Experimental Study of the Flame Retardancy of PMMA-Graphene Composite Materials

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ABSTRACT

In this paper, Polymethyl methacrylate (PMMA)-graphene nano-composites were prepared and tested with the use of a cone calorimeter. Graphene was added to PMMA in limited weight percentages to improve the flame retardancy of PMMA. Two samples of PMMA-graphene, namely 1 and 3 wt%, were investigated. The combustion properties of the tested samples of PMMA-graphene composites, mass loss rate, heat release rate, and time to ignition were measured and calculated. It was found that the peak heat release rate of PMMA-graphene composites reduced by 17% when 3 wt% graphene was added to pure PMMA. Adding graphene to PMMA improves the thermal stability of PMMA by reducing the time of ignition. Also, the presence of graphene enhanced the formation of a continuous carbonized layer at the surface of the burned PMMA.

Keywords-nano-composites; graphene; PMMA; flame retardancy; polymers; heat release rate

I. INTRODUCTION

Polymers are promising materials that can be widely used in a variety of applications and low prices [1, 2]. Polymethyl methacrylate (PMMA) is an example of polymer which has been used in various applications [3]. The most desired properties of the PMMA are its low density, low thermal conductivity, low water absorption, high chemical corrosion resistance, and high flexibility, while its main disadvantages are its low melting temperature and decomposition to volatile combustible products when exposed to heat [4]. In some fields, where flame resistance is required, PMMA is used with additives to enhance its flame retardant properties [5]. The mechanical and thermal properties of PMMA can be enhanced by adding reinforcements [5]. There are many additives used with PMMA to enhance its flame retardancy [6]. However, the choice of flame retardants as additives depends on the specific applications and degree of retardants required [7, 8]. Graphene is often added as a nano-filler of PMMA matrices to enhance flame retardancy [9], since the addition of graphene even at very low loadings up to 0.7 wt.% enhances the flame retardancy of materials [10]. PMMA-graphene as a nano-composite has a widely range of applications [11, 12]. Graphene has a high surface area to volume ratio, and is considered as the thinnest material to date [13, 14]. The presence of graphene as nano-sheets in polymer composites enhances flame retardancy by producing intumescent char during their combustion [15]. When polymer burns, graphene forms a dense carbonized layer, which halts the burning of polymer matrices [16]. Also, incorporation of graphene reduces mass loss rate significantly by altering the diffusion path of pyrolysis products [10].

Flame retardants are used to reduce the fire impact and fire growth and spreading [8]. This study aims to reduce the heat release rate from the combustion of polymers like PMMA. Graphene is selected to be used as a nano filler to retard flame spreading during the combustion of PMMA.

II. PREPERATION OF SAMPLES

In this study, PMMA is used as a base material while graphene is used as nano-filler. Pure PMMA supplied by the SABIC factory was used as a row material. Figure 1 shows the pure form of used PMMA. Graphene is selected as nano-filler to PMMA matrices due to its thermal stability, Graphene will not be a combustion fuel, and can be found in the burned char.

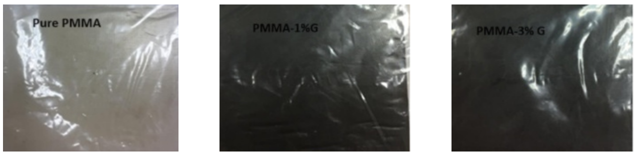
Fig. 1. The used PMMA.

Brabender plastograph EC plus instrument was used to mix the graphene with the base material (PMMA) to get a uniformly homogenous mixture. A total of 30 g of PMMA with two different weight percentages (1 wt% and 3 wt%) of graphene were used as a reinforcement. Graphene and pure PMMA were added to the mixer and processed at 180 ^{o}C and mixing speed of 50 min^{-1} to prepare the nano-composites. The high mixing temperature and the suitable torque leads to good dispersion and homogeneous distribution of grapheme inside the PMMA matrix. Also, pure samples of 30 g weight were prepared with the Brabender plastograph EC plus mixer under the same parameters that used to prepare the PMMA-graphene nano-composites. After the samples got mixed by the Brabender plastograph EC plus mixer, they were put in a stainless steel mold and were pressed by a hot press machine. A stainless-steel mold with dimensions of $100\times100\times3$ mm^3 has been cut and polished to meet the requirements of the sample holder used in the cone calorimeter. The prepared sample was introduced to the sample holder and was tested inside the cone calorimeter which is calibrated according to ISO 5660. The flat square 100×100 mm^2 sample with 3 mm thickness was exposed to heat flux of 50 kW/m^2. The heat release rate was measured with the Clayton Huggett method which is in accordance with ISO 5660. Oxygen consumption was used to determine the heat release rate. For each sample, Peak Heat Release Rate (PHRR), Effective Heat Release Rate (EHRR), and Total Heat Release Rate (THRR), time to ignition t_{ig}, and time to reach the PHRR, ti-peak, were measured and recorded. Heat release and mass of the sample were measured and recorded every 5 s.

