

폴리프로필렌/난연제 함유 산화그래핀 복합재료

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Polypropylene Nanocomposites with Graphene Oxide Containing Flame Retardant Moieties

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초록: 폴리프로필렌(polypropylene, PP)/산화그래핀(graphene oxide, GO) 복합재료의 난연성과 기계적 성질을 향상시키기 위해 GO를 인계 난연제로 개질시켰다. 복합재료는 무수말레인산이 수식된 PP(maleic anhydride-grafted PP, MAPP)를 상용화제로 사용하여 용융 혼합 방식으로 제작되었다. 푸리에 적외선 분광학(Fourier transform infrared, FTIR), 광전자분광법(X-ray photoelectron spectroscopy, XPS)을 통해 난연제와 GO 사이에 공유 결합이 형성된 것을 확인할 수 있었다. GO의 기능화와 상용화제 사용이 PP/GO 복합재료의 형태학, 난연성, 기계적 성질에 미치는 영향을 평가하였다. 주사전자현미경(SEM)을 이용한 형태학 분석 결과, MAPP를 첨가함으로써 충전제와 기지재 사이의 계면 상호작용이 증가되어 GO의 박리 및 분산성이 향상되었다. PP/기능화된 GO 복합재료의 한계산소지수, 영 탄성률, 인장 강도가 PP/GO 복합재료에 비해 증가된 결과를 나타냈다.

Abstract: Graphene oxide (GO) was functionalized with phosphorus-containing groups to give the flame retardancy to the polypropylene (PP)/GO nanocomposites. The composites were prepared *via* melt mixing with maleic anhydride-grafted PP (MAPP) as a compatibilizer. Through the Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), covalently-bonded flame retardant moieties on GO were characterized. The effect of the functionalization of GO and the use of compatibilizer on the morphology, flame retardancy, and mechanical properties of the PP/GO composites were investigated. SEM observation of the composites showed that the addition of MAPP improved the exfoliation and dispersion state of the GO sheets by improving the interfacial interaction between the filler and the matrix. For PP/functionalized GO composites, the limiting oxygen index (LOI), Young's modulus, and tensile strength were increased compared with PP/GO composites.

Keywords: polypropylene, graphene oxide, composite, flame retardant.

Introduction

Polypropylene (PP) is a thermoplastic polymer widely used in many fields due to its low density, processability, and good mechanical properties.^{1,2} Despite these advantages, an inherent flammability issue limits applications in some areas, such as the automotive and electrical industries, where high flame retardancy is required.^{3,4} As a method for increasing the flame

retardancy of PP, a flame retardant containing halogen was widely used. Since halogen radicals generated during combustion can remove radicals generated by thermal decomposition of the polymer, halogen-containing flame retardants are effective in retarding combustion. It has been applied to other polymers, however, its use is prohibited because the halogen halide generated during combustion is toxic and corrosive chemicals.^{5,6}

Metal hydroxides such as aluminum trihydrate and magnesium dihydrate were used as an alternative flame retardant. These metal hydroxides are endothermically decomposed and release water during combustion, reducing heat and tempera-

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ture of the polymer substrate. When using metal hydroxide flame retardants in PP, however, more than 30 wt% was required to achieve the V-0 rating in the UL-94 test, which reduced tensile strength, impact strength, and melt flow index.^{7,8} Another attempt to improve the flame retardancy of PP involves an intumescent flame retardant (IFR) such as ammonium polyphosphate (APP) and melamine polyphosphate (MPP). IFR is halogen-free, and improves flame retardancy by forming an insulating barrier on the polymer surface that prevents heat and mass transfer. This method also reduced tensile strength, flexural strength, and impact strength because more than 25 wt% of flame retardant was required to form a thick insulating barrier.^{9,10}

In recent studies, interest in flame retardants has focused on phosphorus flame retardants with phosphine oxide, such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). They volatilize into the gas phase to form phosphorus-centered radicals such as $\text{PO}\cdot$, $\text{PO}_2\cdot$, and $\text{HPO}\cdot$, which act as radical scavenger. Volatilized compounds are one of the most effective combustion inhibitors because phosphorus-based radicals are 5 times more effective than bromine radicals and 10 times more effective than chlorine radicals.^{11,12} For this reason, it is possible to improve the flame retardancy of the polymer such as polyester and polyamide even in a small amount.^{13,14} In the case of PP, however, it was difficult to apply because of the problem of dispersion due to the large polarity difference between the flame retardant and the matrix. It was observed in a PP/DOPO-GO composite that 30 wt% of filler was required to achieve the V-0 rating, which reduced the tensile strength and impact strength.¹⁵ To increase the flame retardancy of PP with a small amount of flame retardants, it is necessary to improve the dispersibility.

