Scientific Research Journal,
Vol 20, Special Issue (2023) 17-30
https://doi.org/10.24191/srj.v20is.23255

SCIENTIFIC RESEARCH JOURNAL
SRJ
ISSN: 1675-7009
e-ISSN: 2289-649X

Electrical and Electromagnetic Characteristics of Poly (Methyl Methacrylate)/Polyaniline PMMA/PANi Conductive Film

Helyati Abu Hassan Shaari[1, 2,*], Muhammad Mahyiddin Ramli[3],
Mohd Nazim Mohtar[1,4], Norizah Abdul Rahman[1,5], Azizan Ahmad[6],
Nurul Huda Osman[1,7]

[1]Institute of Nanoscience and Nanotechnology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
[2]Faculty of Applied Sciences, Universiti Teknologi MARA Perlis Branch, Arau Campus, Arau 02600, Malaysia.
[3]Instititute of Nano Electronic Engineering (INEE), Universiti Malaysia Perlis (UNiMAP), 01000 Kangar, Perlis, Malaysia.
[4]Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
[5]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
[6]Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Malaysia.
[7]Applied Electromagnetic Laboratory 1, Department of Physics, Faculty of Science, Universiti Putra Malaysia, Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

**Corresponding Author's E-mail: helyati@uitm.edu.my*

Received: 24 July 2023
Accepted: 11 October 2023
Online First: 27 October 2023

ABSTRACT

In this study, a conductive film of poly (methyl methacrylate)/polyaniline (PMMA/PANi) was fabricated through a free radical copolymerization reaction using methyl methacrylate (MMA) and aniline monomers at different aniline-to-MMA ratios, namely, 1:1, 1:3, and 1:5. The PMMA/PANi copolymer films exhibited a total electromagnetic interference (EMI) shielding effectiveness (SE_T) of 0.45, 0.60, and 1.22 dB, respectively, which is more than twice that of the pure PMMA film (0.16 dB). The copolymer films possess the highest conductivity of 2.34 x 10^{-6} S/cm at the optimum value of aniline for films polymerized with a 1:3 PMMA:PANi ratio. Higher conductivity materials exhibited lower resistance and, thus, absorbed more EM energy, resulting in better EMI shielding.

PENERBIT PRESS
UNIVERSITI TEKNOLOGI MARA

Keywords: Thin Film; Copolymer; Electrical Properties

INTRODUCTION

All electronic devices, such as TVs, laptops, kitchen appliances, and mobile phones, emit electromagnetic (EM) radiation that self-propagates in space or through transparent matter. EM radiation consists of electric and magnetic field components that oscillate in phase perpendicular to each other and the direction of energy propagation [1].

Electronic magnetic interference or abbreviated as EMI, on the other hand, is the interference produced by one electronic device to another by the electromagnetic fields set up by its operation. Additionally, interference is the combination of two or even more EM waves that cause the displacement wave that either will be canceled or reinforced. When multiple electronic devices work in the same area, EM radiation produced from each other might be picked up by other electronic devices and cause interference. This may cause the device to malfunction and not perform optimally.

All electronic devices are equipped with EMI shielding material to reduce the impact of EMI. Material with EMI shielding properties is a material that shields the penetration of EM radiation through the reflection and adsorption of EM radiation. Consequently, the amount of EM radiation from the environment penetrating the device’s electronic circuit will be reduced. The ratio of the magnitude of the electric or magnetic field incident on the barrier to the electric or magnetic field transmitted through the barrier wall is used to measure the shield's effectiveness of a material [2].

The most common materials for EMI shielding in electronic devices are steel, pre-tin coated steel, copper, nickel, or carbon. Long before, metal steel was used extensively as EMI shield materials and molded into various shapes depending on the design of the electronic housing or enclosures. Nevertheless, steel and copper are very strong solid materials, making them challenging to mold and deform under pressure. Additionally, despite having high conductivity values, steel and nickel are easily oxidized at high temperatures [3, 4]. Therefore, this work aims to solve the mentioned problem by copolymerization of methyl methacrylate (MMA) and aniline monomers to produce poly (methyl methacylate)/polyaniline) (PMMA/PANi) copolymer film. Alternatively, this study presents a pioneering approach by employing a bulk polymerization method via free radical polymerization reaction to prepare a conducting film known as PMMA/PANi copolymer film. This copolymer film possesses synergistic properties, combining the good conductivity of aniline with the high optical characteristics of PMMA. Since PMMA/PANi is a polymer-based film, the corrosion and scratch resistance of the prepared film are better than that of steel.

