil uptake in an oil-water system increased around 56%. There’s another group of researchers done the modification with the graphene oxide and the results the efficiency and capacity of oil uptake also increase. However, all the research were mostly done in high filler loading which cause high cost for the preparation of the foam to be used in worldwide.

Most of the research that had been done are mostly using the coating method where the superhydrophobic is coated on the surface of the PU foam with surface modification method to improve the efficiency of separating or absorbing the oil from the water and most of them use high filler loading to do research. In this project, the main objective is to investigate how does the one-shot synthesis method of hybrid polyurethane foam affect the oil absorption capacity of the PU foam with the difference in nano filler loading and how does the hybridization of the PU foam help to improve the oil absorption properties with lower filler loading.

1.4 Research Objective

This research focuses the type of nanofiller (HNC and GO) used and the optimum nanofiller content on the oil removal efficiency, mechanical and chemical properties of PU with halloysite nanoclay and reduced graphene oxide, which with research objectives:

I. To investigate the effects of nanofiller (halloysite nanoclay and graphene oxide) on the properties of PU foams.
II. To determine the effects of halloysite nanoclay and graphene oxide on the oil sorption behaviour of the PU foams.
III. To determine the effects of hybridization of halloysite nanoclay and graphene oxide on the oil sorption behaviour of the PU nanocomposite foams.

1.5 Research Scope

There are four stages of this research which are raw material synthesis, sample preparation, oil absorption test with the usage of azeotropic distillation method, and characterization by using SEM, FTIR and density test.

The oil absorption capacity of the PU foam with different nano filler content were investigated. In this research, nanoclay is added into the PU foam to study its effect and possibly to improve the oil removal efficiency of the PU. The nanoclay content that used were 0%, 0.3%, 0.6%, 0.9% and 1.2%. The influences of the nanofiller content regarding to their filler content on the oil absorption capacity is studied through the isotherm of the oil adsorption. After that, GO with the content of 0%, 0.3%, 0.6%, 0.9% and 1.2% were tested with the oil absorption test and hybridized with the optimum NC filler content that is obtained from the result of the oil absorption test. The influence of the GO on the oil absorption capacity is also determined through the oil absorption test.

1.6 Thesis Outline

This thesis consists of five chapters which are:

Chapter 1: Introduction on background, problem statement, research objectives, research approach, research scope and thesis content.

Chapter 2: Literature review of polyurethane which includes the advantages and application of PU, filler reinforced PU, reason of development, oil absorption and oil absorption kinetic.

Chapter 3: Methodology of this study which includes the research flow, method used for sample preparation and testing of the samples, raw materials and equipment used in this research.

Chapter 4: Results and discussion on the effects of nanofiller (nanoclay and graphene oxide) on the properties of PU foams, the effects of nanoclay and graphene oxide on the oil sorption behavior of the PU foams and the effects of hybridization of nanoclay and graphene oxide on the oil sorption behaviour of the PU nanocomposite foams were discussed.

Chapter 5: Conclusion on this research work as well as suggestions for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter provides an overview of previous research on the PU. It describes the advantages and application of PU, types of nanofillers for PU foam oil absorption application, as well as oil absorption techniques, properties enhancement of PNC on oil absorption and also applications of PNC foam.

2.2 Polyurethane (PU)

In year 1973, PU was invented by Otto Von Bayer and his co-workers. In the past 49 years, PU had been used widely by the public in many applications such as furniture, footwear, construction, electronics, automotive, packaging and others type of appliances as PU are consider a broad class of materials (Suleman et. al 2014). According to market research report that produce by Fortune Business Insights, the global PU market size was around USD 56.45 billion in the year 2020 and the PU foam covers almost 29% of the total market of PU according to Molero et. al (2005). According to Li et. al (2021), PU is composed of the urethane links which can be a thermoplastic polymer or a thermoset polymer depending on the application. PU itself possesses many kinds of good properties such as good mechanical properties, excellent elastomeric properties if it is thermoplastic polymer and high durability.