We desire to improve the flame retardancy and mechanical properties of PP at the same time by attaching a phosphorus flame retardant acting as a radical scavenger to GO, and dispersing it in PP. The flame retardants used in this study were DOPO and triphenylphosphine oxide (TPPO), which have been known to be excellent in thermal stability and impart flame retardancy in small amounts. TPPO has been aminated to introduce higher amounts of flame retardants to GO than DOPO, and to increase the dispersion state of the filler by improving the reactivity with MAPP. Since GO is a two-dimensional sheet-like structure, it can be used as not only reinforcing filler but also flame retardant,^{16,17} we chose it as a filler for composite. GO also has the problem of being dispersed in PP due to the polarity from multiple hydrophilic

groups present on the surface. We selected the MAPP as a compatibilizer for the composite, as MAPP was considered to interact with both PP and GO. One method often used to increase the compatibility between PP and fillers having hydroxyl and/or amine groups is to introduce MAPP as a compatibilizer in PP composites.^{18,19}

The effect of functionalized GO as a flame retardant and reinforcing filler on the flame retardancy, mechanical properties, and morphology of PP/GO composites was investigated.

Experimental

Materials. PP was a commercial product of Sumitomo Chemical with the trade name of AY 564. GO powder was obtained from Promico under the trade name of PRM170308. DOPO (97%) was purchased from Tokyo Chemical Industry. MAPP ($M_w \sim 9100$, MA 9~10 wt%) and TPPO (98%) were obtained from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 95%), nitric acid (HNO_3 , 70%), hydrochloric acid (HCl, 35%), Tin(II) chloride anhydrous (SnCl_2 , 98%), sodium hydroxide (NaOH, 20 wt% aq. solution), and tetrahydrofuran (THF, 99%) were purchased from Daejung Chemicals.

Synthesis of Aminated TPPO (TPPO-NH₂). TPPO (10 g, 0.03 mol) was added to 72 mL of H_2SO_4 with stirring under nitrogen condition, and solution was cooled to 0 °C with an ice bath. HNO_3 (36 mL, 0.12 mol) was added over a period of 10 min. The reaction mixture was stood at room temperature for 4 h, and added to 1000 g of ice. After ice was melted, the product (TPPO-NO₂) was filtered, and washed with NaHCO_3 aqueous solution and deionized water before being dried in the oven at 80 °C for 24 h. The obtained TPPO-NO₂ (5 g) was placed in a round-bottomed flask with 30 g of SnCl_2 . A solution of 40 mL HCl in 80 mL of ethanol was added into the flask. The mixture was stirred at room temperature for 5 h, and 500 mL of NaOH aqueous solution was added in order to eliminate the SnCl_2 . The final product (TPPO-NH₂) was filtered, and washed with deionized water until neutral pH. The TPPO-NH₂ was dried in a vacuum oven at 80 °C for 24 h.

Preparation of Functionalized GO. GO (0.5 g) was suspended in 200 mL of THF, and sonicated for 30 min. THF solution (50 mL) with TPPO-NH₂ (1.8 g) was added with stirring. The mixture was heated to 60 °C, and refluxed for 2 h under nitrogen condition. After functionalization, the product (TPPO-GO) was separated by filtration, and washed with anhydrous THF to remove unreacted TPPO-NH₂. The TPPO-GO was dried in a vacuum oven at 80 °C for 24 h. The prepa-

