ENHANCING THE ELECTRICAL CONDUCTIVITY OF NYLON 66 VIA THE INCORPORATION OF SILANE-FUNCTIONALIZED GRAPHENE NANOPLATELETS

M.I. Shueb[1,2], M.E.A. Manaf[1*], J.A. Razak[1], N. Mohamad[1], K.N.K. Umar[2] and V.A. Doan[3]

[1]Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya,
76100 Durian Tunggal, Melaka, Malaysia.

[2]Radiation Processing Technology Division,
Malaysian Nuclear Agency, Bangi,
43000 Kajang, Selangor, Malaysia.

[3]Faculty of Materials Science, Phenikaa University,
Yen Nghia, Ha Dong, Hanoi, Vietnam.

*Corresponding Author's Email: edee@utem.edu.my

ABSTRACT: Polymer composites have been studied recently as electromagnetic interference (EMI) shielding materials as the need for versatile, low-cost and lightweight materials grows. EMI shielding material is heavily affected by electrical conductivity. One problem associated with utilizing polymers as shielding materials is their inherent non-conductive nature. This study aims to investigate the effects of silane treatment using vinyltrimethoxysilane (VTMS) of graphene nanoplatelets (GNP) on the electrical conductivity of nylon 66 composites reinforced with GNP. The pristine GNP and functionalized GNP were incorporated into the nylon 66 via melt compounding method using twin screw extruder and injection moulding. The functionalization of GNP is found to be significantly improving electrical conductivity of nylon 66 by ten orders of magnitude, from 10^{-13} to 10^{-3} S/m. The improvement is attributed to the enhanced dispersion of modified GNP and stronger interfacial interactions between the modified GNP and polymer matrix, which is associated with the covalent linkage of VTMS-GNP with nylon 66. In a nutshell, the VTMS treatment provides an appropriate modification of GNP particles to effectively improve the multifunctional properties of nylon 66/GNP nanocomposites.

1.0   INTRODUCTION

Electromagnetic interference (EMI) refers to the occurrence of disruptive electromagnetic energy that can be transmitted from one electronic device to another via both radiated and conducted paths. It can result in disturbances or malfunctions in the affected devices [1]. EMI occurs when vulnerable electronic devices receive electromagnetic waves emitted by other electronic devices. This interference has the potential to cause malfunctions or disruptions in electronic systems [2].

In the past, metal and alloy shrouds were commonly employed to protect electric and electronic devices from functional disruptions caused by EMI. However, with the growing demand for lightweight and cost-effective electronic devices, there has been a shift in focus towards exploring plastics as potential EMI shielding materials. This increased attention on plastics is driven by the need to develop alternatives that offer both effective EMI shielding capabilities and the desired characteristics of being lightweight and cost-efficient. Electrical conductivity plays a crucial role in the effectiveness of an EMI shielding material.

Two general approaches used to increase conductivity in polymers are by coating with conductive metal, and blending with conductive fibers or particles [3, 4]. On the other hand, coatings for EMI shielding also have certain drawbacks. These include the potential for delamination, the need for additional surface preparation, and the requirement for specialized equipment. These disadvantages ultimately contribute to increased costs associated with the final product [5].

The blending technique enables the creation of conducting polymer composites by incorporating conductive nanofillers with high aspect ratios. Numerous studies have been conducted on different types of conductive polymer composites, employing various conductive fillers such as carbon black, carbon nanotubes, stainless steel fiber, and more, with the aim to explore the potential of these materials for enhancing conductivity and other desired properties in the composites. [6-10]. Incorporating highly conductive metal particles like gold and silver into a polymer is a technique used to enhance electrical conductivity. However, certain conductive fillers such as metal powders and carbon

black may not be suitable as EMI shielding materials due to their high filler loading requirements for such applications. Typically, achieving effective EMI shielding requires a substantial amount of these fillers, ranging from 40 to 60 wt% [5].

