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Effects of Carbon-Based Fillers on the Properties
of Polypropylene Nanocomposites

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仁荷大學校 大學院
高分子工學科

表 혜 리
Effects of Carbon-Based Fillers on the Properties of Polypropylene Nanocomposites

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指導教授 陳 仁 柱
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仁荷大學校 大學院
高分子工學科
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副審 __________________

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Abstract

In this study, in order to enhance the dispersion of carbon materials in polymer, relatively simple modification and functionalization of carbon materials have been studied. The carbon materials of interest were nanometer-scale complex carbon fillers comprising of graphene oxide (GO), carbon nanotube (CNT) or carbon black (CB). And engineering polymers, Polypropylene (PP), are of the most widely used commodity polymers, was used as the main matrix. PP nanocomposites were prepared via solution process and the synergistic effect of complex fillers on the properties of PP was characterized.

GO was modified with alkylation to alkylated-GO (a-GO) to improve miscibility in polymers. And, CNT also was modified by acidification and alkylation to alkylated-CNT (a-CNT) to enhance the miscibility. Two types of complex fillers were prepared as a-CNT/a-GO and CB/a-GO, and incorporated PP nanocomposites.

PP nanocomposites containing carbon complex fillers showed increased thermal, electrical, and mechanical properties. The thermal degradation temperature and re-crystallization temperature of the PP nanocomposites were increased. In addition, Young’s modulus of the
PP nanocomposites was increased. Specifically, PP/CB/a-GO nanocomposites exhibited electrical percolation threshold and sheet resistance was decreased to $2.3 \times 10^7 \, \Omega/cm^2$. Field-emission transmission electron microscopy (FE-TEM) and scanning electron microscopy (FE-SEM) were used to investigate the degree of the dispersion of the nanofillers in the PP matrix, and to analyze the morphology of the PP nanocomposites. Based on the experiment data, carbon-based nanocomposites are expected to be applied as antistatic, electrostatic dissipation (ESD), or electromagnetic interference (EMI) polymers, sensors for biological molecules, anisotropic conductive film (ACF), and corrosion-resistant coatings.

*Keywords*: Carbon nanotube (CNT), Carbon black (CB), Graphene oxide (GO), Polypropylene (PP), Polymer nanocomposites,
국 문 요 약

본 연구에서는 탄소소재의 개질이나 합성을 통해 분산도를 높이기 위한 연구와 간단한 공정으로 탄소소재의 특성을 충분히 발현할 수 있는 데 주력 하였다. 사용한 탄소소재는 산화 그래핀 (graphene oxide, GO)이고, 이 물질 외에도 각각 탄소나노튜브 (carbon nanotube, CNT)와 카본블랙 (carbon black, CB)을 사용하여 복합충전제를 만들었다. 메트릭스가 되는 고분자로는 실생활에 널리 응용되는 범용고분자 폴리프로필렌 (polypropylene, PP)을 사용하였다. PP 나노복합재료는 용액혼합으로 제조하고, 복합충전제를 함유한 PP 나노복합재료의 특성을 분석하였다.

GO 는 Alkylation 으로 CNT 는 산처리 과정과 Alkylation 을 통하여 부족한 상용성을 각각 높여주고자 하였다. Alkylated graphene oxide (a-GO)와 alkylated CNT (a-CNT) 그리고 CB를 이용하여 a-CNT/a-GO, CB/a-GO 로 2 가지 종류의 복합충전제를 제조하였다.

탄소소재 복합충전체를 사용하여 PP 나노복합재료를 제조하였을 때 열적 성질을 향상시키는 결과를 얻었고, 절연특성의 고분자에 전도성이 나타났으며, 기계적 물성 측면으로 보았을 때는 좀 더 brittle 한 성질을 나타내었다. 열분해 온도와 재결정 온도는 다소
상승하였으며, Young's modulus의 수치 또한 증가된 것을 확인할 수 있었다. 특히, electrical percolation이 PP/CB(5wt%)/a-GO(0.2wt%) 나노복합재료에서 일어나며, sheet resistance가 2.3 \times 10^7 \ \Omega/ cm^2로 감소하였다.

연구결과를 바탕으로 고분자 내에서 탄소소재가 어떤 조건에서 최적의 물성을 발휘하는지 연구하였고, 응용분야에 대해서도 고찰하였다. 정전분산(Electrostatic Dissipation, ESD) 고분자 또는, 전자기차폐(Electromagnetic Interference, EMI) 수준의 고분자 복합체까지 응용할 수 있는 가능성을 얻었고, 바이오센서나 이방성 필름, 부식 방지용 대친체 등에 쓰일 수 있는 나노복합재료 등 다양한 분야에서 응용될 수 있을 것으로 기대된다.