According to Suleman et. al (2014), PU are considered as esters or amide esters of the carbonic which were able to synthesize by the chemical reaction between the polyol group with diisocyanates group and after the reaction there is presence of carbamate group ($–NHCO_2$) exist in the molecular backbone of the polyurethane according to Meena (2020). According to Health et. al (2020), the interesting properties that PU possessed were due to their block copolymer structure and the resulting phase separation. In Figure 2.1 shows the chemical reaction to obtain polyurethane. Due to the versatility of the PU possessed, the changing on the synthesizing condition can be altered to obtain desired mechanical properties. In Figure 2.2 shows the example of PU foam and SEM image which was taken from Jaratrotkamjorn et al. (2020).

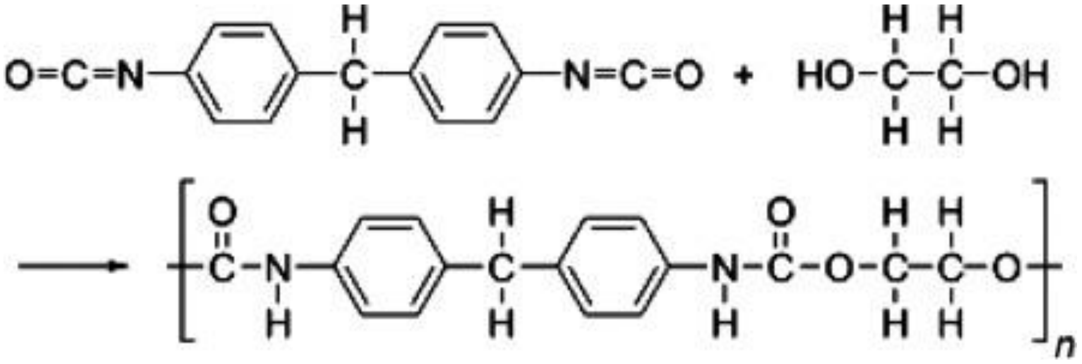

Figure 2.1 : Chemical reaction to form Polyurethane (Meena, 2020).

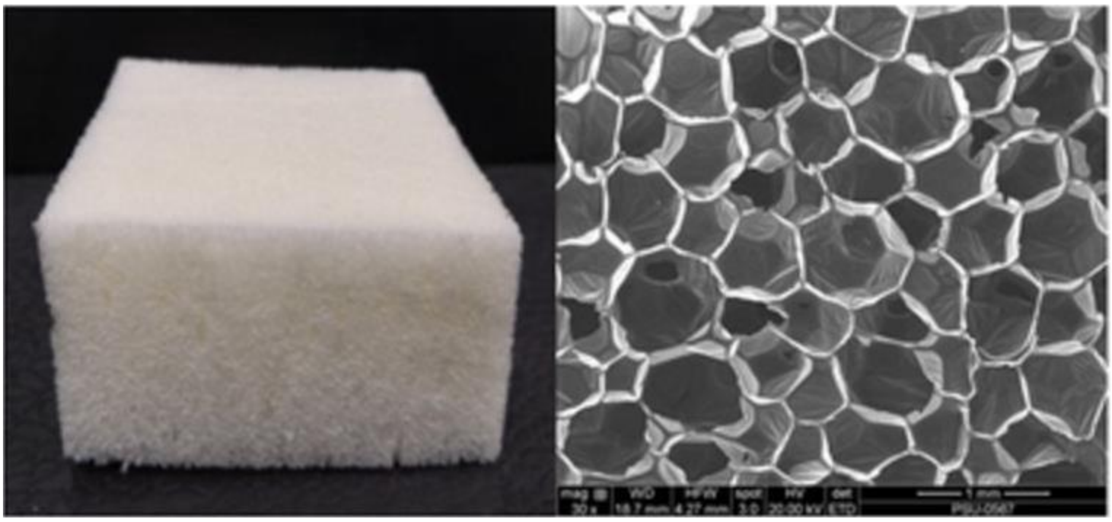

Figure 2.2 : Example of the polyurethane foam (Jaratrotkamjorn et al.,2020).

