EFFECT OF GRAPHENE ON THE FLAMMABILITY BEHAVIOR OF POLYIMIDE-GRAPHENE COMPOSITES

Caroline J. Akinyi 1, Jude O. Iroh 2

University of Cincinnati
Cincinnati, OH, USA

ABSTRACT

The presence of graphene in the composites resulted in a remarkable decrease in the heat of combustion of the polymer by up to 81% at 50 wt.% graphene. An increase from 0- 50 wt.% graphene led to a 77% decrease in HRC indicating that the presence of graphene contributed to the increase in anti-flammability behavior of polyimide. The decrease in HRC slowed down at 30 wt.% graphene, showing only a 2.7% decrease between 30 wt.% and 50 wt.%. The rate of degradation was also shown to significantly decrease by up to 85% from 0-50 wt.% graphene

1. INTRODUCTION

Graphene is a two-dimensional nano-filler with one-atom thick planar sheet sp^2 bonded carbon atoms, tightly packed in a honeycomb crystal lattice[1]. It is the thinnest material known, possessing unusual electrical characteristics (carrier mobilities of up to 200,000 $cm^2V^{-1}s^{-1}$)[[2],[3], [4]], thermal conductivity (4840-5300 $Wm^{-1}K^{-1}$)[5] and Young's modulus (E=1.0 TPA)[6]. Due to these extraordinary properties, the use of graphene has increased in recent years, finding applications in polymer nanocomposites where they are used as nano-fillers to improve the thermal, mechanical, electrical and flame-retardant properties of the polymers [[7],[8],[9],[10],[11],[12],[13]] .

Aromatic polyimide resins have high thermal stability (>300°C), high tensile strength, excellent radiation shielding capability, flexibility and low color. These excellent properties make them attractive for applications in the electronics and aerospace industries [[14],[15],[16],[17],[18],[19],[20],[21],[22],[23],[24],[25]]. Although they are inherently thermally stable and flame retardant, their thermal stability can be improved further for even higher temperature applications hence replacing their metal counterparts, providing the combined benefits of heat resistance and low weight.

SAMPE Conference Proceedings. Charlotte, NC, May 20-23, 2019. Society for the Advancement of Material and Process Engineering – North America.

Most fire retardants developed in the years preceding 2006 were based on halogenated compounds such as bromine and chlorine. Examples include chlorowax, tetrabromobisphenol A, tribromophenol, phosphorus tribromide, among others[26] Although these halogenated flame retardants act effectively to suppress flames, their toxicity and environmental health concerns have led to legislation in various countries that aim to restrict halogenated compounds in the synthesis of flame retardants. These regulations have forced associated industries to come up with innovative and better solutions to formulating flame retardants[27].

Graphene acts by forming char as a barrier protecting the polymer from external heat source and minimizing the transfer of combustible gases generated by the decomposition of the polymer. It's high thermal stability and large specific surface adsorption capability reduces heat and mass transfer[28]. Huang et al. found that the addition of 3 % graphene nanosheets to poly (vinyl alcohol) reduced the peak heat release rate (PHRR) by 49 %[32]

The pyrolytic degradation of an organic polymer in the condensed phase to yield combustible volatile products can be regarded as the first stage in the flaming combustion of the polymer. The presence of flame retardants in the polymer can affect the rate and mode of pyrolysis of the polymer in the condensed phase[33]. The use of thermoanalytical techniques can provide insight into the stages of pyrolytic breakdown of polymers, their thermal stability and the nature and amount of solid residues and volatile products[33]. The role played in combustion by the initial condensed phase burning of the polymer can therefore be well understood from these studies. Direct measurement of the flammability and fire behavior of materials requires large quantities of materials and can be prohibitively expensive. In this work, the thermal and combustion properties of milligram sized samples were obtained using differential scanning calorimetry (DSC).

2. EXPERIMENTATION

Neat polyimide (PI) and polyimide-graphene composites (PI/GNS) with varying graphene compositions (10, 20, 30, 40 and 50 wt.%) were subjected to a heating rate of 10 °C/min in nitrogen and air atmosphere, from 25 °C to 725 °C in a DSC Q20 thermal analyzer purchased from TA instruments, New Castle, Delaware, USA. The samples were used as prepared by Longun and Iroh [34]. Results were analyzed using OriginPro 8.5 software.

