1. Introduction

Friction and wear are very common in daily life and cause energy waste, material loss, and shorter life span of machines. The most effective way to reduce friction and wear is to apply an appropriate lubricant in the contact surfaces. Lubrication effectively controls production facility systems and greatly affects the efficiency of products, the life extension of the machinery, and the stability of the facility system. Therefore, the development of new lubricants has been attracting considerable attention in an attempt to minimize friction coefficients and amount of wear of machinery. Such development is very...
important for the sustainable future of machinery[1-3].

Materials such as graphite, molybdenum disulfide (MoS₂), tungsten disulfide (WS₂), and hexagonal-boron nitride (h-BN) have a layered structure and have shown tremendous potential as solid lubricants. However, they have limitations caused by poor dispersibility as liquid lubricant additives[4-6]. Since graphene with a single layer was discovered in 2004, thin two-dimensional (2D) materials have been developed[7]. In comparison with bulk materials, very thin materials have many beneficial characteristics and potential applications in various fields. These materials have attracted considerable attention in tribological research[8]. Graphene, which is a carbon nanosheet with a sp² hybrid structure, exhibits strong mechanical strength and has high thermal conductivity and thermal properties which are notable in the lubrication industry[9]. In addition, it is a very thin material with the carbon-carbon bond length of 0.142 nm and plane spacing of 0.335 nm. It also has excellent friction characteristics and wear resistance when mixed with a liquid lubricant.

In general, multi-layer graphene is known to have lower friction than single-layer graphene. The tribological characteristics of multi-layer graphene are attributed to anisotropic bonding. The atoms of the basal plane have strong covalent bonds, but have weak van der Waals bonds between basal layers. Due to these weak van der Waals bonds, they are easily separated from each other even at low shear forces, resulting in tribological effects[10].

Graphene can be prepared by mechanical method, chemical method, epitaxial growth method, and chemical vapor deposition. Among these methods, chemical method using graphene oxide (GO) as a precursor is effective for the mass production of graphene, and is advantageous for the graphene preparation process using organic solvents[11]. GO has large numbers of oxygen functional groups on graphene sheets. Large numbers of epoxide groups and hydroxyl groups are mainly distributed on the basal plane of GO. Carboxyl and carboxyl groups are attached to the edge of GO[12]. On the other hand, various methods have been proposed to enhance the physical properties of GO by its reduction, because it is difficult to apply GO to hydrophobic organic solvents due to the large numbers of oxygen functional groups and the remarkably poor physical properties. To solve this problem, many attempts have been made to transform graphene into covalent bonds or noncovalent bonds[13]. Zhang et al. showed that the friction coefficient and wear were reduced by 17% and 14%, respectively, when oleic acid modified graphene was used as a lubricant additive[14]. Mungse et al. improved the dispersion stability of lube oil and effectively reduced the friction coefficient and wear through functionalization of octadecylamine (ODA) on the basal plane of GO. They demonstrated that long-term dispersion stability caused by van der Waals interactions between the alkyl chain of alkylamine and the alkyl chain of the lube oil is very important for the efficient performance of tribological characteristics[15].

In this study, we have functionalized GO nanosheets with hydrocarbon chains using the various alkyl chlorides and investigated the structure, dispersion stability, and tribological characteristics of the graphene nanosheets depending on the various alkyl chain lengths via the various spectroscopic and ball-on-disk techniques.

2. Experimental

2.1. Preparation of NH₂-GO

0.25 g of GO (Angstrom Materials: N002-PS, 0.25 wt%) was mixed with 100 mL of ethanol to prepare a dispersion solution. After 3 mL of ethylenediamine (0.044 mol) was added to the GO dispersion, NH₂-GO was obtained by performing a reflux reaction at 75 °C for 16 h. And NH₂-GO was then sufficiently filtered and washed with enough amount of ethanol, and then dried at 60 °C for 24 h.

2.2. Preparation of Alkyl functionalized GO

The dispersion was prepared by mixing 0.25 g of NH₂-GO with 100 mL of distilled water. Another dispersion was prepared by mixing 0.5 mL of butyl chloride (0.5 wt%) with 100 mL of ethanol. After the butyl chloride dispersion was slowly added to the NH₂-GO dispersion, the reflux reaction was carried out at 80 °C for 24 h. Butyl functionalized GO (FGO-4) was then sufficiently filtered and washed with enough amount of ethanol, and then dried at 60 °C for 24 h. FGO-8 and FGO-14 were also prepared using octyl chloride and tetradeceyl chloride according to the above method.