The ratio of MMA to aniline was varied (1:1, 1:3, and 1:5) to determine the most suitable ratio that yields optimum conductivity and shielding efficiency. To demonstrate the effectiveness of the bulk method in the free radical polymerization approach, interactions between PMMA and PANi chains were investigated using Fourier transform infrared spectroscopy (FTIR). Additionally, conductivity measurements using the 2-probe method were conducted to evaluate the conductivity of the produced copolymers. The potential application of PMMA/PANi copolymers as electromagnetic interference (EMI) shielding materials was also assessed using a vector network analyzer (VNA).

EXPERIMENTAL

Materials

All the materials and method of copolymerization reaction of MMA with aniline monomer via free radical copolymerization reaction has been described elsewhere [5]. The dopant concentration and polymerization time were fixed to 1.5 M and two hours. Meanwhile, the MMA to aniline ratio was varied to 1:1, 1:3, and 1:5.

Synthesis of PMMA/PANi Conductive Film

PMMA/PANi conductive film was synthesized using a free-radical polymerization technique under nitrogen gas to ensure an oxygen-free environment. In a typical procedure, 10 ml of MMA was added to a reaction flask, and BPO was introduced while stirring at a polymerization temperature of 60 °C. Polymerization started prior to the addition of BPO and continued until gelation occurred.

As the polymerization progressed, the solution gradually became more viscous. At this point, HCl-doped aniline (1.0 M, 1.5 M, and 2.0 M), was added to the reaction while adjusting the MMA to aniline monomer ratio to 1:1, 1:3, and 1:5. The copolymerization process continued for 2 h, followed by a reduction in polymerization temperature. To stop the polymerization, methanol was added to the reaction mixture once the desired polymerization time was achieved. Subsequently, the copolymer was subjected to three cycles of washing with distilled water and excess methanol to eliminate contaminants and unreacted monomers. The resulting copolymer precipitate was collected and dried in an oven for 24 h.

Spectral Analysis

The copolymers film was characterized by a 2 cm^{-1} resolution, in the spectral range of 4000 to 500 cm^{-1} wave numbers. The spectral analysis was acquired using a Nicolet 6700 FTIR (Thermo Scientific, Waltham, MA, USA) spectrometer.

Conductivity

In this study, the resistance of PMMA/PANi copolymer produced was measured by two-point probe measurement using 4200-SCS' Keithley Interactive Test Environment (KITE) source meter. The sample used for this measurement was in the form of a thin rectangular film with a dimension of 0.02 m x 0.01 m and a thickness of 0.08 mm. Meanwhile, the length of the needle probe was 0.005 m. This length value was fixed for every measurement of all samples.

The resistivity of PMMA/PANi copolymer was obtained using Eq. (1):

$$\rho = \frac{RA}{L} \ (\Omega\text{-m}) \quad (1)$$

where R is the material's resistance, A is the cross-sectional area (width, w times thickness, t), and L is the needle's length.

In addition, the material’s conductivity is simply the inverse of resistivity. It is denoted by the symbol σ, and the unit for conductivity is S/m. From the resistivity value measured previously, the conductivity of PMMA/PANi copolymer was calculated using Eq. (2).

$$\sigma = \frac{1}{\rho}\ (\text{S-m}^{-1}) \tag{2}$$

EMI Shielding

The shielding efficiency (SE) was acquired using a vector network analyzer (VNA), with the film (5 x 2 cm) placed between the waveguides at a frequency range between 8 to 12 GHz. The thickness of all the films used in this analysis was 0.08 mm. In this analysis, the data of four scattering parameters were obtained; S_{11}, S_{12}, S_{21}, and S_{22}. The value of reflection (R), transmittance (T), and absorbance (A) was calculated from these parameters using the following equations [6];

$$R = IS_{11}I^2 \tag{3}$$
$$T = IS_{21}I^2 \tag{4}$$
$$A = 1\text{-}R\text{-}T \tag{5}$$

S_{11} and S_{21} are the forward reflection coefficient and forward transmission coefficient, respectively.