3. RESULTS

3.1 Degradation in nitrogen

Figure 1 shows DSC thermograms obtained from degradation of the samples in nitrogen. The areas under the peaks correspond to the pyrolytic heat of degradation of the composites. The peak degradation temperature shifts to lower temperatures by up to 33 °C. On the other hand, the onset temperature of degradation slightly shifts towards higher temperatures by up to 20 °C. The peaks become less broad from neat PI to 50 wt.% PI/GNS indicating that less of the polymer resin is being degraded as the graphene content is increased.

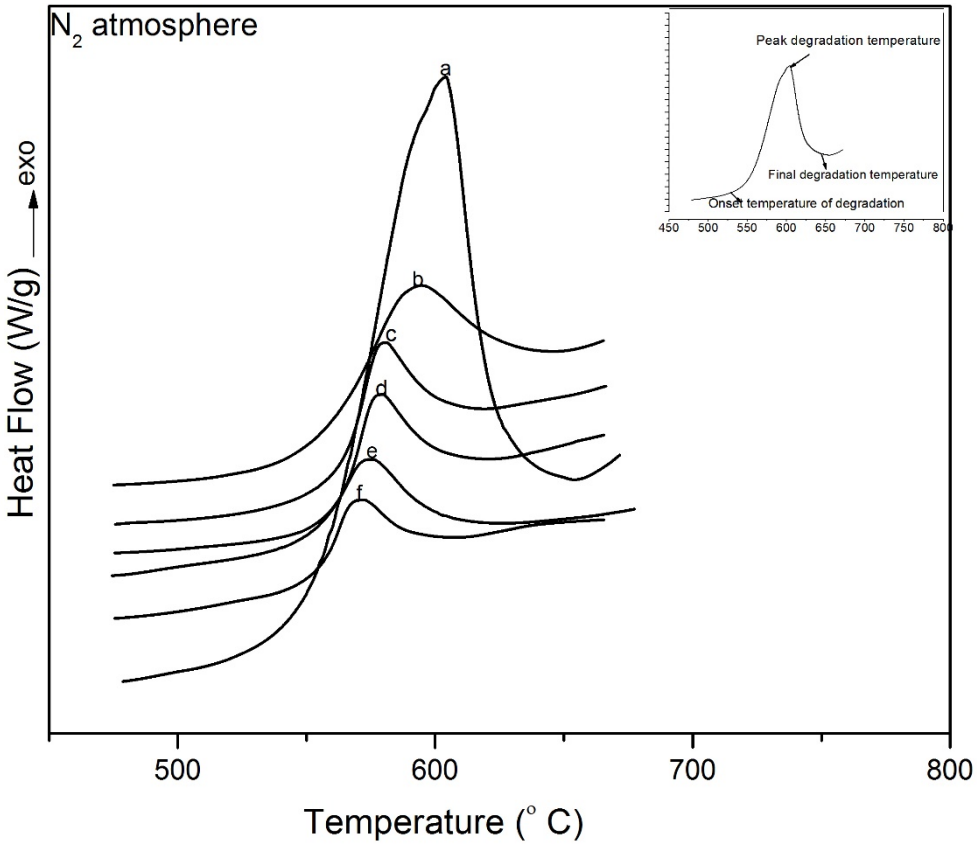

Figure 1: DSC thermograms of neat PI and PI/GNS composites (a) neat PI (b) 10 wt.% (c) 20 wt.% (d) 30 wt.% (e) 40 wt.% (f) 50 wt.% NGS

Figure 2 shows the total heat of degradation of the samples as calculated from the areas under the peaks of the DSC thermograms shown in figure 1. The heat of degradation decreases by 92 % from the neat PI to 50 wt.% PI/GNS. The heat of degradation changes drastically by 75 % from neat PI to 10 wt.% PI/GNS then gradually from 10 wt.% to 50 wt.% PI/GNS. An extrapolation of the data gives the optimum weight percentage of graphene as 8 wt.%. This amount of graphene

in the composite will lead to a low heat of degradation with the added advantage of using less graphene and therefore improving dispersion within the polymer matrix.