GNPs have been discovered to be highly effective in enhancing the electrical conductivity of polymers even at low filler content [11]. The incorporation of GNPs into polymers allows for a significant improvement in electrical conductivity without the need for high concentrations of the filler material. This property makes GNPs an excellent choice for applications where maintaining low filler content is desired while still achieving enhanced electrical conductivity in the polymer matrix. Moreover, GNP shows a much better dispersibility and relatively cheaper than CNT. The two-dimensional nature of GNP makes them a more compelling choice as EMI shielding fillers compared to the one-dimensional CNT.

The unique structure of GNPs, consisting of thin, flat layers, provides a larger surface area for interaction and improved conductivity, which is advantageous for EMI shielding applications. This characteristic allows GNPs to offer enhanced performance in terms of EMI shielding effectiveness, making them a more appealing candidate than CNTs for such purposes [12, 13]. However, the large surface area and strong Van der Waals forces of GNPs often result in the formation of irreversible agglomerates and uneven dispersion within the polymer matrix. To address this challenge, one effective approach is to employ GNP functionalization, which may possibly enhance its dispersion in the polymer matrix.

Nylon 66 is a widely used type of engineering polymer that finds frequent application as housing material in portable electric and electronic devices. It is chosen for its exceptional thermo-mechanical properties, which make it well-suited for demanding environments. Nylon 66 exhibits excellent resistance to severe atmospheric conditions, ensuring durability and stability even in challenging environments. These qualities make Nylon 66 a reliable choice for housing materials, providing protection and longevity to portable electric and electronic devices [14].

However, it should be noted that nylon 66 is inherently an electrically non-conductive material. While nylon 66 excels in numerous mechanical and environmental aspects, its electrical non-conductivity should be taken into account when selecting it for applications such as EMI shield, where electrical conductivity is essential. In other words, if

nylon 66 is to be utilized as a housing material for electronic devices with EMI shielding capability, it becomes crucial to enhance its electrical conductivity. To the best of our knowledge, there is currently no available study or report that investigates the effects of VTMS functionalization of GNP on the properties of nylon 66. This specific research area appears to be unexplored, and no existing literature or publications have documented the findings regarding this subject matter, which make this study significant. The purpose of this study is to investigate the effects of covalently functionalized GNP on the electrical conductivity of nylon 66/GNP nanocomposites. The finding will contribute towards the development of a polymer-based composite that is specifically designed for use as an EMI shielding material.

2.0   METHODOLOGY

In this study, GNP was functionalized using VTMS, prior to mixing with nylon 66 at various weight percent per GNP, to evaluate the effects on electrical conductivity. The composite samples were compounded using melt mixing followed with injection molding to obtain the final samples. The composite samples were characterized using Melt Flow Index, X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM), while electrical conductivity was evaluated using resistance values obtained using LCR meter.

2.1   Materials

Nylon 66 was used as the polymer matrix, without any purification. It was purchased from Terra Techno Engineering with density of melt of 970 kg/m^3. GNP were purchased from Terra Techno Engineering with the surface area of 750 m^2/g and bulk density of 0.4 g/cm^3.

2.2   Sample Preparation

In order to facilitate the exfoliation of the GNPs and achieve better dispersion within nylon 66, a sonication process was employed. The GNPs were dispersed in ethanol and subjected to sonication at 40 Hz for 60 minutes using a Fisher Scientific ultrasonic instrument. The functionalization of GNPs was performed in a mixture of water and ethanol (40:60 ratio). A total of 30 grams of GNPs was added to 300 mL of the ethanol-water mixture, and the mixture was sonicated for 60 minutes to ensure proper dispersion. Subsequently, VTMS was added to the mixture and allowed to react for an additional 60 minutes. The resulting product, VTMS functionalized GNP (abbreviated as GNPf$_n$),

was subsequently subjected to multiple washes using methanol and distilled water in sequential order. The subscript n refers to weight percentage of VTMS, which was varied at 0, 15, 20, 25 wt% per GNP. A dry mixing method was performed prior to melt compounding of nylon 66 and GNP using a high-speed mixture at room temperature for 5 minutes. A constant amount of 0.3 wt% of GNP was applied in this study. Subsequently, the mixtures of nylon 66 with GNP were extruded by co-rotating twin screw extruder. The extrudates were further processed by cutting them into pelletized form, preparing them for injection using an injection molding machine. These pellets are then fed into the injection molding machine, where they are heated, melted, and injected into a mold to form the final samples.

