MODIFICATION OF NYLON 66/GRAPHENE NANOPLATELET COMPOSITES VIA ELECTRON BEAM IRRADIATION

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Abstract. As electrical and electronic devices are becoming an integral part of our life, problems related to electromagnetic interference (EMI) have increased. EMI shielding therefore becomes necessary as to protect vulnerable components within the electric and electronic devices from any interference. As shielding materials, polymer-based composites are highly promising to substitute metal-based materials due to their unique features such as light weight, flexible and excellent corrosion resistance. In this study, we aim to enhance electrical conductivity and shielding effectiveness of nylon 66 composites by improving the dispersion of graphene nanoplatelets (GNP) in the polymer matrix via silane functionalization and electron beam irradiation techniques. Silane treatment of GNP was found to significantly improve the electrical conductivity of the composites with a remarkable increase of 10 orders of magnitude from 10^{-13} to 10^{-3} Sm^{-1}. However, no improvement in the shielding effectiveness was observed. Subsequent exposure to electron beam irradiation at 50 kGy and 100 kGy dosage was found to effectively improve EMI shielding effectiveness over a frequency range of 0.5–18 GHz. Microscopic observation indicated changes in GNP layers of the irradiated samples. Multi-layered GNP was found in the non-irradiated, whereas more single layered GNP sheets were observed in the samples irradiated with 50 kGy and 100 kGy dosage of electron beam.

Keywords: Nylon 66, graphene nanoplatelets, electrical properties, shielding material, electron beam irradiation

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Introduction

Electromagnetic interference (EMI) refers to disturbance caused by transmission of electromagnetic energy from one electronic device to another that affects an electrical circuit by electromagnetic induction, electrostatic coupling or conduction [1,2]. This undesired EMI effect can cause malfunction in electronic systems, disruption on communication as well as affecting human health [3]. As electrical and electronic devices are becoming an integral part of our daily life, shielding for EMI is needed and is increasingly required by governments around the world. EMI shielding uses metals as well as magnetic materials to simultaneously suppress or lessen the electric and magnetic fields. The purpose is to isolate electromagnetic waves and hence, effectively contain the radiation of electromagnetic waves from one area to another [4,5].

Previously, metal and alloy shrouds had been used to avoid EMI induced functional disruption in electrical and electronic devices. However, they were unable to meet the requirements of lightweight, flexible and miniaturized instrument due to their disadvantages such as high density, high cost and low efficiency [6,7]. With the increase in demand for low cost and lighter electronic devices, studies on plastics as EMI shielding materials has gained attention. To enable plastics to be used as shielding materials, their electrical conductivity needs to be enhanced. This can be achieved through two general approaches, i.e., coating with conductive metal, and blending with conductive fibers or particles [8,9]. However, coating has disadvantages such as delamination added with requirement for additional surface preparation and special equipment, which eventually increases the cost of final products [10].

Blending technique is an effective method to fabricate conducting polymer composites by incorporating high aspect ratio conductive nanofillers into polymer matrix. Unfortunately, some conductive filler such as metal powders and carbon black are not suitable as EMI shielding material due to high filler loading requirement for such application, as much as 40 to 60 wt% [11]. On the other hand, graphene nanoplatelet (GNP) is a two-dimensional nanofiller and has been found to be effective for the enhancement of electrical conductivity in polymer composite at low filler content [12,13]. Improvement in thermal stability even at minimal GNP addition has also been reported previously [14]. However, GNP tends to form agglomerates and demonstrates inhomogeneous dispersion in polymer matrix due to large surface area and strong Van der Waals force. One of the approaches to achieve well dispersion of GNP in polymer matrix is by silane functionalization [15].

A more stable conductive behaviour in conductive polymer composites can be achieved either by chemical crosslinking or radiation crosslinking. While chemical crosslinking is limited in applications because it always takes place above the melting temperature, radiation crosslinking is not dependent on temperature, and can be carried out at room temperature. Electron beam (EB) irradiation was found to improve electrical reproducibility of conducting polymer composites and mechanical properties of polymers such as nylon 6 [16,17]. Thus, in this study, we investigate the effects of vinyltrimethoxysilane (VTMS) functionalization of GNP, and EB irradiation on the electrical conductivity and shielding effectiveness of nylon 66/GNP nanocomposites.