Graphene acts by forming a dense, coherent and continuous char layer upon exposure to a flame or heat source. This layer acts like a physical barrier that limits the transfer of heat from the source to the polymer and slows down the diffusion of pyrolysis products from the polymer substrate. The retention of substantial amounts of solid residue due to the presence of graphene helps to minimize the degradation of the underlying polymer, hence conserving its structural integrity.

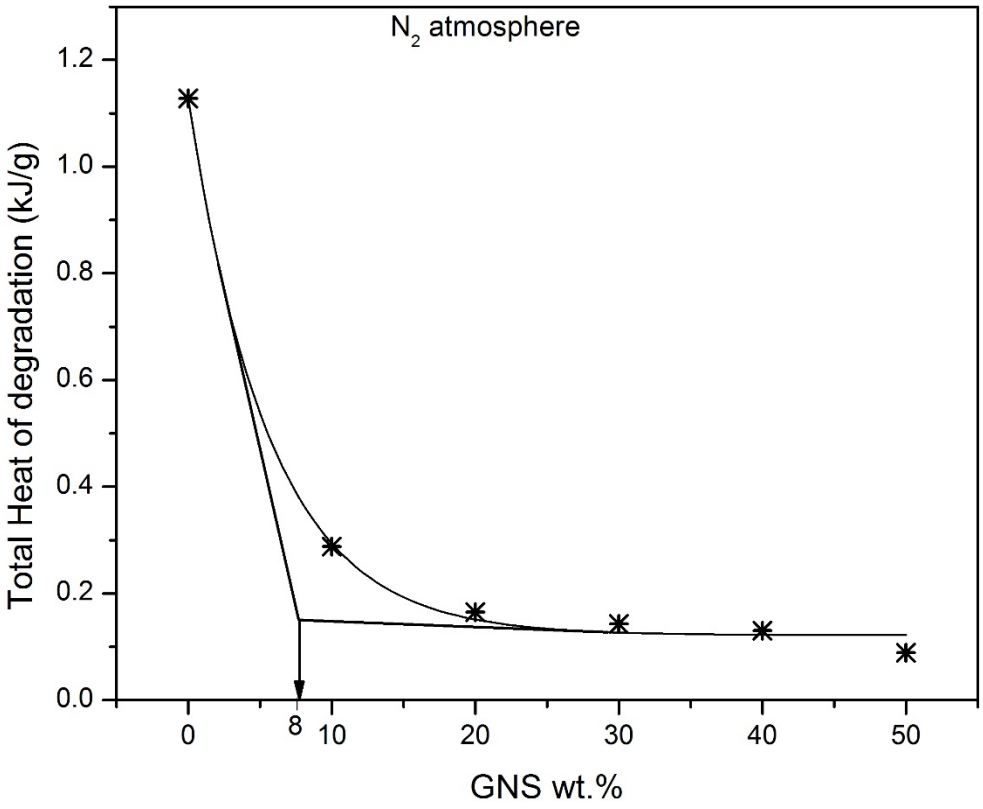

Figure 2: Figure 2: Total heat of degradation of the neat PI and PI/GNS composites as measured by DSC in nitrogen atmosphere at a heating rate of 10°C/min

3.2 Degradation in Air

Figure 3 shows combustion thermograms obtained from DSC in air atmosphere. The thermograms display two decomposition peaks, corresponding to polyimide decomposition and char decomposition. The areas under the peaks decrease with increasing graphene content. The heat of combustion of the polyimide matrix was calculated by integrating the area under the polymer decomposition peak.

