Investigation of Tribological Properties of Hybrid HDPE Polymer Nano Composites

by

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(23053)

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Mechanical Engineering

With Honours

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to verify that I have a full responsibility for the work submitted in this project. My work is original unless stated in the references and acknowledgments. The original work contained in this document was not done by unspecified sources or persons.

NURSYHIRA AZAD BT ABUL KALAM AZAD

ABSTRACT

High-density polyethylene (HDPE) is a thermoplastic polymer, having various applications when used as a primary phase in polymer nanocomposites. However, pure HDPE is vulnerable to fail in tribological properties, particularly bearing applications. Pure HDPE is susceptible to failure in tribological applications owing to the absence of branches in its polymeric chains which make easy for the chain to slide past easily over one another. The high tendency of nanoparticle aggregation in the polymer matrix usually restricts the enhancement in nanocomposite properties. The inter-facial effect between the nanoparticles and the polymer matrix is a critical problem for all types of nanocomposites. Nanofillers (CaCO3/Nano clay) in this research project was developed by masterbatch melt compounding technique. The tribological properties of nanocomposite developed was investigated by Pin-on-Disk method. The mass loss of each sample was noted in the testing, and wear rate of samples were calculated. The morphology properties of nanofillers (CaCO3/Nano clay) in HDPE polymer resin was evaluated by FESEM images. Experimental results proved that the Hybrid samples were preferred combination as compared to non-hybrid. The best sample with the lowest wear rate noted in this experiment are samples 5BC and 15BC with $0.1\text{x}10^{-4}$ kg/Nm. Morphological study was conducted on sample 5BC, and there was a slight to no cavitation around the clay particle and sample display a good encapsulation of $CaCO_3$ by bentonite via the interlocking mechanism. It was confirmed that all samples had a lower wear rate compared to pure polymer except for samples 7BC and 11BC which having filler particles agglomerate for both samples.

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CHAPTER 1

INTRODUCTION

1.1 Background

Polymer composites had been rapidly used in the aviation, automobile and chemical sectors for the past few decades, as they can offer a lower weight of alternative compared to traditional metallic materials. The applications such as bearing and seals, gears, cams, etc., concern on tribological components, where they get particular benefit from the self-lubrication properties of polymers and composites [1]. Tribology is a science that deals with surfaces in relative motion, design, friction, wear and lubricate. Layered clay-based nanocomposite polymers have received considerable attention because they significantly improve wear properties in comparison with those of neat polymer or traditional composites. Such enhancements include increased strength, resilience, heat and fire resistance, and lower gas permeability [2]. HDPE and UHMWPE are most frequently used for bearing materials because of the low friction and the high wear resistance [3]. Due to its extensive tribological uses, including automobile, liners and pressure piped, low- speed gears and bearing, etc., HDPE is increasingly required in various industrial sectors [4].

This article reports on HDPE fabrication using multiple composites (Calcium Carbonate (CaCO3) +Nano clay) with different loadings of (CaCO3+Nano clay). In this research study, Pin-on-Disk technique was used to see the effect of CaCO3 and Nano clay as fillers on the tribological properties of the HDPE composites. Mass loss was measured. Due to its simple configuration, Pin-on-Disk testing is widely used in the laboratory for wear experiments. FESEM was used to characterize the dispersion and distribution state in the composite (CaCO3+Nano clay).

HDPE has a wide range of applications from orthopaedic implants, storage tubes and car parts. This provides excellent chemical resistance, reasonable wear and tear, low friction coefficiency, moderate stiffness and rigidity [5]. Several studies have shown that the integration of fillers with HDPE increases the material properties of polymer. To support the development of robust interfaces between rubber and plastic, HDPE was added, which could draw the components closer to each other. Concerning the compatibility effect, the HDPE application can decrease the temperature of processing, promote interfacial adhesion and reduce costs. Besides, Yuan et al. [3] prove that the incorporation of HDPE in their study contributes significantly to enhance the wear resistance of PP composites.

This study focused on hybrid nano-fillers by combining CaCO3 with nano clay in order to improve the tribology of HDPE polymer. Due to its low cost and abundance, CaCO3 is the highest mineral used in the polymer sector [4]. CaCO3 can be used at a high load point. In fact, for almost all polymers, this material can be commonly used as a filler [6]. However, CaCO3 is difficult to disperse and stabilize in a polymer matrix due to its higher polar nature and higher surface areas [4].

Bukit et al. [7] refer to the hydrophilic properties of Bentonite. The element is usually not compatible with most polymeric materials. Thus, to build a more hydrophobic layer, bentonite must be chemically modified. Therefore, in this study, morphological analysis by FESEM was done to determine the proper state of dispersion and distribution of polymer matrix produced. For composites preparation, melt blending method was applied in this study. In industrial application, melt blending method is frequently used as it is preferable for composite processing. In this process, the polymer is melted in order to produce a viscous liquid. The nanoparticles are then dispersed into the polymer matrix due to the high shear rate and high-temperature diffusion produced. Lastly, compression or injection moulding process takes place to form the nanocomposites [8]. This method can be more effective in the manufacture of PNCs using masterbatch than bulk nanomaterials technique because masterbatch is considered a dust-free additive. Hence it has lower risks to health and safety [6]. Li et al. [9] in his study claim that the homogeneous distribution of fillers in the polymer matrix can be accomplished through the masterbatch filling technique. Melt blending using masterbatch is, therefore considered as one of PNC processing's simplest and most economical methods [6].

A great deal of material is present in the literature on the use of nano inorganic fillers in polymer matrices. The use of calcium carbonate as a filler and nano Bentonite as an additive separately can be found in various studies. Nevertheless, the proposed HDPE nanocomposite would harness the synergy of nano clay and nano calcium carbonate in the same HDPE matrix. The preparation approach is through melting blending "masterbatch" which is also a realistic field of modern research. It is recommended that filler nano calcium carbonate be added as much as possible in order to reduce the cost but not to mitigate the effects of nano-sized particles. For many factors, polymer tribology is different from metal tribology. On the other hand, much less work was done on polymer-based materials (PBMs) tribology. Insufficient knowledge of tribology for polymeric materials is illustrated by the fact that little fundamental texts that talk about the status of polymer science and engineering deal with tribology. Both traditional tribology and traditional methods of experimentation originally developed for metals may not work for polymers. Thereby, the wear rate and tribology of hybrid composites are analyzed in this study.

1.2 Problem Statement

1. Pure HDPE is susceptible to failure in tribological applications owing to the absence of branches in its polymeric chains which make easy for the chain to slide past easily over one another. Wear properties are quite low in values and can be improved by fillers such as nano $CaCO_3$ and Nano clay.
2. To achieve improvement in tribological properties of neat polymers, extensive researched had been done on the incorporation of Nano clay and nano $CaCO_3$ as fillers. The high tendency of nanoparticle aggregation in the polymer matrix limits the continuous improvement of the nanocomposite properties. Therefore, the proper state of distribution and dispersion of nanofillers in HDPE is essential.

1.3 Objective

1. To investigate tribological properties (wear rate) of HDPE polymer composite after incorporation of inorganic hybrid nanofillers, nano clay as an additive and Nano calcium carbonate $CaCO_3$ as a filler.

2. To analyze the morphology of hybrid nanofillers ($CaCO_3$+ Nano clay) in HDPE polymer resin via FESEM analysis in order to determine the proper state of dispersions and distribution in HDPE organic polymer resin.

1.4 Scope of the Study

Many researches had done the addition of nanofiller on the pure polymer to increase mechanical properties, thermal properties, tribological properties, gas barrier properties etc. There are many types of nanofillers available in the market, such as aluminium oxide, zinc oxide, titanium dioxide and many more. In this research, the addition of nano clay and calcium carbonate as fillers are able to produce a synergetic effect on the tribological properties of HDPE. This is an alternative to attain a composite at a cost as low as possible. Filler (nano calcium carbonate) was added as much more in the amount as possible to reduce the cost but not to mitigate the effects of nano-sized particles. This study focused on improving the tribological properties of the HDPE polymer matrix after the addition of a different proportion of fillers. The tribological properties of nanocomposite developed was investigated by using Pin-on-Disk method by calculating the wear rate of samples. Proper dispersion and distribution state were defined to avoid the aggregation of nanoparticles. FESEM was used to study the morphology of the composite.

CHAPTER 2

LITERATURE REVIEW

2.1 Tribological Properties.

Tribology derived from the Greek word *tribos* meaning rubbing. It deals with the subject of friction, wear, lubrication, and related phenomena in a broader sense [10]. Relative surface motion is presented by tribology. It comprises of friction, material wear, scratching and rubbing [11]. Tribology research involves the study of all three factors, namely friction, wear and lubrication of materials. Tribology deals with the studies in relative motion between two or more bodies, including the gears, bearings, piston-cylinder assembly, gyroscopes, etc. Two surface interactions produce friction and cause wear to the material. These interactions lead to forces transmission, which dissipates mass (wear) and energy (friction) [10].

Due to their elasticity, shock loading accommodation, low friction and wear resistance, polymers are being used enormously in tribological applications. Tribology of polymers, for many reasons, varies from tribology of metals [12]. On the other hand, much less work was done in polymer-based materials (PBMs) tribology. It is a complex area because the external lubricants that are widely used for metals are not working for polymers. The lubricant penetrates the polymer, making it swells, and increased material sizes intensify the tribological condition [13]. Lubricants such as greases and oils are newly developed which suitable for polymer composites, but if the wrong lubricant is used, it may cause the element of polymer composites to fail. The lubricants not only able to give low friction and wear, but it is also vital that the lubricants do not lead to degradation. Degradation of the polymer can result in loss of mechanical strength or failure of the fillers to operate as intended [14].

Traditional tribology and conventional experimental methods initially developed for metals may not extend to polymers. For polymers tribology, there are interfacial and functional conditions, including film formation, thermal heat and contact stress [12]. Tribology research aims to minimize and remove frictions and wear losses on all levels in which surfaces are rubbed, melted, polished and cleaned [11].

A vast majority claim that polymers are beneficial for their low friction when reading papers researching polymer tribology, which is not valid for all polymers. Many polymer materials give low friction contacts, but they are often lubricated within the polymer composite itself, either with grease or oil or lubricating additives. Polymers can often have a high coefficient of friction, mainly rubber, which is desirable in some cases [14]. Adding filler or fibres to a polymer matrix enhances the material if the filler and matrix have strong adhesion. Often predicted lower friction and wear, but usually not guaranteed. Many case studies illustrate the effect on tribological and other properties of various additives in polymeric materials but depending on the surface nature of the additives and the extent of interactions with the polymer matrix [11].

One of the applications for tribology property is the use of lining for bulk transport. Ultra-high-molecular-weight polyethylene (UHMWPE) is effectively used for the transport of bulk material particularly in the mining industry, in lining dump trucks and in bobcat buckets for equipment protection. These liners not only enhance wear and corrosion resistance but can also reduce the load of the bed or bucket through the substitution of steel to aluminium. Besides, as the coefficient of the bed or bucket is reduced, the removal of loads becomes more efficient. Figure 2.1 illustrates the application of load removal for a dump truck with and without the use of UHMWPE linings. It shows that linings with UHMWPE produce efficient load transfer [15].

Figure 2.1: Application of load removal for a dump truck with and without the use of UHMWPE linings [15]

2.1.1 Wear

Wear is described as the material loss correlated with sliding to another material. Just like friction, wear between two articulating surfaces is very complicated and generally empirical, depending on the shear strength, stiffness, the pressure applied, and sliding speed [15]. Wear may be mechanical or chemical. Heat during friction usually has accelerated the wear of the material. Adhesion, abrasion, fatigue, and oxidation, like corrosion, is a part of the wear mechanism. Most often, there is no single wear mechanism, but multiple mechanisms are combined [11]. A material's wear rate is traditionally defined as the volume or mass loss from the material per sliding distance unit. Wear is not devastating, but it certainly reduces the efficiency of operations in most cases. It leads to dimensional changes in the components or surface damage. This leads to a related vibration or misalignment problem. In extreme cases, the propagation of cracks formed at or near the stressed surface may result in the component being fractured. Because of surface damage or wear the components lose their applicability. The amount of material removed during the wear cycle is quite low, making it challenging to detect wear through casual testing [10].

2.2 Polymer Nanocomposites

Polymer nanocomposites (PNCs) are a new class of composite materials with at least one nanoscale dimension of the reinforcement filler. The inclusion of these relatively low loading nanofillers can greatly enhance selected polymer properties such as flame retardance, electrical conductance, stiffness, gas barrier, etc. [16]. Generally, nanocomposites with a polymer matrix are developed when the polymer is filled with nanometer-sized particles or fibres [17]. Compared to conventional composites, there are many benefits of nano-reinforcement. For instance, as the diameter of the fibre decreases, the number of surface defects decreases, thereby significantly improving the strength of the fibre. As well as reducing the fibre diameter, the surface area of the nanofiller also increases. The advantage of this effect is that the nanofillers interact with the matrix and allows nanofillers to reinforce the matrix more efficiently at a lower filler concentration. The toughness of the polymer matrix can be retained or in some cases, even strengthened by improving it efficiently at lower concentrations [15]. Blends of two different polymers ideally provide materials with an appealing composition or property balance. Most polymer pairs, nevertheless, are immiscible and many have weak interfaces that lead to unstable morphology and poor mechanical efficiency [18].

The nanosize filler is usually added to the nanocomposites, to enhance the properties of the materials. The element, which is usually present in larger quantity, is called the matrix. Reinforcement usually refers to the component being incorporate into the matrix to improve the properties of nanocomposites, including mechanical properties. In many ways, nanocomposites have more advantages compared to conventional composites. Nanocomposite has the following benefits: [8]

i. The enhancement in nanocomposites ' matrix material properties can be attained by adding a small content of nanofiller materials, while the traditional composites require a high microparticle concentration in order to boost their properties.

ii. The composites produced by the inclusion of nanofillers are lighter compared to the traditional composites.

iii. The size-dependent properties of nanomaterials make them much more useful than conventional composites in their optical, magnetic, thermal, chemical, mechanical and electrical properties.

Polymer nanocomposites are materials with a matrix of polymer, and nano additives are used as reinforcing material. The additives may also include 1D (nano tubing and fibres), 2D (layered materials, such as clay), or 3D (spherical shape particles). The size, form and distribution of two or more phases of the composite can be classified in different ways (Figure 2.2). It can be divided into three groups [19]:

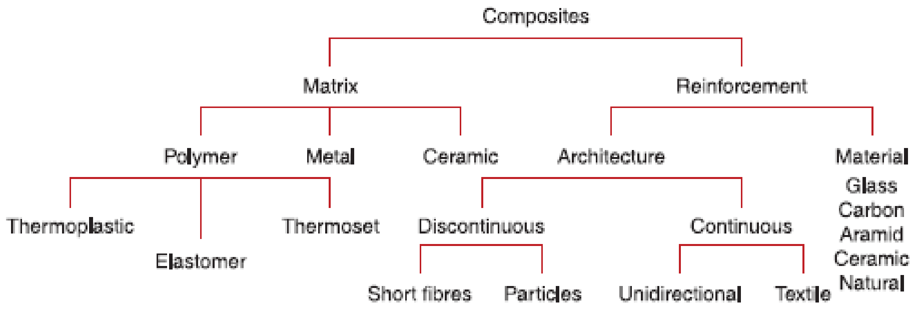


Figure 2.2: Systematic of the structural components of composite materials [19].

2.2.1 Nanofillers

The term nano is used for materials that are nanometer in size, which is in the range of 10 to 9 nm). Nanoparticles are essential and relevant potential materials for improving various properties of the polymer matrix including mechanical and physical properties. The nanometer size is unique, as it is capable of producing vast and sizeable specific area [20]. The term filler is very wide as it contains a wide class of materials. Fillers comprise a variety of substances including organic and inorganic particles. Fillers can be categorized as inorganic or organic substances and further grouped by chemical family as per Figure 2.3 [21]. Adding nanofillers will decrease the size of the dispersed phase due to lower interfacial tension. Due to its prevailing properties compared to conventional fillers such as high surface area, aspect ratio and low percolation threshold, unique chemical, physical and electrical properties, nanofillers are used as reinforcing additives and compatibilizers [22]. Nanoparticle fillers will greatly increase the heat distortion temperature (HDT) of polymeric materials. As high temperatures can develop in the friction contact zone, the increase in HDT will be desirable for tribological characteristics. Nanoparticles inhibit the diffusion of oxygen into the polymer and the escape of reactive thermolysis products. It has also been noted that the repeated heating of the nanocomposite will increase the strength of the barrier due to the backing of silicate in the surface layer of the sample and result in a networked structure. At a good adsorptive interaction between nanofillers and macromolecules, molecular mobility is instantly frozen in the polymer amorphous phase. Functional groups in macromolecules are hindered by interaction with the filler surface. As a response, barriers are formed that avoid adhesive contact with the counter face, and the adhesion component of the friction force decreases [23].