키워드: 탄소나노튜브, 카본블랙, 산화 그래핀, 폴리프로필렌, 고분자복합재료, 정전분산 고분자
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1. INTRODUCTION

Carbon nanotubes (CNTs) were discovered in 1991 and due to their significant physical and mechanical features their applications have been developed [1]. High flexibility, fully reversible blending, semiconducting character, and high electrical conductivity are examples of their remarkable mechanical and physical properties [2-6]. On the basis of the number of walls, carbon nanotubes (SWCNT) [7]. It has been proved that tensile strength of a layer of MWCNT is 100 times higher than that of steel resulting from their graphitic and tubular structure [8, 9]. The diameter of single-walled carbon nanotube (SWNT) is 1.4 nm commonly, and that of multi-walled carbon nanotube (MWNT) is 10–60 nm with a layer distance between walls of 3.4 nm. CNTs have very high aspect ratios and their Young’s modulus may exceed 1.0 TPa [10, 11] and the tensile strength is in the range of 10-50 GPa [12, 13] and thermal conductivity twice as high as that of diamond and electric current-carrying ability 1000 times that of copper wires [14]. Basically, they are fullerene-related structures composed of graphite cylinders, which are closed at either and with caps consisting of pentagonal rings [15]. The chemical stability of CNTs is high
because of their covalent bonds between the carbon atoms [16]. It has been confirmed that chemical activity of CNTs is lower than that of carbon fibers and graphite. Through CNTs, advanced composites can be achieved, and several pieces of research have been conducted to study the feature of diverse matrix materials, polymers, ceramics, and metals [17-19]. Despite of these advantages, they are easy to be aggregated themselves in organic solvents or in the polymer matrices. To improve degree of the dispersion of the CNTs in the polymer matrix, various methods have been developed such as covalent functionalization [20], wrapping of CNTs [21], in-situ polymerization [22], and using organic solvents [23] or surfactants [24]. CNTs can be used in various applications due to their excellent electrical, thermal and mechanical properties such as in field emitting diodes (FEDs) [25], emitting field effect transistors [26], scanning microscopy [27], lithium batteries [28], hydrogen storage [29], single electron transistors [30], gas sensors [31] and composite materials, etc.

Carbon black (CB) is the most widely used nanometer-scale reinforcing filler, because of its abundant source, low density, predominant electrical property, and low cost. They have spherical shape with diameters between a few tens and a few hundreds of
nanometers that are fused together into aggregates. There are many kinds of researches related to CB-polymer nanocomposites, to improve performances of polymer or to achieve new properties of the nanocomposites [32-34]. In case of using the CB as a nanometer-scale filler, properties of polyolefin were noticeably improved. However, few of researches involved with polyolefin nanocomposites were investigated to effects of nanometer-scale complex fillers on the properties of the nanocomposites.

The unique nanostructure and properties have potential applications in polymer composites. Graphene oxide (GO) is easily available through the controlled chemical oxidation of graphite. GO contains graphitic domains and oxidation regions, in which the epoxide and hydroxyl groups are located on the basal planes, and carbonyl and carboxyl groups are found at the edges [35, 36]. The presence of these functional groups makes graphene oxide sheets strongly hydrophilic, which allows GO to readily swell and disperse in water. In addition, the oxygen functionality allows for enhanced interactions with polar polymer matrices. The ability of GOs to disperse well and interact intimately with polar polymers, such as PMMA, creates a percolated domain of an ‘interphase’ polymer that dramatically affects the
thermal and mechanical properties at loadings as low as 0.05 wt% [37]. However, GO require surface modification to disperse in non-polar polymers, such as polyethylene, polypropylene and polystyrene. Fortunately, the surface modification of GO can be induced easily with functional groups, such as epoxide, hydroxyl and carboxyl groups [38, 39].

In this study, we investigated effects of a-CNT/a-GO complex fillers on the properties of PP nanocomposites. The surface of the CNT was modified using a linear alkyl chain in order to create a homogeneous CNT dispersion in the PP matrix. Properties of all samples containing carbon filler were generally enhanced as compared to pristine PP. However, their own progress depends on a type of carbon filler incorporated in PP matrix. Therefore, it is important to choice a filler type for enhancing a property of PP. In some cases, it would be better to use a complex filler system for polymer nanocomposites than to use a single filler system.