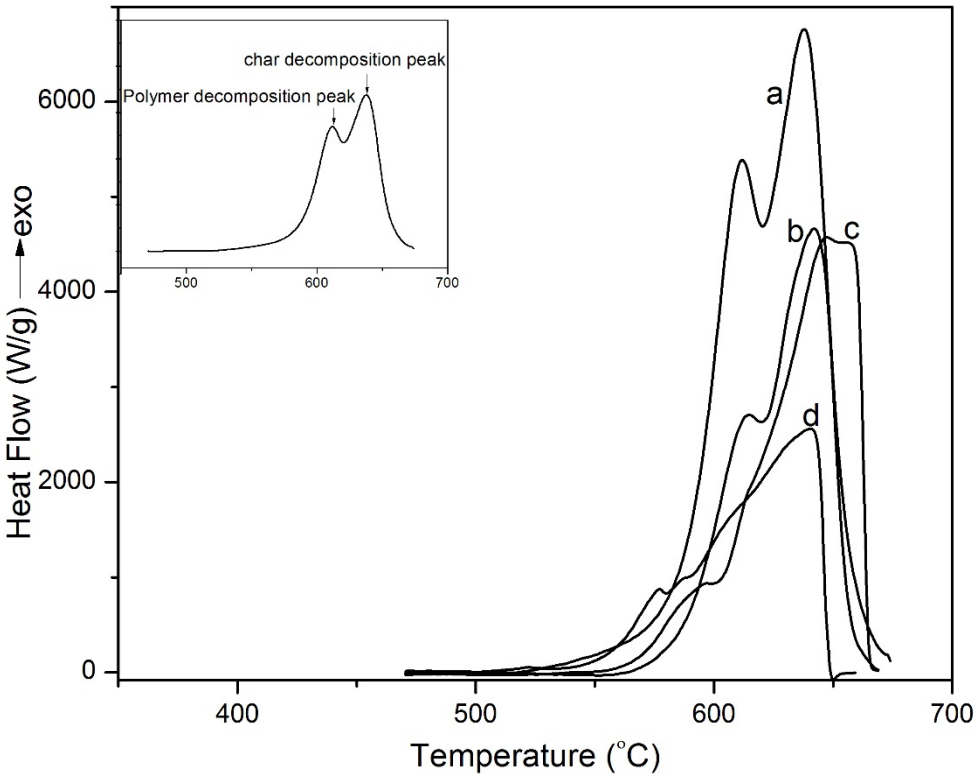

Figure 3: Combustion thermograms (a) Neat PI (b) 10 wt.% (c) 30 wt.% (d) 50 wt.% GNS, at a heating rate of 10°C/min

The heat of combustion of the polyimide matrix decreases by up to 81 % at 50 wt.% graphene. On the other hand, the char retention is shown to increase as the amount of graphene in the composite increases. This indicates that as the char retention increases, the polyimide resin is better shielded from the source of heat, thereby reducing the amount of polymer degraded and in effect, the heat of combustion of the polymer.

3.3 Heat Release Capacity

The heat release capacity is described as the maximum amount of heat released by combustion per degree of temperature rise per unit mass of polymer in mesophase. It combines the thermal stability and combustion properties of a material[35].The heat release capacity was obtained from the combustion thermograms shown in figure 3. The heats of combustion of the polymer matrix was used in the calculations using equation 1 below. Activation energy values were previously calculated using the Horowitz-Metzger method [36]

$$\eta_c = \frac{h_c^o(1-\mu)E_a}{eRT_P^2} \approx \frac{h_{c,p}^o}{\Delta T_p} \quad [1]$$

Where η_c is the heat release capacity, $h_{c,p}^o$ is the heat of combustion of the fuel (polymer), $\Delta T_p = eRT_P^2/E_a$, is the half width of the pyrolysis temperature interval, T_p is the temperature at the maximum fuel generation rate during a linear heating program, E_a is the global activation energy of the single-step pyrolysis process, R is the gas constant and e is the natural number[35].
From the equation above, the heat release capacity is directly proportional to the heat of combustion of the fuel and inversely proportional to its thermal stability.
Figure 4 shows the plot of the heat release capacity against wt.% graphene. This is shown to decrease by up to 77 % from 0- 50 wt.% graphene indicating an improvement in thermal stability.