To produce PU foam, there are three types of foaming system can be used based on the type of the chemicals used in the synthesis process. The three types are:

- One-step-One-shot system
- Quasi-Pre polymer
- Full Pre-polymer system

One step system and Quasi system are mostly used in the foaming industries where One step process mainly just mixing component A and component B for the formation of PU foam. Component A was mostly only diisocyanate component while component B usually consists of polyol, blowing agent, surfactant and catalyst. However, the Quasi Pre polymer system will used component A diisocyanate component is take with polyol and component B with the rest such as polyol, surfactant, blowing agent and catalyst. However, in the Full Pre system, component A were usually the polymer which the diisocyanate component and polyol component was added together and component B was the other chemical such as surfactant, blowing agent and catalyst.

2.2.1 Advantage of PU foam

According to Joy et. al (2020), PU foam is another variety of the polyurethane where it has in flexible state and also rigid state. The foam acquires all the properties that PU had but with lower weight and also better machinability makes the foaming of the PU become an option for required applications. Due to the flexibility of the flexible PU foam, it can act as an impact absorber and able to return to its original dimensional for further usage.

The high porosity characteristic of the PU foam possessed can be used for the oil absorption application where the 3-Dimensional (3D) porous structure that exist in the PU foam were able to hold liquid inside the foam cell. The 3D porous structure that porous material possessed provide room for the liquid to occupied by diffusion of the liquid from high liquid concentrations region to low liquid concentrations region or empty spaces. The higher the porosity of the foam, the better liquid uptake capability of the foam possessed.

2.3 Oil absorption capacity

2.3.1 Factors that effect the foam oil sorption capacity

According to Udayakumar et al. (2021), the factor that effect the oil absorption capacity are ability to hold liquid in their crosslink network, wettability, oil uptake capability and the hydrophobicity of the materials used in oil absorption.

Firstly, the ability to hold liquid were mostly contributed by the crosslink network form in the foam. The denser the crosslink that form inside the foam the better the ability of foam to hold the oil inside. Denser crosslink means smaller pore size will be obtained. According to Harikrishnan et al. (2006), the smaller the size of the pore size of the foam, the better the oil absorption capability as the oil that absorbed into the foam would not escape from the cell easily.

Next, the wettability of the foam also plays a big role in increasing the oil absorption capability. The wettability of the foam toward the oil determine how well does the performance of the foam do in the oil absorption application. The incorporation of the filler such as nanoclay was introduced by Nikkhah et al. (2015) where the nanoclay will improve the hydrophobicity of the foam which will increase the absorption of the foams. The better the wettability of the foam toward oil, the higher oil absorption capability will obtain.

2.3.2 Improvement on the oil sorption capability

According to Nikkhah et al. (2014), they modified the polyurethane foam structure with the integrating of the cloisite 20A nanoclay into the PU foam in order to enhance the oil removal efficiency of their PU foam from water. From the oil absorption testing their done, they claimed that the sorption capacity of modified PU foam increased up to 16% and the oil removal efficiency increased up to 56% in water-oil system. the introduction of the cloisite 20A nanoclay into the PU foam led to cell opening and strengthened it. When optimum filler loading of cloisite 20A was added into the PU formulation, the PU foam shows the highest oil absorption capacity and oil removal efficiency. The introduction of the cloisite 20A help to increase the strength of the foam which also improve the ability of the foam to hold more oil in it structure thereby increase in absorption capacity.