In addition, the shielding effectiveness due to the reflection (SER) , absorbance (SEA), total shielding effectiveness (SET) was calculated using the following equations [6, 7];

$$SE_R = -10 \log (1\text{-}R) \tag{6}$$
$$SE_A = -10 \log (T/(1\text{-}R)) \tag{7}$$
$$SE_T = SER + SEA = 10 \log T \tag{8}$$

In order to be suitable for commercial applications, an electromagnetic interference (EMI) shielding efficiency of 20 dB is necessary, equivalent to effectively blocking 99 % of incoming radiation. SET is converted from dB to % SE by using the formula in Eq. (9) [7];

$$\text{Shielding efficiency (\%)} = 100 - \left(\frac{1}{10^{\frac{SE}{10}}}\right) X\ 100 \tag{9}$$

RESULTS AND DISCUSSION

FTIR Analysis

The copolymers spectrum in Figure 1 indicates that the FTIR spectrum of the lowest PANi ratio (1:1 PMMA/PANi 2h) exhibited a stronger band with lower transmittance and broad character. The decrease in transmittance and broadening of the peak is significant for the peak characteristic attributed to PMMA bands. The bands are C-H stretching vibration (2999 – 2800 cm^{-1}), C=O (1722 cm^{-1}), CH_3 stretching vibration (1482 cm^{-1}, 1448 cm^{-1}), and O-CH_3 stretching (1143 cm^{-1}). The apparent change in intensity of these bands is evidence of lower PANi functional groups in the 1:1 PMMA/PANi 2h sample. The reduction in FTIR band intensity confirms the interaction and formation between PMMA molecules due to the lower amount of PANi molecules in the copolymer [8]. Similarly, when the PANi ratio increases from 1:1 to 1:3 and 1:5, the transmittance of the peaks attributed to both PMMA and PANi molecules increases in the 1:3 and 1:5 samples. The band assigned to N-H stretching (3444 - 3440 cm^{-1}), ring stretching of a quinoid and benzenoid unit of PANi (1400 – 1590 cm^{-1}), and C-N stretching (1386 cm^{-1}) is higher in transmittance in 1:3 PMMA: PANi 2h and 1:5 PMMA: PANi 2h sample to that of the 1:1 PMMA: PANi 2h sample. This indicates that the amount of PANi formation in the copolymers increases with the increasing PANi ratio.

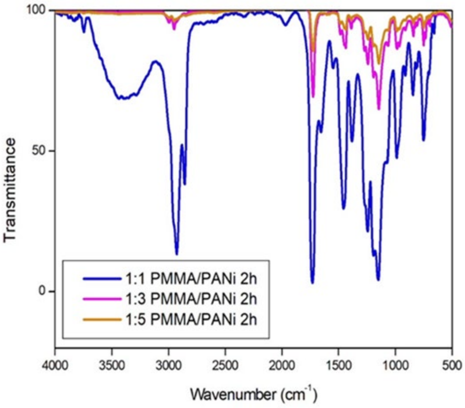

Figure 1: FTIR spectra of PMMA: PANi copolymer with different MMA and aniline ratios

High interaction between PMMA and PANi molecules in the 1:3 and 1:5 copolymer samples is implied with high transmittance of the carbonyl group of PMMA (1722 cm^{-1}) and N-H stretching group of PANi (3444 – 3440 cm^{-1}). The interaction of PMMA and PANi is via hydrogen bonding between the oxygen atom of PMMA and the hydrogen atom of PANi. An increase in intensity due to high molecular interaction was also reported by various researchers in their studies [9–11].

In addition, there is a specific change in the absorption region between 1590 cm^{-1} to 1483 cm^{-1}, which is attributed to a quinoid and benzenoid unit of PANi. The absorption peak around 1483 cm^{-1} disappeared in the 1:1 PMMA: PANi 2h spectrum due to the low transmittance of this band with low PANi content. The strong C-H stretching bond at 1466 cm^{-1} of PMMA tends to cover the functional unit of PANi due to the low amount of PANi [12].