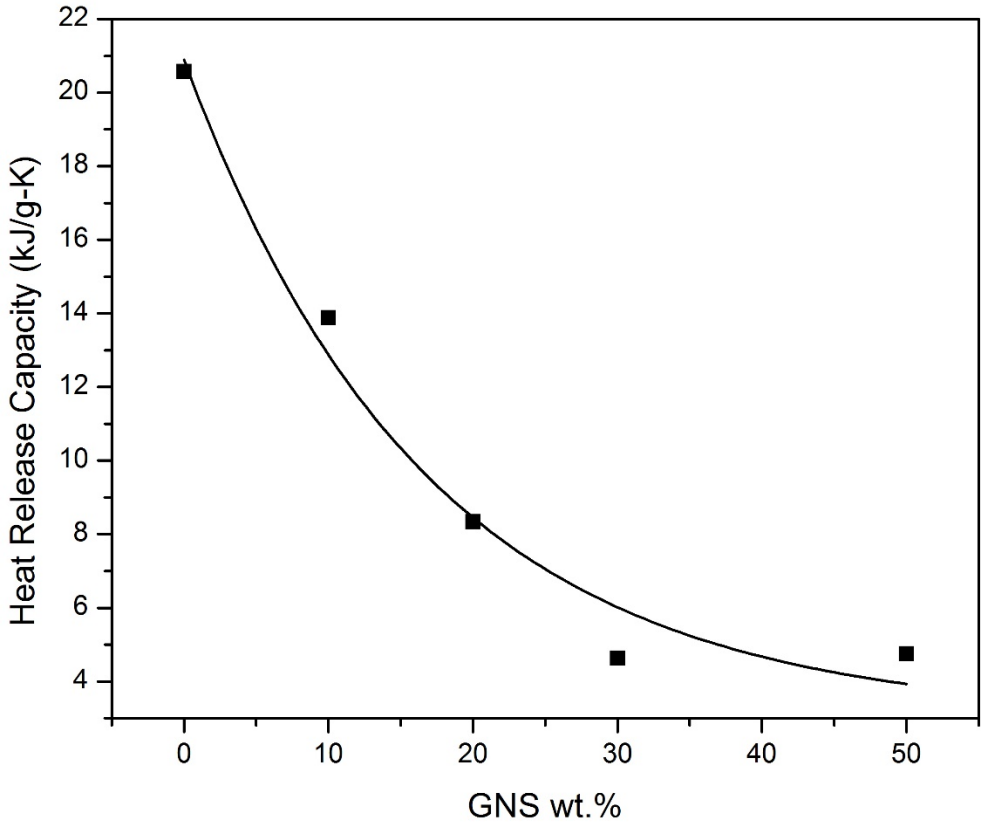

Figure 4: Heat release capacity of polyimide-graphene samples as a function of composition.

4. CONCLUSIONS

The effect of graphene on the combustion properties of polyimide was studied using differential scanning calorimetry. The total heat and the rate of degradation were shown to decrease with increasing graphene content. The heat release capacity was also shown to decrease with increasing graphene content, indicating an improvement in thermal stability and decrease in heat of combustion of the fuel. This is attributed to the shielding properties of graphene sheets by the formation of a continuous char layer around the polyimide matrix.

5. REFERENCES

[1] Kuilla, T., Bhadra, S., Yao, D., Kim, N. H., Bose, S., & Lee, J. H. "Recent advances in graphene based polymer composites." *Progress in Polymer Science* (2010). https://doi.org/10.1016/j.progpolymsci.2010.07.005

[2] Geim, A. K., & Macdonald, A. H. Graphene: "Exploring carbon flatland." *Physics Today*, *60*, 35 (2007). https://doi.org/10.1063/1.2774096

[3] Si, Y., & Samulski, E. T. "Synthesis of Water Soluble Graphene." *23*, 42 (2019). https://doi.org/10.1021/nl080604h

[4] Du, X., Skachko, I., Barker, A., & Andrei, E. Y. "Approaching ballistic transport in suspended graphene." *Nature Nanotechnology*, *3*(8), 491–495 (2008). https://doi.org/10.1038/nnano.2008.199

[5] Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan, D., Miao, F., & Lau, C. N. (n.d.). "Superior Thermal Conductivity of Single-Layer Graphene." https://doi.org/10.1021/nl0731872

[6] Lee, Y. R., Raghu, A. V., Jeong, H. M., & Kim, B. K. "Properties of Waterborne Polyurethane/Functionalized Graphene Sheet Nanocomposites Prepared by an in situ Method." *Macromolecular Chemistry and Physics*, *210*(15), 1247–1254 (2009). https://doi.org/10.1002/macp.200900157