2.3   Characterization

Melt flow index was performed by using melt flow apparatus by Thermo Haake according to Procedure A of ASTM D1238. The electrical resistivity of the nylon 66/GNP composite was determined by measuring the resistance values obtained using an LCR meter. These resistance values were then used to calculate the electrical resistivity, which provides valuable information about the material's conductivity characteristics. The electrical conductivity, σ is determined by taking the reciprocal of resistivity. XRD analysis was conducted using an X-ray diffractometer equipped with nickel filtered copper Kα radiation (λ = 0.154 nm). For the examination of the fractured surface of the samples, Field Emission Scanning Electron Microscope (FESEM) analysis was performed utilizing a Zeiss microscope.

3.0   RESULTS AND DISCUSSION

3.1   Melt Flow Index

The viscosities of nylon 66/VTMS-GNP nanocomposites are determined by their respective MFI values. As seen in Table 1, nanocomposite containing unfunctionalized GNP shows a lower MFI value than neat nylon 66. The MFI value decreases from 37.8 to 25.4 (g/10 min) with the addition of 0.3 wt% GNP. The decrease in flow index indicates an increase in viscosity of the system. The presence of GNP creates a significant energetic barrier for the segmental motions of polymer chains within a confined space. As a result, the flow activation energy of the polymer is increased. This means that the inclusion of GNP into the nylon 66 matrix hinders the mobility and movement of the polymer chains, requiring additional energy for them to flow and deform [15].

The increased flow activation energy indicates that the presence of GNP affects the rheological behavior of the polymer, leading to changes in its flow properties and potentially impacting processing conditions and material behavior. In other words, this effect can be attributed to the fact that the graphene nanoplatelets confine the mobility of the polymer chains. The presence of graphene nanoplatelets restricts the movement and flexibility of the polymer chains, thus, limiting their ability to freely flow and deform.

Table 1: Melt flow indices of nylon 66/VTMS-GNP nanocomposites

Material	VTMS (wt% per GNP)	MFI (g/10 min)
Nylon 66	Not related	37.8
Nylon 66/GNPf$_0$	0	25.4
Nylon 66/GNPf$_{15}$	15	109.2
Nylon 66/GNPf$_{20}$	20	132.6
Nylon 66/GNPf$_{25}$	25	159.0

Contrarily, the MFI value increases in the nanocomposites with functionalized GNP. As the VTMS amount is increased to 25 wt%, there is an increase in the MFI value up to 159.0 g/10 min, therefore a decrease in viscosity or resistance to flow [16]. The overall decrease in viscosity with the addition of VTMS-GNP is likely due to improved flow-capacity properties compared to the composites with non-functionalized GNP and neat nylon 66. This result supports the fact that functionalized graphene can be used as a good lubricant additive for various applications [17]. This is evident from the morphological analyses where functionalised GNP are well dispersed within nylon 66 matrix than unfunctionalized GNP.

3.2   XRD

The purpose of X-ray diffraction (XRD) characterization of nylon 66/GNP is to analyze the crystalline structure and obtain information about the arrangement of atoms or molecules within the material. XRD can provide valuable insights into the orientation, crystallinity, and intermolecular spacing within the polymer/GNP composite.

The XRD patterns for nylon 66/VTMS-GNP nanocomposites are shown in Figure 1. Both nylon 66 and its composites displayed XRD diffraction patterns that indicated a predominant amorphous nature with some degree of crystallinity. Broad diffraction with peaks at 20.4° and 23.1° is observed, which correspond to the reflection of (100) and (110) of α-phase of nylon 66 crystal. The pattern observed aligns with the findings reported by Garcia-Perez et al [18].

It is also demonstrated that the two peaks attributed to the α-phase were less intense for nylon 66 containing functionalized GNP (GNPf15, GNPf20 GNPf25) than for the neat nylon 66, indicating reduction in crystallinity in the composites. The improved interaction between the polymer chains and GNPs at the nylon 66-GNP interface influenced the crystalline structure of nylon/GNP composites. The strong interactions restrict the chain mobility, thus limit crystallization. In other words, VTMS functionalization of GNP is effective to improve interaction between nylon 66 and GNP.