Second, the reinforcing effects of CB/a-GO complex carbon filler on PP nanocomposites [40]. Small amount of a-GO content increased the thermal and mechanical properties of PP nanocomposites. And, the reinforcing effects were more effective than them of alkylated carbon
nanotubes. Small amount of a-GO filler exhibited the synergistic effects in electrical percolation threshold, thermal degradation temperature, re-crystallization temperature and Young’s modulus of the PP/CB nanocomposites.
2. EXPERIMENTAL

2.1. Materials

Two kinds of Multiwalled carbon nanotube (MWNT) were used in these experiments. The one is purchased from Hanwha nanotech, Korea, and other is from NCT, Japan. The MWNTs were synthesized by catalytic chemical vapor deposition (CVD) process, and the diameter was 10-15 nm with a purity of higher than 95wt%. The Carbon black (CB) were used Vulcan XC-72B, supplied by Cabot Cooperation. Polypropylene (PP) was obtained from Aldrich, USA. The PP had number average molecular weight, $M_n$ of 50,000 and mass average molecular weight, $M_w$ of 190,000. Graphene oxide (GO) was prepared from natural graphite (Sigma-Aldrich) using the Hummers method. Figure 1 shows the TEM images of CB and CNT.
2.2. Preparation of alkylated carbon nanotube and graphene oxide

CNT was treated with acid using the following procedure, which was reported in an earlier study [41]. CNT was treated in an acid mixture (sulfuric acid/nitric acid = 3:1 (v/v)) at 60 °C in order to remove any impurities within CNT and the introduction of carboxylic and hydroxyl functional groups onto the surface of CNT. Then, the alkylated CNT was prepared by using a linear alkyl chain [42]. The alkylated MWCNT exhibited a good dispersity and stability in organic solvents. The nomenclatures for the alkylated CNT are a-CNT. Figure 2 shows the alkylation reaction.

GO was prepared from natural graphite using the Hummers method. Aqueous GO suspensions were frozen in liquid nitrogen and then freeze-dried using a lyophilizer (LP3, Jouan, France) at -50 °C and 0.045 mbar for 72h. After lyophilization, low density, loosely packed GO powders were obtained. 100mg of GO powders were exfoliated under ultrasonication in 180 mL of deionized water containing 72 mg of NaOH. Subsequently, 100 mg of a phase transfer agent, tetra-n-octylammonium bromide (TOAB, Fluka), and 5.0 mL of dodecyl iodide (Aldrich, 98%) were added to the black homogeneous sodium salt mixture. After stirring for six hours at 80 °C, a black precipitate
was obtained. The precipitate was filtered with excess chloroform, washed several times with a 15% NaCl aqueous solution and dried under vac-uum.

2.3. Preparation of carbon nanotube/alkylated graphene oxide complex filler

CNT was treated with acid using the following procedure, which was reported in an earlier study [41]. The alkylated MWCNT exhibited a good dispersity and stability in organic solvents. The nomenclatures for the alkylated CNT are a-CNT. Four different kinds of PP/carbon filler nanocomposites containing 0.5 wt% of a-CNT and 0.0, 0.1, 0.5, 1.0 wt% of a-GO were prepared to examine the reinforcing effects according to different filler contents. Their nomenclatures are PP/a-CNT0.5, PP/a-CNT0.5/a-GO0.1, PP/ a-CNT0.5/a-GO0.5 and PP/ a-CNT0.5/a-GO1.0.

Specifically, PP/a-CNT/a-GO nanocomposites were prepared as follow. The PP was added into a 3-neck round flask containing xylene. The flask under protection of nitrogen atmosphere was put into an oil bath set at 130 °C. Before adding a-CNT and a-GO in the flask, they were dispersed homogeneously in xylene. An ultrasound was applied to the
xylene suspension using an ultrasonic generator (Kodo technical research Co., NXCS-600, KOREA) which has a nominal frequency of 28 kHz, with power of 600 W for 3 hour at room temperature. After the PP was dissolved in xylene at 130 °C, the xylene suspension containing a-CNT and a-GO was dropped into the PP solution. The mixture was reprecipitated by excess methanol and then gray solid state of PP/a-CNT/a-GO nanocomposite was obtained. After they were washed several times by methanol, and then dried in a vacuum oven for 72 hours at 70 °C.