After adding PANi to a higher loading ratio (1:5), the N-H stretching mode of PANi at 3440 cm^{-1} is shifted to 3444 cm^{-1} for both 1:3 and 1:5 PMMA/PANi 2h samples than 3430 cm^{-1} for 1:1 PMMA/PANi ratio. A similar finding was also observed for a quinoid and benzenoid unit of PANi where the band attributed to this functional group is shifted from 1590 cm^{-1} to 1583 cm^{-1} (1:5 PMMA/PANi), 1584 cm^{-1} (1:3 PMMA: PANi), and 1544 cm^{-1} (1:1 PMMA: PANi). This is due excessive amount of PANi present in the polymer matrix due to high PANi content rather than bonding with PMMA molecule [9]. Therefore, these peaks are shifted to less frequency than low PANi content.

From the FTIR analysis, the influence of PANi content in the copolymer had been proven based on the presence of the change in intensity and shifts in peak. As discussed previously, the difference in lower intensity with low PANi content may be due to the self-crosslinking of PMMA in the polymer matrix, which results in stronger bonds in the 1:1 PMMA/PANi 2h spectrum [9].

Electrical Conductivity

Figure 2 shows the variation of electrical conductivity of PMMA/PANi copolymers at different ratios of MMA to aniline monomer. According to this measurement, different conductivity values were found for the different MMA to aniline ratio, as shown in Table 1. Pure PMMA is an insulating material with a conductivity of 3.61 x 10^{-11} S/cm. The conductivity of the PMMA/PANi copolymer was found to increase on the addition of aniline to MMA ratio to 2.83 x 10^{-7} S/cm for 1:1 PMMA: PANi film and 2.34 x 10^{-6} S/cm for 1:3 PMMA/PANi film respectively. The increment was due to the formation of conducting network throughout the PMMA matrix [13].

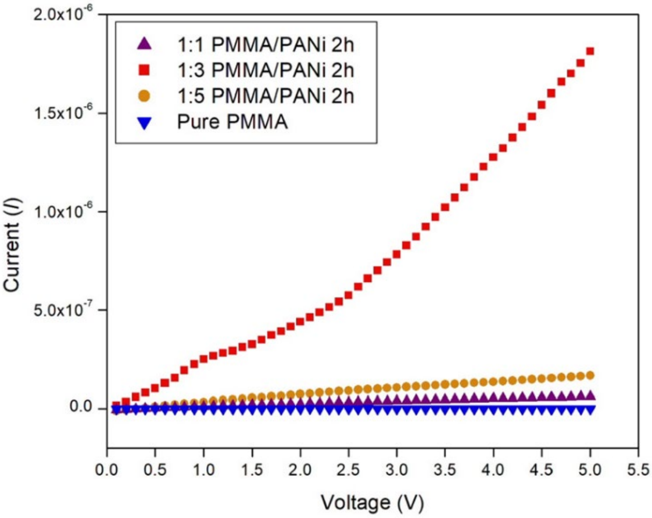

Figure 2: I-V curve of pure PMMA and PMMA/PANi copolymer films polymerized at various MMA: aniline ratios

However, it can be seen that upon further increase of aniline to MMA ratio up to 1:5, the film's conductivity was dropped to 7.23 x 10^{-7} S/cm. In particular, too much aniline incorporation into PMMA molecules would cause non-uniformity and non-bonded PANi molecules with PMMA [14]. Thus, the non-uniformity of PANi results in reduced conductivity of the copolymer.

From the conductivity analysis, it can be concluded that the amount of aniline plays a vital role in determining the conductivity of the PMMA/PANi copolymer produced. It is important to note that the highest conductivity obtained (2.34 x 10^{-6} S/cm) falls under the conductivity range of semiconductor materials (10^{-8} – 10^{2} S/cm), making them a good candidate for EMI shielding material.