Materials and Methods

Materials

Nylon 66 (Dupont, Zytel® 101F NC010) with density of melt of 970 kgm^{-3} was used as the polymer matrix, without any purification. Graphene nanoplatelets (XG Sciences US) with the surface area of 750 m^2g^{-1} and bulk density of 0.4 gcm^{-3} were used as nanofiller. A purified silane coupling agent, vinyltrimethoxysilane (VTMS) was used for functionalizing the GNP and obtained from Degusss-Huls AG, Germany. It is a bifunctional organosilane possessing a reactive vinyl group and a hydrolyzable inorganic trimethoxysilane group. The dual nature of its reactivity allows it to bind chemically to both inorganic materials and organic polymers [18].

Treatment of GNP

Exfoliation of GNP was performed by dispersing it in ethanol and applying sonication at 40 Hz for 60 min using an ultrasonic instrument (Fisher Scientific Sonic Dismembrator) before mixing with nylon 66. Subsequently, functionalization of GNP was carried out by mixing 30 grams of GNP with 300 mL ethanol-water mixture (70:30 ratio) under sonication for 60 minutes before adding VTMS to the mixture and left for another 60 minutes. The product, VTMS functionalized GNP, abbreviated as $GNPf_n$, was then washed several times with methanol and distilled water, sequentially and dried in a vacuum oven at 60 °C for 12 hrs. The subscript n refers to weight percentage of VTMS, which was varied at 0, 15, 20, 25 wt% per GNP.

Composite Fabrication

Initially, a dry mixing of nylon 66 and GNP was performed using a high-speed mixer at room temperature for five minutes, prior to melt compounding. The amount of GNP was kept constant at 0.3 wt%. Next, the compound of nylon 66 and GNP were extruded using co-rotating twin screw extruder (Sino PSM 30). Subsequently, the extrudates were cut into pelletized form, before injected using injection molding machine (Ray Ran). The fabricated composite samples were then exposed to EB produced with three MeV acceleration voltage and 10 mA beam current. The irradiation doses used at each pass were 50 kGy, 100 kGy, 150 kGy and 200 kGy.

Testing and Analysis

XRD analysis was performed using an X-ray diffractometer (PANalytical, X'Pert Pro MRD) with nickel filtered copper Kα radiation at $\lambda = 0.154$ nm. The electrical resistivity of nylon 66/GNP was determined from the resistance values obtained using LCR meter (Agilent, E4980A). Electrical conductivity, σ is then taken as the reciprocal of resistivity. Shielding effectiveness (dB) were measured using vector network analyzer (VNA) instrument to assess the EMI shielding property of nylon 66/GNP nanocomposite samples. Toroidal shaped samples were used (outer diameter = 6.95 mm, inner diameter = 3.05 mm) for this purpose. Transmission electron microscopy (TEM) images were obtained using a JEM-1230 microscope at an acceleration voltage of 120 kV. Samples were cooled below the glass transition of the polymer during cutting, and a speed of 1 mm/s was used to cut 50–100 nm thick sections.

Results and Discussion

XRD Analysis

XRD patterns of GNP particles, neat nylon 66, VTMS-functionalized and EB irradiated nylon 66/GNP nanocomposites are shown in Figure 1. The representative diffraction peaks of GNP are evident at 26.4°, 43.60°and 50.90°. These peaks can be assigned to the (002) (101) and (004) planes of graphitic carbon, respectively [19]. Meanwhile, the XRD pattern for nylon 66/GNP nanocomposite also demonstrates exceptionally wide diffraction (Peak A and Peak B) from 21° to 24° which corresponds to (200) and (002, 220) reflections in α-form crystals of polyamide [20].

In the nylon 66 composite added with 0.3 wt% GNP, the diffraction peaks associated with GNP observed around 26.4°, 43.6°and 50.9° totally disappeared. The XRD results suggest that in the composite, GNP was exfoliated into individual graphene sheets and that the regular and periodic structure of graphene had disappeared, forming loose stacking and disordered GNP in nylon 66/GNP composites [21,22]. The same XRD patterns were observed for the EB irradiated as well as VTMS functionalized nylon 66/GNP composites, indicating no agglomeration and good dispersion of GNP were maintained in these samples.