Another significant finding is that an intense diffraction peak is observed at 2θ = 26.2° in the composite with unfunctionalized GNP. The peak does not appear in neat nylon 66 and composites with functionalized GNP. This diffraction peak is associated with (002) crystalline plane of GNP as reported by Wang et al [19]. The result further proves an improvement in interaction between GNP and nylon 66 in the composites containing VTMS functionalized GNP.

The diffraction peak associated with GNP around 26.2° disappears in the nanocomposites added with functionalized GNP. This observation suggests that the GNPs are exfoliated into individual graphene sheets within the polymer matrix. As a result, the regular and periodic structure of graphene is no longer present, indicating the presence of disordering and loose stacking of GNPs in the nylon 66/VTMS-GNP composites. These findings align with the observations made by Poosala et al [20]. It shows that the VTMS functionalised GNP, especially GNPf15 effectively contributes to the increase in surface interaction hence resulted in exfoliated morphology of GNP within the matrix. This is in good agreement with the SEM micrographs of the nanocomposites, in which the VTMS functionalised GNP in nylon 66/GNPf15 are well dispersed and free from aggregation or agglomeration in the nylon 66 matrix. It can be summarised that the functionalization of GNP has significant influence on the aggregation or assembly behaviors of nylon 66 chains.
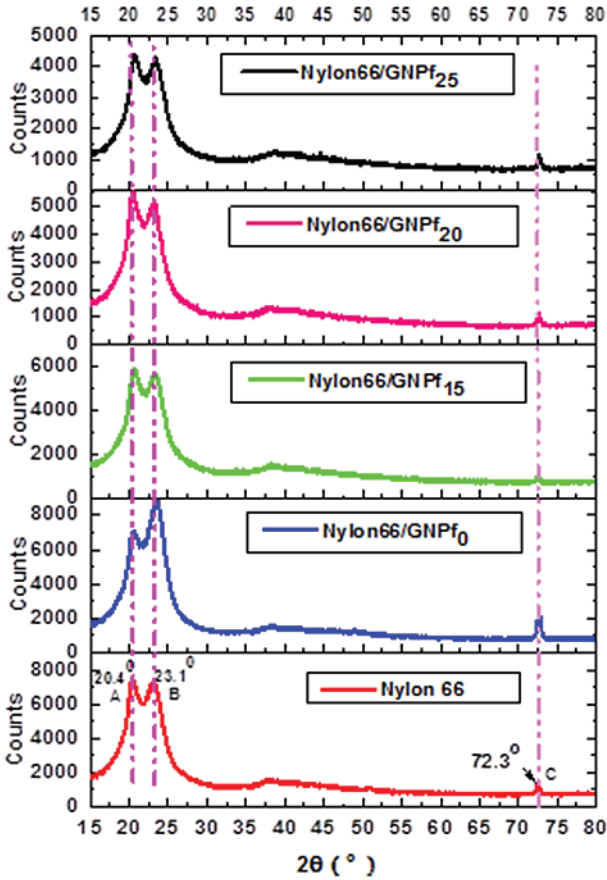
Figure 1: XRD spectra (15° ≤ 2θ ≤ 80°) for nylon 66 added with differently functionalised GNP

3.3 Electrical Conductivity

Electrical conductivity values of the nylon 66/VTMS-GNP nanocomposites are presented in Figure 2. The incorporation of a minimal quantity (0.3 wt%) of VTMS functionalized GNP has been shown to markedly enhance the electrical conductivity of nylon 66. The conductivity shows a significant improvement by ten orders of magnitude (from 10^{-13} to 10^{-3} S/m) , which recorded by nylon 66/GNPf$_{15}$. The obtained result demonstrates a comparable level of conductivity, albeit at much lower filler content, to that of the same polymer incorporating CNT as a conductive filler. In the case of the CNT-filled nylon (2 wt%), a conductivity of 7×10^{-3} S/m was recorded [21]. However, as the concentration of VTMS increases further to 20 and 25 wt%, the conductivity value does not exhibit any additional improvement. This could be attributed to the system reaching a