The morphologies of CB and a-CNT were observed using transmission electron microscopy (TEM, CM200, Philips, USA). Fourier transform infrared (FT-IR, Bruker, VERTEX 80V, Germany) spectroscopy was used to investigate the existence of alkyl chains for CNT. The amount of alkyl chains, which was introduced in the CNT and thermal degradation behavior of the nanocomposites, were calculated using thermogravimetric analysis (TGA, Q50, TA instruments, USA) by scanning from 20 to 750 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The morphology of GO was observed by transmission electron microscopy (TEM, CM200, Philips, USA) and atomic force microscopy (AFM, a Digital Instrument Nanoscope IVA).
The structure of GO and a-GO was examined by Fourier transform infrared spectroscopy (FT-IR, VERTEX 80v, Bruker Optics, Germany). Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer 7 instrument, with dry nitrogen gas at a flow rate of 10 mL/min. The DSC was calibrated using indium as the standard, and the sample weight was maintained at 4.0 ± 0.1mg. The thermal history of the products was removed by scanning them from 25 to 250 °C at a heating rate of 10 °C/min, and the specimen was cooled to 25 °C using scan rates of 10 °C/min. The tensile properties were tested on an Instron 4665 ultimate tensile testing machine (UTM) at 20 °C and a humidity of 30%. The cross-head speed was set at 50 mm/min for both of the dumb-bell samples. At least 5 specimens of a given sample were collected and averaged for the tensile property tests.

2.4. Preparation of carbon black/alkylated graphene oxide complex filler

The alkylated graphene oxide was treated with acid using the following procedure, which was reported in an earlier study. Four different types of PP/CB nanocomposites, containing 1, 3, 5 and 10 wt% CB were prepared to examine the reinforcing effects according
to different filler contents. The nomenclature of these four nanocomposites was PP/CB1, PP/CB3, PP/CB5 and PP/CB10. Four different types of 0.1 wt% a-GO incorporated PP/CB nanocomposites and four different types of 0.2 wt% a-GO incorporated PP/CB nanocomposites were prepared to investigate the synergistic effects of a-GO on properties of PP nanocomposites. The nomenclature of the nanocomposites was PP/CB1/a-GO0.1, PP/CB3/a-GO0.1, PP/CB5/a-GO0.1, PP/CB10/a-GO0.1, PP/CB1/a-GO0.1, PP/CB3/a-GO0.2, PP/CB5/a-GO0.2 and PP/CB10/a-GO0.2. Specifically, the PP/CB nanocomposites and PP/CB/a-GO nanocomposites were prepared using the following method. First, PP was added to a 3-neck round flask containing xylene. The flask was placed in an oil bath at 130 °C under nitrogen atmosphere. The a-GO and CB were homogeneously dispersed in xylene before they were added to the flask. An ultrasound was applied to the xylene suspension using an ultrasonic generator (Kodo technical research Co., NXCS-600, KOREA), with a nominal frequency of 28 kHz and a power of 600 W for 1 hour at room temperature. After the PP was dissolved in xylene at 130 °C, the xylene suspension containing the a-GO and CB was dropped into the PP solution. The mixture was precipitated with excess methanol until gray
solid PP/CB/a-GO nanocomposites were obtained. After the nanocomposites were washed several times with methanol, they were dried in a vacuum oven for 72 hours at 80 °C.

The morphologies of PP and PP/CB/a-GO nanocomposites were observed using field emission scanning electron microscopy (FESEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV after the samples were pre-coated with a homogeneous Pt layer through ion sputtering (E-1030, Hitachi, Japan). The thermal degradation behavior of the nanocomposites was calculated using the thermogravimetric analysis (TGA, Q50, TA instruments, UK) from 20 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer 7 instrument, with dry nitrogen gas at a flow rate of 10 mL/min. The DSC was calibrated using indium as the standard, and the sample weight was maintained at 7.0 ± 0.1 mg. The thermal history of the products was removed by scanning them from 30 to 220 °C at a heating rate of 10 °C/min, and the specimen was cooled to 25 °C at a scan rate of 10 °C/min. The Young’s modulus and tensile properties were tested using an Instron 4665 universal materials testing machine (UTM) at 20 °C and a humidity of 30%. The cross-head speed was set at 50
mm/min for both of the dumb-bell samples. The dumb-bell specimens were made according to the ASTM D 638 standard for tensile testing. At least 5 samples of a given product were collected, and the tensile property tests results were averaged. The thermal conductivities of nanocomposites were tested on a Quick Thermal conductivity meter (QTM-500, Kyoto Electronics, Japan). The electrical conductivities of the nanocomposites were measured using a four-probe method with an electrical conductivity meter (Hiresta-UMCP-HT450, Mitsubishi Chemical, Japan).
3. RESULT AND DISCUSSION