2.3. Chemical and structural analysis

Fourier transform-infrared (FT-IR, Vertex-80/Hyperion-3000) spectroscopy was used to investigate the functional groups present in the samples. The binding energies of the atoms in each sample were measured and compared using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Multilab-2000). The crystal structures of the samples were analyzed using X-ray diffraction (XRD, Ultima IV) and Raman spectroscopy (Horiba Jobin-Yvon, LabRam HR). The morphology and structure of the samples were examined using scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, JEM-2100F).

2.4. Tribological Characteristics

In this study, the tribological characteristics of the friction coefficient and wear of the prepared samples were examined using a high frequency friction/wear tester (TE 77 AUTO). The reciprocating ball-on-disk method was used for the test. Bearing steel SUJ2 (Ø = 10 mm, HRC: 60-63) was used as the material for the ball and disk. Figure 1 shows a schematic diagram of ball-on-disk testing in which the steel disk is pressed by a steel ball with the reciprocating motion under rubbing condition. PAO-0W40 engine oil (poly alpha olefin, GS Caltex Corporation) was used as a base lubricant. The FGO was dispersed into PAO-0W40 oil through ultrasonic treatment for 1,800 s. The concentration of the dispersion in which the FGO was added in PAO-0W40 oil was 0.02 wt%. The ball and disk were ultrasonically cleaned with acetone before testing their friction characteristics. Then, 10 mL of lubricant was poured into a bath placed between the ball and disk. The tribological tester was run at a reciprocation frequency of 10 Hz and a load of 50 N for 360 s. During the test, the disk was fixed.
to the bottom of the measuring device and the disk was pressed by the ball through the reciprocating motion. A new ball and disk were used for each test. After the test, the disk was ultrasonically cleaned with acetone in order to observe the surface condition. Morphological characteristics of wear track were observed using an optical microscope (Nikon Eclipse Ni-U).

3. Results and Discussion

In this study, alkyl functionalized GO synthesis was carried out in a two-step reaction. In the first step, an amide bond was formed between the carboxyl groups distributed on the edge of GO and the -NH\textsubscript{2} groups of ethylenediamine. In the second step, Cl acted as a good leaving group between NH\textsubscript{2}-GO prepared in the first step and alkyl chloride, followed by the formation of N-R bond. This alkyl functionalized GO reaction consists of the strong two-step nucleophilic substitution reaction. Figure 2 shows a schematic diagram of the synthesis and preparation steps of the GO nanosheets in which alkyl chloride is introduced.

FT-IR spectra analysis of the synthesized samples provides direct evidence of the functionalization of GO because it presents information on the functional groups present in the sample\cite{16}. The FT-IR spectra of the GO and FGOs are shown in Figure 3. As shown in Figure 3, the spectrum of the GO exhibits a wide range of typical peaks related to the hydroxyl groups at 3,244~3,777 cm\textsuperscript{-1}. 1,725 cm\textsuperscript{-1} corresponds to the carboxyl groups and 1,588 cm\textsuperscript{-1} corresponds to the aromatic ring, C = C. 1,042 cm\textsuperscript{-1} and 1,113 cm\textsuperscript{-1} correspond to the epoxide groups. Therefore, the FT-IR spectra confirm that the oxygen functional groups are present in GO. For the FGO samples in which the surface of the GO nanosheets is functionalized with alkyl chloride, the
peak is observed at 761 cm\(^{-1}\). The peak corresponding to the C-H stretching vibration of alkyl chain is observed at 2,834-2,978 cm\(^{-1}\). In the FGO samples, the peak at 1,581 cm\(^{-1}\) corresponds to the N-H band and represents the successful amination of the GO. After functionalization of the GO, the bands corresponding to the carboxyl and epoxide at 1,725 cm\(^{-1}\) and 1,042 cm\(^{-1}\) are attenuated. A new peak representing the formation of the N-H band appears at 1,581 cm\(^{-1}\).

Successful alkyl functionalization of the GO is confirmed by XPS analysis and the results are shown in Figure 4. As shown in Figure 4a, the survey spectrum results of the GO show two strong peaks at 287 eV and 532 eV corresponding to the C1s and O1s peaks, respectively. With the introduction of long alkyl chains in the nanosheets of the GO, the O1s peak (532 eV) is substantially decreased, while the intensity of the C1s peak (280 eV) is significantly increased. In addition, successful functionalization shows a new peak of N1s at 399 eV. The high-resolution spectra of C1s, O1s, and N1s are measured. C1s scans of the GO and FGO-14 are shown in Figures 4b and 4c. The deconvolution of the C1s scan of the GO shows four main peaks corresponding to C-C (284.64 eV), C-O (284.48 eV), C=O (288.08 eV), and COO (289.04 eV) (Figure 4b). They indicate the substantially high degree of oxidation of the GO representing the presence of oxygen functional groups in the GO nanosheet. In the case of FGO-14, the peaks corresponding to C-O and COO decrease drastically due to the functionalization of the GO by alkyl chloride such as tetradecyl chloride, and a C-N peak appears at 285.88 eV (Figure 4c). This is confirmed by the deconvoluted N1s spectra showing three peaks at 399.49 eV (C-N), 400.50 eV (N-H), and 398.68 eV (N-O) (Figure 4d).