saturation limit for functionalization, where further increases in VTMS concentration do not lead to significant enhancements in conductivity.
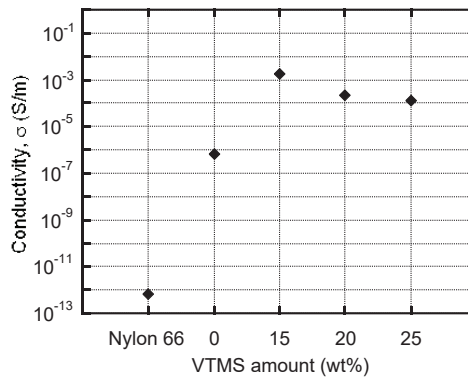

Figure 2: Electrical conductivity of neat nylon and nylon 66/VTMS-GNP nanocomposites at various VTMS amount

The level of dispersion of GNPs plays a critical role in determining the ultimate electrical properties of the nanocomposites. The excellent dispersion of GNPs in nylon 66/GNPf$_{15}$ composites results in the formation of a highly effective network for transmitting electron paths. This network formation is responsible for the remarkable electrical conductivity observed in the composites. This is obtained by a highly dispersed GNP nanocomposites system.

3.4 Morphological Analysis

Figure 3 (a-d) show the FESEM micrographs of neat nylon 66 and nylon 66/GNP nanocomposites. The fracture surface of nylon 66 (Figure 3(a)) appears lighter with smoother and flatter surface. Meanwhile, nylon 66/GNP nanocomposites (Figure 3 (b-d)) show darker constrast with rougher surface and clear plate-like structure distributed uniformly throughout the matrix; attributed to the presence of graphene platelets. Serious thickening of graphene platelets are observed in the composite with 25% VTMS functionalised level (Figure 3(d)), which resulted from stacking of graphene sheets. This is in agreement with the results shown in Figure 2, in which a slight decrease in electrical conductivity is observed in naocomposites filled with 20 and 25 wt% VTMS functionalized GNP.
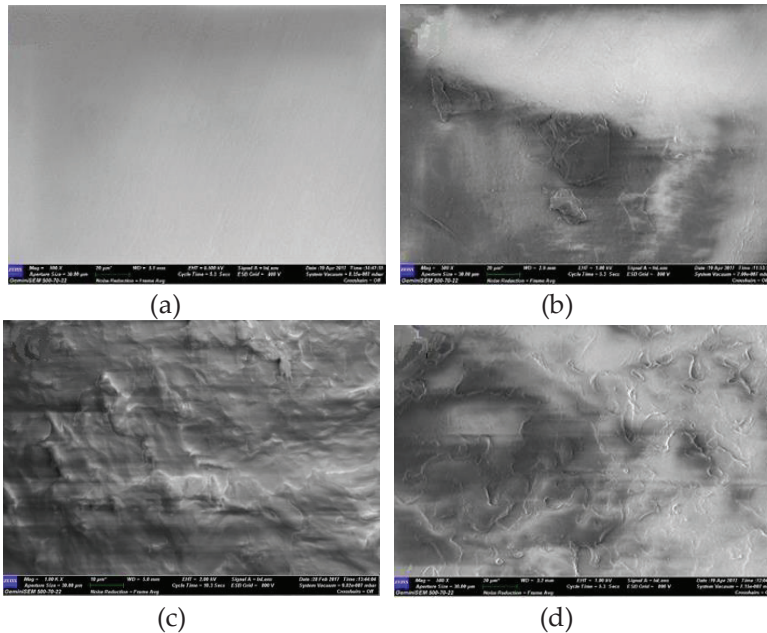
Figure 3: FESEM images of (a) unfilled; (b) unfunctionalized GNP; (c) 15 wt% VTMS-functionalized GNP; (d) 25 wt% VTMS-functionalized GNP filled nylon 66 at 500x magnification

In contrast, seemingly thin platelets of GNPs are observed to be uniformly dispersed and distributed in the composite with 15% VTMS-GNP (Figure 3(c)), hence better interaction between fillers and matrices. The chemical interaction formed between the functionalised GNP and nylon 66, as observed in FTIR results enables a better stress transfer under applied forces. The externally applied stresses can be transferred and distributed efficiently from matrix to fillers, thus only small proportion of the load will be sustained by the matrix phase.