III. RESULTS AND DISCUSSION

Many methods are used to enhance the flame retardancy of materials, one of these is by char formation [17]. Some materials like graphene and its derivatives when exposed to heat or flame form a char. This leads to the formation of a layer of carbonized material that can act as a barrier between the flame and the underlying material, preventing or slowing further combustion [18]. The addition of small load of graphite up to 5 wt% can significantly enhance the flame retardancy and mechanical properties [3].

Three samples of pure PMMA and PMMA-graphene composites were prepared and tested by the cone calorimeter. Figure 2 shows the prepared samples of pure PMMA and its composites.



(a) (b) (c)

Fig. 2. The prepared samples: (a) Pure PMMA, (b) PMMA-1 % graphene, (c) PMMA-3% graphene.

Figure 3 shows the results of heat release rate from the pure samples. The results of pure PMMA and PMMA-graphene composites indicate the consistency of the tests. Also, it can be concluded that the samples resulted from Brabender plastograph EC plus instrument are homogeneous and uniformly mixed, where the heat release rate is approximately the same for the three samples taken from the mixed batch. The average measured values are shown in Table I. For PMMA-graphene composites, two weight percentages of graphene were considered (1 wt% and 3 wt%).

TABLE I. AVERAGE RESULTS OF THE CONE CALORIMETER TEST

Sample	PHRR (kW/m^2)	EHRR (kW/m^2)	THRR (MJ/m^2)	t_{ig} (s)	ti-peak (s)
Pure PMMA	964	95.94	104.26	41	138.3
PMM-graphene (1 wt%)	858.16	46.77	102.9	23	140
PMMA-graphene (3 wt%)	801.3	47.22	100.5	20.6	131.6

Figure 4 shows the average values of heat release rate for pure PMMA and PMMA-graphene composites from the cone calorimeter test. Pure PMMA has larger PHRR (964 kw/m^2) than PMMA-graphene composites. However, the addition of 1 wt% of graphene to PMMA reduced the PHRR by 11%. With further increment of the addition of graphene to 3 wt%, the PHRR was further reduced to 17% of pure PMMA's. Authors in [19] found that addition of 1 wt% of Graphene Nano Plates (GNPs) leads to 12% reduction in peak release rate compared to pure PMMA. Also, authors in [5] found that the PHRR reduces from 950 to about 780 kW/m^2, when 0.5 ml/mg of carbon nano tubes were added to PMMA [19]. The mechanism of reducing the PHRR of PMMA in the presence of grapheme is attributed to the formation of a carbon layer when the composites are ignited. This low conductivity of carbon layers covered the surface of the matrix, reducing the heat release of the material [20]. Authors in [21] found the same results when adding grapheme oxide to polypropylene where the PHRR reduced from 1140 to 936 kW/m^2 when 1 wt% of grapheme oxide was added. However, the time to reach the PHRR has the same importance as the PHRR itself. It was found that addition of 3 wt% of grapheme to PMMA reduces this time from 140 s for pure PMMA to 131 s for PMMA-3 wt% grapheme nanocomposite, as shown in Table I.