2.4 Nanofiller for PU oil absorption application

2.4.1 Nanoclay (NC)

According to Zawrah et al. (2017), the organo modified nanoclay shows a results high absorption of hydrocarbon. The hydrocarbon used in the process were diesel, gasoline and lubricant oil. Organo modified nanoclay was able to absorb 3 times more than its own weight for both gasoline and diesel and 2 times for the lubricant oil. From the results it shows that organo modified nanoclay shows that’s nanoclay type of filler were able to absorb oil which indicate that nanoclay might be a promising nanofiller to be used in the oil absorption application.

2.4.2 Silicone

According to Guo et al. (2014), the silicone that added into the PU formulation were act as the surface modifications where the pore size of the PU foams was decreased when the concentration of silicone in the PU foam formulation increase. However, the research also said that the pore size of the silicone modified PU foam become too small which even the oil molecules where not able to be absorbed in due to the concentration of the silicone in the PU foam formulation was too high. The excessive decrease of the pore size causes the permeability of the foam to liquid where the liquid unable to pass through the pore to fill up the void in the foam which decreases the oil uptake efficiency of the foam.

2.4.3 Graphene Oxide (GO)

According to Dideikin et al. (2019), Benjamin Brody was the first person to synthesize graphene oxide in 1859 which was much earlier that the discovery for the graphene. According to Park et. Al (2009), GO were produced by the chemical exfoliation and oxidizing of layered crystalline graphite. At the definite condition, the oxidizing graphite carbon atoms will conserve the integrity 2-Dimensional structure with oxygen which containing functional groups that attached to both carbon plane layer and to the edge according to Chen et. Al (2012).

According to Rahmani et al. (2017), a good absorbance usually has porous structure in it. The modified PU sponges possess of porous structure and hydrophobic surface make the sponges an outstanding sorbent for oil and hydrocarbon remove. The hydrophobic surface that the modified PU foam are more selectively to oil once modified sponges were on contact with oil and water. This shows that sponges that modify with graphene oxide give good hydrophobic surface where the sponges will then absorb oil or hydrocarbon in a water-oil/hydrocarbon system.

2.5 Absorption Kinetic

Absorption is a process of mass transfer where the pollutants or the sorbate move from the liquid phase to the solid absorbent. Through the year of research of the absorption kinetic by the scientist, there are various kind of the absorption kinetic model had been proposed and accepted worldwide for example Psuedo-First-Order kinetic model (PFO) by Lagergren in 1898, Pseudo-Second-Order kinetic model (PSO) by Ho in 1996, Mixed-Order by GUO and Wang in 2019, Ritchie's equation in 1997 and others (J. Wang & Guo, 2020).

Among all the absorption kinetic model that proposed, the most widely used absorption kinetic model was the PFO and PSO that was proposed by Lagergren and

HO. Throughout the absorption kinetic model studies, it provides us the information about the absorption rate, the capability or the performance of the absorbent and also the mass transfer mechanism.

In absorption step, there are 3 steps of mass transfer steps which are external internal and the absorption on the active sites. The first step is the external absorption where the absorbate where transfer through the liquid film around the absorbent and this always happen due to the concentration difference between the bulk solution and the surface of the absorbent. The next step is internal diffusion where the absorbate was diffuse into the pore of the absorbent. The last step would be the absorption of the absorbate in the active site of the absorbent.

2.5.1 Pseudo-First-Order Kinetic Model

According to Wang et al. (2020), PFO kinetic model was introduced by Lagergren in 1898, starting from the sorption capacity which define the sorption phenomenon that occurs at the interface between solid and liquid according to the following equation:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \ (1)$$

where q_e (g/L) and q_t (g/L) are the sorption capacities (expressed as the amount of the sorbate sorbed on the sorbent unit mass) at the equilibrium conditions and at time t, respectively. K_1 (s^{-1}) is the rate constant of the PFO sorption reaction. Integrating Equation (1) with boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t a linear relation can be obtained, as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \ (2)$$

By using Equation (2), the K_1 value were calculated as the slope of $\ln(q_e - q_t)$ versus time t.