[7] Eda, G., & Chhowalla, M. (n.d.). "Graphene-based Composite Thin Films for Electronics." https://doi.org/10.1021/nl8035367

[8] Liang, J., Xu, Y., Huang, Y., Zhang, L., Wang, Y., Ma, Y., … Chen, Y. (n.d.). "Infrared-

Triggered Actuators from Graphene-Based Nanocomposites." https://doi.org/10.1021/jp901284d

[9] Kim, H., & Macosko, C. W. "Processing-property relationships of polycarbonate/graphene composites." *Polymer*, *50*(15), 3797–3809 (2009). https://doi.org/10.1016/J.POLYMER.2009.05.038

[10] Quan, H., Zhang, B., Zhao, Q., Yuen, R. K. K., & Li, R. K. Y. "Facile preparation and thermal degradation studies of graphite nanoplatelets (GNPs) filled thermoplastic polyurethane (TPU) nanocomposites." *Composites Part A: Applied Science and Manufacturing*, *40*(9), 1506–1513 (2009). https://doi.org/10.1016/J.COMPOSITESA.2009.06.012

[11] Xu, Y., Wang, Y., Liang, J., Huang, Y., Ma, Y., Wan, X., & Chen, Y. "A hybrid material of graphene and poly (3,4-ethyldioxythiophene) with high conductivity, flexibility, and transparency." *Nano Research*, *2*(4), 343–348 (2009). https://doi.org/10.1007/s12274-009-9032-9

[12] Lee, Y. R., Raghu, A. V., Jeong, H. M., & Kim, B. K. "Properties of Waterborne Polyurethane/Functionalized Graphene Sheet Nanocomposites Prepared by an in situ Method." *Macromolecular Chemistry and Physics*, *210*(15), 1247–1254 (2009). https://doi.org/10.1002/macp.200900157

[13] Ramanathan, T., Abdala, A. A., Stankovich, S., Dikin, D. A., Herrera-Alonso, M., Piner, R. D., … Brinson, L. C. "Functionalized graphene sheets for polymer nanocomposites." *Nature Nanotechnology*, *3*(6), 327–331 (2008a). https://doi.org/10.1038/nnano.2008.96

[14] Yoonessi, M., Shi, Y., Scheiman, D. A., Lebron-Colon, M., Tigelaar, D. M., Weiss, R. A., & Meador, M. A. "Graphene polyimide nanocomposites; Thermal, mechanical, and high-temperature shape memory effects." *ACS Nano*, *6*(9), 7644–7655 (2012). https://doi.org/10.1021/nn302871y

[15] Adamczak, A. D., Spriggs, A. A., Fitch, D. M., Awad, W., Wilkie, C. A., & Grunlan, J. C. "Thermal Degradation of High-Temperature Fluorinated Polyimide and its Carbon Fiber Composite." *J Appl Polym Sci*, *115*, 2254–2261 (2009). https://doi.org/10.1002/app.31321

[16] Meador, M. A. "Recent advances in the development of processable high-temperature polymers." *Annu. Rev. Mater. Sci* (Vol. 28) (1998). Retrieved from www.annualreviews.org

[17] Li, Y., & Morgan, R. J. "Thermal cure of phenylethynyl-terminated AFR-PEPA-4 imide oligomer and a model compound." *Journal of Applied Polymer Science*, *101*(6), 4446–4453 (2006). https://doi.org/10.1002/app.24047

[18] Ju, J., & Morgan, R. J. "Characterization of Microcrack Development in BMI-Carbon Fiber Composite under Stress and Thermal Cycling." *Journal of Composite Materials*, *38*(22) (2004). https://doi.org/10.1177/0021998304044773

[19] Li, Y., Obando, N., Tschen, F., & Morgan, R. J. "Thermal analysis of phenylethynyl end-capped fluorinated imide oligomer afr-pepa-4." *Journal of Thermal Analysis and Calorimetry*, *85*(1), 125–129 (2006). https://doi.org/10.1007/s10973-005-7355-7

[20] Cella, J. A." Degradation and stability of polyimides." *Polymer Degradation and Stability*, *36*(2), 99–110 (1992). https://doi.org/10.1016/0141-3910(92)90145-U

