MRS Advances
https://doi.org/10.1557/s43580-023-00602-5

ORIGINAL PAPER

Testing and modeling of an in situ shear exfoliated 2D nanocomposite coating casing material for the suppression of Li-ion battery fires in electric vehicles

Md Abdur Rahman Bin Abdus Salam[1] · **Md Ashiqur Rahman**[1] · **Mohammad Humaun Kabir**[2] · **Elmmer Vera Alvarado**[1] · **Tousif Sadman**[3] · **Rajib Mahamud**[4] · **Lawrence Cano**[1] · **Ali Ashraf**[1]

Received: 16 May 2023 / Accepted: 9 June 2023

Abstract

A two-dimensional nanocomposite coating material, a mixture of dragon skin®(DS) (flame-resistant silicone elastomer and hexagonal boron nitride(hBN) (DS/hBN), was applied on the traditional polycarbonate battery casing material to study its effect on flame retardancy. A micro-batch mixer was used to simultaneously exfoliate hBN nanosheets from bulk layered hBN raw materials and disperse these nanolayers into both dragon skin polymer precursor and curing agent. Standard 'UL94 Flammability Test' protocol was followed to measure the flame retardancy of the prepared coating. The test showed enhanced flame retardancy in horizontal and vertical tests for DS/hBN sample as compared to the DS sample, which followed the trend found in numerical simulation. Additionally, the mechanical strength of DS/hBN-coated battery casing material remained intact even after prolonged flame exposure. This opens the door for manufacturing of low-cost hBN coating for robust electric vehicle battery casings.

Introduction

The requirements of high energy density Li-ion battery, along with its flammable electrolyte in electric and hybrid electric vehicles, makes it susceptible to abusive operating conditions leading to thermal runaway, gas venting, fires, and explosions [1–3].Though there are external cooling and in situ measures (e.g., coating of the cathode with inert materials) to prevent thermal runaway, still managing the generated heat as well as reducing the cell weight of the Lithium-ion battery (LIB) is a major challenge in the current research world [4, 5]. To resolve the issue, the demand for polymer composite based battery casing is growing tremendously due to their multifunctional properties and easy large-scale production [6]. However, low mechanical strength under thermal stress, easily ignitable nature, and low thermal conductivity limits their applications in this field [7, 8]. To reduce flammability, heat release rate, and smoke production of polycarbonate sheet, Vahabi et al. incorporated polyhedral oligomeric silsesquioxane (POSS) and resorcinol bis (diphenyl phosphate) (RDP) using melt blending [9]. The promotion of char layer formation was attributed to the phosphorus group in RDP, while POSS was found to enhance the thermo-oxidative resistance of this protective layer [9]. Addition of 0.5% wt. MgO into polycarbonate via melt compounding, the LOI (Limiting Oxygen Index) value increased from 26.5 for pure polycarbonate to 32.7 [10]. Catalyzing the thermal-oxidative degradation, MgO accelerated the formation of a thermal protection/mass loss barrier at the burning surface [10]. So, introducing new pathways to design new cell housing for LIBs opens a new research window in the current scientific world.

Cell housing for a battery demands a strong physical barrier that can resist mechanical abuse, electrical abuse, and thermal abuse [11]. Introducing 2D materials with

---

✉ Ali Ashraf
ali.ashraf@utrgv.edu

Md Abdur Rahman Bin Abdus Salam
mdabdurrahmanbinabdus.salam01@utrgv.edu

[1] Department of Mechanical Engineering, University of Texas Rio Grande Valley, Texas 78539, USA

[2] Department of Materials Science & Engineering, Texas A&M University, College Station, TX 77840, USA

[3] Department of Mechanical Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