Equation (2) is the linearized equation for the PFO kinetic model, and the equation is widely used by researchers to fit the kinetics data and calculate the parameters required which are q_e and K_1. However, the linearization process of the PFO kinetic model might causes inaccurate estimation and calculation of the parameters according to Ho (2006). Therefore, correlation coefficient R^2 was used to identify how does the fitting of experimental data with the theoretical data. If the R^2 is smaller than 0.9, it should be considered that the experiment data obtained didn't follow the PFO. The PFO parameter q_e is the equilibrium absorption amount and K_1 is frequently used researcher to describe how fast the absorption equilibrium is achieved.

2.5.2 Pseudo-Second-Order Kinetic Model

PSO kinetic model was developed by Ho in 1999 (Ho & Mckay, 1999). The PSO kinetic model is generally applied for sold-liquid systems, and it is based on the expression on the following expression:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 (3)$$

By integrating Equation (3) at boundary conditions ($q_t = 0$ at t = 0 and $q_t = q_t$ at t = t), the PSO kinetic can be expressed in linear form as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \ (4)$$

Where K_2 $[g/(gmin)]$ is Equation (4) rate constant. The intercept and slope of linear t/q_t versus time plot was used to determine the PSO rate constant, K_2, and maximum equilibrium sorption q_e, respectively.

The Equation (4) shown above is the linearization of the PSO kinetic model and this model was widely used to describe the absorption process. Most of the research paper that study about the absorption kinetic used PSO model as their prediction of their absorption experimental data and used to calculate the absorption rate constant for their absorption testing.

2.6 Hybridization

Hybridization always the favorable topic in the polymer industry as most of the company want to obtain a good mechanical properties with the addition of different kind of filler to improve or obtain desired properties. According to Aswathy et al. (2021), the hybridization between different filler was able to achieve to obtain some specific properties such as the hybridization synergy between filler that have high surface area-to-volume ratio will give higher mechanical properties when compared to composite that using only individual filler.

CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter provided the overview of the chosen research methods and the detailed research flow of this study. The understanding of the research methodology is important as the further investigations and improvements are understand by the readers. The information and details on the materials, instruments used, test specimen preparation steps and tests been carried out are presented.

3.2 Research Flow

A detailed methodology of this project is prepared to provide clear path with the most appropriate ways to investigate the effects of nanofiller (HNC and GO) on the properties of PU foams, the effects of HNC and GO on the oil absorption behavior of the PU foams and the effects of hybridization of HNC and GO on the oil absorption behavior of the PU nanocomposite foams. The GO and the HNC is then dispersed into the PU part A. The PU part A and part B is then mixed, and PU nanocomposite foam is obtained. Oil absorption test is done to test the oil absorption ability of the PU foam with the usage of xylene to wash out oil and water and azeotropic distillation is then done to obtain the oil that had been absorb by the PU foam. Once obtaining the good testing result, foam samples are prepared again with the PU + GO. The filler loading with best result from the PU + HNC and PU + GO were selected and form PU + (NC/GO) nanocomposite foam. The GO/HNC hybrid PU nanocomposite foam is then tested with oil absorption test. After that, surface morphology (SEM), FTIR, compression test and oil absorption properties were studied. Figure 3.1 shows the research flow of this project.