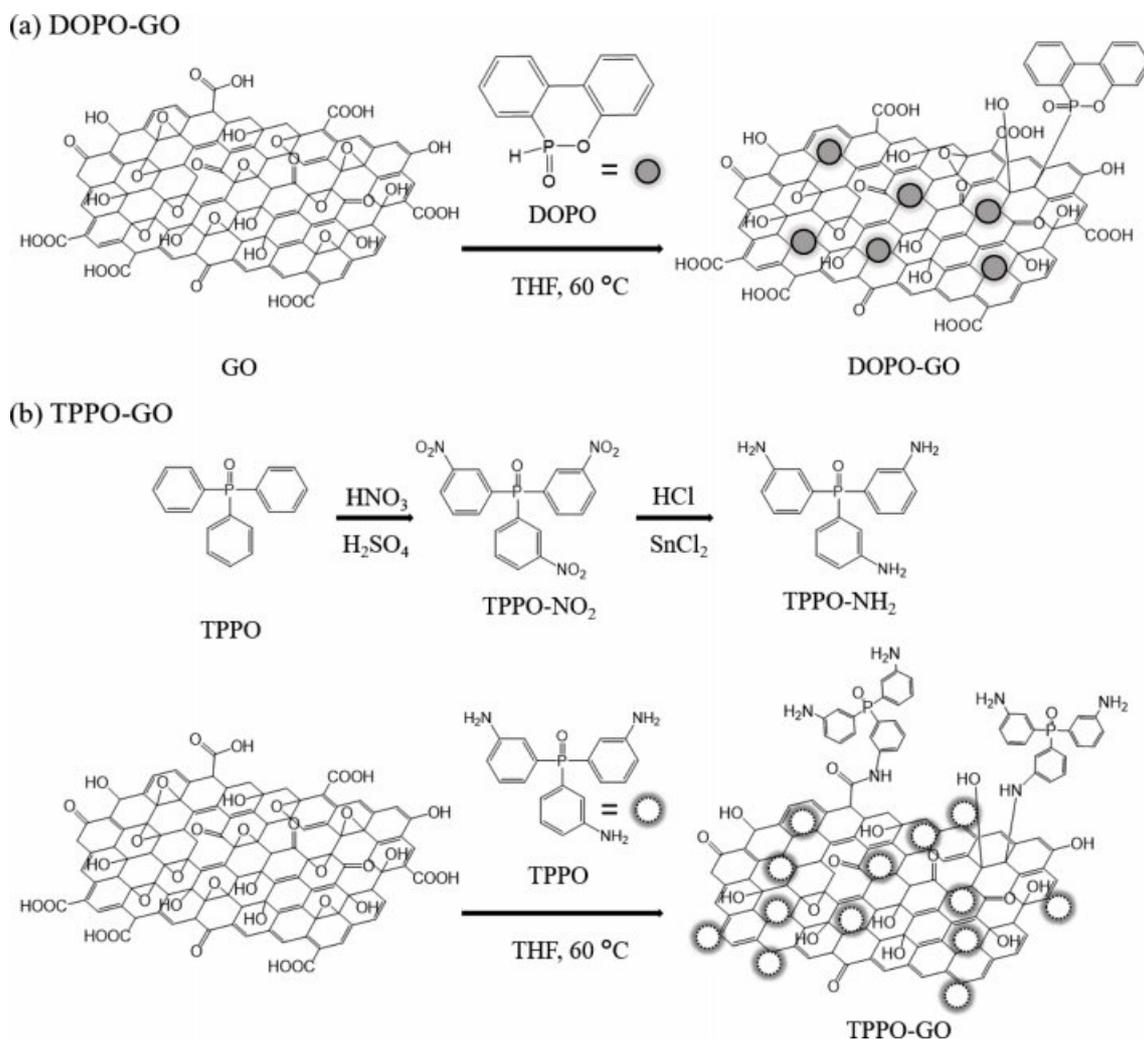


Figure 1. Schematics of synthesis of (a) DOPO-GO; (b) TPPO-GO.

ration of DOPO-GO was done by the same synthesis procedure as TPPO-GO. Figure 1 shows the synthesis scheme of TPPO-GO and DOPO-GO.

Preparation of PP/MAPP/Functionalized GO Nanocomposites. Prior to preparation of nanocomposites, PP/MAPP/functionalized GO master batches containing 4 wt% of functionalized GO were prepared by reactive extrusion using an internal mixer (Thermo scientific, Haake PolyLab QC). The extrusion temperature and rotor speed were 190 °C and 60 rpm, respectively. The master batches were melt blended with PP in a co-rotating twin-screw extruder (Thermo Electron, Prism TSE 16TC) with temperature profile of 190 to 200 °C from hopper to die at the rotating speed of 200 rpm. The composites extruded using a strand die were water-cooled, pelletized, and dried.

Characterization and Measurement. The attenuated total

reflection Fourier transform infrared (ATR-FTIR) spectra were recorded using a FTIR spectrometer (Agilent, Cary 600) equipped with an ATR accessory in the range from 4000 to 650 cm^{-1} . X-ray photoelectron spectroscopy (XPS) of each sample was recorded on X-ray photoelectron spectrometer (Thermo scientific, K-Alpha Spectrometer) using monochromatic Al K α radiation as the exciting source.

Morphology was investigated with a field emission scanning electron microscope (FE-SEM, JEOL, JSM-6701F). To investigate the phase morphology, specimens were fractured under cryogenic conditions using liquid nitrogen.

Young's modulus and tensile strength were determined using a universal testing machine (UTM, LR10K, Lloyds Instruments). The tests were carried out with a crosshead speed of 10 mm/min and specimens of $63.1 \times 3.1 \times 3.2 \text{ mm}^3$ in dimension according to the ASTM D638 Type V method.

The limiting oxygen index (LOI) was measured using an oxygen index meter (Fire Testing Technology, Oxygen Index) according to the ASTM D2863 Type I method, which is for specimens of $90 \times 10 \times 4 \text{ mm}^3$ in dimensions.