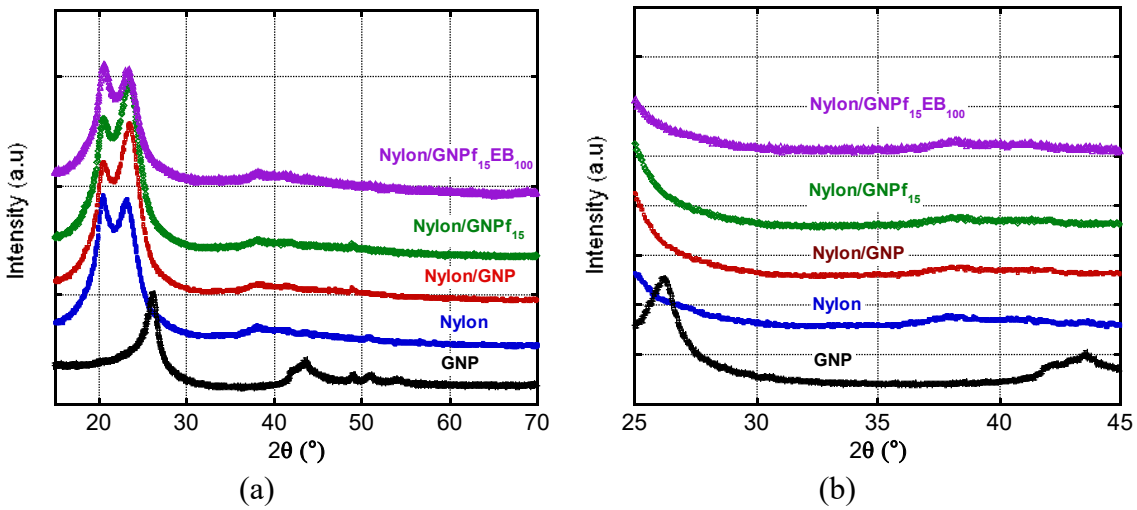


Figure 1: (a) XRD spectra of GNP, nylon 66 and various nylon 66/GNP nanocomposites and (b) enlarged version of the spectra

Electrical Conductivity

Changes in electrical conductivity values in VTMS-functionalized nylon 66/GNP composites and EB irradiated nylon 66/GNP composites as compared to the non-functionalized composite and neat nylon 66 are presented in Figure 2(a) and (b), respectively. Addition of a minimal amount (0.3 wt%) of GNP (non-functionalized), significantly increases the electrical conductivity of nylon 66 from 10^{-13} to 10^{-6} Sm^{-1} as shown by the second bar of Figure 2(a). The improvement in conductivity becomes more evident when VTMS functionalized GNP is applied as nanofiller. The electrical conductivity shows a significant increase by ten orders of magnitude (from 10^{-13} to 10^{-3}) for nylon 66/GNPf15. The conductivity value is comparable to that of polyvinylidene fluoride (PVDF) added with 0.5

wt% functionalized graphene, which is 10^{-4} Sm^{-1} [23]. However, the electrical conductivity does not increase with a further increase of VTMS concentration to 20 and 25 wt%. This is perhaps due to attainment of saturation limit of functionalization in the system [24].

The dispersion level of GNP is important in determining the final electrical properties of the nanocomposites. The increase in conductivity as observed in nylon 66/GNPf$_{15}$ indicates good dispersion level of GNP in nylon 66 polymer matrix. This produces a formation of an effective network for electron path transmittance, which is responsible for high electrical conductivity. On the other hand, exposure to EB irradiation does not seem to further increase the electrical conductivity of nylon 66/GNP nanocomposites as shown in Figure 2(b). It should be noted that 0 EB dosage in the right figure refers to the non-irradiated nylon 66/GNPf$_{15}$ nanocomposite of the left figure. There is no significant change in conductivity observed in the EB irradiated samples.