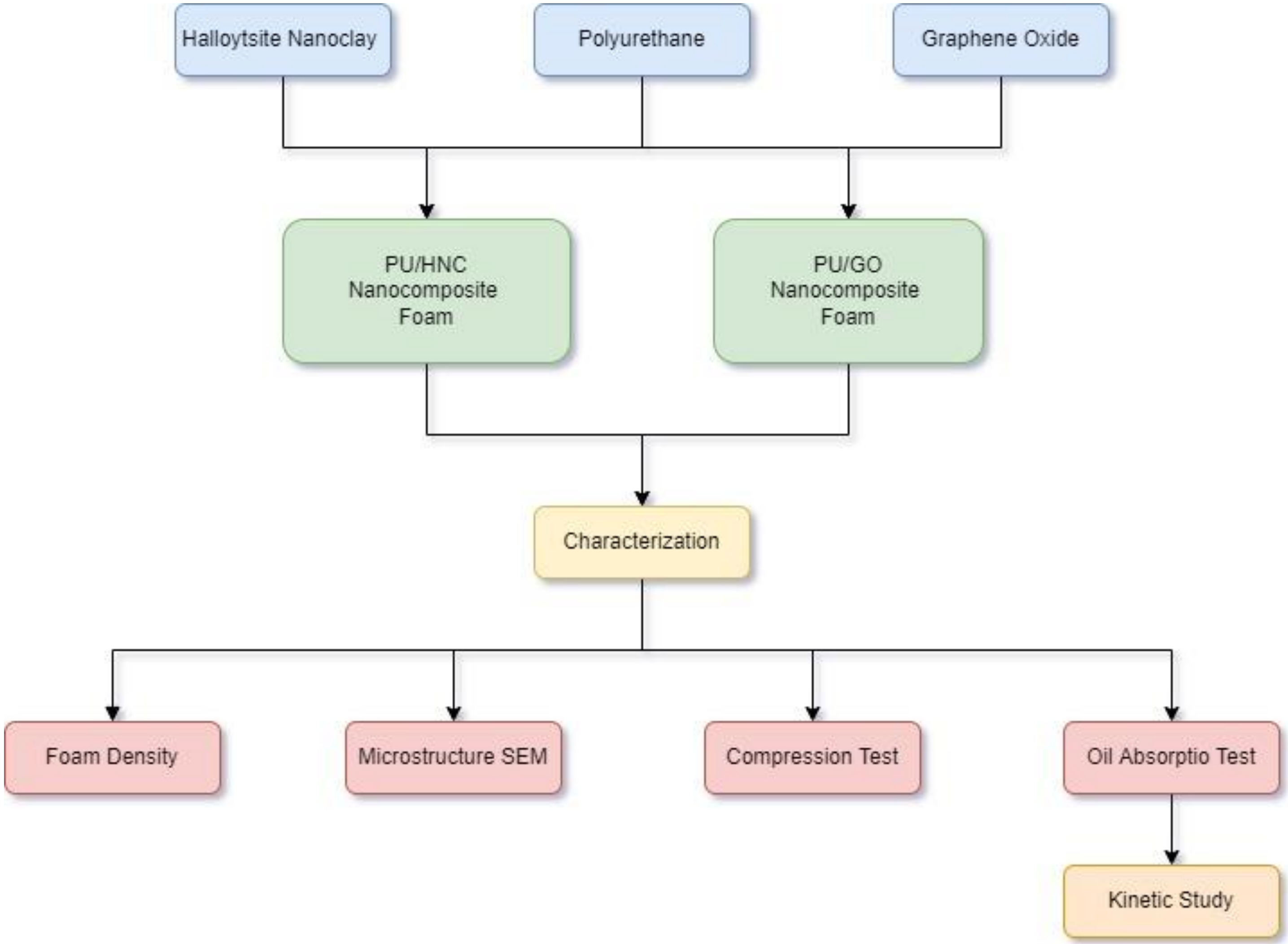

Figure 3.1 : Flow chart of the preparation and characterization of PU/HNC and PU/GO nanocomposite foam.