Chemical Family	**Examples**
Inorganic Oxides	Glass (Fibers, Spheres, Hollow spheres, flakes), MgO, SiO_2, Sb_2O_3,
Hydroxides	$Al(OH)_3$, $Mg(OH)_2$
Salts	$CaCO_3$, $BaSO_4$,$CaSO_4$, Phosphates
Silicates	Talc, Mica, Kaolin, Wollastonite, Montmorillonite, Nanoclay, Feldspar, Asbestos
Metals	Boron, Steel
Carbon – Graphite	Carbon fibers, Graphite fibers, and Flakes, Carbon nanotubes, Carbon black
Natural Polymers	Cellulose fibers, Wood flour and fibers, flax, cotton, sisal, starch
Synthetic Polymers	Polyamide, Polyester, Aramid, Polyvinyl alcohol fibers

Figure 2.3: Chemical families of filler for polymer [21]

2.2.2 Filler loading

The amount of fillers is usually addressed as volume fraction or weight percent. Overloading of filler might contribute to poor properties of composites. Hsueh [24] in his study revealed that the stress transfer decreases with the rise of the volume fraction of filler and increases with the rise of the aspect ratio of the inclusion. Wang et al. [25] reported that epoxy/slurry clay tensile strength declines minimally with an increase in clay content. Flaws found in nanocomposites are the causes for the decline in tensile strength. These defects involve the weak boundaries between particles and the bubbles trapped during the preparation of samples. With increasing volume fraction of the filler, the number of such flaws will rise. This implies that the clay layers were behaving as stress concentrators and facilitating the creation of a substantial number of microcracks as the sample was loaded. The weakly bound silicate layers are claimed to be the source of microcrack nucleation occurring easily inside the stacked layers, instead of in the polar zone. The more enormous clay aggregates generate a lot of high local stress causing the premature fracture. A linear polymer is known to be a network of rigid rod chains linked to a junction. Mechanical loading triggers the chain, which means that certain bond conformations change. Loading changes the bond conformation. Chain rupture happens as the strain per bond reaches its critical value [26].

2.3 Hybrid High-Density Polyethylene Polymer nanocomposites

2.3.1 Hybrid composites

Hybrid composite, formulated by different researchers through the combination of various natural and synthetic fibres including epoxy, phenolic, polyester, polyurethane resins, polyvinyl ester, etc. However, due to environmental sustainability, the researchers had taken wise action by establishing new composites by using more than one natural fibres in order to avoid the usage of synthetic fibre. Hybridization of nanofiller with natural fibre in the matrix results in the reduction of water absorption properties and improved mechanical properties. All these aspects are represented in several research works [20].

2.3.2 High-Density Polyethylene

Due to availability and recyclability, high-density polyethylene (HDPE) is considered as commodity material in the material substitution chain. High-density polyethylene (HDPE) is a common polymer abundantly used in various applications. Its outstanding characteristics such as ordered structure, low-energy grouping, processing costs, excellent biocompatibility and good mechanical properties made HDPE desirable material for usage in different areas. It is recently used in the medical field for manufacturing of implants, despite its frequent use in the production of single or multiple medical equipment. For contrast with other polymers such as Ultra-High Molecular Weight Polyethylene (UHMWPE), HDPE exhibit excellent creep properties, but it has low wear resistance. HDPE and UHMWPE were widely used as bearing material because of their low friction and good wear resistance. Additionally, with the increase in demand for HDPE, their usage is popular in many application (Figure 2.4) including automotive parts, pressure pipe, low-speed gears and bearing [16].

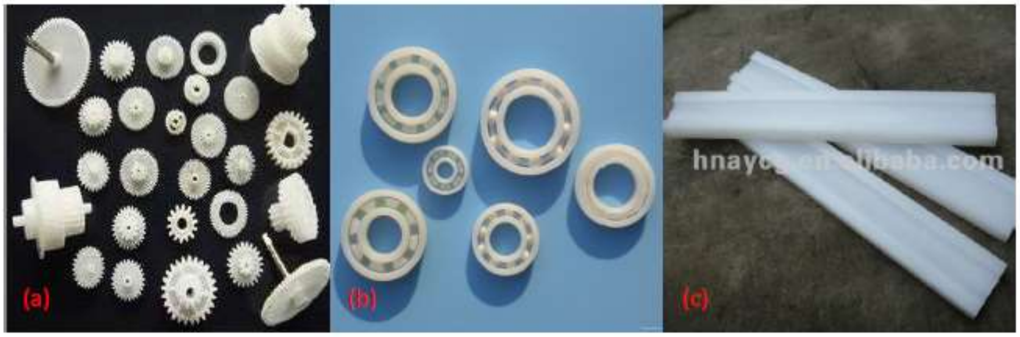
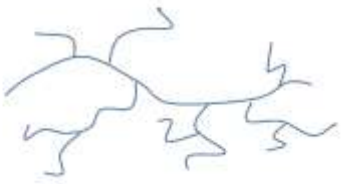


Figure 2.4: Parts produced from HDPE [16].

HDPE has a higher tensile strength compared to Low-density polyethylene (LDPE). It consists of long, linear chains of polymerized ethylene. The improvement of strength exceeds the difference in density, giving HDPE a higher specific strength compared to LDPE. Moreover, with the lack of chiral centres and linearity of the chain, HDPE can rapidly change to a high crystalline structure when below the melting point. Figure 2.5 shows the macromolecular of HDPE and LDPE [16].

(a) A macromolecular of HDPE (linear polyethylene)



(b) A macromolecular of LDPE (branched polyethylene)

Figure 2.5: Macromolecular of HDPE and LDPE [16].

Modification of HDPE matrix using nano clay which is a nanoparticle of layered mineral silicates is widely used in industrial and medical applications to adjust the desired mechanical and thermal properties. The literature study shows that considerable attention is needed to evaluate the mechanical and thermal properties of HDPE / nano clay. Inadequate data or experimental results on the effects of nano clay as fillers are available. Therefore, extensive research is required to produce useful information concerning on material synthesis and advancement.

Numerous researches were done to study the effect of HDPE on the incorporations with other of fillers. The research of Liu et al. [27] focuses on improving the wear resistance of high-density polyethylene composites by reinforcing with organosilane-graphitic nanoplatelets. Pin-on-disk wear testing was conducted at sliding velocities of 0.3 m/s, 1.3 m/s and 2.0 m/s, normal force of 36 N and corresponding wear times for 27h, 6h and 4h. The results show exceptional improvements in wear resistance at different sliding velocities were noticed in silanized-GNP reinforced with HDPE compared to pure composites. In their study, Wear resistance increase by 97% was noticeable below sliding velocity of 1.3 m/s.

Yuan et al. [3] reported on the tribological properties of Polypropylene (PP), Ethylene propylene diene monomer (EPDM), Calcium Carbonate (CaCO3) composites modified by HDPE. Pin-on-disk wears testing was carried on with 200r/min sliding velocity, 200 N normal force, and 120min corresponding wear times. Throughout this study, it is observed that HDPE improves the tribological properties of composites PP, EPDM, CaCO3. Results revealed that the lowest composite coefficient of friction is 0.27with 0.40 mg weight loss as the HDPE content is 25 g.

Xue et al. [28] claim that their research is concerned with the wear resistance and creep resistance of composite material consisting of (UHMWPE) and (HDPE) incorporate with multi-wall carbon nanotubes (CNT). They conducted Ball-on-prism tribometer testing against two types of polished steel. To find the optimum filler content, the CNT content in the experiment was ranged between 0.2 and 2 wt%. The results indicate that carbon nanotubes could enhance the wear performance of UHMWPE / HDPE composite. However, the specific wear rate of the composites reduced with increasing CNT content.

2.3.3 Calcium Carbonate

Calcium Carbonate is an inorganic filler, widely use in the polymer composites for the alteration of the properties due to its, low cost and non-toxic features [29]. Calcium carbonate has been used to produce polymer composites at an early stage because it is one of the world's most abundant materials. The mineralogical hardness of fillers is usually measured by the scale Mohs hardness scale, which is based on the mineral's ability to scratch another. The common thermoplastic fillers have a hardness of less than 4. The CaCO3 has the hardness of 3 according to the Mohs scale [30].

The usage of CaCO3 mineral as fillers can further enhance the performance of composites, as gasses and liquids cannot dissolve or pass through them. Often, the effect of fillers on barrier properties very much depends on whether the polymer wets the filler. If the fillers are not properly wetted, the void will produce around each particle which initiates the pathway for crack initiation. However, if the filler is wetted properly, particulate fillers will decrease in permeability [31].

Sudeepan et al. [31], investigate the tribological properties of acrylonitrile-butadiene-styrene (ABS) polymer filled with micron-sized calcium carbonate (CaCO3). Multi-tribometer with the block on- roller configuration based on L27 orthogonal array (OA) was used. From the experimental study, it was concluded that five weight percent of filler with 35N load applied and 120 rpm of speed produced an optimum value of gray relational grade of composites. The tribological properties are further improved if the addition of Calcium Carbonate is at the right amount.

However, addition of $CaCO_3$ filler could cause problem. Due to its higher polar nature and high surface area, Calcium Carbonate is difficult to be dispersed and stabilize in a polymer matrix. The effects of filler on the mechanical and other properties of the composites depend strongly on filler origin, particle shape and size, aggregate size, the fraction of filler, surface characteristics, and degree of dispersion [32]. Such agglomerated particles can serve as stress concentrator and may affect the composite's final performance. Therefore, the particle size of this mineral needs to be better optimized before being used in HDPE polymer. Poor filler dispersion and adhesion lead to a composite with poor physical properties [33].

2.3.4 Nano Clay

A group of hybrid organic-inorganic materials is made up of nano clays which are known as nanoparticles of layered mineral silicates. Nano clays are categorized in multiple groups, including kaolinite, hectorite, montmorillonite, bentonite and halloysite, according to their morphology and chemical composition [8].

Clays are one of the nanofiller materials frequently used for the construction of polymer nanocomposites. Combination of polymer and clay as an addictive have recently been very popular in academia and industry due to their superior properties compared to traditional composites. The layered silicates of clay particles are either natural or synthetic mineral materials composed of regular stacks of aluminosilicate layers which having high surface area and high-aspect-ratio [8].

In this study, we are using bentonite as our nano clay. Bentonite is classified as dioctahedral species of the smectite mineral group which has montmorillonite content up to 70-95% [34]. As Bentonite is mainly composed of montmorillonite, it is considered as an essential source of montmorillonite in nature [35]. Despite high montmorillonite content, bentonite also consists of crystalline cristobalite, feldspar and quartz. Bentonite has a lot of minerals contents and has the properties of typical montmorillonite include the ability to swell in water. This material is commonly used as catalyst nano and nano clay polymer composites due to intercalation and ion exchangers ability. The usage of bentonite is low, in the material composites. The usage of Bentonite as nanofillers is currently under evaluation by many national and international research [7]. However, Montmorillonite is one of the most common clays used in polymer nanocomposites, because of its good swelling ability, high cation exchange capacity, high aspect ratio and ease for modification. In spites of its widespread usage, hydrophilic montmorillonite is difficult to be exfoliated and well-dispersed in a hydrophobic polymer matrix [36]. Chen et al. [37] in their studies highlight the fact that nano clays can toughen a polymer matrix, at least in the case of a highly intercalated morphology, by enhancing the energy-absorbing mechanisms in front of the process zone of crack tip fracture.

Organoclays have recently been introduced as compatibilizers for polymer mixtures. It has been shown that adding organoclay to polymer blends has drastic effects on the morphology of mixtures, usually an even finer dispersion. Tiwari et al. [38] acknowledged that the presence of Montmorillonite in the matrix and at the interface was more effective in reducing the particle size of the phase dispersed.

The reinforcement and compatibilizing efficiency of bentonite clay in the natural rubber/polystyrene blends shows that the dispersion of bentonite clay results in a practical reinforcement effect of these inorganic fillers even at a low content, resulting in enhanced stiffness and strength [39].

The usage of Organoclay as nanofillers have progressively raised intense research concerns as a remarkable compatibilizer for many types of insoluble polymer mixtures by essentially reducing the size of the dispersed phases at very low concentrations. When the clay platelets disperse during the continuous phase of the polymer mixing process, the high aspect ratio of the clay platelets can prevent the dispersed domains from coalescing during the melting process. The addition of organoclay will improve the viscosity of the continuous process, avoid the coagulation of domains and increase the size of the domain. Once the amount of clay platelets per unit volume is greater than the critical value of the physical cross-linking structure, the clay platelets will be linked together by electrostatic attraction. Giving an overview of the complete morphological distribution of polypropylene (PP)/polystyrene (PS)/organoclay mixtures, in the dispersed domain, the organoclay spontaneously arranges in the dispersed domain to develop a "clay knife" structure that "splits" the domain apart and then results in a reduction of the dispersed domain size [40].

Bukit et al. [7] in their study, add bentonite as fillers in HDPE polymer. Results show increases in tensile strength which enhance the mechanical properties of HDPE with the addition of nano-bentonite mixture 2wt% to 6wt%. However, there is a decrease in the maximum tensile strength of composites with eight wt% to 10wt% of nano bentonite. This is because clumping occurs in the composites, thereby reducing the tensile strength.

Carrión et al. [41] conduct their research on the physical and tribological properties of a polycarbonate-organoclay nanocomposite. The pin-on-disc wear testing (ASTM G 99-05) was carried out at 0.10 m / s sliding speeds and 0.98 N Normal force. The friction coefficient of the new nanocomposite was determined to be reduced by 88%. The tribological performance was improved due to uniform dispersion of the nano clay.

2.4 Wear testing

There are many types of wear testing available in laboratories. Each testing is depending on the research parameters. Proper choice of tribometer is very important in every experiment. The choice of wear test should consider on the value to be measured, load and stresses applied must be the same as the actual application, the environmental condition, the test duration and the surface roughness of rubbing faces [42]. The most popular type of wear testing includes:

1. Sliding Wear Test.
2. Scratch Wear Test.
3. Abrasion Wear Test.

2.4.1 Sliding Wear Test

There are two types of sliding wear test applications which is unidirectional sliding and reciprocating sliding. For unidirectional sliding, the pin-on-disk machine is one of the most common laboratory devices used for measuring friction and wear. Thus, its usage involves the friction properties at controlled atmospheres, elevated temperatures, as well as lubrication and wear of the material. Figure 2.6 shows the Pin-On-Disk set up. The basic structure of this system is a pin that slides against a rotating counterface disk. The motion is typically in a single direction with a constant speed. The test components including the size and shape of the pin, the load applied, the sliding speed and material pairs [42].

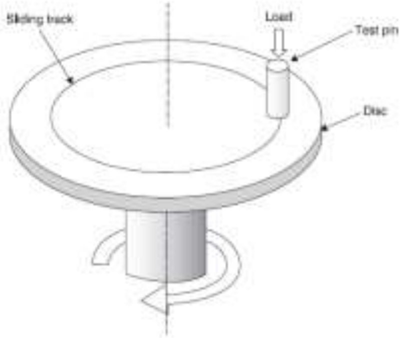


Figure 2.6: Pin-on-Disk device [42].

For reciprocating sliding, the common laboratory device used is the pin-on-plate or ball-on-plane testing. Both the testing can estimate the wear and friction during reciprocating sliding. The results of same material used for both sliding method will be differed. In the Sliding wear testing, Wear results are usually obtained by conducting an experiment according to the selected load value, sliding speed and sliding distance. The reciprocating sliding test be used to simulate fretting situations by reducing the stroke of the motion to the fretting range [42].

2.4.2 Scratch Wear Test

Since an approximately linear correlation exists between wear resistance and hardness, the scratch wear test acts as a reference for materials such as polymers, in which to give an insight about abrasive wear resistance. This involves the creation of a scratch, under constant normal force and speed, without the risk of fracturing, spalling or delaminating the surface of the specimen. This is done by moving a hard and sharp stylus of a specified geometry along a specified path (Figure 2.7). The main aim of this test is to determine the amount of wear in a given state in a polymer. The experiment can be done in two setups. The first one is under dry condition and room temperature, while the second is under lubricated and elevated room temperature. The stylus indenter consists of circular cross section and square-based pyramid shape. Moreover, scratch speed, scratch load, loading rates, number of scratches and scratch length can be the parameter to give enough flexibility to define a required test [42].