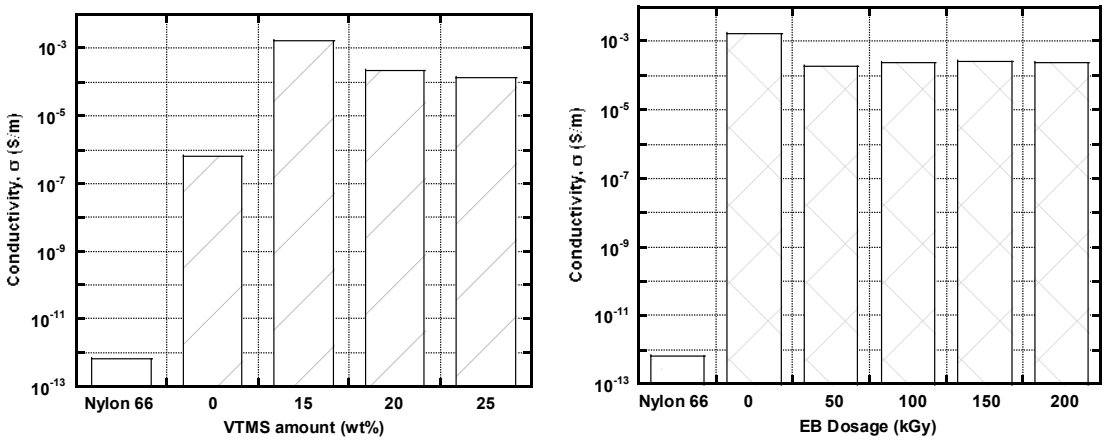


Figure 2: Electrical conductivity of nylon 66 and nylon 66/GNP composites modified with (a) chemical treatment using various VTMS amount and (b) exposure to various dosages of EB irradiation

EMI Shielding Effectiveness

In general, efficiency of any shielding material is expressed in decibels (dB). The higher the decibel level of EMI shielding effectiveness (SE), the less energy is transmitted through shielding material. EMI shielding effectiveness of composites can be analyzed in the X-band region (8 GHz-12 GHz) and in the broad band (1 GHz to 8 GHz) [23]. The SE values of nylon 66/GNP nanocomposites are shown in Figure 3. As expected, the shielding efficiency is 0 dB for neat nylon 66 in the frequency domain of 1–18 GHz. Similarly, by adding 0.3 wt% GNP, the attenuation is almost 0 dB, clearly indicating that interconnected conductive networks of polymer filler interfaces between the GNPs and nylon 66 matrix are not established. Figure 4(a) shows some agglomeration or partially exfoliated graphene nanoplatelets in the non-irradiated nylon 66/GNP sample, probably as a result of filler–filler interaction and strong shearing GNP were subjected to during melt extrusion process [25].

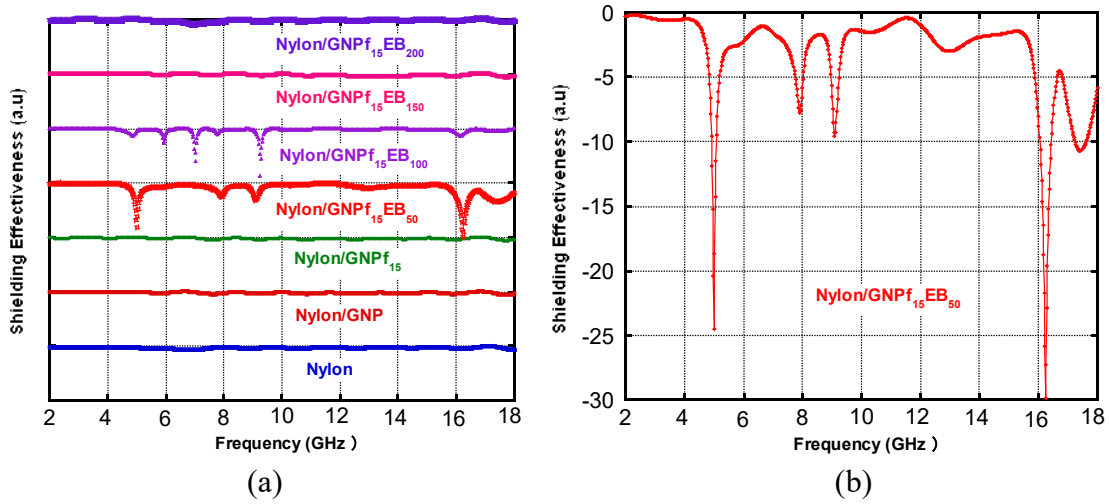
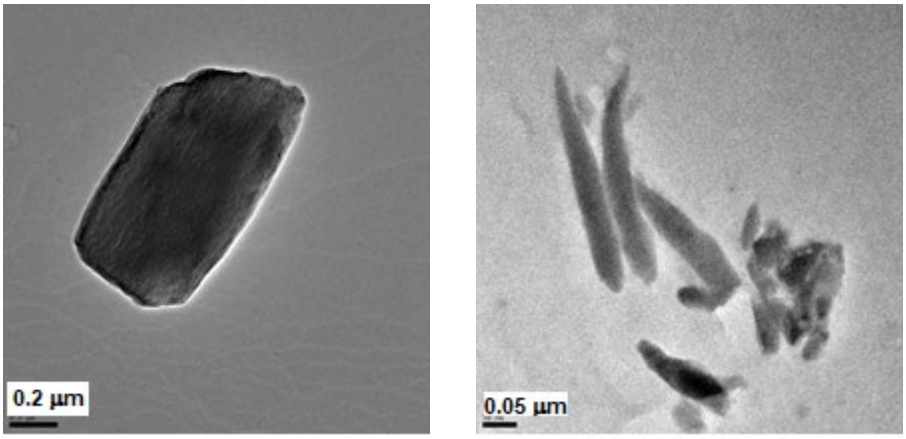


