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Highly oil-dispersed functionalized reduced graphene oxide nanosheets as lube oil friction modifier

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ABSTRACT

Unique mechanical properties of graphene make it an attractive candidate for many tribological applications such as additives for lube oil. However, within a few days of its preparation, graphene suffers from agglomeration and it can be prevented by introducing large structure molecules on the surface of GO. Covalent functionalization of GO is possible because there are multiple oxygen-containing functionalities on GO sheets. The conversion of highly water-soluble GO to high oil-soluble GO was also possible by covalent functionalization method. In this study, oil-soluble GO sheets were fabricated via functionalization of GO with organic moiety using CuAAC via Click chemistry. This study demonstrates that chemical strategy to provide graphene with organic moiety is important to obtain highly oil-dispersed GO sheets. This study revealed that the rGO_f shows a significant effect in reducing friction and wear by 16% and 30% respectively and proved to be easily dispersed in oil.

1. Introduction

Increasing transportation activities have been consuming much of our energy resources, and a significant portion of the energy produced is spent overcoming the friction in moving mechanical systems [1]. To lubricate moving mechanical systems, lube oil is required. Unfortunately, the based oil itself as a lubricant cannot provide excellent reduction of friction. So far, there are three types of lubricant additives commonly used. They are solid, semi-solid and liquid additives. Compare to others, solid additives were widely used due to their benefits in applications that involve low sliding speeds and high contact loads. Semi-solid and liquid additives will squeeze-out when high loads and contact stresses on bearing points of mating surfaces occurred, resulting in lubricant starvation [2]. Graphene is proposed as solid additives to improve the lube oil lubrication in moving mechanical systems [3].

Graphene is chemically inert, having the high extreme strength and ability to shear easily on its densely layered and atomically smooth surface is the major favorable attributes for its impressive tribological behavior [4,5]. The mechanical properties of graphene are confirmed to be one of the strongest materials ever measured by previous studies [6]. Graphene also has been shown to be impermeable to liquid and gasses [7], thus slowing down the corrosive and oxidative processes that usually caused more damage to rubbing surfaces.

So far, many studies on graphene have been reported in the tribological application [3,8,9]. Graphite [10] and some graphite derivatives [11] together have the desirable properties mentioned earlier. Graphite has low strength shearing and weak interatomic interactions, and strong van der Waals forces between their layers [12].

Research on the tribological properties of graphite nanosheets as an additive for lube oil have been done by Lin et. al. [13]. Tribology studies on graphite nanosheets as an additive for lube oil found that when their sheets were added to the paraffin oil at optimum concentration the anti-wear ability and frictional behavior of the lubricant oil were improved [14]. There were few methods that can be used to synthesize graphene oxide [15–17]. However, Hummers method was commonly used. Graphene oxide (GO) films with two-dimensional structure were successfully prepared by the modified Hummers method through oxidation of graphite flakes [18].

However, studies show that the graphene platelets are a failure as oil additives due to the significant increase in agglomerations within the lubricant [19]. Therefore, the application of graphene is limited. Fortunately, the problem with aggregation can be solved by using some chemical modification process. By doing some chemical modification on GO, the requirement to be an effective friction modifier additives which are a polar group and straight hydrocarbon tail can be introduced to the surface of GO. One of

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the methods to do the modification is by doing the covalent functionalization method.

Over the last decades, several approaches have been established to modify GO by a chemical process. Gusain et al. reported that the covalently attached graphene-ionic liquid hybrid (Gr-IL) nanomaterials can significantly improve their dispersion and tribological properties [20]. Alkylated graphene with a variation of chain length also has been prepared to be used in the lubrication application. A chemical approach to modify graphene with alkyl chains was developed through the amide linkage between the alkyl and the edges or defects on reduced graphene oxide [21,22].

In particular, to prevent sedimentation of GO and to have uniform dispersion in the oil, taking advantage of the –OH and –COOH on the surface of the GO and do a covalent functionalization with long hydrocarbon chain compounds enhances the dispersion in nonpolar solvents [23,24]. To enhance the dispersion stability of the additives, the dispersant must have a polar head that attaches itself to the metal surfaces and a very long hydrocarbon tail that keeps it suspended and solubilized in the oil [25]. The different head groups can be a carboxylic acid, phosphoric acid, amines, amides and all their derivatives.

By taking advantage of the oxygen functional groups in GO, functionalization of GO via Click chemistry can be done. Click chemistry was described as reactions that are simple to perform, create only byproducts that can be removed without chromatography, can be conducted in easily removable solvents [26,27]. The reactions also high yielding, wide in scope and stereospecific [28]. Via Click chemistry, both straight hydrocarbon tail and the polar group will be introduced on the GO to meet the requirement to be an effective friction modifier additive. Therefore, in this study, the focused is more on the functionalization of GO by click chemistry to increase the dispersibility of this solid additive in oil while providing advantages in properties of the oil.