XRD patterns of the GO and FGO are analyzed to calculate the interlayer spacing[15]. The d-spacing of the XRD patterns can be calcu-
lated by Bragg’s equation (1).

\[ n \lambda = 2d \sin \theta \]  

(1)

where \( \lambda \) is the wavelength of the characteristic x-rays, \( \theta \) is the x-ray incidence angle, and \( d \) is the lattice interplanar spacing of the crystal. As shown in Figure 5, the GO shows the diffraction peak at \( 2 \theta = 9.75^\circ \) and the corresponding d-spacing is 0.91 nm[17]. Graphite has only one diffraction peak near \( 2 \theta = 26.4^\circ \) and its d-spacing is about 0.334 nm[16]. The interlayer distance of the GO is higher than that of graphite, because oxygen functional groups exist in the basal plane and edge. The introduction of long alkyl chains to the graphene interlayer reduces the degree of graphite crystallinity, lowering the main diffraction peak. FGO-4, FGO-8, and FGO-14 exhibited broad peaks at \( 2 \theta = 3.70^\circ \), \( 3.50^\circ \), and \( 3.30^\circ \), respectively. The d-spacing between the FGO-4, FGO-8, and FGO-14 nanosheets was 2.39 nm, 2.49 nm, and 2.67 nm, respectively. This was higher than 0.91 nm of GO d-spacing due to the successful functionalization of alkyl chloride. At the same time, the XRD pattern of the FGO shows a new peak at \( 2 \theta = 23-24^\circ \), which approaches closer to the diffraction peak of graphite (\( 2 \theta = 26^\circ \)). This is caused by the formation of disordered graphene nanosheets which are rearranged due to the reduction of the oxygen functional groups on the GO nanosheets[18].

Most of carbon-based materials have various nanostructures such as diamond, graphite, carbon nanotube (CNT), and graphene depending on the carbon allotropes. Carbon nanostructures are composed of C-C bonds with different orientations. Raman spectrum is a powerful means of characterizing the degree of graphite of these carbon-based materials [19]. The Raman spectra of the GO and FGOs are shown in Figure 6. The D-band at 1,349 cm\(^{-1}\) in the GO nanosheets corresponds to sp\(^3\)-hybridized carbon or a structural defect, and G-band at 1,579 cm\(^{-1}\) corresponds to planar sp\(^2\)-hybridized carbon. The relative intensity ratio (ID/IG) of the D and G bands has been known to depend on the structural characteristics of carbon[20]. The G-band of the functionalized FGOs is red-shifted due to the reduction of the oxygen functional groups on the GO nanosheets in comparison with the conventional GO[21]. FGOs approach closer to the G-band (1,579 cm\(^{-1}\)) of typical graphite than the GO, which implies the restoration of the sp\(^2\) network.
The intensity ratio \(I_D/I_G\) of the GO and FGO-4, FGO-8, and FGO-14 are 0.94, 1.13, 1.12, and 1.08, respectively. This indicates that the \(I_D/I_G\) is slightly increased after the functionalization of GO. These changes demonstrate that amorphous carbon is formed with reduced regularity as long alkyl chains increase the spacing of the nanosheets[22].

In tribological applications, nanostructured materials must be completely dispersed in lubricants to ensure efficient lubrication. In this context, the surface characteristics of the nanomaterials are important parameters that control their dispersibility when applied to lubricants [23]. Figure 7 and Figure 8 show SEM and TEM images, respectively, of the surface morphology and characteristics of the GO and FGOs. As shown in Figure 7 and Figure 8, the conventional GO (Figure 7a and Figure 8a) has a similar morphology to a flat sheet with a smooth surface in comparison with the FGOs (Figures 7b-7d and Figures 8b-8d). However, after the introduction of long alkyl chains to the GO, the FGOs show crumpled sheets with wrinkles and some folded areas in random orientations resembling crumpled paper. This indicates that long alkyl chloride chains have been successfully introduced to the GO surface indicated by the thick area which becomes more crumpled and rougher with the longer alkyl chloride chains.

Figure 9 shows the elemental mapping results of TEM images for the GO and FGO-14. The results of elemental mapping for the GO show abundant oxygen and carbon. This indicates the oxygen functional groups present on the GO nanosheets. On the other hand, the results of elemental mapping for the FGO-14 functionalized with long alkyl chains show that nitrogen appears due to the reduction of oxygen functional groups on the existing GO nanosheets and successful amination. Thus, as a result of the elemental mapping, it has been confirmed that the two-step synthetic reaction was successfully performed in this study.