The morphologies of CB and the pristine CNT are depicted in Figure 1. The CNT exhibited straight line morphology with a high aspect ratio and a long contour length, and CB had a spherical shape with a diameter of a few tens of nanometers. These CB particles were fused together into aggregates. The surface of CNT was functionalized with linear alkyl chains in order to enhance the dispersion-stability in organic solvents and the polymer matrix. Figure 3 shows the IR spectroscopy and TGA data of the pristine CNT and a-CNT. The functionality of a-CNT was monitored using IR spectroscopy, with the new peaks at 2981 and 2831 cm\(^{-1}\), corresponding to the C-H stretching of the alkyl chains [40]. The curves of the a-CNT exhibited an obvious weight loss at 200 °C, which was attributed to the loss of the alkyl chains. The weight loss between 200 and 430 °C was used to estimate the weight percentage (9 wt %) of the alkyl chains that were attached to the nanotubes. The samples without the a-CNT did not exhibit an electrical percolation threshold. However, the a-CNT incorporated PP/CB/a-CNT nanocomposites exhibited an electrical percolation threshold at relatively low CB contents (Figure 4). When 0.5 wt% and 1 wt% of the a-CNT were introduced into the PP/CB4 nanocomposite,
the sheet resistances of the PP/CB4/a-CNT0.5 and PP/CB4/a-CNT1 nanocomposites greatly increased over 8 orders of magnitude to values of $5.3 \times 10^7 \, \Omega/\text{cm}^2$ and $9.5 \times 10^6 \, \Omega/\text{cm}^2$, corresponding to electrostatic dissipative plastics. Figure 5 shows the alkylation reaction. Idododecane and TOAB were used as the precursor of the alkyl chain as a phase transfer agent, respectively. a-GO was prepared by a $S_n2$ reaction between the oxygen groups of GO and the reactants. Figure 6 shows the morphology of GO. GO exhibited a two-dimensional sheet morphology, which had a thickness < 2 nm and a mean lateral size of 850 nm. Surface functional groups of the GO were modified to a linear alkyl chain to disperse them homogeneously in an organic solvent and increase the interfacial adhesion between GO and the non-polar polymer matrix. The existence of alkyl groups incorporated on the surface was confirmed by FT-IR spectroscopy. Figure 7 presents the FT-IR spectra of (a) GO and (b) a-GO. Peaks corresponding to the presence of hydroxyl and carboxyl groups were observed at 3455 and 1727 cm$^{-1}$ in the GO, and the peaks at 1110 and 1086 cm$^{-1}$ were assigned to epoxide groups on the surface. These peaks indicate the oxidation of graphite by concentrated acid. The functional groups induced by oxidation allow GO to readily swell and disperse in water.
Consequently, GO is exfoliated by ultrasonication in water and the functional groups of GO provide reaction sites for the alkyl groups. In the case of a-GO, the bands at 2924 and 2852 cm$^{-1}$ was assigned to the CH$_2$ stretching vibration and the peak at 1457 cm$^{-1}$ was attributed to the CH$_3$ degeneration deformation. These peaks suggest the presence of alkyl groups on the surface of the GO. The degree of functionalization of GO and the a-GO were characterized by TGA (Figure 8). The TGA curve of GO exhibited an obvious weight loss between 120 and 230 °C, which was attributed to the loss of oxygen groups on the GO. In the case of the a-GO, weight losses of oxygen groups and alkyl chains were observed between 180 and 480 °C. The difference in weight loss between GO and a-GO indicates the contents of alkyl groups incorporated on the GO, which comprise approximately 22%. These alkyl groups make a-GO hydrophobic, which allows a-GO disperse readily in organic solvents [43]. Figure 9, 10, 11 shows optical images of a-CNT and CB, a-GO dispersions in different solvents, from non-polar solvents, such as toluene to polar solvents, such as water. Contrary to the case of CNT, a-CNT was dispersed homogeneously in xylene, toluene, DMF, chloroform, methanol but not in water. CB also was dispersed homogeneously in xylene, DMF, chloroform except for
toluene and water. GO was dispersed in both polar aprotic solvents with a high dipole moment and polar aprotic solvents [44-46]. Contrary to the case of GO, a-GO was dispersed homogeneously in non-polar solvents containing xylene but not in polar solvents, such as methanol and water. The ability of a-GO to disperse well and interact intimately with hydrophobic polymer matrices can easily create a percolated domain of a-GO, which affects dramatically the thermal and mechanical properties at low filler loadings. PP/a-GO composites were prepared using a-GO dispersions in xylene. The thermal degradation of PP and the PP/a-GO composites was examined by determining the mass loss during heating [43].