[4] Department of Mechanical Engineering, Idaho State University, 1002 Sam Nixon Dr, Pocatello, ID 83201, USA

the polymer can be considered an excellent option for this application [12, 13]. They react to form a compact char layer which insulates the unburned polymer from ignition, thus increasing the fire retardancy of the polymer [13]. Moreover, 2D materials create tortuous paths to decrease the permeability of gas and water, eventually increasing the safety factor for the battery cell [14, 15]. Bin Yu et al. found that adding 2% functional reduced graphene oxide (FRGO) to epoxy reduced the peak heat release rate by 43% compared to pure epoxy resin. Incorporating 4% FRGO (FRGO/EP4) reduced the total heat release rate by 30.2% compared to pure epoxy resin [16]. Muratov et al. showed, addition of 29% ultrasonic exfoliated hBN with polypropylene enhanced the thermal conductivity to $0.721\text{Wm}^{-1}\ \text{k}^{-1}$ which is 4 times the pristine polypropylene [17]. As one of the graphene analogs with a unique isoelectronic structure, hBN exhibits an array of outstanding properties, including good in-plane thermal conductivity (200–600 W/mK), exceptionally high electrical insulation and breakdown strength, outstanding dielectric property, and low friction coefficients. These features make hBN a promising candidate for creating polymer composites with high integrated properties, containing the high thermal conductivity and flame retardancy because of the combined effect of its high aspect ratio 2D structure [18]. On the polymer side, silicone-based elastomers such as Dragon skin® have intrinsic flame retardancy. In addition, Dragon skin exhibits good thermal stability, chemical inertness, and an operating temperature range of a constant − 65°F to + 450°F. These 2D nanomaterial-composites have high flame retardancy by forming a 3D thermal conductive network that can quickly dissipate heat. [13, 19]. However, the high cost associated with nanomaterial fabrication and their agglomeration in polymer nanocomposite has hindered their applicability as advanced coating material. Here, we have proposed a facile fabrication technique using in situ shear exfoliation of inexpensive bulk hBN powder within silicone elastomer to obtain multifunctional nanocomposite coating with uniform nanofiller dispersion. Capable of large-scale production, this micro-batch mixer-based system can simultaneously exfoliate hBN nanosheets from bulk layered hBN raw materials and disperse these nanolayers into both dragon skin polymer precursor and curing agent. Batch mixing outperformed planetary and hand mixing in terms of dispersion, with a dispersion index (DI) of 0.07 compared to 0.0865 and 0.163 for planetary and manual mixing, respectively [20]. Polycarbonate (PC), a high-strength thermoplastic with excellent fatigue resistance, elastic modulus, impact strength, and heat aging resistance, has become a widely used engineering plastic used in battery casing [21]. This study examined polycarbonate as a candidate for cell housing by coating the sample with h-BN nanosheet combined elastomer.

Materials and methods

Materials

Hexagonal boron nitride (hBN) powder (surface area-$15\text{m}^2/\text{g}$) was purchased from ACS material, LLC. Dragon skin elastomer was provided by Smooth-on, Inc. Polycarbonate sheet (9″X8″X0.25″) was acquired from ‘Buy plastic’, an online shop via Amazon.

Method

A 2D nanocomposite coating material, a mixture of dragon skin® (flame-resistant silicone elastomer from Smooth on, Inc.), and hexagonal boron nitride (DS/hBN), was applied on the traditional polycarbonate casing material to study its effect on flame retardancy. Dragon skin polymer precursor (dragon skin part A) and curing agent (dragon skin part B) with 10% low-cost layered hBN were mixed separately in a Hauschild planetary mixer to get homogenous mixing (at 2500 rpm for 2 min). A micro-batch mixer was used to simultaneously exfoliate hBN nanosheets from bulk layered hBN raw materials and disperse these nanolayers into both dragon skin polymer precursor and curing agent separately (at 100 rpm for 10 min). Dragon skin polymer precursor and curing agent with exfoliated hBN were mixed in a 1:1 weight ratio to coat the polycarbonate and dried for 24 h.