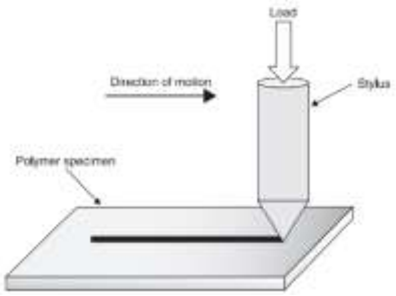


Figure 2.7: Scratch wear test device [42].

2.4.3 Abrasion Wear Test.

Abrasion resistance of a material is defined as the ability of the material to withstand mechanical action such as rubbing, scraping or erosion, which tends progressively to remove material from its surface. Abrasive wear test which is tabor abrader is very useful for characterizing the abrasion resistance of polymers, composites, blends and wood plastic composites. Firstly, a specimen is conditioned according to the conditioning standard before it is used for testing. Then, the specimen is rotated on a turn table as shown in Figure 2.8, that varies in terms of abrasiveness, by using a pair of weighted abraded wheels which produces abrasion through slid slip. Most of the time, in carrying out such test, the specimen is exposed to the turn table for at least 5000 revolutions. Finally, the result of the test is reported through the loss of the specimen’s weight in milligram per 1000 cycles. Many different types of abrasion measuring equipment are available, but the relation between test results and actual abrasion-related wear remains very poor [10].

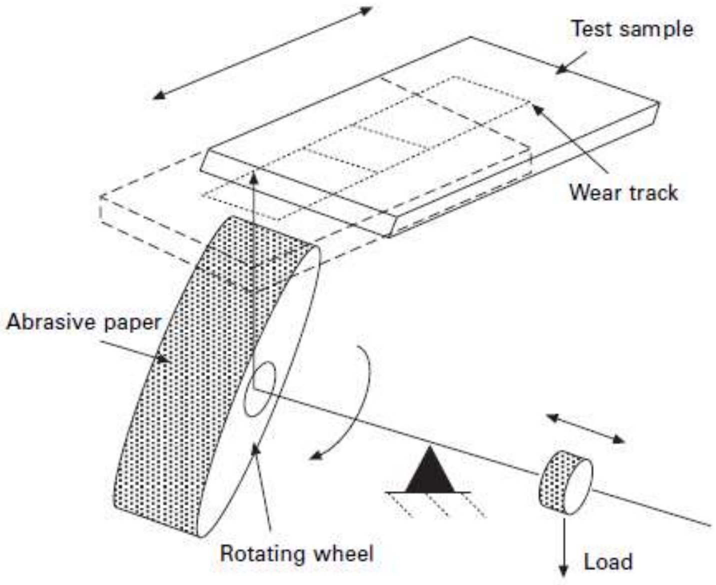


Figure 2.8: Abrasive Wear Test apparatus [10].

2.5 Morphological analysis

Blending is an excellent and cost-efficient way to improve product material properties. However, polymer mixtures usually have a coarse morphology and low interfacial adhesion between the mixing phases [22]. In the polymer matrix, the strong tendency of agglomeration in nanoparticles limits the further enhancement of nano-composite properties. This is because the aggregates act as defect in the nanocomposites. Therefore, it is very important that the nanofillers are properly distributed and dispersed to achieve maximum enhancement. It is stated that uniform distribution is important to enhance particles and polymers interactions in a way that it able to improve mechanical properties [33]. Figure 4.1 shows the distribution of different types of nanoparticles in the matrix material. Figure (a) portray a good distribution but poor dispersion of nano particles while figure (b) shows a poor distribution and poor dispersion. Figure (c) shows a poor distribution, but good dispersion, and (d) shows a good distribution and good dispersion. The best condition that should be achieved is portrayed in figure 2.6 (d) [16].

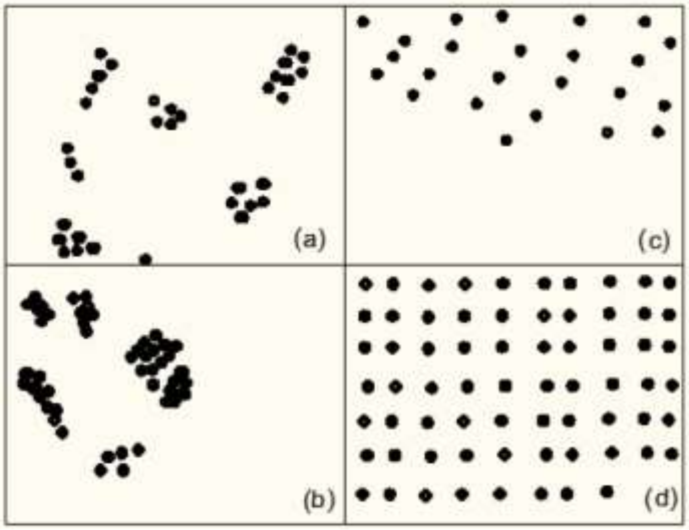


Figure 2.9: Distribution of nanoparticles in Matrix [16].

Liu et al. [43] done an analysis on the characterization of high-density polyethylene (HDPE) /silane montmorillonite composites through Scanning Electron Microscopy (SEM). Results on the surface morphology of HDPE-TPO-MMT composites, show a relatively rough pattern compared to the neat HDPE. Thus, it shows that the wear resistance of HDPE does not effectively increase by the addition of Montmorillonite (MMT) and thermoplastic polyolefin elastomers (TPO).

Liu et al. [27] have been studying the filler dispersions, the worn surface of nanocomposites and the interaction between filler and polymer matrix. FESEM (field emission scanning electron microscope) was used to see the morphology of the composites. Wear resistance decreases in both high temperature purified GNP (ht-GNPs) and as- received GNP (as-GNPs) composites due to poor dispersion and interfaces.

Yuan et al. [3] used scanning electron microscopy (SEM) to study the morphology of PP / EPDM / CaCO3 composites after the wear testing. From the results, it shows that there are many clastic found on the contact surface of samples without the presence of HDPE. By adding HDPE to the composites, the clastic was reduced. Hence, they conclude that the incorporation of HDPE with PP/EPDM/CaCO3 composite help in improving the tribological performance.

CHAPTER 3

METHODOLOGY

Figure 3.1 shows the outline of the research methodology. Theoretical and experimental steps involved throughout the research study are mentioned below in details.

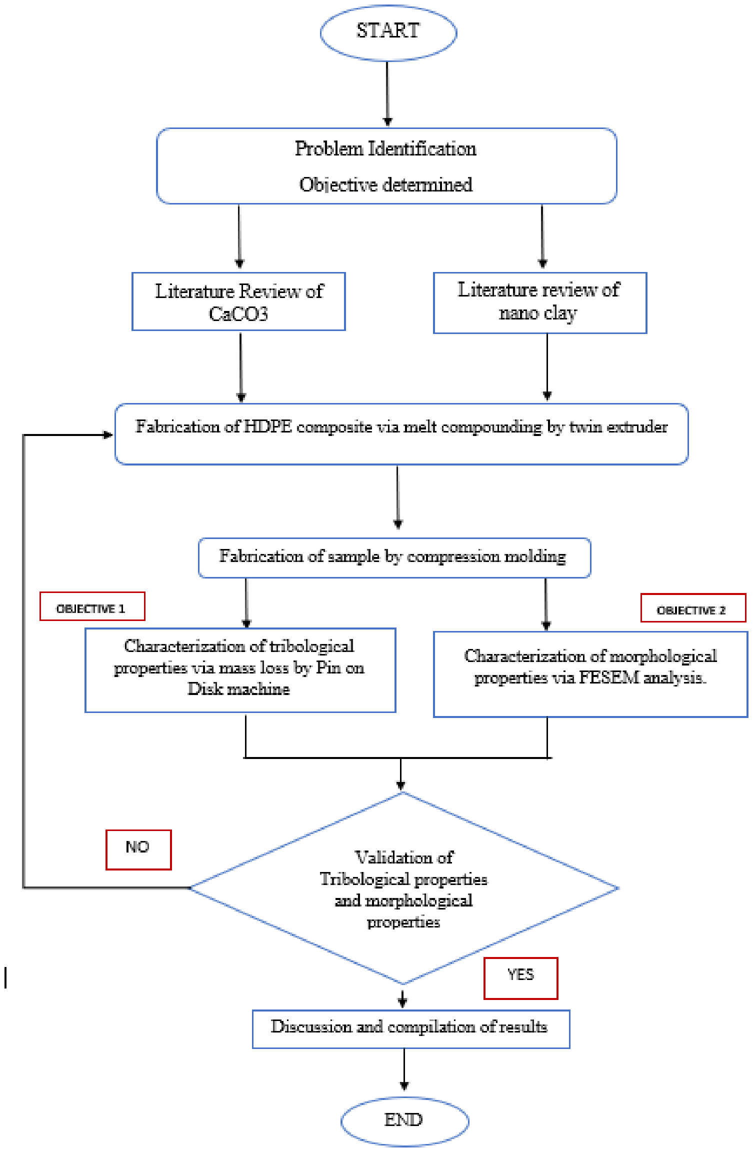


Figure 3.1: Methodology Outline

3.1 Theoretical Study:

As Shown earlier in the research outline, there were a few theoretical steps involved in this study, including:

i. Microstructural characteristics of CaCO3 was analyzed. The effects of different weight percentages and different particle sizes on polymer composite were studied. A fix particle size and weight percentage of CaCO3 was selected in the light of literature reviews after applying DOE analysis.

ii. Analyzation on the microstructural characteristics of Nano Clay. The effects of different weight percentages on composite were studied. The appropriate Nano size and weight percentage of (Nano clay) Nanoparticle were selected in the light of literature review after applying DOE analysis.

iii. The Masterbatch melt compounding method was used because of its effectiveness based on the study of the literature review. Pin on disk method had been identified to be the best method in investigating the tribological properties of polymer because it is the most popular method among researcher in conducting their study. Based on the literature review, we can see that SEM method are not able to give the best image which could interfere with the analyzation of morphology on the composites. Therefore, FESEM was used as we need a more precise and spatial resolution.

3.2 Experimental flow chart:

Figure 3.2 shows the experimental process flow for this research study. The details of each testing will be explained further in the procedure.

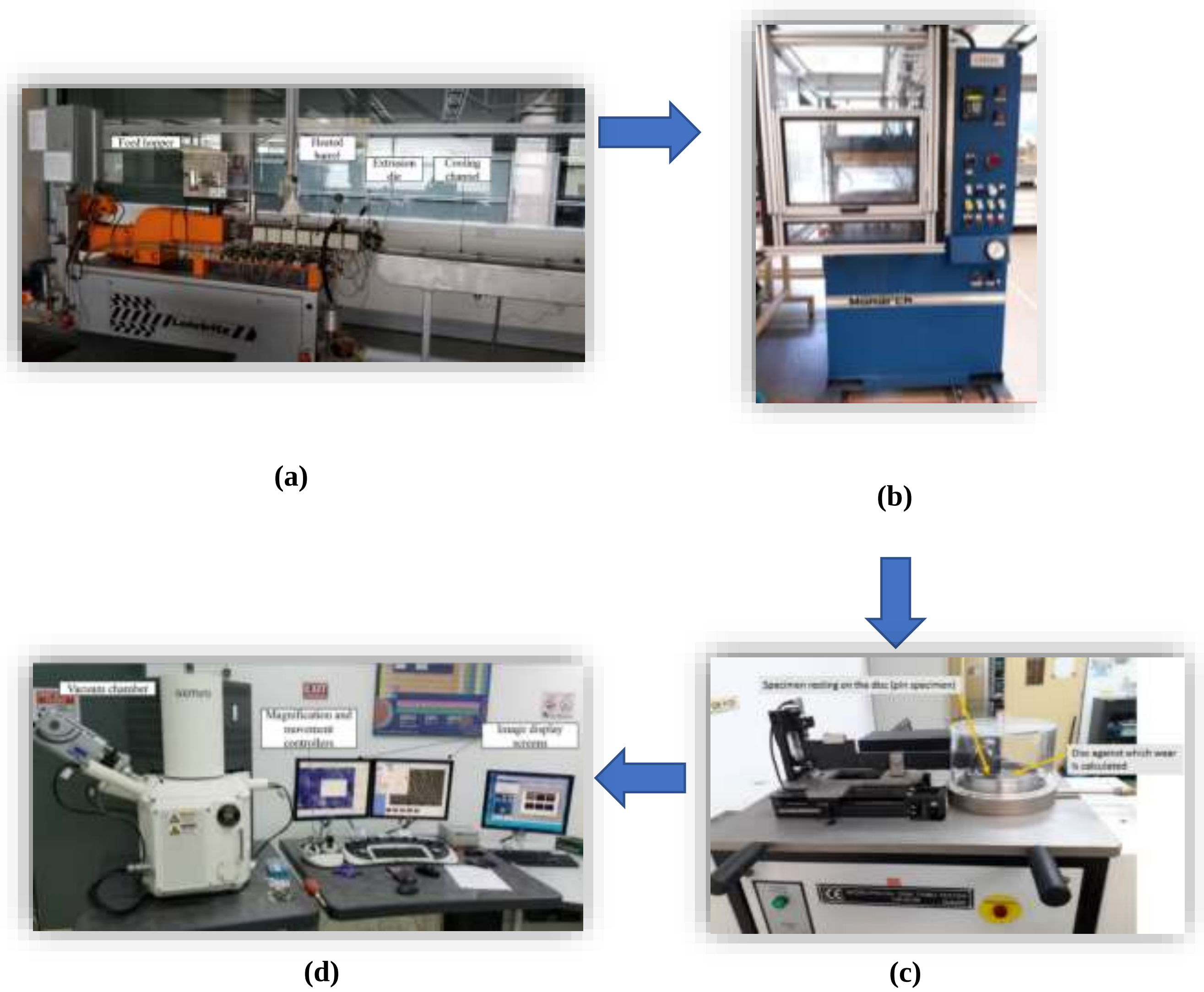


Figure 3.2: Experimental process flow: (a) Melt Compounding Machine; (b) Compression Molding Machine; (c) Pin-on-Disk machine; (d) FESEM.

3.3 Experimental Procedures:

i. Materials

HDPE Polymer was supplied in the form of pellets from Titanvene Malaysia. It has MFI of 18g/10 min and a nominal density of 0.950 gm/cm^3, respectively. CaCO3 (33295 Calcium carbonate) was supplied in the form of precipitated nanopowder with the density of 2.930 gm/cm^3, formula weight of 100.09 and melting point of 800 °C. Sodium bentonite with high montmorillonite content (61.5 % by mass) and cation exchange capacity of 66.5 meq/100 g (determined by methylene blue test) were obtained from Alfa Aesar.

ii. Sample Fabrication:

To remove moisture from the CaCO3 and trapped water molecules from bentonite, both the nanofillers were dried in a vacuum oven for 48 hours. The dry mixing processing method was applied to fabricate HDPE composites reinforced by either single or hybrid graphitic nanofillers. Formulations selected were on the base of weight percent of fillers (CaCO3 + Nano Clay) and were melt compounded with HDPE resin via twin-screw extruder shown in Figure 3.3. There was a total of 16 samples. Each sample was having different weight %, and different nanofiller. Temperature for the fabrication of melt compounding of composite and fabrication of samples selected was 120 °C. Moreover, the rpm for melt compounding chosen was 14 such that to have proper mixing and to avoid unwanted degradation of polymer chains as a result of excessive shear. The nanocomposites were subsequently hot-pressed at 180 °C for 15 min via a compression moulding machine shown in Figure 3.4. The panels were allowed to cool down to room temperature naturally after turning off the heat. All samples were cut with specific sizes for wear testing to meet the requirement of the pin-on-disk machine, respectively. Table 3.1 clearly shows the detailed composition of each sample. The sample had different weight % of Calcium Carbonate and Bentonite fillers. However, for sample no 16, it consists of 100% pure HDPE. Design of experiment were done using Minitab software.

Figure 3.4: Melt Compounding Machine.