[21] Chen Shiyong Yang Zhiqiang Tao Aijun Lin Fan, J. H. (n.d.). "Processing and Properties of Carbon Fiber-reinforced PMR Type Polyimide Composites." https://doi.org/10.1177/0954008306063395

[22] Lincoln, J. E., Morgan, R. J., & Shin, E. E. "Effect of thermal history on the deformation and failure of polyimides." *Journal of Polymer Science Part B: Polymer Physics*, *39*(23), 2947–2959 (2001). https://doi.org/10.1002/polb.10043

[23] Kung, H.-K. (n.d.). "Effects of Surface Roughness on High-temperature Oxidation of Carbon-fiber-reinforced Polyimide Composites." https://doi.org/10.1177/0021998305051801

[24] Cho, D., & Drzal, L. T. "Characterization, properties, and processing of LaRC PETI-5 as a high-temperature sizing material. II. Thermal characterization." *Journal of Applied Polymer Science*, *75*(10), 1278–1287 (2000). https://doi.org/10.1002/(SICI)1097-4628(20000307)75:10<1278::AID-APP9>3.0.CO;2-M

[25] Li, Y., Murphy, L. A., Lincoln, J. E., & Morgan, R. J."Phenylethynyl End-Capped Fluorinated Imide Oligomer AFR-PEPA-N: Morphology and Processibility

Characteristics." *Macromolecular Materials and Engineering*, *292*(1), 78–84 (2007). https://doi.org/10.1002/mame.200600306

[26] Lewin, M., Atlas, S. M., & Pearce, E. M. . *Flame - Retardant Polymeric Materials : Volume 3*. Springer New York (1982)

[27] Morgan, A. B., & Wilkie, C. A. Non-Halogenated Flame Retardant Handbook. *Non-Halogenated Flame Retardant Handbook*, 1–419 (2014). https://doi.org/10.1002/9781118939239

[28] Sang, B., Li, Z. wei, Li, X. hong, Yu, L. gui, & Zhang, Z. jun. "Graphene-based flame retardants: a review." *Journal of Materials Science*, *51*(18), 8271–8295 (2016). https://doi.org/10.1007/s10853-016-0124-0

[29] Ramanathan, T., Abdala, A. A., Stankovich, S., Dikin, D. A., Herrera-Alonso, M., Piner, R. D., … Brinson, L. C. "Functionalized graphene sheets for polymer nanocomposites." *Nature Nanotechnology*, *3*(6), 327–331 (2008b). https://doi.org/10.1038/nnano.2008.96

[30] Eda, G., & Chhowalla, M. "Graphene-based Composite Thin Films for Electronics." *Nano Letters*, *9*(2), 814–818 (2009). https://doi.org/10.1021/nl8035367

[31] Longun, J., & Iroh, J. O. "Polyimide/substituted polyaniline-copolymer-nanoclay composite thin films with high damping abilities." *Journal of Applied Polymer Science* (2013). https://doi.org/10.1002/app.36794

[32] Huang, G., Gao, J., Wang, X., Liang, H., & Ge, C. "How can graphene reduce the flammability of polymer nanocomposites."*Materials Letters*, *66*(1), 187–189 (2012). https://doi.org/10.1016/J.MATLET.2011.08.063

[33] Cullis, C. F. "The role of pyrolysis in polymer combustion and flame retardance." *Journal of Analytical and Applied Pyrolysis* (1987). https://doi.org/10.1016/0165-2370(87)85047-7

[34] Longun, J., & Iroh, J. O. "Nano-graphene/polyimide composites with extremely high rubbery plateau modulus." *Carbon*, *50*(5), 1823–1832 (2012). https://doi.org/10.1016/J.CARBON.2011.12.032

[35] Janssens, M. (2005). *Polymer Flammability*. Retrieved from

https://www.fire.tc.faa.gov/pdf/05-14.pdf

[36] Horowitz H. Hugh, & Metzger Gershon. "A New Analysis of Thermogravimetric Traces." *Analytical Chemistry*, *35*(10), 1464–1468 (1963). Retrieved from https://pubs.acs.org/doi/pdf/10.1021/ac60203a013