The polycarbonate sheets were cut to dog bone shape using a bench top band saw according to ASTM D638-08, a standard test method for tensile properties of plastics. The specimens were 165 mm (about 6.5 in) in length, 19 mm (about 0.75 in) in width, and 6.7 mm (about 0.26 in) in thickness. The cut sample was coated with the DS/hBN nanomaterial using a film casting knife—Micrometer Adjustable Film Applicator—50 mm to ensure the uniform thickness of the coating. We measured thickness of the DS/hBN coating for 4 samples at 5 different areas for each sample using optical microscope (Celestron, USA). The maximum temperature of the samples was determined by taking the average temperature of ~ 50 pixels from the sample area in contact with the flame.

Characterization

UL-94 Standard has been followed for the flame resistance test of the samples [22]. Two tests, horizontal and vertical test were conducted (Fig. 1a, b). In the horizontal test, samples were kept horizontal, and two lines at 1″ and 4″ from the free end were marked. Samples were ignited in a high blue flame for 30 s and then allowed the flame to propagate until it extinguished spontaneously. The burn rate was calculated by measuring the burn length and time the

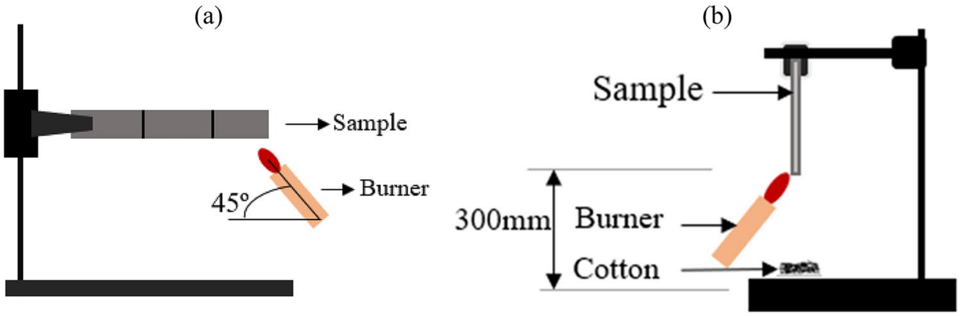


Fig. 1 UL-94 standard flame retardancy test setup. **a** Horizontal, **b** vertical test

sample took to extinguish. In the vertical test, samples were kept vertical and ignited with a blue flame. The flame was kept for 5 s, then 5-s rest and done 10 times for each sample tested. According to the test result, samples were categorized in UL 94 V-0, V-1, and V2.

Temperature distribution was measured using a Fluke RSE600 thermal camera with a close-up lens (Macro Infrared Lens RSE, 0.5x). Morphology was investigated before and after the flame test to check the distribution and characteristics of char formed due to the presence of hBN by a Zeiss ΣIGMA VP Scanning Electron Microscope. The tensile strength was tested on the MTS model 45 universal testing machine, according to ASTM D638-08, at a stretching speed or crosshead speed of 20 mm/min at ambient temperature. In mechanical testing, coatings were removed at two ends of the samples to ensure proper gripping in the instrument.

Results and discussion

In the UL-94 standard horizontal test, the DS/hBN-PC samples were fully quenched within 3 min and the flame could not reach the 1-inch marked line (Fig. 2). The burn rate was 9 mm/min. Whereas DS/PC sample took 11 min to be fully extinguished and the flame passed 1-inch line but could not propagate to reach 4-inch marked lines with a burn rate of 33 mm/min. The traditional polycarbonate stripe was also observed under this UL-94 test, and it was not extinguished naturally. It took 3 min 30 s to reach the 4-inch marked line. As the burn rate was lower than 75 mm for the DS and DS/hBN coating, they were categorized as 'Horizontal burning' (HB), and the traditional polycarbonate stripe was labeled as "Failed" illustrated in Fig. 2a.