Figure 3.3: Compression Molding Machine

Table 3.1: List of samples fabrication,

Samples	**Weight %** **B: Bentonite** **C:CaCO3**
PURE HDPE	
16	B/C-0/0
1	B/C-0/5
2	B/C-0/10
6	B/C-5/10
3	B/C-0/15
7	B/C-5/15
11	B/C-10/15
GROUP B	
4	B/C-5/0
8	B/C-10/0
9	B/C-10/5
12	B/C-15/0
13	B/C-15/5
14	B/C-15/10
GROUP C	
5	B/C-5/5
10	B/C-10/10
15	B/C-15/15

iii. Wear testing:

To determine the tribological properties of the composite, wear testing was done by using the pin on disk machine shown in Figure 3.5. 1020 Carbon Steel pin was used in this experiment. The test was performed on the sample according to ASTM G-99-04. The diameter of the wear track was 30 mm. 20 N normal force was applied to the specimen. In this study, the wear testing was conducted under 120 rpm sliding speed and 30 minutes of testing time. The mass loss was recorded, and the wear rate was calculated by the following equation:

$$w = \frac{\triangle m}{Fd} \qquad (1)$$

Where w is wear rate, $\Delta m = (m_1 - m_2)$ where $m_{1,}$ mass of wear sample before wear testing and m_2 is the mass of the sample after wear testing, Δm is the mass loss during each wear period, F is normal force, and d is the diameter of wear track.

Figure 3.5: Pin- On-Disk Machine

iv. Characterization:

After the sample had been tested on the pin-on-disk machine, characterization of the samples were performed, by FESEM microscopy as showed in Figure 3.6. This study was done to examine the distribution and dispersion of the fillers as well as the worn surface of the nanocomposites. This is to ensure the composites produce the best performance.

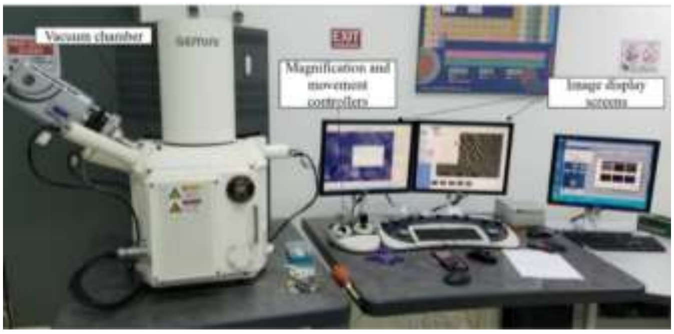
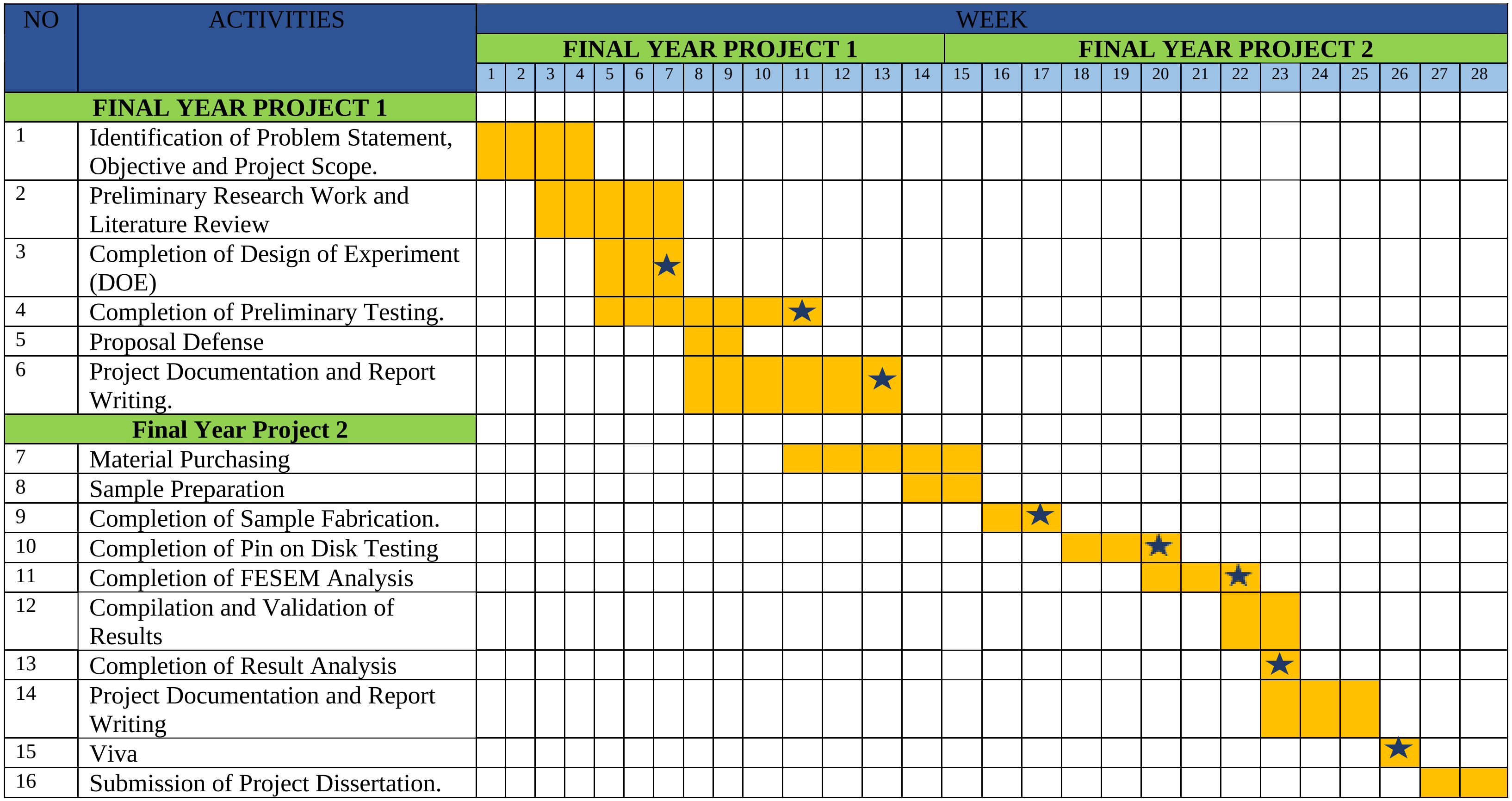


Figure 3.6: Field Emission Scanning Electron Microscopy

3.4 Gantt chart

Figure 3.7 shows the Gant Chart and milestones of this study. Gant Chart and key milestones were critical elements in every research study to ensure all objectives are achieved within the expected time.



NO	ACTIVITIES	WEEK																											
		FINAL YEAR PROJECT 1														FINAL YEAR PROJECT 2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
FINAL YEAR PROJECT 1																													
1	Identification of Problem Statement, Objective and Project Scope.	🟨	🟨	🟨	🟨																								
2	Preliminary Research Work and Literature Review			🟨	🟨	🟨	🟨	🟨																					
3	Completion of Design of Experiment (DOE)					🟨	🟨	★																					
4	Completion of Preliminary Testing.					🟨	🟨	🟨	🟨	🟨	🟨	★																	
5	Proposal Defense								🟨	🟨																			
6	Project Documentation and Report Writing.								🟨	🟨	🟨	🟨	🟨	★															
Final Year Project 2																													
7	Material Purchasing											🟨	🟨	🟨	🟨	🟨													
8	Sample Preparation														🟨	🟨													
9	Completion of Sample Fabrication.																🟨	★											
10	Completion of Pin on Disk Testing																		🟨	🟨	★								
11	Completion of FESEM Analysis																				🟨	🟨	★						
12	Compilation and Validation of Results																						🟨	🟨					
13	Completion of Result Analysis																							★					
14	Project Documentation and Report Writing																							🟨	🟨	🟨			
15	Viva																										★		
16	Submission of Project Dissertation.																											🟨	🟨

COURSE	PROJECT MILESTONE	
	WEEK	MILESTONE
FYP 1	7	Completion of Design of Experiment (DOE)
	11	Completion of Preliminary Testing.
	13	Project Documentation and Report Writing.
FYP 2	17	Completion of Sample Fabrication.
	20	Completion of Pin on Disk Testing
	22	Completion of FESEM Analysis
	23	Completion of Result Analysis
	26	Viva

🟨	Progress
★	Project Milestone

Figure 3.7: Gant Chart and Milestone

3.7 Key Milestones

Table 3.2 shows all the key milestone for FYP 1 and FYP 2. There is a total of 8 milestones. Three milestones should be completed in FYP 1, and the other five milestones should be completed in FYP 2. The milestones include:

Milestone 1: The first milestone in this research project was the completion of the design of experiment. Where the wt% of both fillers in each sample was determined, and the parameter of testing were determined by considering to the literature review.

Milestone 2: Second milestone is the completion of the preliminary testing. Testing were done to ensure the best parameter chosen for each experiment. Preliminary test was completed on 25th November 2019 because of the unavailability of wear testing machine.

Milestone 3: The third milestone was the project documentation and report writing. All literature review, methodology, expected results etc. had been documented to produce high quality report.

Milestone 4: Completion of Sample preparation and fabrication had completely done by week 17 of academic calendar. This is to ensure a smooth process on the other testing as it may take a lot of time.

Milestone 5: Pin-on-Disk testing were done on week 20 of academic calendar which was specifically on 14th February 2020.

Milestone 6: Completion of FESEM analysis was done on 28th February 2020.

Milestone 7: Analysis of results was done on week 23. Full commitment was given on the analysis to produce an accurate research data and discussion.

Milestone 8: Viva should be done by week 26 but there was a delay because of some reasons.

Table 3.2:Key Milestone for FYP 1 and FYP 2

KEY MILESTONES		
M1	Completion of Design of Experiment (DOE)	19th October 2019
M2	Completion of Preliminary Testing.	15th November 2019
M3	Completion of Project Documentation and Report Writing.	29th November 2019
M4	Completion of Sample Fabrication.	24th January 2020
M5	Completion of Pin on Disk Testing	14th February 2020
M6	Completion of FESEM Analysis	28th February 2020
M7	Completion of Result Analysis	6th March 2020
M8	Completion of Viva	27th March 2020

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Morphological study

Morphological analysis of the nanocomposite fabricated, lead to engrossing details, indicating a physio mechanical phenomenon that enhanced wear of polymers. As shown by the wear rate values (Table.4.1), the comparative weight percent of bentonite versus calcium carbonate (CaCO3) had a great influence on the wear mechanism, and distinctive pattern changes were also noticed in the morphology of Group A (GA), Group B (GB) and Group C (GC), where there was little difference between GB and GC.

Table 4.1: Wear rate of samples

Samples	Weight % B: Bentonite C:CaCO3	Wear rate (10-4 (kg/N-m))
PURE HDPE		
16	B/C-0/0	1.6
GROUP A		
1	B/C-0/5	1
2	B/C-0/10	0.3
6	B/C-5/10	1.1
3	B/C-0/15	1.3
7	B/C-5/15	3.1
11	B/C-10/15	2.6
GROUP B		
4	B/C-5/0	1.3
8	B/C-10/0	1
9	B/C-10/5	0.8
12	B/C-15/0	1.5
13	B/C-15/5	0.3
14	B/C-15/10	0.2
GROUP C		
5	B/C-5/5	0.1
10	B/C-10/10	0.3
15	B/C-15/15	0.1

As an illustration in Fig.4.1, there is a visible difference of cavitation in a, b and c indicated by arrows around the filler particles. Fig.4.1 (a) is the Field Emission Scanning Electron Microscope (FESEM) image of the sample 5BC holding equal content of bentonite and CaCO3. There is minor or no cavitation around clay particles owing to the reason that the clay possesses the property of finer compatibilization. The thermodynamic compatibilizing effects of the clay platelets can be objectively taken into consideration for effective bonding effect with polymer [37, 38]. The sample 5BC belongs to GC and all the samples having equal weight % of both the filler possessed the same morphological pattern. Fig.4.1 (b) represents the case of minor voids and cavitation around the filler particles. Overall, the values of wear rates of GB were in low to intermediate stage as displayed in the Table.4.1. This efficient response of the samples as in case of 13BC, was due to effective stress transfer between polymer/filler because the particles were adequately bonded to the matrix [24]. However, the morphological patterns changed completely when the content of CaCO3 particles dominated the composite as seen from Fig.4.1 (c) which is 7BC (5 wt% of Bentonite, 15 wt% of CaCO3), a representative sample from GA. This noticeable difference is caused by the extent of inhomogeneity caused by the CaCO3 particles.

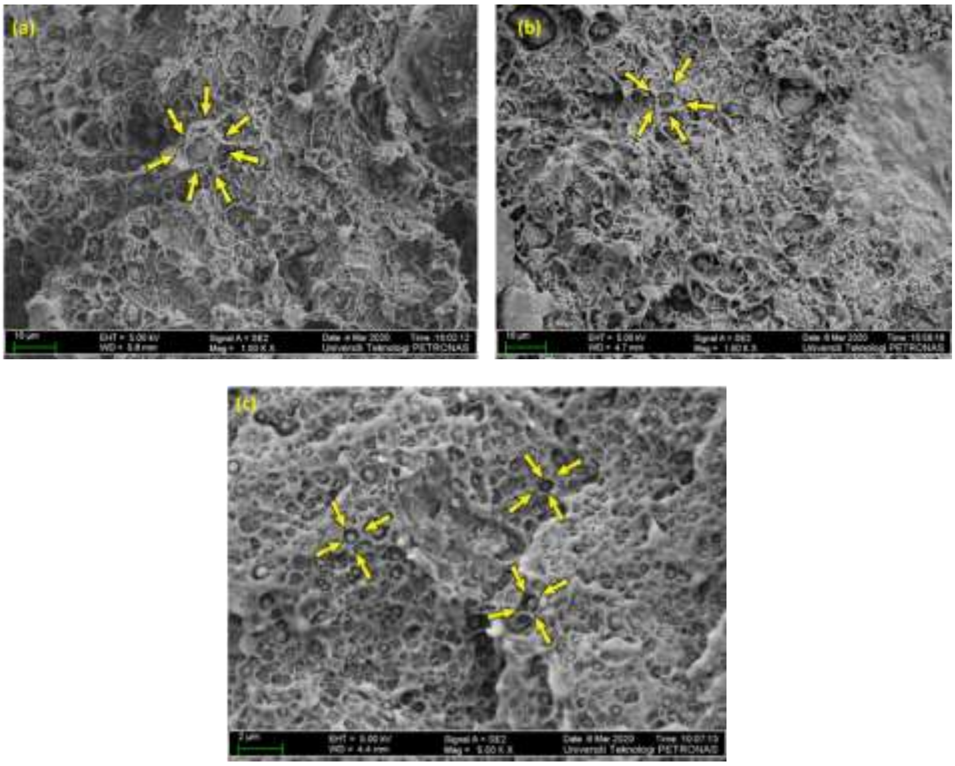


Figure 4.1:Comparison of morphological patterns (a) 5BC no cavitation around the filler (b) minor cavitation in 13BC, (c) noticeable cavitation around the CaCO3 fillers in 7BC.

That is to say, excessive loading of rigid filler increases chances of air bubbles due to inhomogeneous network density in HDPE matrix [25]. Moreover, the chance of cavitation increases as the weight % of the filler particles increase which is responsible for creating flaws in the composites [36] .This existence of flaws, particularly around the filler particles hinders the processes of stress transfer between polymer/fillers which can be considered the reason for high wear rate of samples of GA as shown in the Table.4.1 [24]. From the wear testing results (Table.4.1) the wear rate values of non-hybrid samples decreased progressively by the mechanical restraint to the easy sliding of polymer chains over one another. Furthermore, CaCO3 particles are hard particles having a higher modulus than the virgin HDPE matrix. The degree of restrain to chain sliding increases as a result of repulsive potential to the matrix which is closer in the vicinity of a hard particle. This entanglement of chains with filler particle have possibly contributed majorly to perform well as compared to virgin polymer [44]. This phenomenon can be effective when there is not enough amount of fillers particles to undergo agglomeration, however excessive loading of the fillers adversely effects the process of wear.

As seen in the Fig.4.2 (a) and (b) the filler particles agglomerates possibly have acted as “stony pulled out” particles during the test, causing further abrasion of the surface giving high value of wear even more as compared to virgin polymer. But even so, these effects of inhomogeneity were observed to be reduced due to shear generated during mixing by the platelets like structure and the ability of being a solid compatibilizer. This “knifing” effect introduced by Zhu et al. which was more prominent in samples from GB and GC owning to high loading of bentonite as compared to CaCO3 [40].