Table 1: Conductivity of PMMA and PMMA/PANi copolymer

Sample	MMA:Aniline Ratio	Conductivity (S/cm)
Pure PMMA	-	3.61×10^{-11}
1:1 PMMA/PANi 2h	1:1	2.83×10^{-7}
1:3 PMMA/PANi 2h	1:3	2.34×10^{-6}
1:5 PMMA/PANi 2h	1:5	7.23×10^{-7}

Shielding Effectiveness

From Figure 3 (a) and (b), it can be seen that the average reflection shielding effectiveness (SE_R) of all copolymer films is found to be lower than that of pure PMMA film. Additionally, as for absorbance shielding effectiveness (SE_A), a gradual increment of the trend can be observed. The SE_A for 1:1 PMMA/PANi 2h film is 0. 45 dB and increases to 1.22 dB when the MMA: aniline ratio increases to 1:3. The huge difference in the SE_R and SE_A trends of the copolymer films suggest that the absorption mechanism is dominant in the PMMA/PANi copolymer. Meanwhile, the SE_A value for pure PMMA is only 0.15 dB. Thus, even though the value of SE_A of the copolymers is considered low, it is proven that adding the conductive material, such as PANi, in the PMMA matrix can improve the absorption of EM radiation. This suggests that the interfacial polarization of the PMMA molecule by PANi molecules increases, leading to an increase in the absorption mechanism [15].

The total shielding effectiveness (SE_T) of PMMA/PANi copolymer depends on the content of the conductive element in the copolymer. As seen in Figure 3(c), the trend of the total shielding effectiveness (SE_T) is increased with an increase in the aniline ratio. The average SE_T of 1:1 PMMA/PANi 2 h film is 0.45 dB and increases to 1.22 dB and 0.60 dB at 1:3 and 1:5 MMA: aniline ratio, respectively. The increase in the shielding effectiveness of the PMMA/PANi copolymer over the pure PMMA is due to the formation of a conductive network of PANi in the PMMA matrix. However, too much aniline content in the polymer matrix causes non-homogenous molecules in the PMMA matrix, thereby reducing the shielding effectiveness [15].

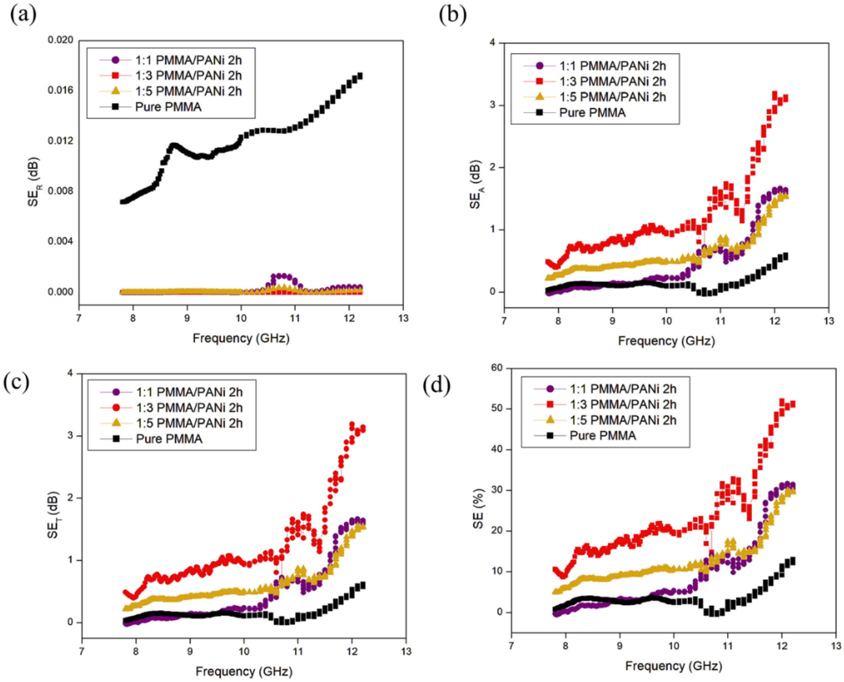

Figure 3: (a) Shielding effectiveness due to reflection (SE_R) (b) Shielding effectiveness due to absorption (SE_A) (c) Total shielding effectiveness (SE_T) (d) Shielding efficiency (SE) of the PMMA/PANi copolymers and pure PMMA film.