In the vertical test, the flame extinguished spontaneously after 5 s and 15 s for DS/hBN and DS coating, respectively, after exposure to ignition. For the DS-coated sample, a crack was induced by the flame on the coating layer, which quickened the flame propagation from the inside (Fig. 2b). The DS/hBN-coated sample passed the vertical test with a V-0 rating as the flame extinguished spontaneously within 10 s of burning without the dripping of combustible material, while only the DS-coated sample failed the test as it had severe dripping. The char residue for DS/hBN was smooth and tightly packed (Fig. 2c). The protective char surface acts as a barrier to spread oxygen for further propagation of flame. Unlike DS/hBN-coated sample, char residue was fragile and cotton-like for DS-coated sample (Fig. 2b). A vertical test was also performed with multiple periodic flame exposure for 5 s (Fig. 3). After the first ignition for 5 s in the DS-coated sample, the flame spread quickly to the sample holder, leading to extensive damage to the sample and no

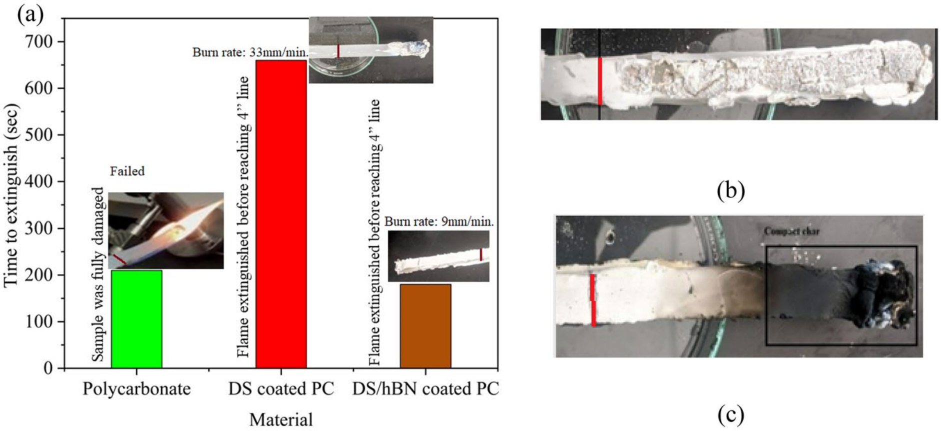
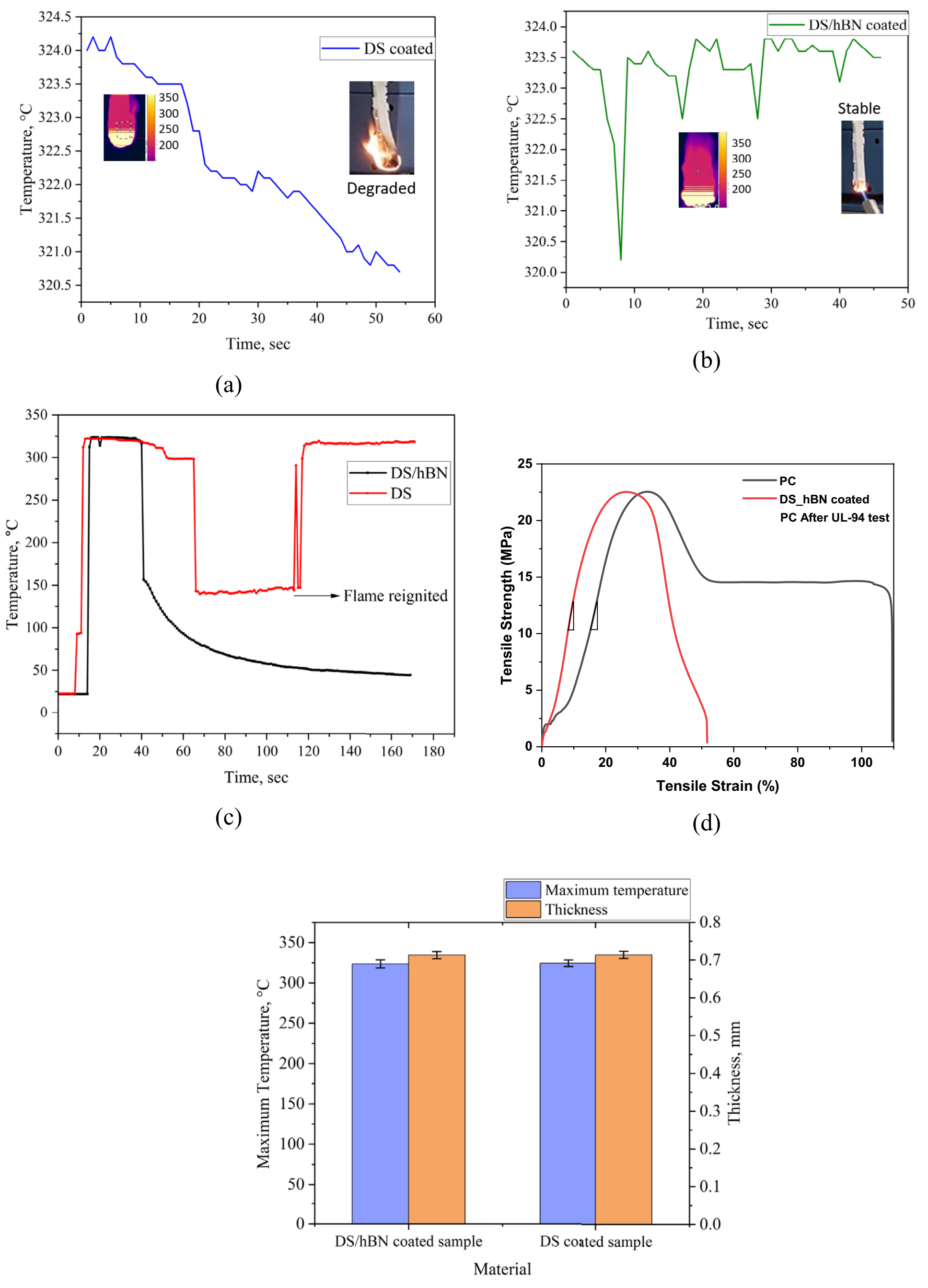