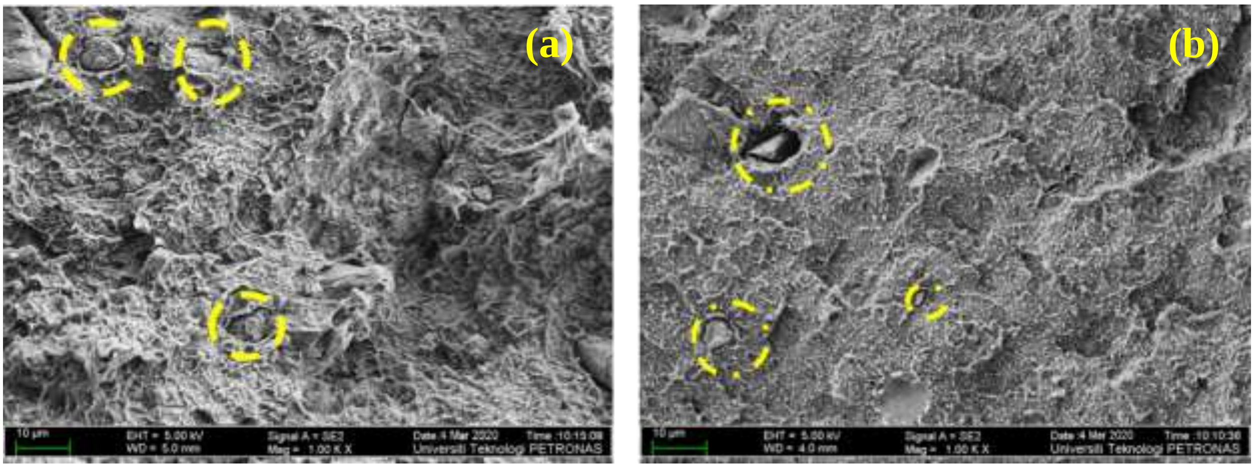


Figure 4.2: Agglomerated CaCO3 particles in samples (a) 7BC, and (b) 11BC

The explanation for enhanced wear properties is fundamentally by an enhanced polymer/filler adherence of GC and GB as compared to GA. Furthermore, it was not postulated that there could have been two possibilities of distribution of fillers particles in the HDPE matrix. Yet, the hybrid samples dominated by the contents of bentonite can be seen to undergo distribution "jointly" as compared to separate distribution of particles in the samples of G.A. This difference can be viewed by comparing Fig.4.3 and Fig.4.4.

The work of wang et.al showed that during fabrication the clay particle have likelihood chance under the external shear of melt compounding to "open up" [25]. The clay aggregates were partially or fully dismantled under the effect of shear and the CaCO3 were encapsulated by the clay in this process. This combination of "encapsulation" and "opening" of clay reduced the incompatibility of CaCO3 to minor. These encapsulated particles were held up together by interlocking, as can be viewed at a much higher magnification of the Fig.4.3. The interlocking/encapsulation of CaCO3 filler particles as shown by FESEM image in Fig.4.3. is well analogous to the physio mechanical phenomenon proposed as in Fig.4.5. given these points, when content of bentonite was more, they adequately encapsulated CaCO3particles minimizing the exposure and by distribution of CaCO3 particles were enhanced by interlocking them separately as displayed in Fig.4.5.

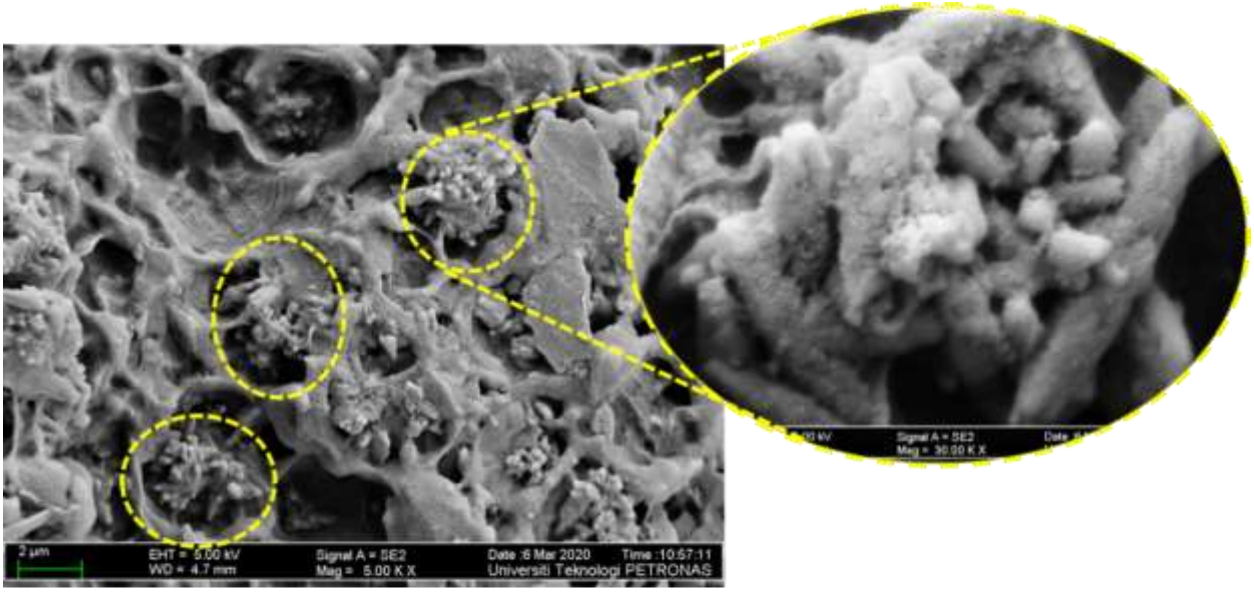


Figure 4.3:FESEM image of the hybrid sample 5BC displaying encapsulation of $CaCO_3$ by bentonite via interlocking mechanism.

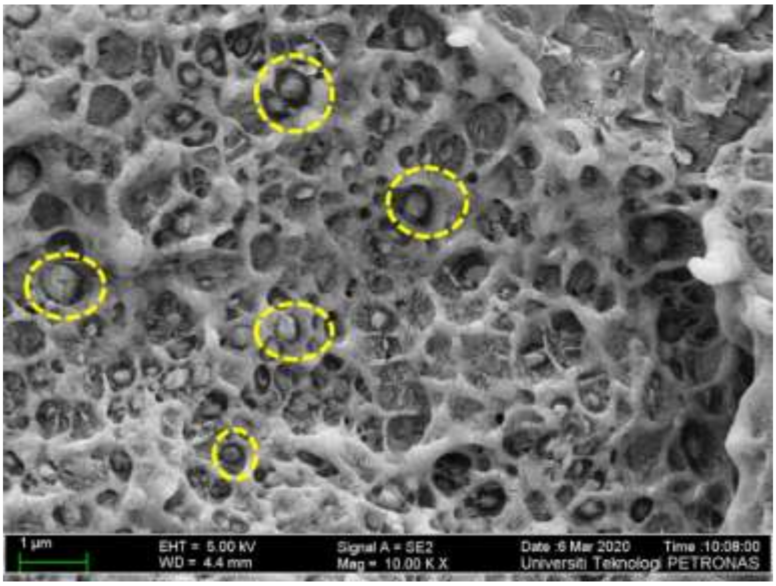


Figure 4.4: FESEM image of the sample 7BC displaying separate distribution of filler particles with no encapsulation.

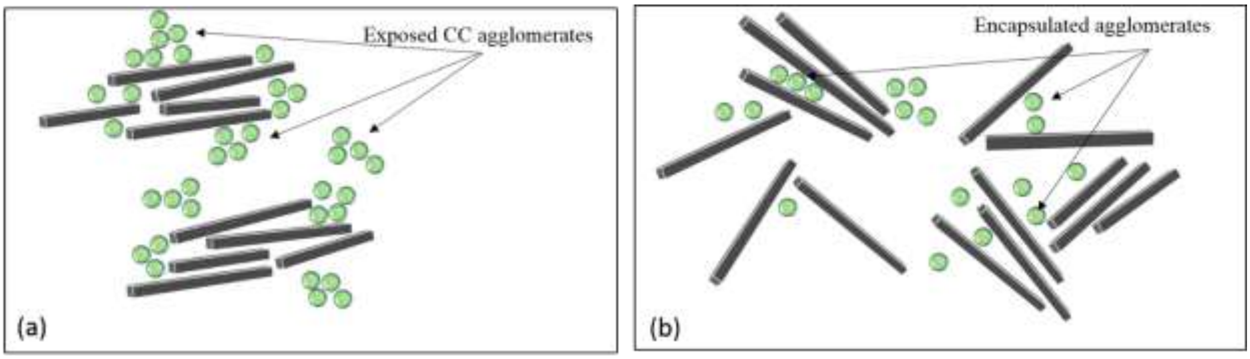


Figure 4.5: Physio-mechanical phenomenon for strengthening of the composite (a) agglomerate particles distributed separately, (b) particles distributed jointly rendering encapsulation of C.C particles.

4.3 Wear resistance

Table 4.2:Wear rate of each sample in Pure HDPE, (a) Group A, (b) Group B, (c) Group C

PURE HDPE		
Sample	Weight % B:Bentonite C:CaCO3	Wear rate (10^{-4} (kg/Nm))
16	B/C-0/0	1.6

(a)

GROUP A		
Sample	Weight % B: Bentonite C:CaCO3	Wear rate (10^{-4}) (kg/Nm)
1	B/C-0/5	1
2	B/C-0/10	0.3
6	B/C-5/10	1.1
3	B/C-0/15	1.3
7	B/C-5/15	3.1
11	B/C-10/15	2.6

(b)

GROUP B		
Sample	Weight % B: Bentonite C:CaCO3	Wear rate (10^{-4}) (kg/Nm)
4	B/C-5/0	1.3
8	B/C-10/0	1
9	B/C-10/5	0.8
12	B/C-15/0	1.5
13	B/C-15/5	0.3
14	B/C-15/10	0.2

(c)

GROUP C		
Sample	Weight % B:Bentonite C:CaCO3	Wear rate (10^{-4} (kg/Nm))
5	B/C-5/5	0.1
10	B/C-10/10	0.3
15	B/C-15/15	0.1

In order to explore whether the incorporation of bentonite and calcium carbonate as hybrid nanofiller in pure HDPE results in a promising reinforcement for tribological applications, the wear property of HDPE/Bentonite–$CaCO_3$ system was investigated to compare with that of the pure HDPE polymer. The weight loss of nanocomposite prepared in this study, was determined by a pin-on-disk wear testing apparatus. The comparison of wear rate calculated by Eq. (1) is exhibited in Figure 4.6. Design of Experiment was divided into three groups as shown in Table 4.2. Moreover, the comparative weight percent of bentonite versus CaCO3 is a sample substantially influenced wear properties, such that experimental design space can be explained as three different groups. The wear rate of the three groups A, B, and C were compared with Pure HDPE. The Samples of Group A having more weight percent (wt%) of CaCO3 as compared to wt% of Bentonite, Group B consists of more wt% of Bentonite than wt% of CaCO3 and lastly Group C own an equal weight percentage of both filler particles.

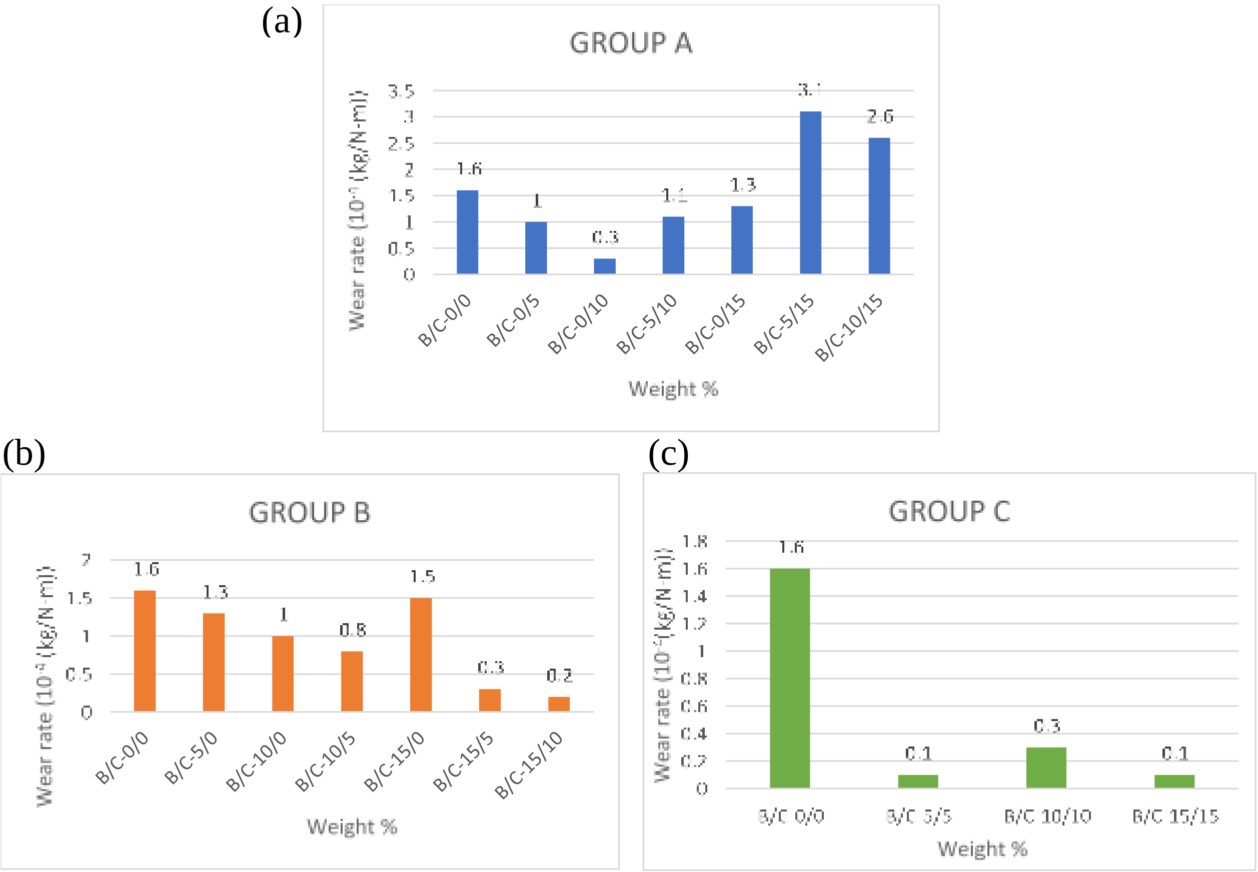


Figure 4.6: Wear rate comparison of (a) Group A , (b) Group B and (c) Group C under Pin-on-Disk wear tests with varying Bentonite% and CaCO3 % content by weight.

There were hybrid and non- hybrid samples in each group. It was observed that the experimental design space (16 samples) displayed wear resistance of two distinctive levels of high and low due to the comparative weight percentage of Bentonite versus $CaCO_3$. More than 80 percent of design space showed good results in this experiment. In this experiment, three key factors influence the wear properties of composites including:1) An adequate dispersion and distribution of fillers, 2) Dissipation of heat generated during the wear process, 3) An adequate polymer/fillers interfacial bonding.

The value of ware rate in each sample was compared with the wear rate of pure HDPE which is 1.6x10^{-4} (kg/N-m). (Fig. 4.6) shows a significantly low wear rate of Group B, and Group C as compared to Group A, because of effective load transfer between polymer fillers. It was revealed that Group C has an impressive improvement in wear rate among all three groups. 80 percent of the samples were good because presence of rigid fillers hindered the process of easy sliding of polymer chains over one another. This process is known as freezing effect. CaCO3 and Bentonite are rigid filler and polymer chains can entangle well effectively.

Group A consist of mostly samples which have high loading of CaCO3 fillers. Figure 4.6 denote the wear rate of hybrid and non-hybrid samples of group A showed a slight decrease in wear rate compared to the Pure HDPE composites. The observable difference was explained by the degree of inhomogeneity generated by CaCO3 particles. CaCO3 inclusion may be problematic. The higher polar structure and high surfaces of CaCO3 make it difficult to disperse and stabilize into a polymer matrix [31]. However, sample 7BC and 11BC exhibit the highest wear rate compared to all samples from this study. Excessive loading of filler particles lead to an adverse effect on wear rates as can be seen from the results of samples 11BC and 7BC. Confirmation had been made through the morphology of the samples that were investigated as shown in Figure.4.2. Tribological properties can be enhanced if the addition of CaCO3 is in an appropriate combination of design parameters [30]. Bad dispersion and distribution of the filler can also contribute to a composition with low physical properties [32].