Table 1 shows the mechanical and thermal properties of PP nanocomposites containing a-CNT and a-CNT/a-GO complex carbon filler. From the results, we can check the improved thermal degradation temperature of PP nanocomposites. In case of PP nanocomposites containing a-CNT/a-GO complex carbon filler, it enhanced approximately 28 °C than PP nanocomposites containing only a-CNT carbon filler. In contrast, the tensile strength and Young’s modulus were increased by 20% and 37%, respectively. In figure 12, the mass loss curves of the samples are presented at a heating rate of 10 °C/min.
During thermal degradation, the samples exhibited a single step degradation behavior. The mass loss curve of pristine PP showed a 10 wt% weight loss at approximately 401.99 °C. After blending with a-CNT, thermal degradation temperature of PP/a-CNT nanocomposites was decreased remarkably. The mass loss curve of PP/a-CNT nanocomposites was occurred about 389.96 °C. However, the TGA curve of a-GO carbon filler incorporated PP nanocomposites exhibited weight loss between 400.68 to 417.83 °C. This result shows that a-GO was more effective enhancing thermal property of PP nanocomposites than a-CNT. Also, this enhancement was induced by the high thermal conductivity of percolated a-CNT. And, with increasing a-GO content, thermal degradation temperature of PP/a-CNT/a-GO nanocomposites was gradually increased. Figure 13 shows the DSC thermograms for melting temperature of PP and PP nanocomposites containing a-CNT, a-CNT/a-GO carbon filler. The melting temperatures of the PP nanocomposites were increased gradually with increasing a-CNT, a-CNT/a-GO carbon filler contents. In the PP/a-CNT nanocomposites, the synergistic effects of a-CNT resulted in the increases of 9.91 °C. And, In the PP/a-CNT/a-GO nanocomposites, the synergistic effects of a-GO resulted in the increases of 1.71 °C (0.5 wt% a-GO) and 2.46 °C
(1.0 wt% a-GO), respectively. Figure 14 shows DSC thermograms of the 1st cooling for the pristine PP and PP nanocomposites. The recrystallization temperatures of the PP/a-CNT and PP/a-CNT/a-GO nanocomposites were higher than the pristine PP. And, a-GO is more effective on the recrystallization of PP nanocomposite than a-CNT. In the PP/a-CNT/a-GO nanocomposites, their recrystallization temperatures are higher than the pristine PP approximately 10 °C. In this case of PP/a-CNT/a-GO nanocomposites, a-GO played a major role in recrystallization of PP ahead of a-CNT. Based on the results, it seems to be no synergy effects. Figure 15 shows the mechanical properties of PP nanocomposites. Young’s modulus of the PP nanocomposites containing a-CNT/a-GO complex carbon filler was increased by 39% compared to pristine PP. In contrast, tensile strength of the PP nanocomposites complex carbon filler was decreased by 20%. The carbon filler has low mobility considering the structure of PP nanocomposites, which has a segment as the toughening part.