2. Experimental section

2.1. Materials

Graphite flake, sodium hydride (NaH), dimethyl malonate, lithium aluminium hydride ($LiAlH_4$), magnesium sulphate ($MgSO_4$), potassium permanganate ($KMnO_4$, 99.9%) chloroform, thionyl chloride ($SOCl_2$), sulphuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 85%), chloroform (CH_3Cl) and hydrogen peroxide (H_2O_2, 30%) were purchased from Merck. Hydrochloric acid (HCl, 37%), 1-bromodecane and sodium azide (NaN_3) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF), sodium hydroxide (NaOH), diethyl ether, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), and trimethylamine (Et_3N) were purchased from Friendemann Schmidt. Dichloromethane (DCM), sodium ascorbate and copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) were purchased from Fischer Scientific and propargyl bromide was purchased from Sigma-Aldrich. Group II 500 N petroleum-based oil used was obtained from Caltex Korea.

2.2. Synthesis of graphene oxide

The graphene oxide in this experiment was prepared by using the Improved Hummers method. The detailed procedure is as follows, H_2SO_4 and H_3PO_4 were stirred in an ice bath to keep the mixture cold. After 10 min, graphite powder is added to the mixture. After mixing the suspension for 10 min, $KMnO_4$ was slowly added to make sure the temperature of the mixture doesn't exceed 40 °C. The reaction suspension was then heated to about 35 °C and kept the mixture stirring at this temperature for 3 days. As the reaction progressed, the reaction suspension became brownish in color. At the ends of the 3 days period, cold deionized water was poured into the suspension. The suspension was then maintained at room temperature for 15 min. The suspension was then further added with 30% hydrogen peroxide and left to cool at room temperature. The suspension was subsequently washed with HCl and followed with water. Finally, the suspension was subjected to mild sonication to exfoliate graphite oxide into graphene oxide [18,29,30]. Finally, the product was dried at 75 °C.

2.3. Preparation of alkyne-functionalized graphene oxide

2.3.1. Synthesis of 2,2-di(propynyl)malonate

In an ice bath, dimethyl malonate was added to a NaH suspension (60% wt in mineral oil) in dry THF and left stirring for 10 min. Propargyl bromide (80% wt in toluene) was added dropwise to the mixture and left stirred for overnight. The mixture was extracted with water, followed by DCM. The combined organic phase was concentrated using a rotary evaporator leaving 2,2-di(propynyl) malonate, DiMDiPM.

2.3.2. Synthesis of 2,2-dipropargyl-1,3-propanediol

2,2-di(propynyl)malonate stirred in anhydrous THF and then $LiAlH_4$ was added**.** The mixture left stirred overnight. Water and 10% NaOH solution was added slowly to quench the reaction. The mixture was then stirred for 30 min until the suspended solids become white. The mixture was filtered and the filtrate dried over $MgSO_4$. Concentrate the product using a rotary evaporator to have the 2,2-dipropargyl-1,3-propanediol, DiPPOH.

2.3.3. Synthesis of chlorinated graphene oxide

Graphene oxide was stirred in chloroform. In an ice bath, $SOCl_2$ and triethylamine were added dropwise into the mixture. The mixture was then stirred for 2 h to produce chlorinated graphene oxide that was concentrated using a rotary evaporator. In anhydrous THF, NaH was added, followed by DiPPOH and chlorinated graphene oxide prepared. The mixture was stirred overnight. The mixture concentrated using a rotary evaporator to produce alkyne-functionalized graphene oxide, GO_f.

2.4. Preparation of azidodecane

1-bromodecane and anhydrous NaN_3 was added to DMF and then left stirred at 80 °C under reflux for overnight. The mixture was extracted with water and diethyl ether. The combined organic phases were added with $MgSO_4$ to remove water. The mixture was filtered and then the filtrate was concentrated by rotary evaporator.

2.5. Click reaction of alkyne-functionalized graphene oxide and azidodecane

Alkyne-functionalized, azido decane and sodium ascorbate were added to the mixture of water and DMSO (20:10) and sonicated for 1 h. $CuSO_4{\cdot}5H_2O$ was added and then sonicated for 2 h. The mixture was stirred overnight and then wash with water and ethanol. The product dried overnight.

2.6. Characterization

Fourier-Transform Infrared (FTIR) spectra are obtained using a Perkin-Elmer FTIR spectrophotometer within the wave number in the range of 4,000–400 cm^{-1}. Samples are finely ground with potassium bromide, KBr and then compressed into pellet form. PANalytical diffractometer used to obtain the pattern of X-ray diffraction (XRD) of the sample with a 2θ angle ranging from 5 to 50° and scan rate of 10°/min. Thermal Gravimetric Analysis