In contrast, in Group B, the hybrid samples showed satisfactory results as compared to non-hybrid samples because of, 1) heat dissipation and 2) proper dispersion and distribution, both variables play significant role to enhance the wear rate of composites. CaCO3 acted as an agent for heat storing and dissipation while Bentonite reduced wear by rendering minor voids and inhomogeneity. Wear resistance of GB increased because the samples were dominated by contents of bentonite reducing voids, imperfections in the samples. Bentonite resisted the nucleation of cracks generated by the shear stresses generated during the wear test. It was observed that the introduction of clay to polymer materials increases their heat resistance as well as their thermal stability, including tolerance to thermal-oxidative degradation [23].

As clearly seen in group B the non-hybrids have the higher wear rates and no consistent order of increased or decrease with increase weight percentage. This can be assigned to the processing which depends upon likelihood chance of interlocking of fillers with one another. The more interlocking the more effect. This chance is substantially affected by the comparative weight percentage. This freezing effect was effective more when there were no filler particles for agglomeration [23]. From Fig. 4.6 (b) the wear rate of samples decreased gradually as compared to the wear rate of pure HDPE. However, there were sudden increased of wear rate for sample 12 (Table 4.1) with 15wt% Bentonite and 0wt% CaCO3. The result of samples dominated by bentonite increases progressively as bentonite weight increase. Yet sample 12 is inconsistent because of agglomeration. Nevertheless, this sample still noted a better wear rate compared to pure HDPE. This phenomenon happened owning to the improper processing of samples and agglomeration happened in the composites.

Apart from experimental setup, Heat generated during the sliding of pin on disc specimen also effect significantly on the samples. This effect can be viewed by comparing hybrid of GA and GB. Clay is a layered silicate having good heat properties and this ability of clay is reflected by the clay rich samples or the samples having equal weight percent of clay as compared to CC.

Figure 4.7:Wear debris generated during pin on disc experiment (a) low wear rate (b) wear rate of the sample 11BC (c) wear rate of the sample 7BC

GC shows the best and improved wear. Chances of interlocking are increased by a similar of wear rate generated by the morphology as a result of equal weight percentage of fillers. For Group B and Group C as prerequisites, uniform dispersion and strong interfacial bonding with the polymer allowed CaCO3 to act as effective heat storage and emission channel which can extract and release friction heat. This can protect the polymer matrix from oxidation and degradation caused by heat generated during wear. Clay can act as a solid compatibilizer having more compatibility with polymer. there is an adequate polymer filler debonding so there was very low to no wear debris generated for GB and GC and representation can be seen as Fig 4.7 (a). However, 7bc and 11bc shows a very high wear debris (Figure 4.7 (b) and (c) due to low content of Bentonite.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This work gives a deep insight into microstructural features and wears behavior of bentonite nano clay and nano CaCO3, acting as fillers for HDPE polymer.

From wear testing, it can be concluded that the incorporation of nano CaCO3 and nano clay (Bentonite) in HDPE polymer significantly improve the tribological properties of composites (wear rate). However, it can be summarized that the Hybrid samples are preferred combination as compared to non-hybrid. The best hybrid samples with the lowest wear rate noted in this experiment are samples 5BC and 15BC with $0.1\text{x}10^{-4}$ kg/Nm. It was observed that all samples were having lower wear rate compared to pure polymer except for samples 7BC and 11BC, which having higher weight percent of CaCO3.

From Morphological study, it can be deduced that sample 5BC has no cavitation around the clay particle, which contribute to its high performance. The hybrid samples dominated by the contents of bentonite (5BC) can be seen to undergo distribution “jointly” as compared to the separate distribution of particles in the samples of 7BC. FESEM analysis reveals that the agglomerate particles for both samples may have behaved as "Stony pulled out" particles during the experiment, causing further abrasion. It is due to the higher polar density and the large surfaces of CaCO3, which make it impossible to distribute and stabilize into a polymer matrix.

As there is time and budget constraint, the morphologic analysis cannot be done for all samples. FESEM analysis should be done to all samples to see the filler distribution. Thus, more reliable and accurate results can be obtained. Experiment should be repeated by having more samples from Group C to produce the best and effective composites that can be commercialized to the industry.

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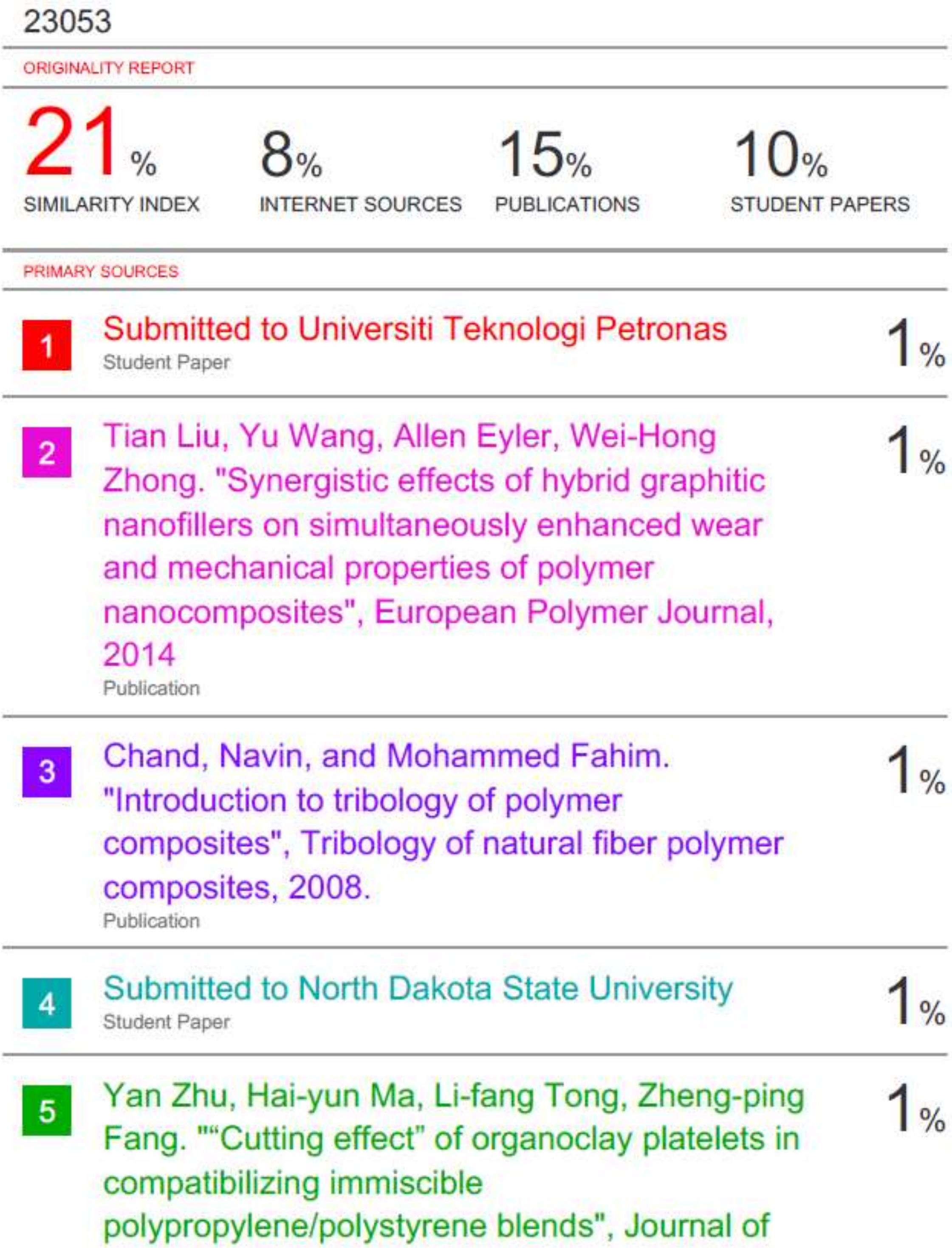

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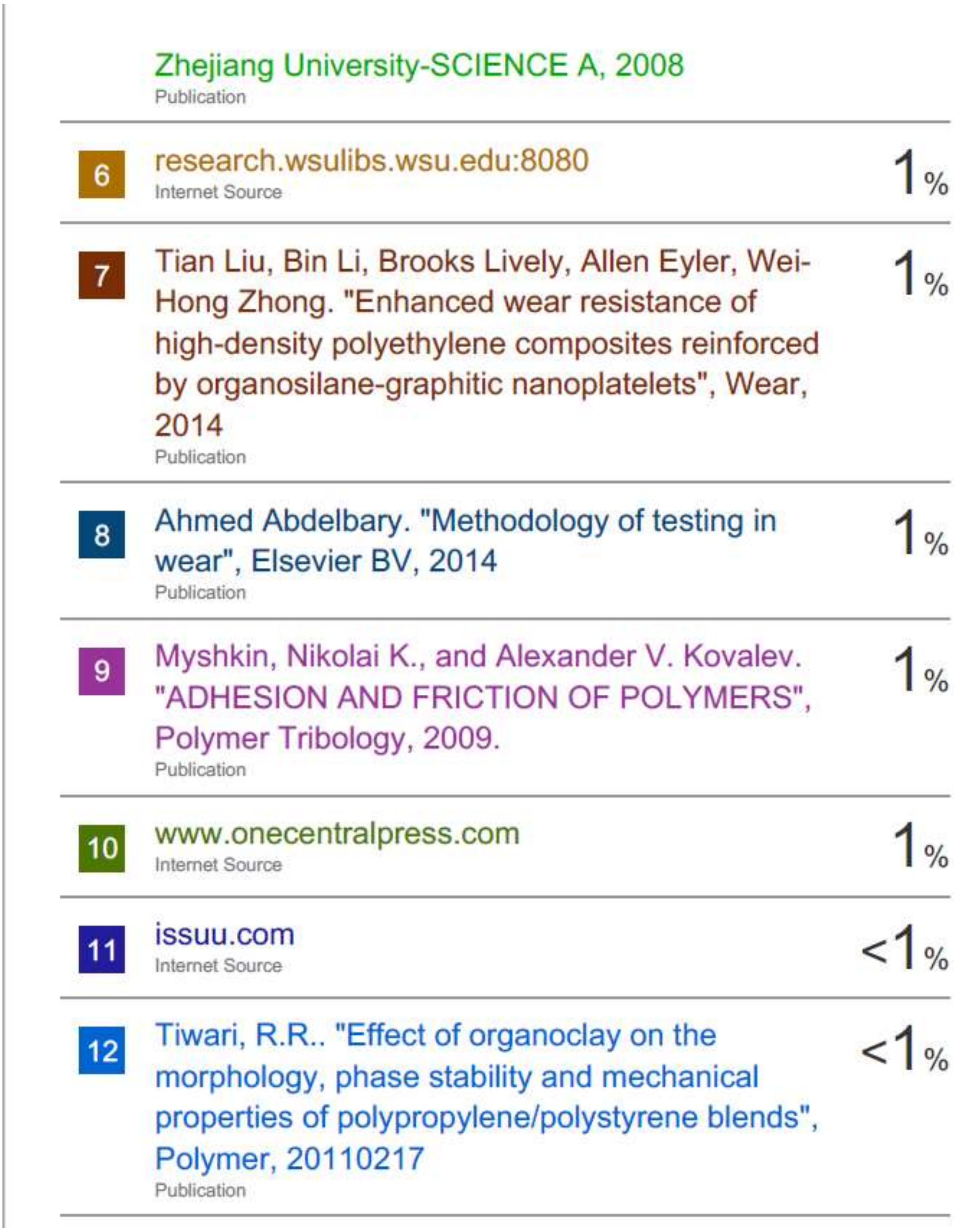

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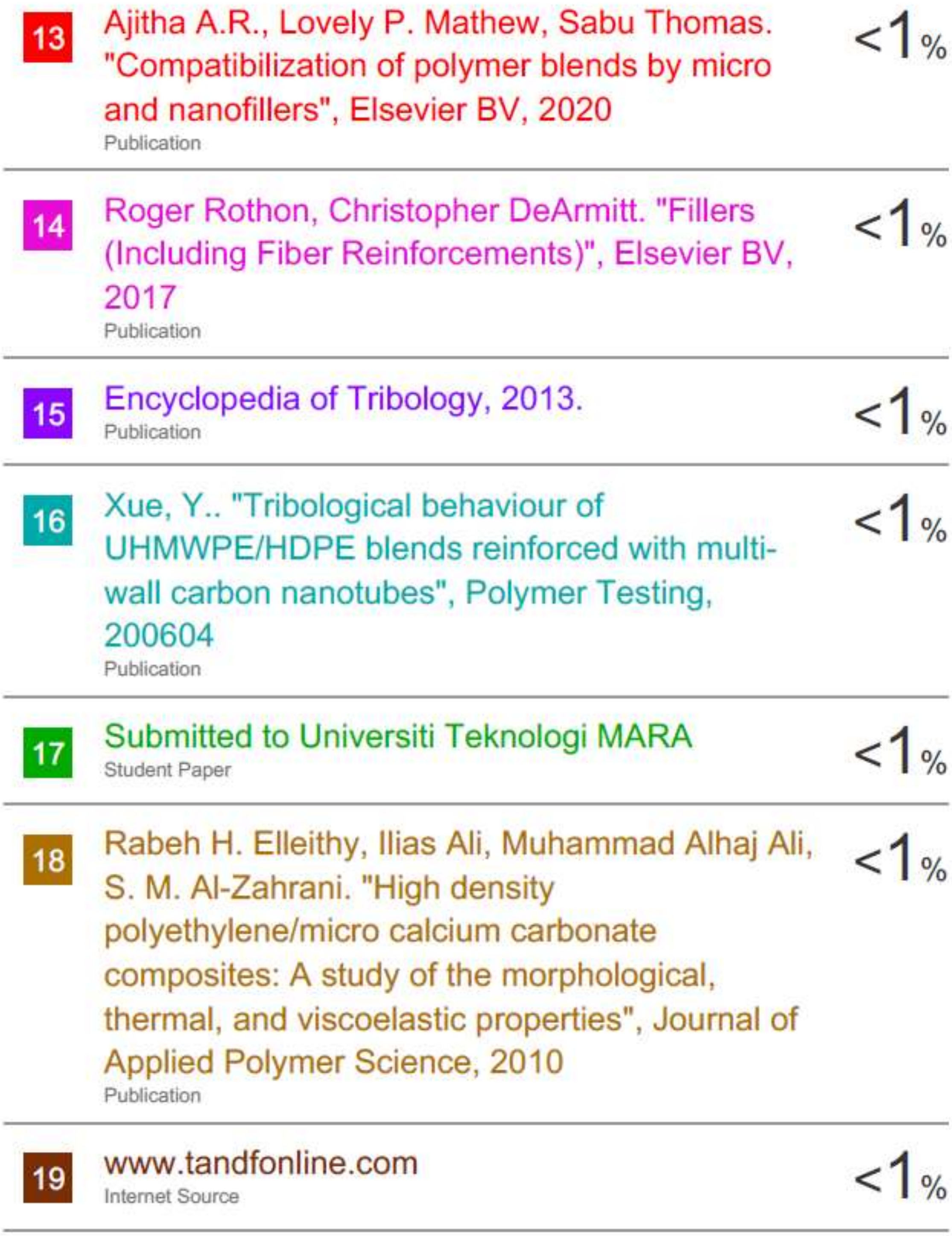