Table 2 represents the mechanical and thermal properties of CB reinforced pristine PP. The overall thermal properties of composites were enhanced by CB contents. The mechanical properties of composites were decreased with increasing CB contents except for
Young’s modulus. Young’s modulus of PP composites improved gradually with increasing CB contents. Table 3 shows the mechanical and thermal properties of all the samples. The overall thermal properties of composites were enhanced by CB and a-GO complex carbon filler. The DSC thermograms show the 1st cooling stage of the PP/CB nanocomposites. The re-crystallization temperatures of the nanocomposites were increased gradually with increasing CB and CB/a-GO contents. This suggests that CB and a-GO act as nucleation agents for crystallization of the PP matrix by providing a very large surface area for adsorption of the PP chain, resulting in easier nucleation. In the PP/CB10 nanocomposites, the synergistic effects of a-GO resulted in the increases of 1.5 °C (0.1 wt% a-GO) and 1.6 °C (0.2 wt% a-GO). From the standpoint of mechanical properties, a-GO is only advantageous for the young’s modulus of the composites. The tensile strength and strain to maximum decreased gradually with increasing a-GO content compared to those values of homo PP. However, Young’s modulus of PP/CB/a-GO composites increased considerably. 0.2 wt% a-GO increased the Young’s modulus of composite by more than 70%. These differences between CB and a-GO in the composites are interesting. According to the shapes of the nano-
sized fillers, their reinforcing effects on the composite were obviously different. This suggests that a dual or triple filler system might be more effective on composites than a single filler system. Figure 16 shows the morphologies of the pristine PP and PP/CB/a-GO nanocomposites. CB was homogeneously dispersed in PP matrix and the fractured surface was covered by a-GO with several micrometer lateral sizes. Only 0.2 wt% a-GO was overlapped each other. Figure 17 and figure 18 show the mass loss curves of the PP/CB, PP/CB/a-GO nanocomposites at a heating rate of 10 °C/min, respectively. During thermal degradation, the samples exhibited a single step degradation behavior. The mass loss curve of pristine PP showed a 10 wt% weight loss at nearly 402.0 °C. With increasing CB contents, thermal degradation temperatures of the PP/CB composites were increased 401.99 to 442.41 °C, respectively. The increase of thermal degradation temperatures continued in PP nanocomposites containing a-GO carbon filler. The synergistic effects of a-GO in thermal degradation temperatures brought about the increases of 5.5 °C (0.1 wt% a-GO) and 11.3 °C (0.2 wt% a-GO) on the PP/CB10 nanocomposites. The thermal degradation temperature of PP/CB10/a-GO0.2 was increased by 51.7 °C compared to pristine PP. Table 4 represented on the effective thermal conductivity of PP
nanocomposites containing CB, CB/a-GO carbon filler. The thermal conductivity of pristine PP shows approximately 0.16 W/m·K. However, thermal conductivity of PP nanocomposites was increased by the addition of carbon filler, gradually. It could be different from percolation at specific carbon filler content in electrical conductivity. Using based technique, we discovered that PP/CB10 nanocomposites manifest thermal conductivity of up to 0.28 W/m·K. And, PP/CB10/a-GO0.1 nanocomposites increased by 0.7 W/m·K than PP/CB10 nanocompsoties. As a result, increasing with CB/a-GO complex carbon filler contents induced better thermal conductivity through interaction each other. Figure 19 shows the mechanical properties of the CB and CB/a-GO reinforced PP nanocomposites. Young’s modulus of the CB reinforced PP nanocomposites was increased gradually with increasing CB contents, and addition of 0.1 wt% a-GO more sharply increased the Young’s modulus from 438.1 (PP/CB10) to 524.9 (PP/CB10/a-GO0.1) and 540.1 MPa (PP/CB10/a-GO0.2). The enhanced Young’s modulus is due to the mechanical interlocking at the wrinkled surface of a-GO. The overlapped network of a-GO restricts segmental mobility of the polymer chains near the a-GO surfaces. As a result, the synergistic effect of CB/a-GO is clearly exhibited in Young’s modulus of PP
nanocomposites. However, the tensile strength decreased with incorporation of a-GO. This result is similar to previous result [40]. The overlapped network induced electrical percolation threshold in low carbon black contents although electrical conductivity of a-GO was considerably damaged by strong oxidation process (Figure 20). CB incorporated PP matrix exhibited electrical percolation threshold in over 5 wt% CB contents. However, 0.1 wt% a-GO and 0.2 wt% a-GO incorporated PP/CB nanocomposites exhibited electrical percolation threshold in CB contents between 3 wt% and 5 wt%, and sheet resistance of the 5 wt CB incorporated composites were also decreased to $1.8 \times 10^{10} \, \Omega/\text{cm}^2$ (0.1 wt% a-GO) and $2.3 \times 10^7 \, \Omega/\text{cm}^2$ (0.2 wt% a-GO).
4. CONCLUSION

The reinforcing effects of a-CNT/a-GO complex carbon fillers on the properties of PP nanocomposites were investigated by various methods. The thermal properties of PP nanocomposites containing a-CNT carbon filler contents were decreased approximately 12.03 °C, %. However, tensile strength and Young’s modulus of PP/a-CNT nanocomposites were increased by 12% and 35%, respectively. When a-GO carbon filler was added in PP/a-CNT nanocomposites, thermal and mechanical properties of PP nanocomposites were enhanced. The thermal stabilities of PP nanocomposites containing complex carbon filler were higher than PP nanocomposites containing single carbon filler. And, PP/a-CNT/a-GO nanocomposites exhibited better mechanical properties than PP/a-CNT nanocomposites approximately 39%. In addition, electrical percolation thresholds were observed at a-CNT filler contents. Their sheet resistance was enough to show the anti-static function.