Results and Discussion

Structure of TPPO-NH₂ and Functionalized GOs. TPPO-NH₂ was synthesized via a two-step route. As shown in Figure 1(b), the nitro compound (TPPO-NO₂) was first obtained as an intermediate, and hydrogenated to result in the amine compound (TPPO-NH₂). Nitration and reduction of TPPO have been well-established to obtain amino derivatives.²⁰ FTIR spectrum of TPPO-NH₂ was shown in Figure 2(a). The formation of aromatic primary amine group was confirmed by IR absorption peaks from 3300 to 3500 cm⁻¹. The formation of amine was also observed by XPS N 1s peak at 398.5 eV as shown in Figure 3(a) and 3(c). Similar results were observed for the synthesis of bis(4-aminophenoxy)phenyl phosphine oxide.^{21,22}

To identify the chemical reactions that took place during the modification of GO, we investigated the FTIR spectra of GO and the functionalized GOs, which were shown in Figure 2(b), 2(c), and 2(d). In the spectrum of DOPO-GO, the ring-opening reaction of GO with DOPO could be confirmed by analyzing the epoxy ring peak of GO. The asymmetrical vibration peak of the epoxy ring of GO at 982 cm⁻¹ was decreased when the epoxy group reacted with DOPO (Figure 2(c)). The DOPO-GO spectrum exhibited a new characteristic band at 755 cm⁻¹ due to the stretching vibration of P-O-Ph in DOPO, which was formed by the reaction between the GO and DOPO. The same result was previously observed in the IR analysis of preparation of phosphorous-containing epoxy resin with DOPO-GO.²³ Unlike DOPO, amine groups in the TPPO-NH₂ react with both epoxy and carboxylic acid groups in GO. As a result, absorption bands corresponding to carboxylic acid (1730 cm⁻¹) and epoxy (982 cm⁻¹) were reduced in TPPO-GO. The similar result was observed for the GO treated with *p*-phenylenediamine.²⁴ Also, spectrum of TPPO-GO included peaks for the C-N (1120 cm⁻¹), N-H (1600, 695 cm⁻¹), and P-Ph (1448 cm⁻¹) groups, implying the presence of TPPO on the GO surface.

The XPS spectra of GO and functionalized GO was shown in Figure 3(b), and the atomic percent of each sample was summarized in Table 1. As the flame retardants were introduced into GO, a peak of P which was not present in GO was formed, and the ratio of C and O was changed. In the case of

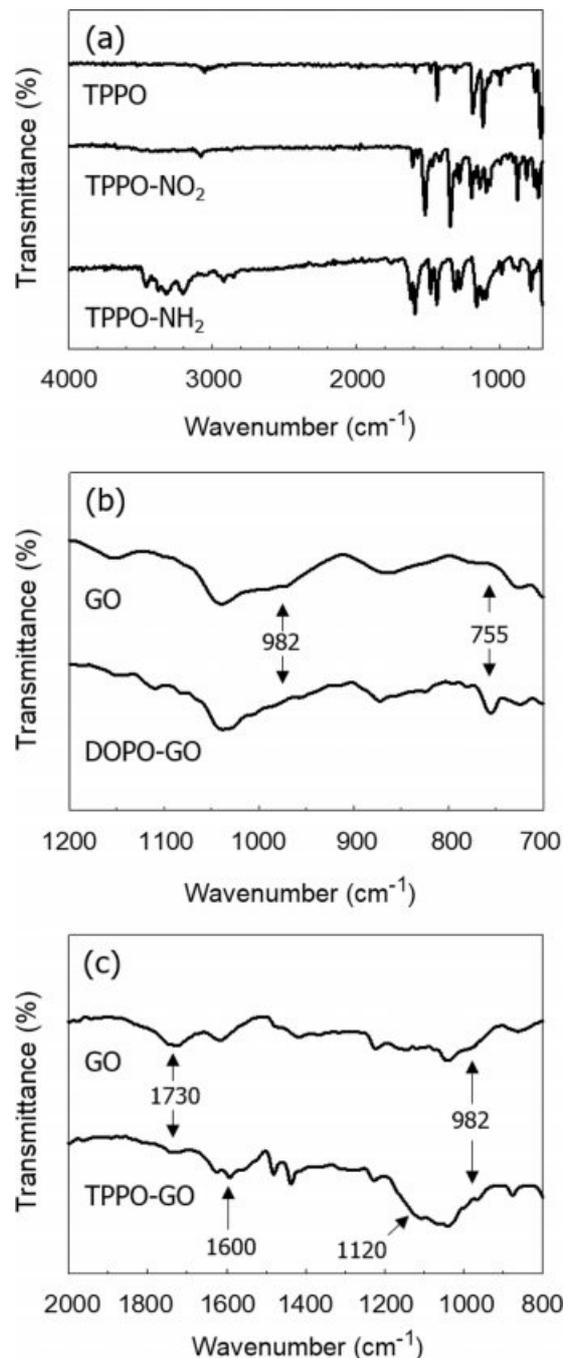


Figure 2. FTIR spectra of (a) TPPO-NH₂; (b) DOPO-GO; (c) TPPO-GO.