Fig. 2 **a** UL-94 horizontal test data. The red dotted line represents the 4-inch mark, **b** DS-coated PC sheet and **c** DS/hBN-coated PC sheet after UL-94 test

Fig. 3 Infrared thermography data. **a** DS-coated polycarbonate, **b** DS/hBN-coated polycarbonate stripe, **c** Maximum temperature profile DS and DS/hBN sample, **d** results from tensile strength test of polycarbonate stripe and DS/hBN-coated polycarbonate stripe after UL-94 flame retardancy test, **e** Variation of coating thickness and maximum temperature of the tested sample



(a) (b) (c) (d) (e)

further flame test could be performed (Fig. 3a). On the other hand, the temperature peak of the DS/hBN-coated sample after flame exposure decreased during 5 s of delay times, and the cyclic flame test was performed a total of 10 times (the first 4 times are shown in Fig. 3b). Figure 3c shows the temperature profile after the flame was removed from the samples at the end of the cyclic test. DS/hBN sample dissipates heat rapidly preventing the damage of the sample by quenching the flame and the temperature decreases close to 50 ºC from 324 °C (during flame exposure). DS-coated sample was slow in dissipating heat, which allowed flame to reach PC underneath the coating and again raising the temperature and damaging the sample (Fig. 3c).

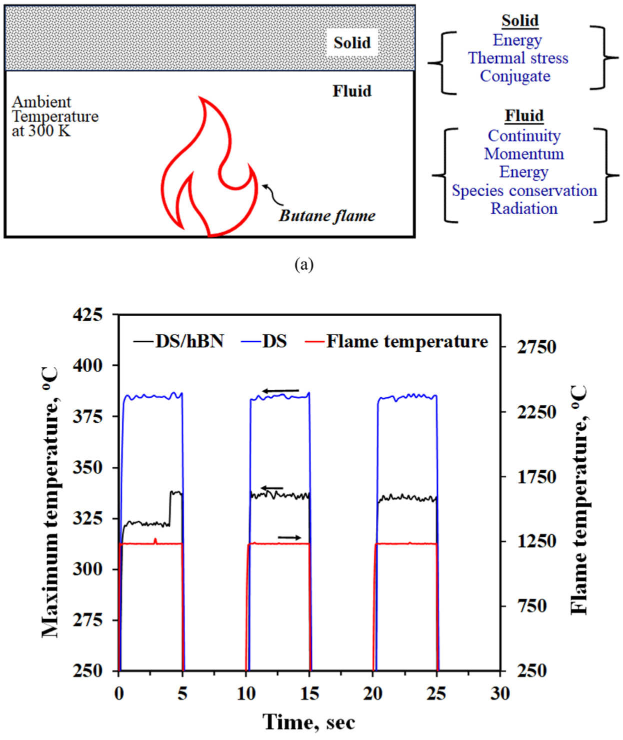
Coated and uncoated PC samples were tested for their mechanical strength. The representative stress–strain curve in Fig. 3d shows that the ultimate tensile strength of the unburned Polycarbonate stripe and the UL-94 tested sample are 22.4 MPa and 22.6 MPa, respectively, indicating that mechanical strength hasn't changed (0.9% difference) upon coating and exposure to flame.

The average film thickness of all the samples was 0.7135 ± 0.0095 mm and temperature variation were 321 ± 3.5 °C With variation of coating thickness, maximum temperature variation is negligible (Fig. 3e). Therefore, the coating showed reproducibility with regards to its flame-retardant characteristics.

Figure 4a, b shows the scanning electron microscopy image of the flame-tested DS/hBN-coated polycarbonate sheet. The surface morphology of the sample is composed of a regular three-dimensional network structure of hBN nanosheets and elastomer. The pores visible in the morphology of the burnt sample can prevent the heat transfer from the outside zone to the inside zone and thus achieve the excellent flame-retardant effect [23]. It is noteworthy that a significant portion of the h-BN sheets with the layer-by-layer structure are effectively coated on the surface of the polycarbonate sheet. This coating is crucial in achieving efficient flame retardancy of the casing material.

Numerical modeling

We developed a numerical model using a custom-made finite volume solver based on OpenFOAM [24]. The solver combined the capabilities of reactingFoam, chtMultiregionFoam, and solidDisplacementFoam. The model solves for a single-stage stoichiometric reaction, continuity, momentum, energy, and the radiation equation in the fluid region. In the solid region, the model considers conjugating heat transfer and thermal stress for both DS-coated and DS/hBN-coated materials. The schematic of the problem can be seen in Fig. 5a, while Fig. 5b illustrates the temperature in the solid region as well as the flame temperature. The results obtained from the numerical model agreed with the experimental findings. The DS/hBN sample demonstrated efficient heat dissipation, effectively preventing temperature elevation within the sample. Consequently, the maximum temperature calculated for the DS/hBN sample was approximately 330 °C, while the DS sample exhibited a maximum temperature of around 380 °C.



(a)

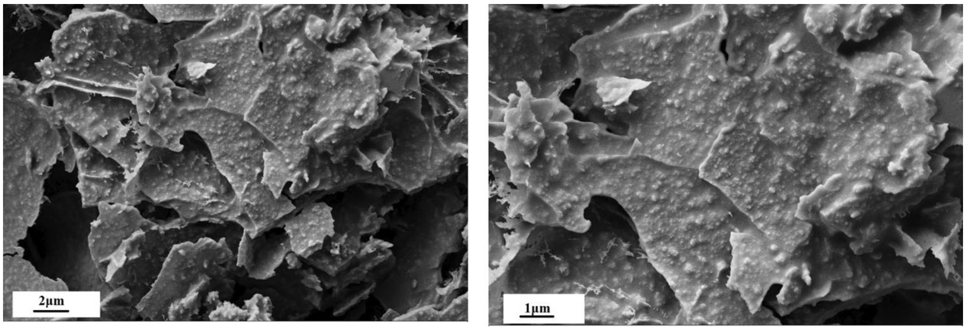
(b)