Figure 3: Shielding effectiveness for (a) nylon 66 and various nylon 66/GNP nanocomposites and (b) nylon 66/GNP irradiated with 50 kGy of EB irradiation

Theoretically, shielding effectiveness and electrical conductivity of composites are directly related. For nylon/GNPf$_{15}$, however, no significant value of SE is observed despite a huge improvement in its electrical conductivity. This suggests that the shielding process is largely controlled by resistance. As the conductivity of the composite increases, so does its electromagnetic impedance [26]. The impedance mismatch to the air decreases in size. As a result, the electromagnetic wave's resistance loss is magnified, thus resulted in the decrease of SE.

The effects of EB irradiation dose on the EMI shielding effectiveness of nylon 66/GNP nanocomposites can be observed in Figure 3. Electron beam irradiation at 50 kGy and 100 kGy of radiation dosages is found to effectively improve SE of nylon 66/GNP nanocomposite, probably due to the presence of more single layered GNP sheets as shown in Figure 4(b). From Figure 3, up to 30.3 and 26.7 dB of SE is obtained for nylon 66/GNPf$_{15}$EB$_{50}$ and nylon/GNPf$_{15}$EB$_{100}$, respectively. The results indicate that they may be used as lightweight, effective EMI shielding materials for commercial applications over a frequency range of 0.5–18 GHz. Irradiation promotes formation and recombination of free radicals in the polymer-filler interface, which makes the easy movement of mobile charge career that eventually lead to formation of more interconnected conductive networks [27]. The increases of SE at 50 kGy and 100 kGy EB dose may also be due to the formation of a greater number of interconnected conductive networks through the free radical combination in these nanocomposites [28].



(a) (b)

Figure 4: TEM images of (a) unirradiated and (b) irradiated nylon 66/GNP nanocomposites

Conclusions

In this study, the potential of using GNP functionalization and EB irradiation for producing nylon 66/GNP nanocomposites with improved electrical and SE performance has been explored. It is found that VTMS treatment of GNP greatly improves the electrical conductivity of the composites with a significant increase of 10 orders of magnitude from 10^{-13} to 10^{-3} Sm^{-1}. However, VTMS functionalization of GNP seems to have no impact to the improvement of shielding effectiveness in nylon 66/GNP composites. Subsequent exposure to electron beam irradiation at 50 kGy and 100 kGy dosage was found to effectively improve EMI shielding effectiveness over a frequency range of 0.5–18 GHz. This probably relates with the changes in GNP arrangement upon EB irradiation. Microscopic observation indicated changes in GNP layers of the irradiated samples. While multi-layered GNP was found in the non-irradiated, more single layered GNP sheets were observed in the samples irradiated with 50 kGy and 100 kGy dosage of electron beam.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors declare that no known competing financial interests or personal relationships that could have appeared to influence the work reported in the paper.

Compliance with Ethical Standards

The work is compliant with ethical standards

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