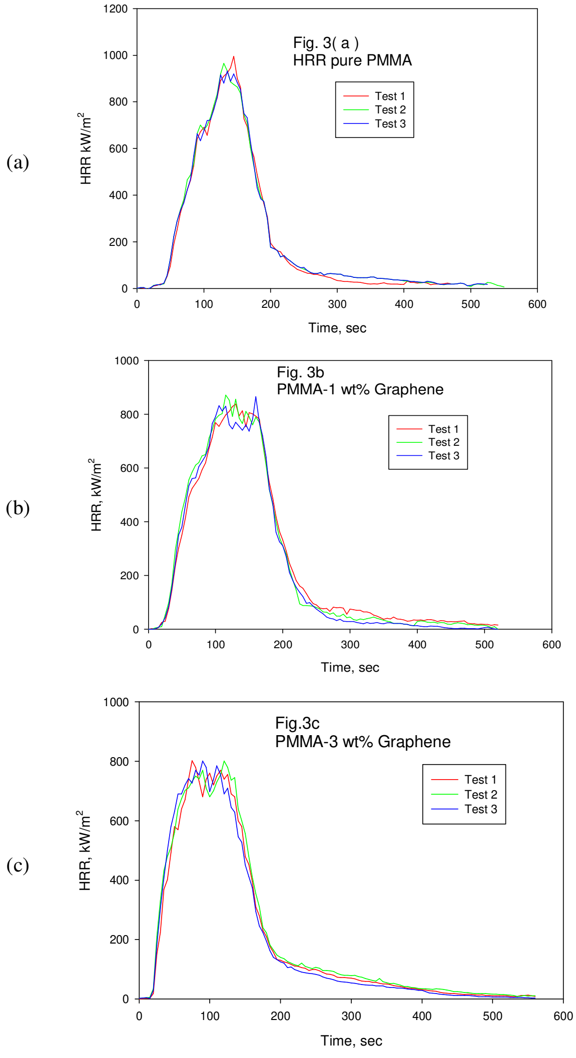


Fig. 3. Heat release rate from: (a) pure PMMA, (b) PMMA-1 wt% graphene, and (c) PMMA- 3 wt% graphene.

Figure 5 shows the images of char residues of PMMA and PMMA – 3 wt% grapheme composite. The char of pure PMMA contains white and black areas. However, PMMA-3 wt% grapheme has exterior black char as shown. This black char slows the combustion of interior layers and prevents the pyrolysis gases to release. Figure 6 shows the microstructure of pure PMMA char and PMMA-3 wt% grapheme char. The presence of graphene enhances the formation of a continuous carbonized layer at the surface of PMMA-3 wt% graphene. This compact continuous carbonized layer protects the sublayers of the nanocomposite in two ways: by hindering the pyrolysis gases to transfer to the upper layer and acts as an insulator reducing the amount of heat transferred from the surface toward the sublayers. It has been found that the presence of graphene in the epoxy matrix produces a continuous and compacted char layer which exhibits lower thermal conductivity from pure epoxy [22].

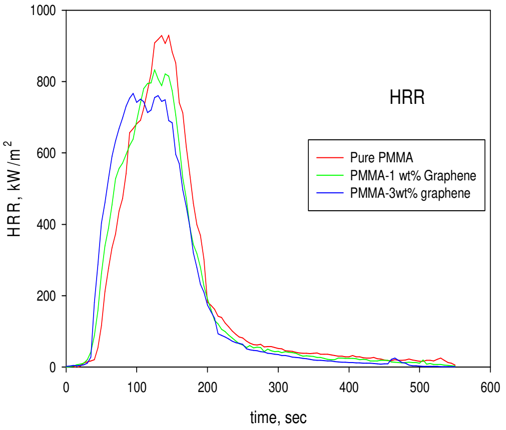


Fig. 4. Average heat release rate for pure PMMA and PMMA-graphene composites.


(a) (b)

Fig. 5. Char images from (a) PMMA and (b) PMMA-3 wt% grapheme.

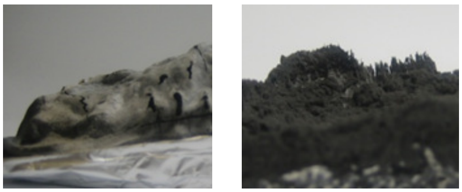

(a) (b)

Fig. 6. Char microstructure of: (a) PMMA and (b) PMMA-3 wt% graphene.

Table I reveals that the induction of graphene in low percentages (1 wt% and 3 wt%) has less effect in reducing the THRR values of PMMA-graphene composites. This is expected, because the heat generated from the combustion of 1 g of composites will not change, so all the samples approximately have the same values of THRR. PHRR has more influence on the fire spreading. So, for the same THRR, a lower PHRR means lower fire hazard and flame spreading [20].

Graphene and its products in general improve the thermal stability of the polymers and reduce the time to ignition t_{ig} as shown in Table I [21]. Time to ignition is recorded when the HRR exceeds 10 kW/m^2 for the first time. Adding 1 wt% graphene reduces t_{ig} from 41 s for pure PMMA to 23 s. Authors in [23] reported that the addition of 1 wt% graphene oxide to polypropylene decreases the t_{ig} to 39 s from 49 s.