Fig. 5 **a** The schematic of the numerical model, the governing equations, and the boundary conditions for the numerical simulation, **b** the results from the numerical model, which predict the maximum temperature for DS and DS/hBN composite, along with the maximum flame temperature, are presented (Red lines for flame temperature on left scale)

Conclusion

A flame-resistant coating on polycarbonate containing a low percentage (10%) of hBN nanomaterial manufactured by in situ shear exfoliation method showed promising results in flame retardancy test making it suitable for use as casing material of Li-ion battery. In UL-94 flame retardancy test, the DS/hBN-coated sample successfully

Fig. 4 SEM images of hBN on polycarbonate sheet



(a)

(b)

suppressed the flame propagation with rating “HB” while the traditional and only DS-coated sample failed in resisting the flame propagation. The char layer formed prevented the decomposition of the thermoplastic and the addition of hBN nanomaterial reduced the burn rate to 9 mm/min from 33 mm/min. In the vertical test, the DS/hBN-coated sample passed the vertical test with a V-0 rating, while burning and degradation of the traditional and DS-coated sample resulted in fail rating. Mechanical testing of the coated and flame-tested sample showed only 0.9% change in tensile strength from pristine polycarbonate sheet. This opens the door to manufacturing robust hBN-elastomeric coating from low-cost bulk material via shear exfoliation for flame retardancy and thermal management applications.

Acknowledgments This research is financially supported by the National Science Foundation (NSF) under grant number ERI 2138574. The authors kindly acknowledge the experimental support provided by Dr. Victoria Padilla from the University of Texas Rio Grande Valley.