GO, the atomic percent ratio of the XPS result was 7:3 for carbon and oxygen. It can be considered that 70 carbon atoms and 30 oxygen atoms exist among 100 atoms, and that 70 carbon atoms can constitute about 30 numbers of 6-membered rings. The number of flame retardants introduced to the GO surface can be deduced based on the atomic percent of C and O atoms

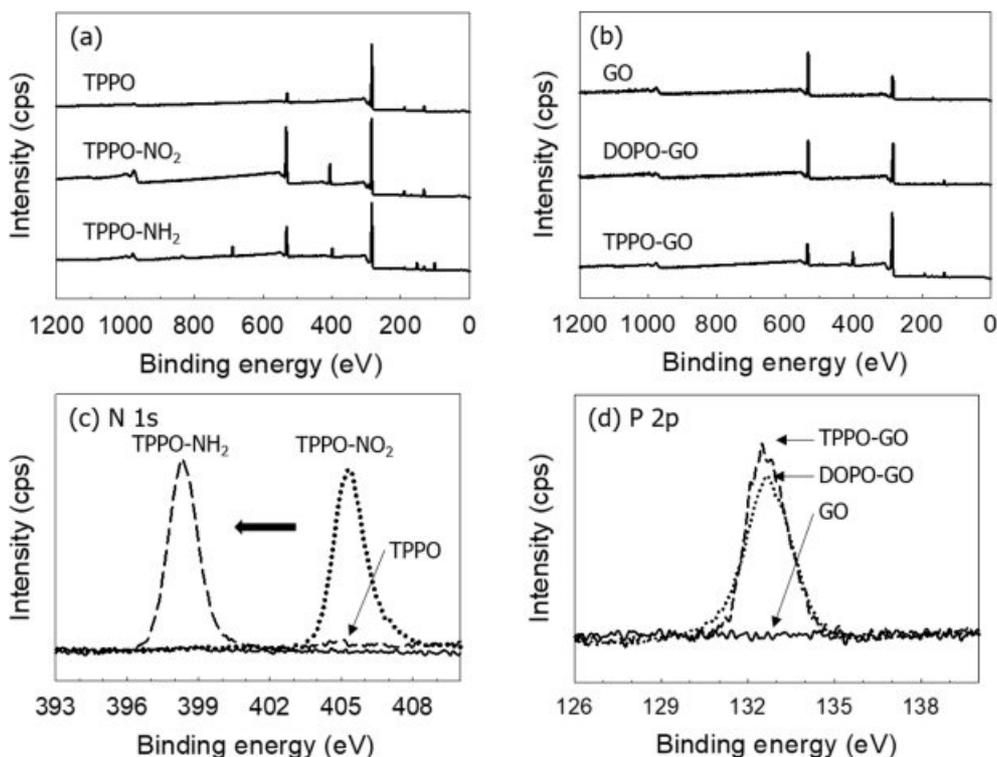


Figure 3. XPS survey spectra of (a) TPPO-NH₂; (b) DOPO-GO and TPPO-GO. XPS high resolution spectra of (c) N 1s in TPPO-NH₂; (d) P 2p in DOPO-GO and TPPO-GO.

Table 1. Atomic Percent of Element Obtained from XPS

Sample	Element (at%)			
	C	O	P	N
GO	70.9	29.1	-	-
DOPO-GO	73.1	23.9	3.0	
TPPO-GO	76.8	11.5	3.2	8.5

changed by the added flame retardant, as well as the atomic percent of newly generated P and N atoms. As a result, it is simply calculated that one DOPO per 5.4 rings is formed on the surface of DOPO-GO, and one TPPO per 2.5 rings on TPPO-GO. For TPPO-GO, TPPO-NH₂ interacts with carboxylic acid groups and epoxy groups on the GO surface as mentioned above. It can be confirmed that a larger amount of flame retardant is attached on TPPO-GO surface than DOPO-GO.

Morphology. As flame retardancy and mechanical properties of GO reinforced composites should be dependent on the dispersion of filler including particle size as well as the filler content, morphology of the composites was examined. The cryo-fractured surfaces of the composites were shown in Figure 4.

As shown in Figure 4(a) and 4(c), the functionalized GO particles in PP/DOPO-GO and PP/TPPO-GO composites were aggregated to a size of 20.7 and 20.6 μm , respectively. When the GO was functionalized with flame retardants, there was no effect to improve the interfacial interaction with the PP. For this reason, the GO was not effectively exfoliated, resulting in the aggregation.