A similar trend can also be observed for the shielding efficiency of the copolymer films. As depicted in Figure 3 (d), the highest shielding efficiency of the PMMA/PANi copolymer films is 51 % at 12 GHz for 1:3 PMMA/PANi 2h film, more than that of pure PMMA film (13 %). A further increase in the aniline content (1:5 PMMA/PANi) decreases the shielding efficiency of the PMMA/PANi copolymer to 30 %. The high shielding performance at 12 GHz at the optimum amount of aniline content is ascribed to the higher electrical conductivity of the PMMA/PANi copolymer.

Based on the shielding effectiveness test, the copolymer films showed an improvement in shielding properties over the pure PMMA film through the absorption mechanism. The PMMA/PANi copolymer polymerized with a 1:3 MMA to aniline ratio was proven to have the highest shielding effectiveness among the other copolymer films due to better conductivity. The conductivity of PANi facilitates the reflection of electromagnetic waves inside the film matrix, thereby reducing the probability of the EM waves transmitting through the material [16]. Excessive aniline, up to a 1:5 MMA:aniline ratio, will only cause agglomeration to occur within PANi particles. Agglomeration disrupts the alignment of PANi chains and leads to a reduction in conductivity due to the difficulties faced by charge carriers in moving through the material [17]. However, the shielding properties of the copolymer film were not sufficient for commercial use. Nevertheless, with further improvements and modifications, PMMA/PANi copolymers have the potential to advance significantly in terms of EMI shielding properties.

CONCLUSION

In this work, we have investigated the electromagnetic interference (EMI) shielding effectiveness of PMMA/PANi copolymers. Co-polymerizing MMA fabricated the film with aniline monomer using different ratios of MMA to aniline. We found that a copolymer film produced with a 1:3 MMA to aniline ratio has the highest conductivity and shielding effectiveness of EM radiation over pure PMMA film. Since the conductivity of the copolymer is largely depending on the polarons site of aniline, the optimum amount of aniline monomer is found to give enhancement of the conductivity performance of the copolymer as supported by the results obtained in FTIR analysis where the optimum amount of aniline provides a better PMMA-PANi network through strong π-π interactions by hydrogen bonding. Moreover, material with high conductivity gives better EM shielding due to more efficient in dissipating and redirecting EM energy. On the other hand, the conductivity of the copolymer film is highly influenced by the amount of aniline content. Still, too high aniline causes non-homogeneity in the PMMA matrix, resulting in a reduction in conductivity. With further studies, the prepared conducting polymer-based film is expected to be commercially used in EMI shield applications due to its cost-effectiveness and ease of fabrication using simple equipment and processing, but with better EMI shielding performance.

ACKNOWLEDGEMENTS

We thank Universiti Teknologi MARA (UiTM), Perlis Branch, Universiti Putra Malaysia (UPM), and Universiti Malaysia Perlis (UniMAP) for providing financial support and research equipment for this work.

REFERENCES

[1] R. C. Radha and P. Gurupranesh, 2014. Electromagnetic radiation from electronic appliances, *IOSR Journal of Mechanical and Civil Engineering,* pp. 41–46.

[2] R. K. Kotnala and J. Shah, 2015. Chapter 4: Ferrite Materials: Nano to Spintronics Regime, *Handbook of Magnetic Materials*, vol. 23, 291-379.

[3] S. S. Pradhan, L. Unnikrishnan, S. Mohanty, and S. K. Nayak, 2020. Thermally conducting polymer composites with EMI shielding: A review, *Journal of Electronics Material*s, 49(3), 1749–1764. doi: 10.1007/s11664-019-07908-x.

[4] V. Bhingardive, M. Sharma, S. Suwas, G. Madras, and S. Bose, 2015. Polyvinylidene fluoride based lightweight and corrosion resistant electromagnetic shielding materials, *RSC Advances*, 5(45), 35909–35916. doi: 10.1039/c5ra05625j.