Figure 7 shows the mass loss rate for pure PMMA and PMMA-graphene composites materials recorded in the cone calorimeter tests. The heat release rate from the samples depends on the amount of gas volatiles released from the sample. So, the mass loss rate curves have identical trends as the heat released rate curves. PMMA has the largest Peak Mass Loss Rate (PMLR) of 33 g/m^2 s. The PMLR of PMMA-1 wt% graphene composite is reduced by 22% and even more PMLR reduction was obtained (30%) when graphene increased to 3 wt%.

The thermal conductivity of PMMA is reduced by the addition of graphene [24]. The presence of graphene in PMMA suppresses the transfer of the heat generated by the cone calorimeter from the surface layer of the tested sample to the inner layers, reducing the pyrolysis of PMMA. As a result, the volatile gases are reduced and the mass loss rate is affected. In addition, the mass loss rate depends on the rate of volatile gases released from the surface of the sample. The presence of nano fillers in polymers reduces gas permeability [25]. Authors in [26] found that the gas permeability of PMMA matrix reduced by 50% when 1 wt% oxide grapheme was inserted and with further addition to 10 wt%, the nancomposite became impermeable. However, the gas permeability of nanocomposites depends on the nanofiller aspect ratio, volume fraction, and the distribution uniformity inside the polymer. Graphene as a single layer of graphite has a high aspect ratio of 2630 m^2/g [27].

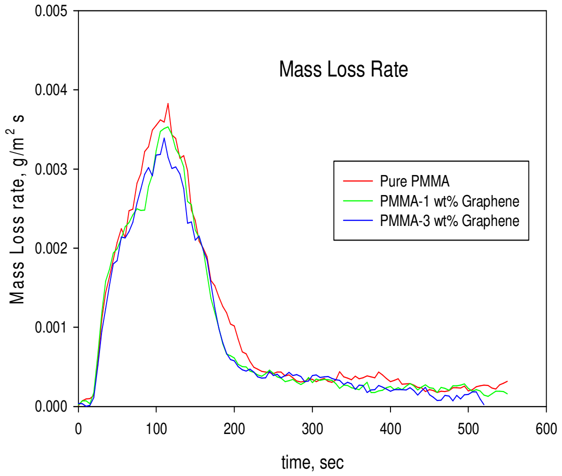


Fig. 7. Mass loss rate of PMMA and its composites.

The effect of the addition of graphene to PMMA to produce composite materials can be observed from the rate production of CO and CO_2 generated from the combustion of volatile gases. Figure 8 shows the production rate of CO and CO_2 from pure PMMA and PMMA-graphene composites. It seems that the production of CO and CO_2 shows the same trends of heat release rate.

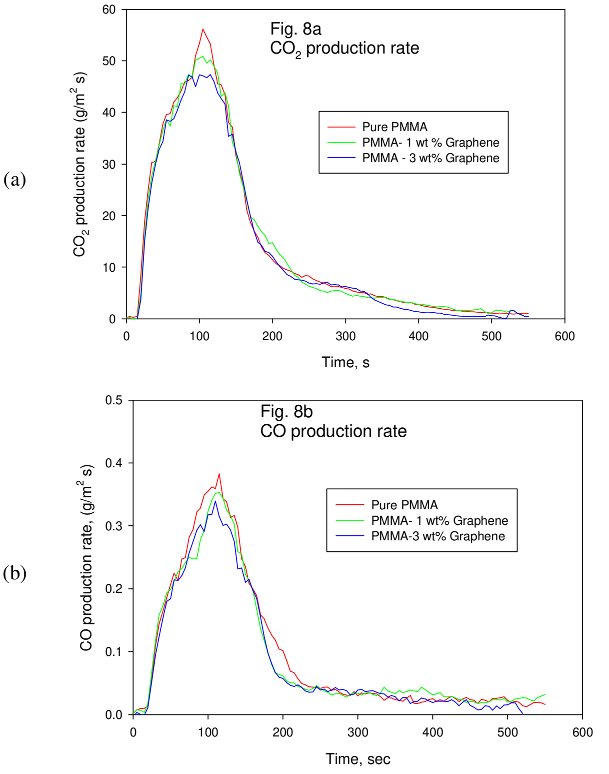


Fig. 8. Production rate of (a) CO_2 and (b) CO during combustion.

IV. CONCLUSIONS

In this study, two levels of graphene particles were mixed with pure PMMA and pressed in a prepared mold, and the resulting composite materials were studied with regard to their flame retardancy. The main conclusions of the current study are:

- The addition of graphene particles enhances the flame retardancy of PMMA
- The peak heat release rate of composite materials (PMMA-graphene) is less than pure PMMA's, while there is no change between the total heat release rate.
- The time to ignition decreases from 40 s for pure PMMA to 20 s for 3 wt% added graphene to PMMA.
- Mass loss rate decreases when graphene is added to PMMA.
- The production of CO_2 and CO from the combustion of pure PMMA and PMMA-graphene nanocomposites have the same trends.