In comparison, smaller and thinner GO particles were found on the fracture surface of PP/MAPP/DOPO-GO and PP/MAPP/TPPO-GO composites as shown in Figure 4(b) and 4(d). This indicated that MAPP act as a compatibilizer. It is considered that the polypropylene chains of the MAPP, with the same structure as PP matrix, were exposed on the surface of functionalized GO in the composites. These chains diffused into the PP matrix phase to form entanglement and cocrystallization with the PP chains, creating a bridge at the interface between the functionalized GO and the PP matrix.^{25,26} This interaction led to increase compatibility between GO and PP, resulting in effective exfoliation of GO sheets.

The size and thickness of particles in PP/MAPP/TPPO-GO was smaller than those in PP/MAPP/DOPO-GO, which was a result of better interfacial interaction between functionalized

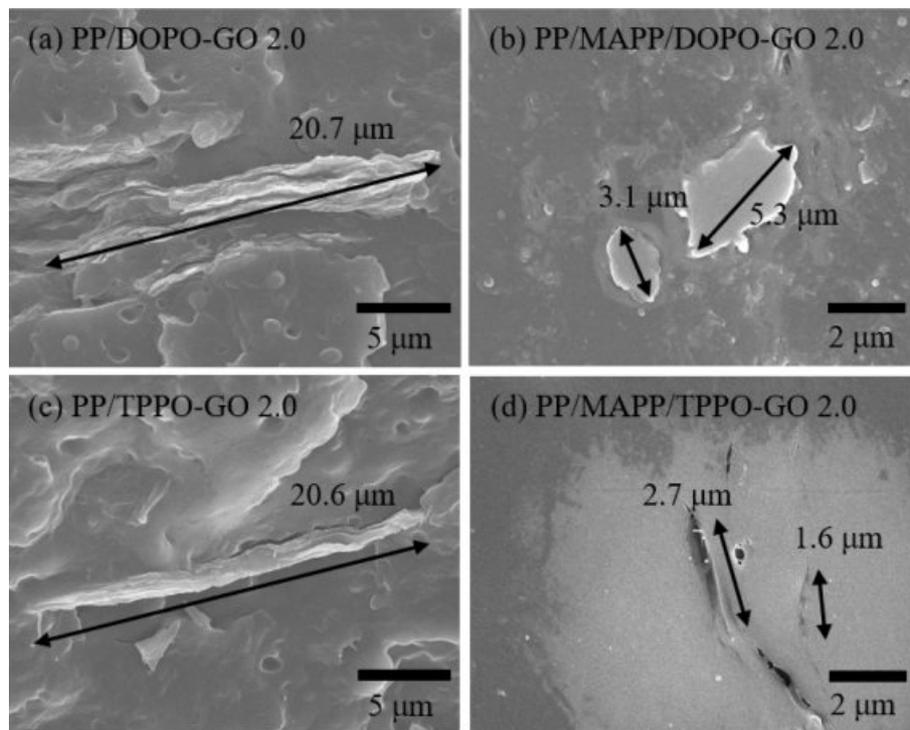


Figure 4. SEM images of the cryofractured surface of (a) PP/DOPO-GO; (b) PP/MAPP/DOPO-GO; (c) PP/TPPO-GO; (d) PP/MAPP/TPPO-GO composites.

GO and PP. In PP/MAPP/functionalized GO composites, maleic anhydride group in MAPP reacts with hydroxyl groups on DOPO-GO surface and amine groups on TPPO-GO surface, and make a covalent bond between MAPP and functionalized GO.²⁷ The surface of DOPO-GO was functionalized with bulky molecules (i.e. biphenyl structure of DOPO), the amount of hydroxyl groups in DOPO-GO exposed to MAPP was relatively decreased compared to that of the before functionalization. The amine groups on the of TPPO-GO in PP/MAPP/TPPO-GO composite, however, exist on the outer surface of TPPO-GO, and approach to MAPP easily. The effective exfoliation of TPPO-GO in the PP matrix is considered to be the result of increased reactivity of MAPP, which improves the compatibility between PP and TPPO-GO in composite.

Flame Retardancy. The LOI values of both PP/GO and PP/functionalized GO with phosphorous flame retardant composites were increased with the filler content increased, as shown in Figure 5(a). It has been explained that the origin of the flame-retarding behavior of GO was thought to be its ability to form a continuous protective layer that acts as a thermal insulator and mass transport barrier.²⁸⁻³⁰ For PP/TPPO-GO composite, TPPO-GO was functionalized with higher amounts

of flame retardants than DOPO-GO, and the LOI of the PP/TPPO-GO composites was higher than that of the PP/DOPO-GO composites. The higher amount of radical scavenger formed during the combustion process of PP/TPPO-GO composite prevented the degradation of PP more effectively than PP/DOPO-GO composite, resulting in higher LOI. In the case of DOPO, radicals are formed as the P-H bond is homolytically cleaved during the degradation process. The radicals formed in this process are stabilized by dividing into dibenzofuran and PO radicals.^{31,32} For TPPO, it has been reported that TPPO is rather poor char promoter, but are more active in the gas phase than other phosphorous flame retardants with higher oxidation numbers like phosphate.³³ It has been also reported that as the oxidation state of TPPO increased, the production of stable char layers increased and the release of phosphorous-containing radicals decreased.³⁴ The enhanced flame retardancy of the composites with GO containing phosphorous flame retardants is considered to be a result of the radical scavenging mechanism in the gas phase.