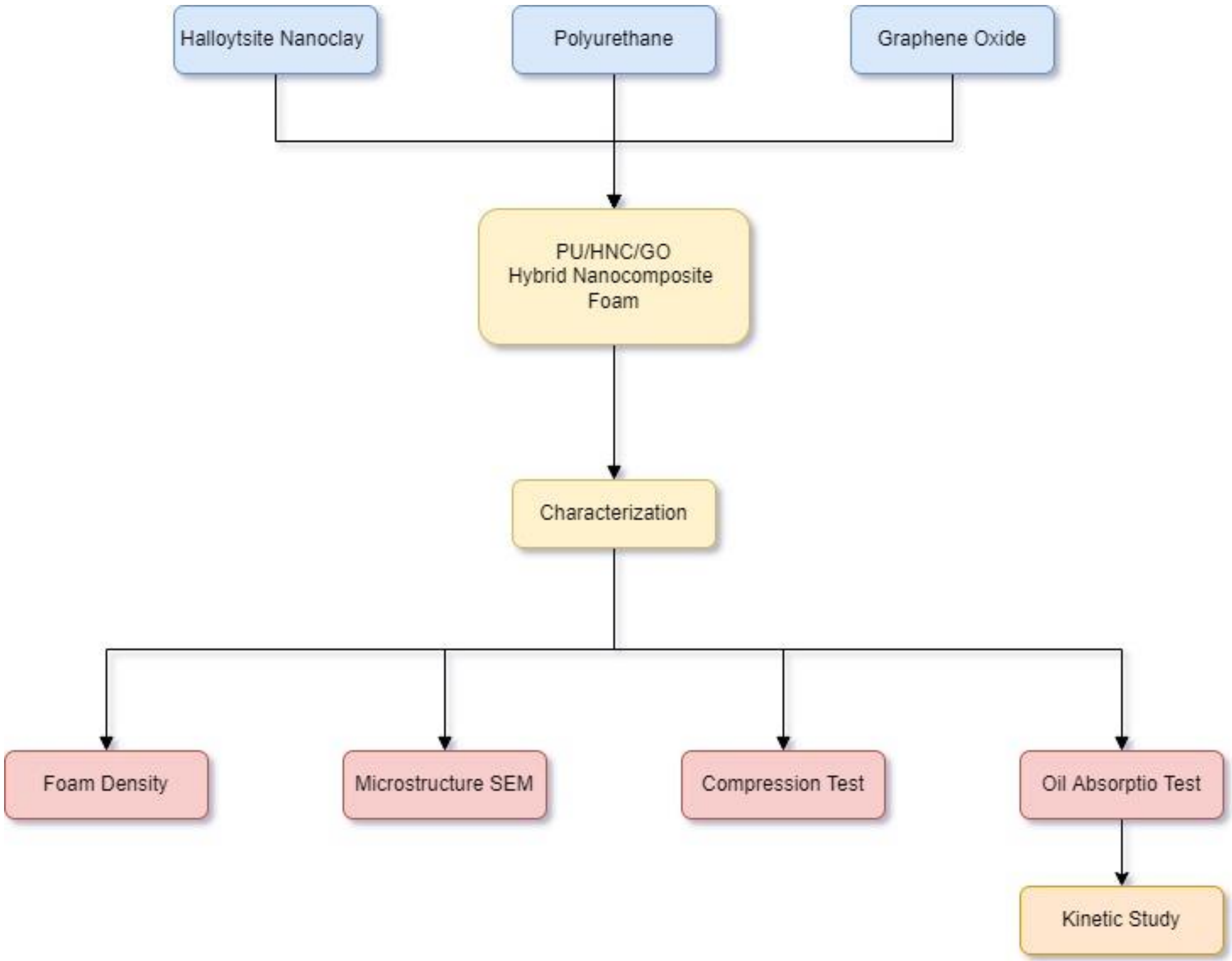

Figure 3.2 : Flow chart of the preparation and characterization of PU/HNC/GO nanocomposite foam.

3.3 Material

Polyurethane Part A (polyether polyol, surfactant, catalyst) and Polyurethane Part B (diphenylmethane diisocyanate and higher oligomers of diisocyanate for example dimers, trimers or tetramers) that used in this study were supplied by Euro Chemo-Pharma Sdn. Bhd. Halloysite nanoclay (HNC) in powder form was used as nanofiller. The diameter and length of the HNC was in the range of 30-70nm and 1-3μm respectively. Graphene oxide (GO) in powder form was used as nanofiller with bulk density ~1.8g/cm^3. Halloysite nanoclay (HNC) and Graphene Oxide (GO) were from Sigma-Aldrich Chemistry Sdn. Bhd.