Data availability The dataset generated and analyzed during the current study is available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Q. Wang, B. Mao, S.I. Stoliarov, J. Sun, A review of lithium ion battery failure mechanisms and fire prevention strategies. Prog. Energy Combust. Sci. (2019). https://doi.org/10.1016/j.pecs.2019.03.002
2. H. Chen et al., An experimental study on thermal runaway characteristics of lithium-ion batteries with high specific energy and prediction of heat release rate. J. Power Sources (2020). https://doi.org/10.1016/j.jpowsour.2020.228585
3. D. Kong, G. Wang, P. Ping, J. Wen, A coupled conjugate heat transfer and CFD model for the thermal runaway evolution and jet fire of 18650 lithium-ion battery under thermal abuse. eTransportation (2022). https://doi.org/10.1016/j.etran.2022.100157
4. A.N. Jansen, K. Amine, A.E. Newman, D.R. Vissers, G.L. Henriksen, Low-cost, flexible battery packaging materials. JOM (2002). https://doi.org/10.1007/bf02822616
5. E. Maiser, Battery packaging—Technology review. AIP Conf. Proc. (2014). https://doi.org/10.1063/1.4878489
6. F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta, P. Dubois, New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. Mater. Sci. Eng. (2009). https://doi.org/10.1016/j.mser.2008.09.002
7. R.E. Lyon, M.T. Takemori, N. Safronava, S.I. Stoliarov, R.N. Walters, A molecular basis for polymer flammability. Polymer (2009). https://doi.org/10.1016/j.polymer.2009.03.047
8. K. Babu et al., A review on the flammability properties of carbon-based polymeric composites: state-of-the-art and future trends. Polymers (2020). https://doi.org/10.3390/polym12071518
9. H. Vahabi, O. Eterradossi, L. Ferry, C. Longuet, R. Sonnier, J.-M. Lopez-Cuesta, Polycarbonate nanocomposite with improved fire behavior, physical and psychophysical transparency. Eur. Polym. J. **49**(2), 319–327 (2013). https://doi.org/10.1016/j.eurpolymj.2012.10.031
10. Q. Dong et al., A polycarbonate/magnesium oxide nanocomposite with high flame retardancy. J. Appl. Polym. Sci. **123**(2), 1085–1093 (2012). https://doi.org/10.1002/app.34574
11. X. Feng, M. Ouyang, X. Liu, L. Lu, Y. Xia, X. He, Thermal runaway mechanism of lithium ion battery for electric vehicles: a review. Energy Storage Mater. (2018). https://doi.org/10.1016/j.ensm.2017.05.013
12. X. Yue, C. Li, Y. Ni, Y. Xu, J. Wang, Flame retardant nanocomposites based on 2D layered nanomaterials: a review. J. Mater. Sci. (2019). https://doi.org/10.1007/s10853-019-03841-w
13. S. Lu, W. Hong, X. Chen, Nanoreinforcements of two-dimensional nanomaterials for flame retardant polymeric composites: an overview. Adv. Polym. Technol. (2019). https://doi.org/10.1155/2019/4273253
14. R. Silva-Leyton, R. Quijada, R. Bastías, N. Zamora, F. Olate-Moya, H. Palza, Polyethylene/graphene oxide composites toward multifunctional active packaging films. Compos. Sci. Technol. (2019). https://doi.org/10.1016/j.compscitech.2019.107888
15. Q. Bian et al., Effect of graphene oxide on the structure and properties of poly(vinyl alcohol) composite films. Polym. Sci. Ser. A (2015). https://doi.org/10.1134/S0965545X15060048
16. B. Yu et al., Enhanced thermal and flame retardant properties of flame-retardant-wrapped graphene/epoxy resin nanocomposites. J. Mater. Chem. A **3**(15), 8034–8044 (2015). https://doi.org/10.1039/C4TA06613H
17. D.S. Muratov et al., Improved thermal conductivity of polypropylene filled with exfoliated hexagonal boron nitride (hBN) particles. Mater Res Express **8**(3), 35010 (2021). https://doi.org/10.1088/2053-1591/abed0f
18. G. Han et al., Highly flame-retardant epoxy-based thermal conductive composites with functionalized boron nitride nanosheets exfoliated by one-step ball milling. Chem. Eng. J. **407**, 127099 (2021). https://doi.org/10.1016/J.CEJ.2020.127099
19. H. Song, J. Liu, B. Liu, J. Wu, H.M. Cheng, F. Kang, Two-dimensional materials for thermal management applications. Joule (2018). https://doi.org/10.1016/j.joule.2018.01.006
20. M.A. Rahman, M.M. Rahman, A. Ashraf, Automatic dispersion, defect, curing, and thermal characteristics determination of polymer composites using micro-scale infrared thermography and machine learning algorithm. Sci. Rep. **13**(1), 2787 (2023). https://doi.org/10.1038/s41598-023-29270-z
21. X. Mu et al., High-performance flame-retardant polycarbonate composites: mechanisms investigation and fire-safety evaluation systems establishment. Compos B Eng **238**, 109873 (2022). https://doi.org/10.1016/J.COMPOSITESB.2022.109873
22. Underwriters Laboratories, *Tests for flammability of plastic materials for parts in devices and appliance* (Underwriters Laboratories, Northbrook, 1990)
23. Z.R. Yu et al., Enhanced mechanical property and flame resistance of graphene oxide nanocomposite paper modified with functionalized silica nanoparticles. Compos. B Eng. (2019). https://doi.org/10.1016/j.compositesb.2019.107347

24. N. Muhammad, F.D. Zaman, M.T. Mustafa, OpenFOAM for computational combustion dynamics. Eur. Phys. J. Spec. Top. **231**(13), 2821–2835 (2022). https://doi.org/10.1140/epjs/s11734-022-00606-6