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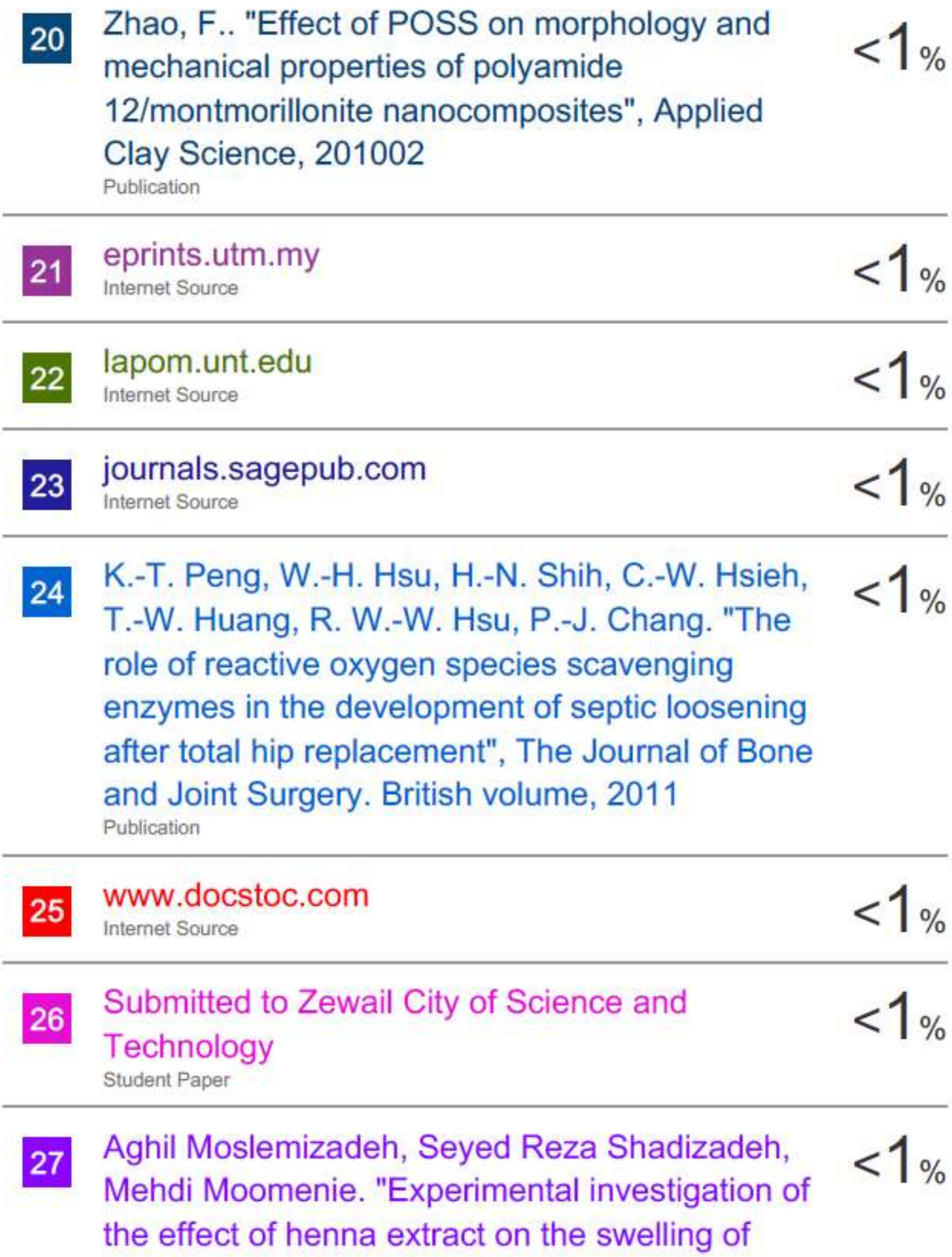

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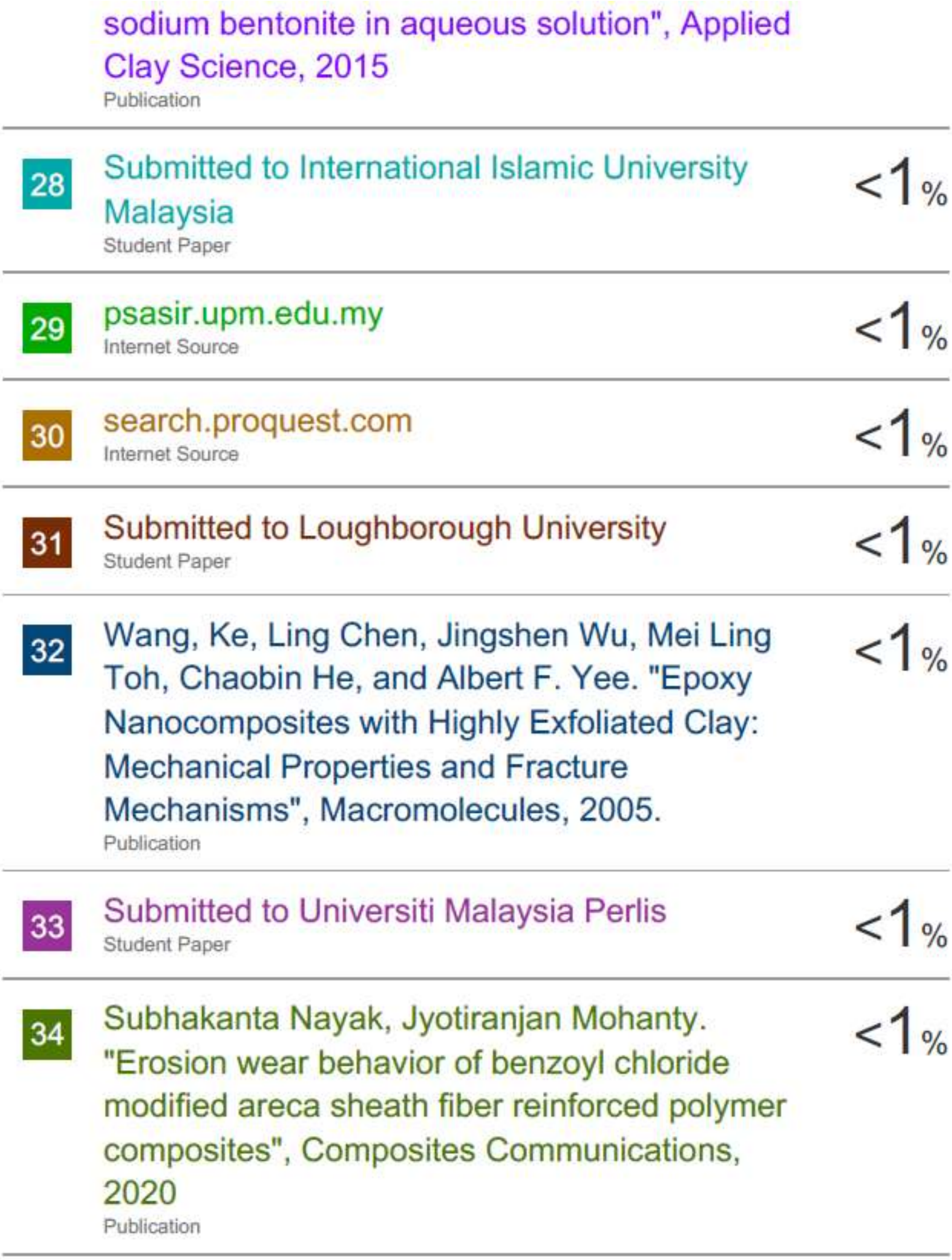

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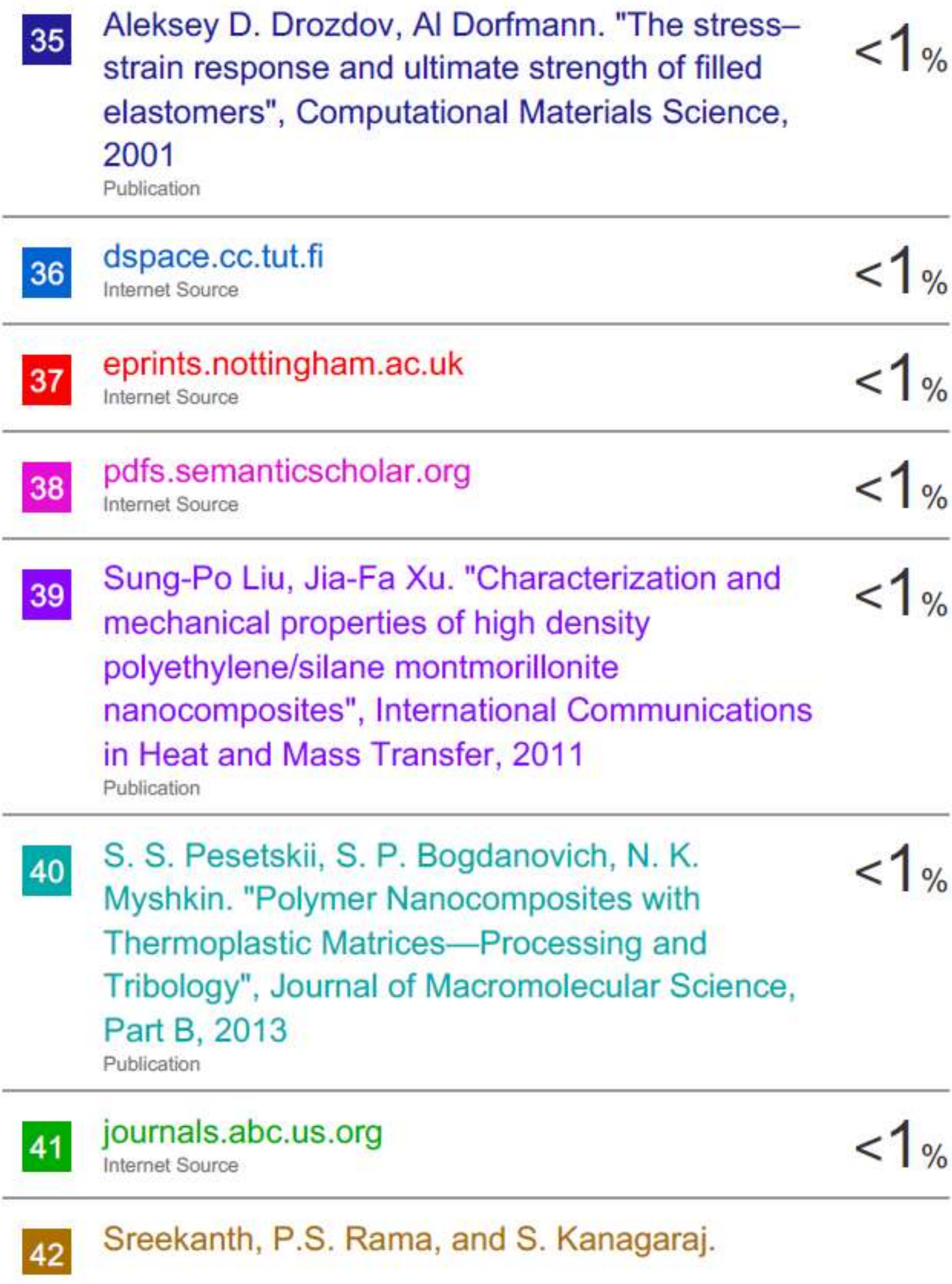

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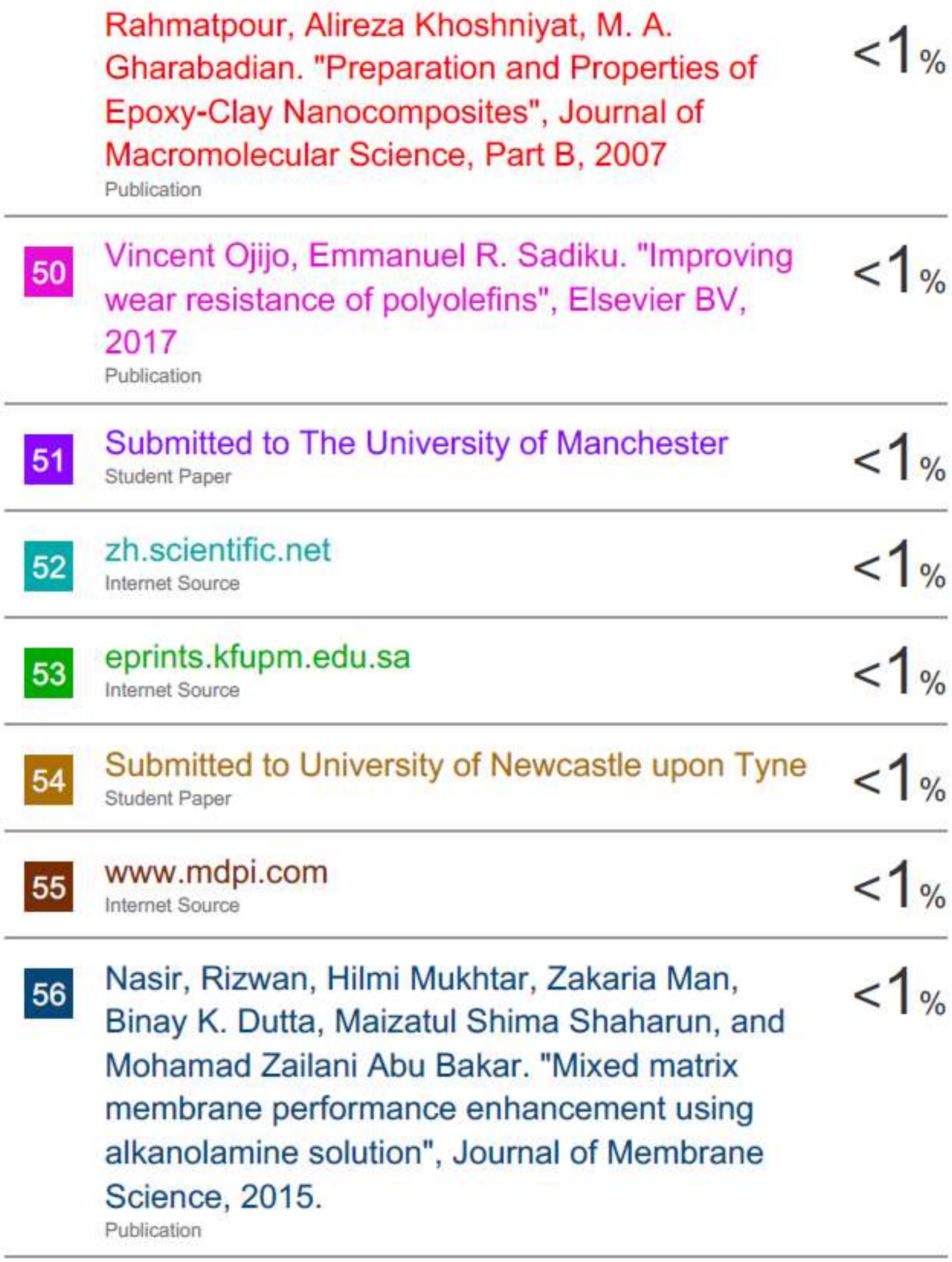

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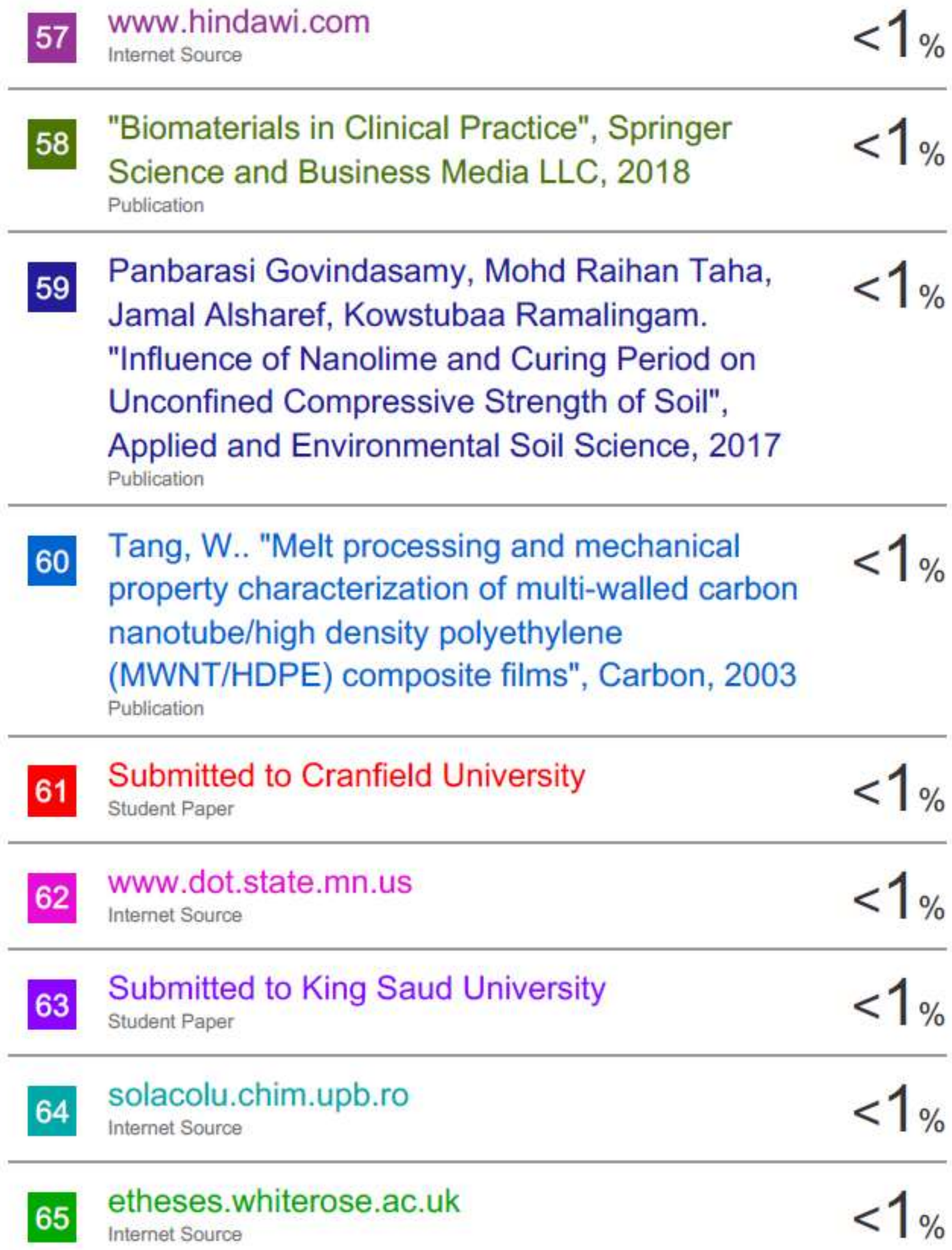