When the compatibilizer was used to improve the dispersion state of the fillers in composites, the LOI value was further increased. To create an effective protective layer with GO

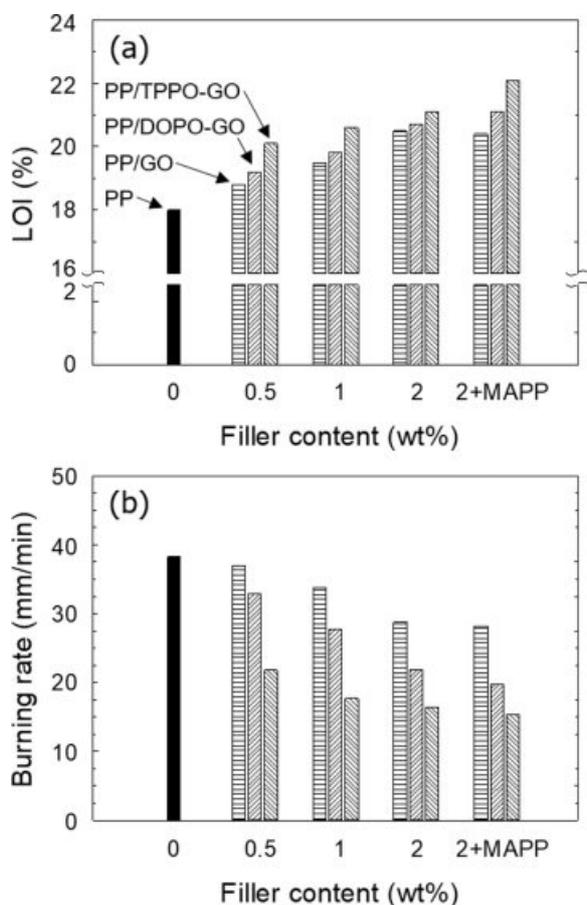


Figure 5. (a) LOI; (b) burning rate of PP and its composites with various filler content (wt%).

sheets, they must be dispersed in the matrix, not agglomerated, so that they accumulate continuously in the condensed phase during combustion. Effective dispersion of fillers increases the interfacial area with matrix, which means that the amount of phosphorous flame retardant exposed is increased. The further increase in LOI was due to an increase in the amount of PO radicals produced as the amount of flame retardant exposed increased.

The results of the UL-94 horizontal burning test were summarized in Figure 5(b). The result showed that all composites showed lower burning rates than neat PP, and the tendency was similar to that of LOI. As the filler content increased, the burning rate gradually decreased, and showed the minimum point when the compatibilizer was added. As mentioned above, GO formed a protective layer during the combustion process, and phosphorus flame retardant acted as a radical scavenger, which delayed the thermal degradation of PP. As a result, the burning rate of the composites decreased, but all of the composites

classified as an HB rating. The specimens had to be self-extinguished to pass the vertical burning test, which measures the time to stop combustion after vertically igniting the specimen, but was not found in this study. It was expected that more filler would be needed to achieve higher LOI values or UL-94 vertical rating. The use of larger amounts of GO, however, is limited due to aggregation of GO that reduce the tensile strength,^{15,27} and environmental problems caused by the GO production process.³⁵

Mechanical Properties. The tensile properties of PP and the composites were shown in Figure 6. For the PP/GO composites, the Young's modulus and tensile strength were increased than those of neat PP, which indicated the reinforcing effect of GO. The Young's modulus and tensile strength of PP/DOPO-GO composite did not show any significant increase compared to PP/GO composite. It was expected to reduce the interaction between GO sheets by attaching bulky DOPO to the GO surface, however, exfoliation of the GO sheets was not effective because there was no change to improve the interfacial interaction with PP. Since the compatibility with PP was not improved, the dispersion state was also not improved, and there was no further increase in mechanical properties. Recent researches reported that the mechanical properties of a polymer composite reinforced with GO affected by dispersion states of filler in the matrix as well as filler content.^{27,36}