3.4 Sample Preparation

3.4.1 Preparation of PU Foams

10 g polyol (Part A) was mixed with 7.5 g of diisocyanate (Part B) and mix for 30 seconds. After 30 seconds of continuous stirring, it was observed that polyurethane (PU) foam was formed with a volume of about 25-30 times that of the reactants. It was allowed to cure for about 1 hour.

3.4.2 Preparation of PU/Halloysite Nanoclay Foams

Halloysite Nanoclay (HNC) was dried in an oven under the temperature of 100 °C for 24 h, and then mixed with Part A for the filler dispersion. Next, the mixture was then mix with Part B for the PU foam formation. The final mixture wad then left for foaming and curing for 30 minutes. Prepared foam was cut into 1.5 cm-3 cubes to be used in the sorption experiments. Table 3.1 shows the materials composition and designation of the PU/HNC nanocomposites foam.

Table 3.1 : Materials composition and designation of the PU/HNC nanocomposite foams

Materials designation	Polyol (g) Part A	Diisocyanate (g) Part B	HNC (phr)
PU	10	7.5	0
PU/HNC-0.3	10	7.5	0.3
PU/HNC-0.6	10	7.5	0.6
PU/HNC-0.9	10	7.5	0.9
PU/HNC-1.2	10	7.5	1.2

3.4.3 Preparation of PU/Graphene Oxide Foams and PU/HNC/GO hybrid nanocomposite foams

Graphene Oxide (GO) was dried in an oven under the temperature of 100 °C for 24 h, and then mixed with Part A for the filler dispersion. Next, the mixture was then mix with Part B for the PU foam formation. The final mixture wad then left for foaming and curing for 30 minutes. Prepared foam was cut into 1.5 cm x 1.5cm x 1.5cm cubes to be used in the sorption experiments. Table 3.2 shows the materials composition and designation of the PU/GO nanocomposites foam.

Table 3.2 : Materials composition and designation of the PU/HNC nanocomposite foams

Materials designation	Polyol (g) Part A	Diisocyanate (g) Part B	GO (phr)
PU	10	7.5	0
PU/GO-0.3	10	7.5	0.3
PU/GO-0.6	10	7.5	0.6
PU/GO-0.9	10	7.5	0.9
PU/GO-1.2	10	7.5	1.2

3.4.4 Preparation of PU/HNC/GO hybrid nanocomposite foams

For the PU/HNC/GO hybrid nanocomposite foams, the preparation procedure was similar to the preparation of HNC and GO but the difference was that both HNC and GO were mixed with part A. After that, the mixture was mixed with part B and left for 1 hour to provide enough time for the foaming and curing reaction. Prepared foam was cut into 1.5cm x 1.5cm x 1.5cm cubes to be used in the sorption experiments. Table 3.3 shows the materials composition and designation of the PU/HNC/GO hybrid nanocomposites foam.

Table 3.3 : Materials composition and designation of the PU/HNC/GO hybrid nanocomposite foams

Materials designation	Polyol (g) Part A	Diisocyanate (g) Part B	HNC (phr)	GO (phr)
PU/HNC/GO	10	7.5	0.3	0.3

3.5 Characterization

3.5.1 Absorption determination method

The method for the measurement of the oil and water absorption capacity was based on the Standard Test Method for sorbent performance of adsorbents (ASTM F726-99). All the sorption experiments were performed in water–diesel system with same initial weight of oil which is 5g of diesel. In water–diesel system test, 5g of diesel was poured into a 100 ml beaker containing 50 ml of deionized water. Then, the adsorbent cubes were added to the system. The content of the beaker was allowed to settle for a period of 5, 10, 15, 30, 45 and 60 min. Then, adsorbent cubes were removed and put into glass beaker using forceps and weighted accurately using balance to