REFERENCES

[1] Y. Zhang, X. Yu, and Z. Cheng, "Research on the Application of Synthetic Polymer Materials in Contemporary Public Art," *Polymers*,

vol. 14, no. 6, Jan. 2022, Art. no. 1208, https://doi.org/10.3390/polym14061208.

[2] M. Danikas and S. Morsalin, "A Short Review on Polymer Nanocomposites for Enameled Wires: Possibilities and Perspectives," *Engineering, Technology & Applied Science Research*, vol. 9, no. 3, pp. 4079–4084, Jun. 2019, https://doi.org/10.48084/etasr.2678.

[3] T. Rajkumar, N. Muthupandiyan, and C. T. Vijayakumar, "Synthesis and investigation of thermal properties of PMMA-maleimide-functionalized reduced graphene oxide nanocomposites," *Journal of Thermoplastic Composite Materials*, vol. 33, no. 1, pp. 85–96, Jan. 2020, https://doi.org/10.1177/0892705718804595.

[4] B. Sang, Z. Li, X. Li, L. Yu, and Z. Zhang, "Graphene-based flame retardants: a review," *Journal of Materials Science*, vol. 51, no. 18, pp. 8271–8295, Sep. 2016, https://doi.org/10.1007/s10853-016-0124-0.

[5] L. Xu *et al.*, "Preparation and Study on the Flame-Retardant Properties of CNTs/PMMA Microspheres," *ACS Omega*, vol. 7, no. 1, pp. 1347–1356, Jan. 2022, https://doi.org/10.1021/acsomega.1c05606.

[6] Q. Liu *et al.*, "Recent advances in the flame retardancy role of graphene and its derivatives in epoxy resin materials," *Composites Part A: Applied Science and Manufacturing*, vol. 149, Oct. 2021, Art. no. 106539, https://doi.org/10.1016/j.compositesa.2021.106539.

[7] J. Shen, J. Liang, X. Lin, H. Lin, J. Yu, and S. Wang, "The Flame-Retardant Mechanisms and Preparation of Polymer Composites and Their Potential Application in Construction Engineering," *Polymers*, vol. 14, no. 1, Jan. 2022, Art. no. 82, https://doi.org/10.3390/polym14010082.

[8] L. Xu, J. Jiang, L. Ni, Z. Chen, and C. Li, "Preparation and study of the flame retardant properties of C 60 /PMMA microspheres," *RSC Advances*, vol. 12, no. 35, pp. 22623–22630, 2022, https://doi.org/10.1039/D2RA03642H.

[9] Z. Wang, P. Wei, Y. Qian, and J. Liu, "The synthesis of a novel graphene-based inorganic–organic hybrid flame retardant and its application in epoxy resin," *Composites Part B: Engineering*, vol. 60, pp. 341–349, Apr. 2014, https://doi.org/10.1016/j.compositesb.2013.12.033.

[10] A. Kausar, "Poly(methyl methacrylate) nanocomposite reinforced with graphene, graphene oxide, and graphite: a review," *Polymer-Plastics Technology and Materials*, vol. 58, no. 8, pp. 821–842, May 2019, https://doi.org/10.1080/25740881.2018.1563112.

[11] A. S. Alghamdi, "Synthesis and Mechanical Characterization of High Density Polyethylene/Graphene Nanocomposites," *Engineering, Technology & Applied Science Research*, vol. 8, no. 2, pp. 2814–2817, Apr. 2018, https://doi.org/10.48084/etasr.1961.

[12] M. J. Allen, V. C. Tung, and R. B. Kaner, "Honeycomb Carbon: A Review of Graphene," *Chemical Reviews*, vol. 110, no. 1, pp. 132–145, Jan. 2010, https://doi.org/10.1021/cr900070d.

[13] G. Huang, S. Wang, P. Song, C. Wu, S. Chen, and X. Wang, "Combination effect of carbon nanotubes with graphene on intumescent flame-retardant polypropylene nanocomposites," *Composites Part A: Applied Science and Manufacturing*, vol. 59, pp. 18–25, Apr. 2014, https://doi.org/10.1016/j.compositesa.2013.12.010.