4.0   CONCLUSION

The potential of using VTMS functionalized GNP for producing nylon 66/GNP nanocomposite with improved electrical performance has been explored. The incorporation of 0.3 wt% of functionalized GNP has been found to significantly improve the melt flow index, filler dispersion and electrical conductivity of nylon 66. The electrical conductivity showed a significant increase by ten orders of magnitude (10^{-13} to 10^{-3} S/m) at 15 wt% of VTMS. However no further increase was observed when the concentration of VTMS was further increased to 20 and 25 wt%. The results can be attributed to the improved dispersion of GNP in nylon 66/GNPf$_{15}$ and good interaction between GNP and matrixIn conclusion, the addition of a small quantity of VTMS functionalized GNP has

proven to be highly effective in significantly improving the electrical properties of nylon 66. The conductivity is enhanced by ten orders of magnitude, from 10^{-13} to 10^{-3} S/m. Importantly, achieving a high level of GNP dispersion is crucial for realizing the full potential of this addition and maximizing its impact on the electrical conductivity of the composite.

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AUTHOR CONTRIBUTIONS

M.I. Shueb: Conceptualization, Methodology, Writing- Original Draft Preparation; M.E.A. Manaf: Validation, Supervision, Final Editing; J.A. Razak: Writing-Reviewing, Editing; N. Mohamad: Conceptualization, Validation; K.N.K. Umar: Methodology; V.A. Doan: Validation.

CONFLICTS OF INTEREST

The manuscript has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agree with its submission, and declare no conflict of interest on the manuscript.

REFERENCES

[1] X.C. Tong, *Advanced Materials and Design for Electromagnetic Interference Shielding.* Boca Raton: CRC Press, 2016.

[2] S.B. Kondawar and P.R. Modak, "Theory of EMI Shielding", in *Materials for Potential EMI Shielding Applications: Processing, Properties and Current Trends*, K. Joseph, R. Wilson and G. George. Cambridge: Elsevier, 2019, pp. 9-26.

[3] S. Geetha, K.K. Satheesh Kumar, C.R. Rao, M. Vijayan and D.C. Trivedi, "EMI shielding: Methods and materials—A review", *Journal of Applied Polymer Science*, vol. 112, no. 4, pp. 2073–2086, 2019.

[4]   M. Wang, X.H. Tang, J.H. Cai, H. Wu, J.B. Shen and S.Y. Guo. "Construction, mechanism and prospective of conductive polymer composites with multiple interfaces for electromagnetic interference shielding: A review", *Carbon*, vol. 177, pp. 377-402, 2021.

[5]   M.H. Al-Saleh and U. Sundararaj, "Microstructure, electrical and electromagnetic interference shielding properties of carbon nanotube/acrylonitrile–butadiene–styrene nanocomposites", *Journal of Polymer Science Part B: Polymer Physics*, vol. 50, no. 19, pp. 1356–1362, 2012.

[6]   T. Kuang, M. Zhang, F. Chen, Y. Fei, J. Yang, M. Zhong, B. Wu and T. Liu, "Creating poly (lactic acid)/carbon nanotubes/carbon black nanocomposites with high electrical conductivity and good mechanical properties by constructing a segregated double network with a low content of hybrid nanofiller", *Advanced Composites and Hybrid Materials*, vol. 6, no. 1, pp. 48, 2023.

[7]   A.M. Alkaseh, M.E.A. Manaf and N. Mohamad. "Electrical and shielding properties of acrylonitrile butadiene styrene filled with differently treated recycled carbon fibers", *Journal of Advanced Manufacturing Technology*, vol. 16, no. 2, pp. 81-92, 2022.

[8]   A. Ameli, M. Nofar, S. Wang and C.B. Park, "Lightweight polypropylene/stainless-steel fiber composite foams with low percolation for efficient electromagnetic interference shielding", *ACS Applied Materials & Interfaces*, vol. 6, no. 14, pp. 11091–11100, 2014.