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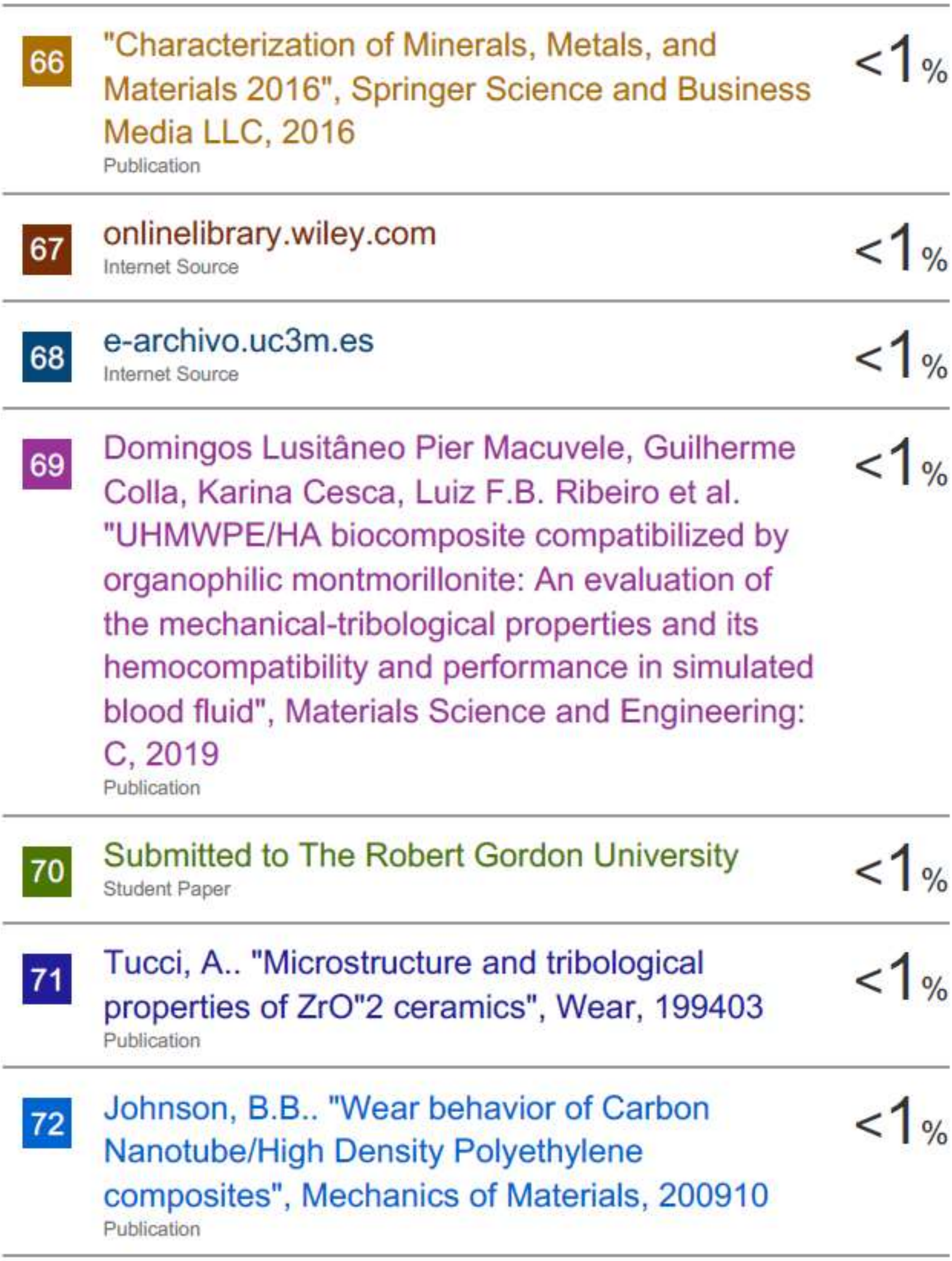

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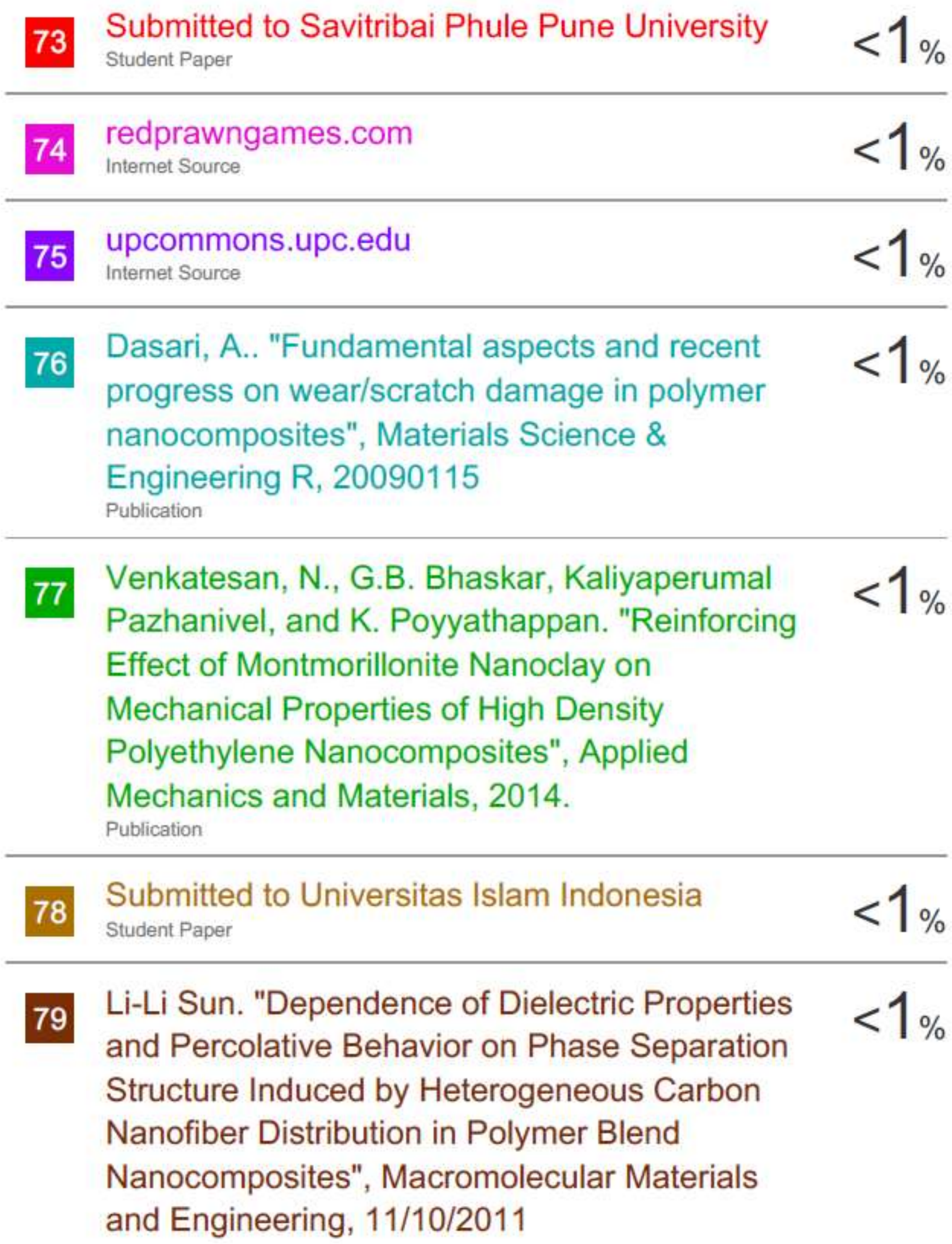

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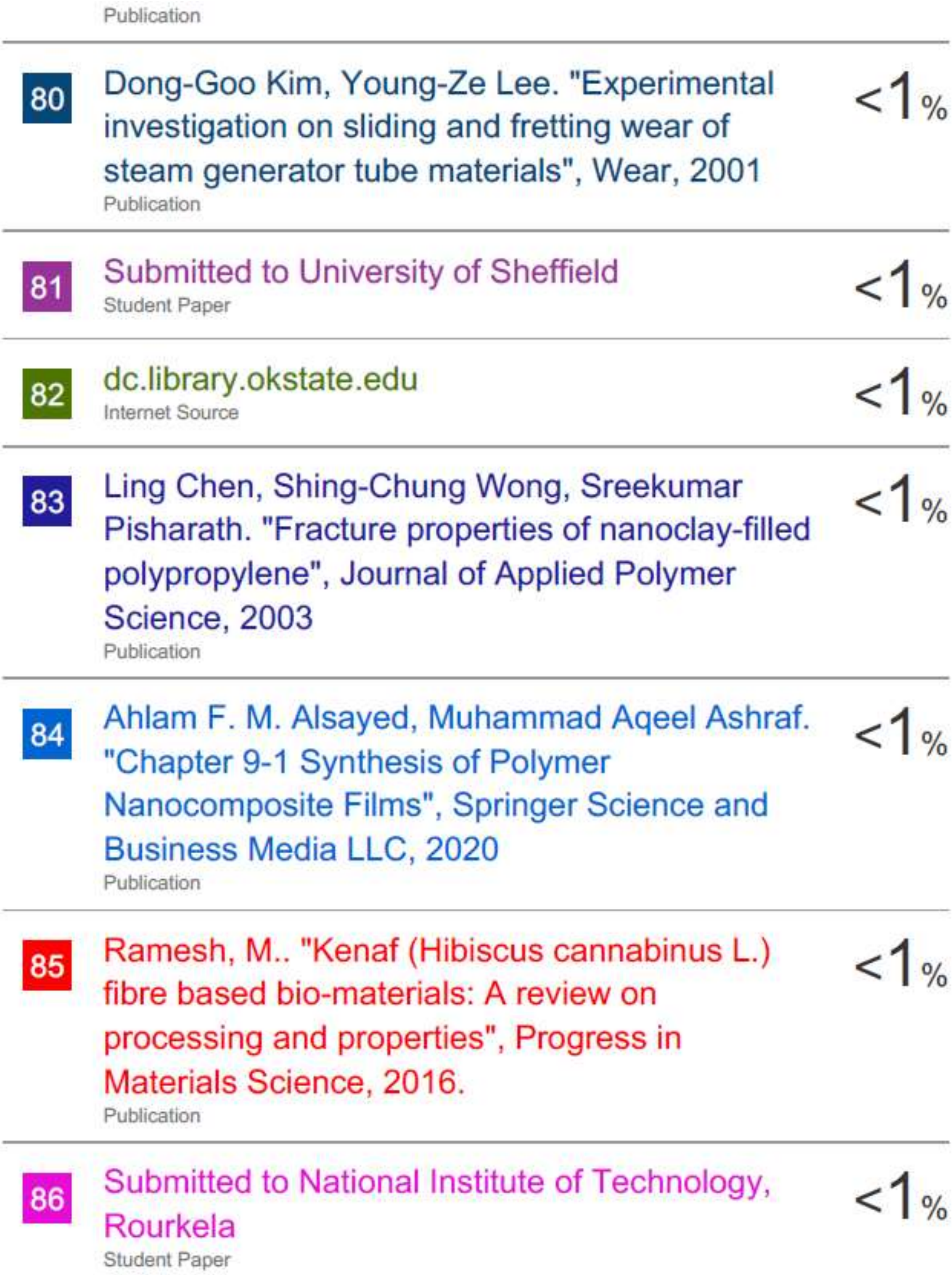

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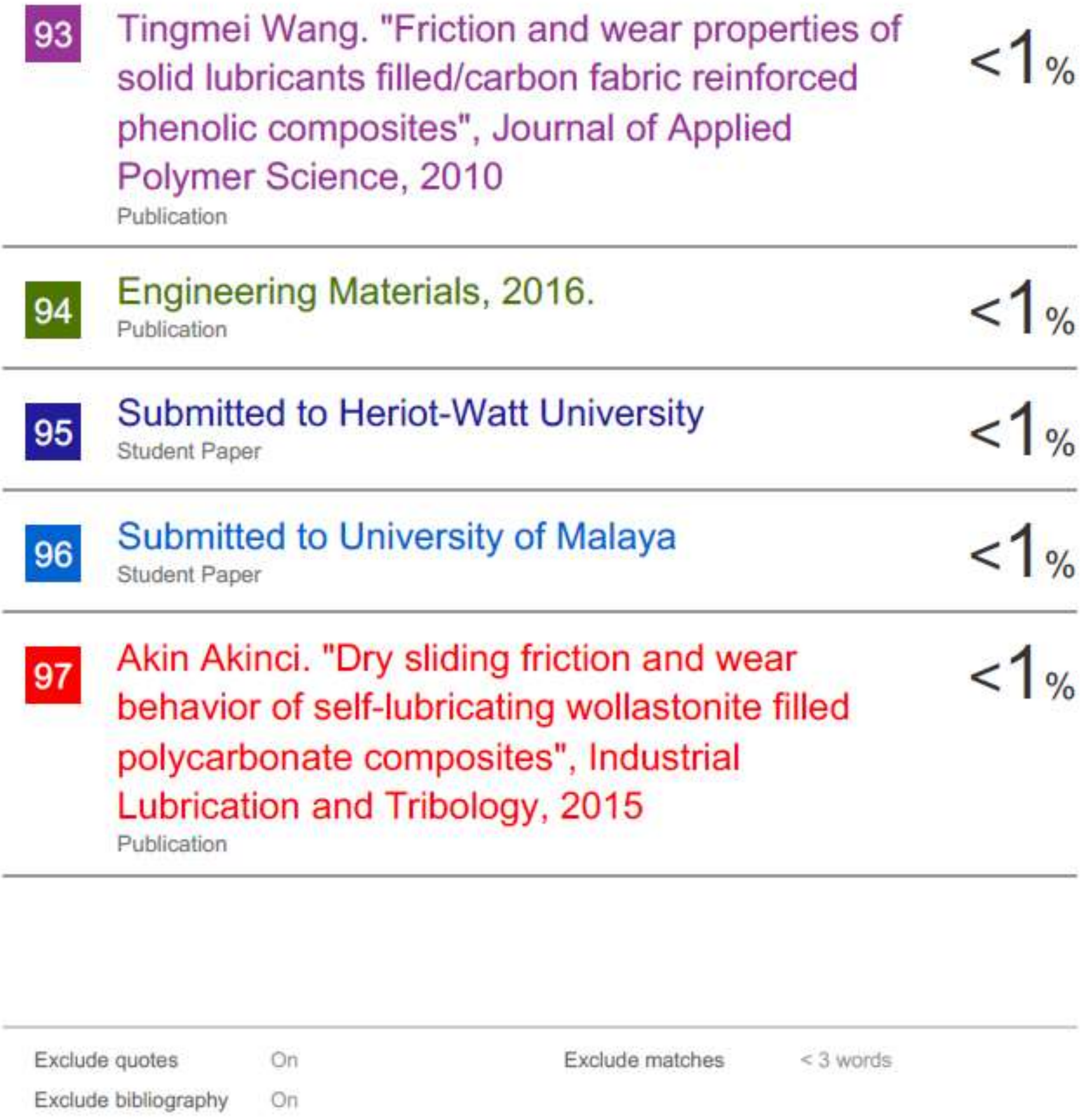

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