GO is not mixed with PAO oil, but the FGOs nanosheets are mixed with PAO oil and are then ultrasonically treated. These samples are carefully observed for 1 month. As analyzed by FTIR and XPS, the FGOs could be dispersed in the PAO lubricant due to the presence of
long alkyl chains. Figure 10 shows the test results of the dispersion stability of the GO, FGO-4, FGO-8, and FGO-14 in PAO oil. As shown in Figure 10b, after ultrasonic treatment, the FGO-4, FGO-8, and FGO-14 are successfully dispersed in PAO oil, but only FGO-14 shows a very stable dispersion status after 30 days. The long-term dispersion stability of the FGO-14 is caused by the introduction of hydrophobicity to the GO as well as the high specific surface area of the FGOs like crumpled paper[24]. Thus, as the van der Waals interactions between the tetradecyl chains of the FGO-14 and the alkyl chain of PAO oil increased, these nanosheets are fully dispersed and long-term dispersion stability is provided.

The tribological characteristics of the FGOs mixed with lubricant additives are analyzed under ball-on-disk rubbing for 360 s at a reciprocation frequency of 10 Hz and a load of 50 N. Figure 11 shows the changes of the friction coefficient of the FGOs depending on the length of various alkyl chains and conventional base lubricant. In comparison with PAO-0W40 oil, the friction coefficient of the FGO-4 and FGO-8 is increased by ~34.48% and ~9.70%, respectively, but the friction coefficient of the FGO-14 is decreased by ~5.88%. In the case of FGO-4 and FGO-8, the increases in the friction coefficient are caused by their poor dispersion stability. In the case of FGO-14, the tribological characteristics and wear resistance are improved. GO is a type of nanosheet material similar to a smooth plate and tends to aggregate due to strong van der Waals interactions between the layers. However, the FGOs functionalized with long alkyl chains is a type of nanosheet material similar to crumpled paper and maintains excellent mechanical strength of the existing graphene while reducing the aggregation between layers due to high specific surface area. Thus, the mechanism of a reinforced nano bearing could improve the tribological characteristics[25].

Figure 12 shows images of the wear track of the steel disk lubricated with base lubricant and the FGOs blended lubricants acquired by the optical microscope. As shown in Figure 12, the width of the wear track of the lubricants added with the PAO oil and FGOs are ~155 µm and ~165 µm, ~159 µm and ~149 µm, respectively. As mentioned above, the FGO-4 and FGO-8 have poor dispersion stability which decreases their tribological characteristics, resulting in increases in the width of the wear track in comparison with that of base lubricants. On the other hand, the width of the wear track of FGO-14 is decreased by ~3.8%. The decrease in the width of the wear track could be caused by the improvement in the wear resistance of the steel disk due to the morphology of the FGO-14, like crumpled paper, which reduces the friction.

4. Conclusions

FGOs are functionalized on the surface of the GO by introducing alkyl chloride with various alkyl chain lengths. From the results of the FT-IR and XPS analyses, the introduction of long alkyl chains and appearance of C-N bonds are found together with the decreases in the oxygen functional groups of the GO. The results of XRD and Raman spectra analyses show that the structure of the FGO is characterized by wider interlayer spacing and the formation of amorphous carbon of disordered SP². In addition, SEM and TEM images show that the FGOs have a morphology like crumpled paper after functionalization. The results of the friction test show that the FGO-14 has a reduced friction coefficient of ~5.88% and a width of wear track of ~3.8% under the rubbing action of the ball-on-disk in comparison with those of the existing PAO oil, even when the concentration is as low as 0.02 wt%. Thus, the wear resistance of the PAO oil has been found to be improved. The van der Waals interactions between the tetradecyl chain of FGO-14 and the alkyl chain of the lubricant have provided long-term stable dispersion in the lubricant, which has been proved to be very important for the efficient friction wear performance. In this study, we confirm the successful functionalization of GO and the dispersion stability and tribological characteristics depending on various alkyl chain lengths. In particular, it has been proved that the most im-

Figure 12. Wear tracks of (a) PAO oil, (b) FGO-4, (c) FGO-8, and (d) FGO-14 dispersed in PAO oil, after tested by ball-on-disk method.

Figure 13. Distributions of wear tracks of PAO oil and FGOs with the various numbers of hydrocarbon chain.
provement in the dispersion stability and tribological characteristics is shown when the number of carbon atoms in the functionalized alkyl chains is 14. It enhances a lipophilicity of FGO in PAO oil and enables to functionalize FGO-14 as solid lubricant in PAO oil to the optimum condition.

References