When MAPP was used as a compatibilizer, both Young's modulus and tensile strength were further increased. As described in the morphology part, MAPP increased the interfacial interaction between functionalized GO and PP, which improved the dispersion state of filler. Improved dispersion meant that the GO sheets were effectively exfoliated and reduced in size and thickness. When the size of the filler is decreased to nanometer size, fillers interfere with polymer chain movement (blockage effect) that decreases the molecular mobility leading to an increase in the stiffness and strength of the composites.³⁷ As the size decreased, the contact area also increased significantly compared to the same weight or volume ratio. When the contact area increases, the stress transfer area increases, and the total stress value measured during the tensile test increases. Therefore, even with fillers having the same weight content, the increased dispersion leads to an increase in modulus and strength by effectively achieving stress transfer.^{38,39}

It is notable that the PP/MAPP/TPPO-GO composite showed the highest Young's modulus and tensile strength, which meant that the dispersion state of GO was better than the

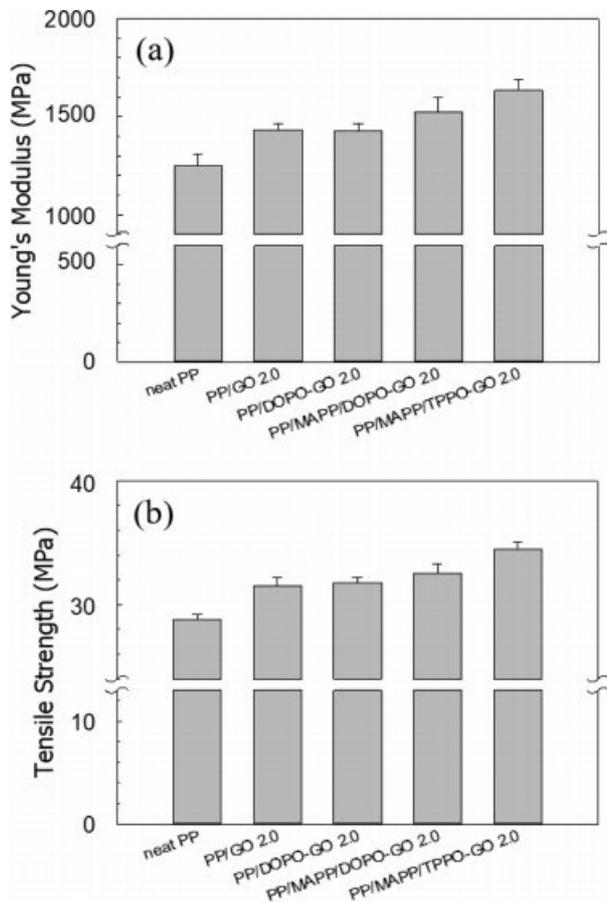


Figure 6. (a) Young's modulus; (b) tensile strength of the composites.

rest of the composites. The reason for this was considered to be the better interfacial interaction between TPPO-GO and MAPP. The hydroxyl groups in DOPO-GO were hindered by bulky molecules and blocked from the approaching of MAPP. For TPPO-GO, however, amine groups were present on the outer surface of TPPO-GO, making them less susceptible to steric hindrance by bulky molecules. The improved dispersion of TPPO-GO was due to the increased interfacial interaction with the matrix than DOPO-GO by effectively grafting MAPP onto the surface. Similar result was reported in the case of PP/MAPP/aminated GO composite.²⁷ Ryu *et al.* have reported that in their PP/MAPP/aminated GO with hexamethylene diamine composite, Young's modulus and tensile strength increased to about 35% and 14%, respectively, on loading 2 wt% of aminated GO. When the content of more than 2 wt% was added, however, the fillers were reaggregated, and tensile strength tended to decrease. Similar result was reported in the mechanical properties of PP/silane coupled DOPO-GO composite.

Tensile strength of PP composite decreased from 31.0 to 28.3 MPa when DOPO-GO loaded at 10 wt%.¹⁵

Conclusions

PP/functionalized GO composites were prepared using MAPP as the compatibilizer *via* melt blending. The DOPO and aminated TPPO were chemically grafted onto the GO surface and its influence on the morphology, flame retardancy, and mechanical properties was investigated. Successful formation of covalent bonding between GO and phosphorous-based flame retardants was corroborated using FTIR and XPS spectroscopy. Dispersion state of functionalized GOs in PP/functionalized GO and PP/MAPP/functionalized GO composites was confirmed by the characterization of cryofractured surface of composites using FE-SEM. The effective interfacial interaction between TPPO-GO and MAPP resulted in the better exfoliation and dispersion of TPPO-GO. By reinforcing with flame retardant grafted GO fillers, the flame retardancy and mechanical properties of PP were increased simultaneously. As the phosphorous content of functionalized GO increased, the LOI value increased. Young's modulus and tensile strength of the PP/MAPP/TPPO-GO composite were higher than those of PP and other composites due to the better interfacial interaction between filler and matrix.

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