[14] R. N. Singh and C. S. Sharma, "Preparation of Bimetallic Pd-Co Nanoparticles on Graphene Support for Use as Methanol Tolerant Oxygen Reduction Electrocatalysts," *Engineering, Technology & Applied Science Research*, vol. 2, no. 6, pp. 295–301, Dec. 2012, https://doi.org/10.48084/etasr.215.

[15] B. Tawiah *et al.*, "Highly efficient flame retardant and smoke suppression mechanism of boron modified graphene Oxide/Poly(Lactic acid) nanocomposites," *Carbon*, vol. 150, pp. 8–20, Sep. 2019, https://doi.org/10.1016/j.carbon.2019.05.002.

[16] X. Wang, E. N. Kalali, J.-T. Wan, and D.-Y. Wang, "Carbon-family materials for flame retardant polymeric materials," *Progress in Polymer Science*, vol. 69, pp. 22–46, Jun. 2017, https://doi.org/10.1016/j.progpolymsci.2017.02.001.

[17] W. Liu, D.-Q. Chen, Y.-Z. Wang, D.-Y. Wang, and M.-H. Qu, "Char-forming mechanism of a novel polymeric flame retardant with char agent," *Polymer Degradation and Stability*, vol. 92, no. 6, pp. 1046–1052, Jun. 2007, https://doi.org/10.1016/j.polymdegradstab.2007.02.009.

[18] P. Yang, H. Wu, F. Yang, J. Yang, R. Wang, and Z. Zhu, "A Novel Self-Assembled Graphene-Based Flame Retardant: Synthesis and Flame Retardant Performance in PLA," *Polymers*, vol. 13, no. 23, Jan. 2021, Art. no. 4216, https://doi.org/10.3390/polym13234216.

[19] Z. Wang, S. H. Xu, L. X. Wu, and D. X. Zhuo, "Flammability and Thermal Degradation of PMMA/Graphene Composites," *Advanced Materials Research*, vol. 910, pp. 31–34, 2014, https://doi.org/10.4028/www.scientific.net/AMR.910.31.

[20] M. M. Hirschler, "Flame retardants and heat release: review of traditional studies on products and on groups of polymers," *Fire and Materials*, vol. 39, no. 3, pp. 207–231, 2015, https://doi.org/10.1002/fam.2243.

[21] M. Sabet, H. Soleimani, E. Mohammadian, and S. Hosseini, "The Effect of Graphene Oxide on Flame Retardancy of Polypropylene and Polystyrene," *Materials Performance and Characterization*, vol. 9, no. 1, pp. 284–292, Jul. 2020, https://doi.org/10.1520/MPC20190256.

[22] X. Wang, W. Xing, X. Feng, B. Yu, L. Song, and Y. Hu, "Functionalization of graphene with grafted polyphosphamide for flame retardant epoxy composites: synthesis, flammability and mechanism," *Polymer Chemistry*, vol. 5, no. 4, pp. 1145–1154, Jan. 2014, https://doi.org/10.1039/C3PY00963G.

[23] M. Sabet and H. Soleiman, "Graphene Impact on Thermal Characteristics of LDPE," *Polymer Science, Series A*, vol. 61, no. 6, pp. 922–930, Nov. 2019, https://doi.org/10.1134/S0965545X20010095.

[24] D. Mohanalakshmi, S. Duggal, V. V. Nandini, and D. Charles, "Thermal conductivity of graphene incorporated heat activated polymethyl methacryate: A pilot study," *The Journal of Prosthetic and Implant Dentistry*, vol. 3, no. 1, pp. 51–56, 2019.

[25] M. A. Priolo, D. Gamboa, K. M. Holder, and J. C. Grunlan, "Super Gas Barrier of Transparent Polymer−Clay Multilayer Ultrathin Films," *Nano Letters*, vol. 10, no. 12, pp. 4970–4974, Dec. 2010, https://doi.org/10.1021/nl103047k.

[26] S. Morimune, T. Nishino, and T. Goto, "Ecological Approach to Graphene Oxide Reinforced Poly (methyl methacrylate) Nanocomposites," *ACS Applied Materials & Interfaces*, vol. 4, no. 7, pp. 3596–3601, Jul. 2012, https://doi.org/10.1021/am3006687.

[27] Y. Arao, Y. Mizuno, K. Araki, and M. Kubouchi, "Mass production of high-aspect-ratio few-layer-graphene by high-speed laminar flow," *Carbon*, vol. 102, pp. 330–338, Jun. 2016, https://doi.org/10.1016/j.carbon.2016.02.046.