The PP/CB/a-GO nanocomposites were successfully prepared and synergistic effects of a-GO on the properties of PP/CB nanocomposites were investigated. PP/CB nanocomposites containing 0.1 wt% and 0.2 wt% a-GO exhibited electrical percolation threshold in lower CB
contents than that of PP/CB nanocomposites. Sheet resistances of the PP/CB5 nanocomposites were also decreased to $1.8 \times 10^{10} \Omega/\text{cm}^2$ (0.1 wt% a-GO) and $2.3 \times 10^7 \Omega/\text{cm}^2$ (0.2 wt% a-GO). The thermal degradation temperature of the PP/CB10 nanocomposites were increased by 5.5 °C (0.1 wt% a-GO) and 11.3 °C (0.2 wt% a-GO), respectively. The re-crystallization temperatures of the PP/CB10 nanocomposites were also increased by 1.5 °C (0.1 wt% a-GO) and 1.6 °C (0.2 wt% a-GO), respectively. Addition of 0.1 wt% a-GO to the PP/CB nanocomposites sharply increased the Young’s modulus from 438.1 (PP/CB10) to 524.9 (PP/CB10/a-GO0.1) and 540.1 MPa (PP/CB10/a-GO0.2), respectively. However, the tensile strength decreased with the incorporation of a-GO.
5. REFERENCES


[44] K. Chrissafis, K. M. Paraskevopoulos, S. Y. Stavrev, A. Docoslis, 


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<tr>
<th>Composition</th>
<th>Strain to max (%)</th>
<th>Tensile strength (MPa)</th>
<th>$E^*$ (GPa)</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_d^*$ (°C)</th>
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Table 1 Mechanical and Thermal Properties of PP Nanocomposites Containing a-CNT and a-CNT/a-GO Complex Carbon Filler
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<th>E* (GPa)</th>
<th>Tc (°C)</th>
<th>Td* (°C)</th>
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Table 3 Mechanical and Thermal Properties of PP Nanocomposites Containing CB/a-GO0.1 and CB/a-GO0.2 Complex Carbon Filler

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<th>E* (GPa)</th>
<th>Tc (°C)</th>
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Table 4 Thermal Conductivities of PP Nanocomposites Containing CB and CB/a-GO01 Complex Carbon Filler

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<tr>
<td>PP/CB1</td>
<td>0.26</td>
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<tr>
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<td>0.27</td>
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<td>PP/CB5</td>
<td>0.28</td>
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<td>PP/CB10</td>
<td>0.28</td>
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<td>PP/CB1/GO0.1</td>
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Figure 1. TEM images of (a) CB and (b) pristine CNT.
Figure 2. Schematic of alkylation reaction of CNT.
Figure 3. (a) IR spectroscopy and (b) TGA data of the pristine CNT and the a-CNT.
Figure 4. Electrical properties of PP nanocomposites containing CB/a-CNT complex carbon fillers.
Figure 5. Alkylation reaction of graphene oxide using a linear alkyl chain.
Figure 6. (a) AFM scan and (b) TEM image of graphene oxide.
Figure 7. (a) IR spectrum of graphene oxide and (b) alkylated graphene oxide.
Figure 8. TGA data of (a) graphene oxide and (b) alkylated graphene oxide.
**Figure 9.** Optical image of a-CNT dispersions in different solvents. (0.01 mg a-CNT/10 g solution)
Figure 10. Optical image of CB dispersions in different solvents. (0.01 mg CB/10 g solution)
Figure 11. Optical image of a-GO dispersions in different solvents.
(0.01 mg a-GO/10 g solution)
Figure 12. TGA data of PP nanocomposites containing a-CNT, a-CNT/a-GO carbon filler.
Figure 13. DSC thermograms of PP nanocomposites containing a-CNT and a-CNT/a-GO carbon filler.
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Figure 15. Mechanical properties of PP nanocomposites containing a-CNT and a-CNT/a-GO carbon filler: (a) Tensile strength, (b) Young’s modulus
Figure 16. FE-SEM images of the fracture surfaces of (a) pristine PP, (b)-(d) PP nanocomposites containing CB3/a-GO0.2 complex carbon filler in different magnification.
Figure 17. TGA data of CB incorporated PP nanocomposite.
Figure 18. TGA data of PP nanocomposites containing (a) CB/a-GO0.1 and (b) CB/a-GO0.2 complex carbon filler.
Figure 19. Mechanical properties of PP nanocomposites containing CB and CB/a-GO0.1, CB/a-GO0.2 carbon filler: (a) Tensile strength, (b) Young’s modulus.
Figure 20. Electrical properties of PP nanocomposites containing CB and CB/a-GO0.1, CB/a-GO0.2 complex carbon filler.