[9]   D. Shahdan, S. Ahmad, R.S. Chen, A. Omar, F.D. Zailan and N.A.A. Hassan, "Mechanical performance, heat transfer and conduction of ultrasonication treated polyaniline bio-based blends", *International Communications in Heat and Mass Transfer*, vol. 117, pp. 104742, 2020.

[10]   M.I. Shueb, M.E Abd Manaf, C.T. Ratnam and N. Mohamad, "Influence of sonication assisted dispersion method on the mechanical and electrical properties of nylon 66/nano-copper nanocomposite", *Jurnal Teknologi*, vol. 79, no. 5–2, pp. 77–81, 2017.

[11]   V. Eswaraiah, V. Sankaranarayanan and S. Ramaprabhu, "Functionalized graphene–PVDF foam composites for EMI shielding", *Macromolecular Materials and Engineering*, vol. 296, no. 10, pp. 894–898, 2011.

[12]   J. Liang, Y. Wang, Y. Huang, Y. Ma, Z. Liu, J. Cai, C. Zhang, H. Gao and Y. Chen, "Electromagnetic interference shielding of graphene/epoxy composites", *Carbon*, vol. 47, no. 3, pp. 922–925, 2009.

[13]   Z. Chen, C. Xu, C. Ma, W. Ren and H.M. Cheng, "Lightweight and flexible graphene foam composites for high-performance electromagnetic interference shielding", *Advanced Materials*, vol. 25, no. 9, pp. 1296–1300, 2013.

[14]   R.K. Goyal, K.R. Kambale, S.S. Nene, B.S. Selukar, S. Arbuj and U.P. Mulik, "Fabrication, thermal and electrical properties of polyphenylene sulphide/copper composites", *Materials Chemistry and Physics*, vol. 128, no. 1–2, pp. 114–120, 2011.

[15]   L. Altay, M. Atagur, K. Sever, I. Sen, T. Uysalman, Y. Seki and M. Sarikanat, "Synergistic effects of graphene nanoplatelets in thermally conductive synthetic graphite filled polypropylene composite", *Polymer Composites*, vol. 40, no. 1, pp. 277–287, 2019.

[16]   G. Zhang, F. Wang, J. Dai and Z. Huang, "Effect of functionalization of graphene nanoplatelets on the mechanical and thermal properties of silicone rubber composites", *Materials*, vol. 9, no. 2, pp. 92, 2016.

[17]   I.M. Inuwa, A. Hassan, D.Y. Wang, S.A. Samsudin, M.M. Haafiz, S.L. Wong and M. Jawaid, "Influence of exfoliated graphite nanoplatelets on the flammability and thermal properties of polyethylene terephthalate/polypropylene nanocomposites", *Polymer Degradation and Stability*, vol. 110, pp. 137–148, 2014.

[18]   C. García-Pérez, C. Menchaca-Campos, M.A. García-Sánchez, E. Pereyra-Laguna, O. Rodríguez-Pérez and J. Uruchurtu-Chavarín, "Nylon/porphyrin/graphene oxide fiber ternary composite, synthesis and characterization", *Open Journal of Composite Materials*, vol. 7, no. 3, pp. 146-165, 2017.

[19]   Q. Wang, Y. Wang, Q. Meng, T. Wang, W. Guo, G. Wu and L. You, "Preparation of high antistatic HDPE/polyaniline encapsulated graphene nanoplatelet composites by solution blending", *RSC Advances*, vol. 7, no. 5, pp. 2796-2803, 2017.

[20]   A. Poosala, K. Hrimchum, D. Aussawasathien and D. Pentrakoon, "The effect of oxygen-plasma treated graphene nanoplatelets upon the properties of multiwalled carbon nanotube and polycarbonate hybrid nanocomposites used for electrostatic dissipative applications", *Journal of Nanomaterials*, vol. 16, no. 1, pp. 91-92, 2015.

[21]   V.J. Cruz-Delgado, B.L. España-Sánchez, C.A. Avila-Orta and F.J. Medellín-Rodríguez, "Nanocomposites based on plasma-polymerized carbon nanotubes and Nylon-6", *Polymer Journal*, vo. 44, no. 9, pp. 952-958, 2012.