[5] H. A. H. Shaari, M. M. Ramli, M. M. A. B. Abdullah, M. N. Mohtar, N. A. Rahman, N. H. Osman, 2022. Effects of polymerization time towards conductivity and properties of poly (methyl methacrylate)/ Polyaniline (PMMA / PANi) copolymer, *Sustainability,* 14(14), 894.

[6] J. Cheng, C. Li, Y. Xiong, H. Zhang, H. Raza, S. Ullah, J. Wu, G. Zheng, Q. Cao, D. Zhang, Q. Zheng, R. Che, 2022. Recent advances in design strategies and multifunctionality of flexible electromagnetic interference shielding materials, *Nano-Micro Letters*, 14(1).

[7] H. Li, X. Lu, D. Yuan, J. Sun, F. Erden, F. Wang, C. He, 2017. Lightweight flexible carbon nanotube/polyaniline films with outstanding EMI shielding properties," *Journal of Materials Chemistry* C, 5(34), 8694–8698. doi: 10.1039/c7tc02394d.

[8] S. B. Aziz, O. G. Abdullah, A. M. Hussein, and H. M. Ahmed, 2017, From insulating PMMA polymer to conjugated double bond behavior: Green chemistry as a novel approach to fabricate small band gap polymers, *Polymers (Basel)*, 9(11), 1–15. doi: 10.3390/polym9110626.

[9] S. Ramesh and L. C. Wen, 2010. Investigation on the effects of addition of SiO2 nanoparticles on ionic conductivity, FTIR, and thermal properties of nanocomposite PMMA-LiCF3SO3-SiO_2, *Ionics (Kiel),* 16(3), 255–262. doi: 10.1007/s11581-009-0388-3.

[10] S. Ramesh, K. H. Leen, K. Kumutha, and A. K. Arof, 2007. FTIR studies of PVC/PMMA blend based polymer electrolytes, Spectrochimica *Acta Part A: Molecular and Biomolecular Spectroscopy,* 66, no. 4–5, 1237–1242. doi: 10.1016/j.saa.2006.06.012.

[11] M. Chalid, Y. A. Husnil, S. Puspitasari, and A. Cifriadi, 2020. Experimental and modelling study of the effect of adding starch-modified natural rubber hybrid to the vulcanization of sorghum fibers-filled natural rubber, *Polymers (Basel),* 12(12), 1–19. doi: 10.3390/polym12123017.

[12] L. Guo, H. Sato, T. Hashimoto, and Y. Ozaki, 2010. FTIR study on hydrogen-bonding interactions in biodegradable polymer blends of poly(3-hydroxybutyrate) and poly(4-vinylphenol), *Macromolecules*, 43(8), 3897–3902. doi: 10.1021/ma100307m.

[13] S. N. Tripathi, P. Saini, D. Gupta, and V. Choudhary, 2013. Electrical and mechanical properties of PMMA/reduced graphene oxide nanocomposites prepared via in situ polymerization, *Journal of Materials Science,* 48(18), 6223–6232. doi: 10.1007/s10853-013-7420-8.

[14] N. N. Rozik, A. I. Khalaf, and A. A. Ward, 2016. Studies the behaviors of polyaniline on the properties of PS/PMMA blends, Proceedings of the Institution of Mechanical Engineers, *Part L: Journal of Materials: Design and Applications,* 230(2), 526–536. doi: 10.1177/1464420715581196.

[15] A. K. Gupta, M. Bafna, S. Srivastava, R. K. Khanna, and Y. K. Vijay, 2021. Study of electromagnetic shielding effectiveness of metal oxide polymer composite in their bulk and layered forms, *Environmental Science and Pollution Research*, 28(4), 3880–3887. doi: 10.1007/s11356-020-09322-x.

[16] S. Khasim, 2018. Polyaniline-Graphene nanoplatelet composite films with improved conductivity for high performance X-band microwave shielding applications, *Results in Physics*, 12, 1073–1081. doi: 10.1016/j.rinp.2018.12.087.

[17] K. Yusupov and A. Vomiero, 2020. Polymer-based low-temperature thermoelectric composites, *Advanced Functional Materials,* 30(52), p. 2002015. doi: https://doi.org/10.1002/adfm.202002015.