Influence of Graphene Nano Fillers and Carbon Nano Tubes on the Mechanical and Thermal Properties of Hollow Glass Microsphere Epoxy Composites

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Abstract: The present work aimed to analyze the roll of carbon nano tubes and graphene nano fillers on the mechanical and thermal characteristics of hollow glass microsphere reinforced epoxy composites. Composites with varying content of hollow glass microballoons (2, 4, 6, 8, and 10 wt %) reinforced in epoxy matrix were fabricated. Additionally, two more types of composites, one with graphene nano fillers and the other with carbon nano tube at a constant 0.5 wt %, were fabricated with varying weight percentages of hollow glass microballoons (2, 4, 6, 8, and 10%). The composites were fabricated using an open mold casting process. Composites were tested for thermal and mechanical properties. The tensile and flexural moduli were found to rise as the HGM concentration increased. Graphene-filled HGM/epoxy composites revealed the highest modulus compared with HGM/epoxy and HGM/CNT/epoxy composites. The impact strength of all composite types decreased as the HGM content increased. Neat epoxy specimens revealed low response as compared with all the composites tested. Further, the thermal conductivity of HGM/epoxy compositions was lower as compared with other compositions and neat epoxy. Scanning electron microscopy was used to analyze the surface morphological behavior of the composites subjected to flexural test. It was found that HGM/G/E composites with 10% of HGM and 0.5% of graphene by weight in epoxy matrix were the optimum.

Keywords: epoxy; hollow glass microsphere; nano fillers; carbon nano tube; graphene; mechanical and thermal properties

1. Introduction
Closed cell hollow particles are reinforced in matrix to realize syntactic foams [1–3]. These foams offer advantages of lower moisture inclusion, high compression response,
and higher damage tolerances [4,5]. High flexibility in design can be attained by selecting suitable hollow spheres and matrices. These hollow particles are widely employed with polymer matrix composites because they are lightweight, have a high strength-to-weight ratio, and are stiff [6]. They are widely used in a variety of industries, including electrical, aerospace, marine, automotive, and sports, among others [7]. Ferreira et al. examined the influence of HGM filler with carbon short fiber and glass-reinforced epoxy composites and found that with the increase of HGM content, there was an increase in flexural, compressive, and impact properties. The carbon content increased flexural and fracture toughness properties, and the glass fiber content increased impact properties, while hybrid composites did not improve the impact properties [8]. Mohammed Imran et al. have investigated the effect of compressive strength of carbon nanofibers grown on HGM epoxy composite foam and observed that the compressive strength increased, owing to the high modulus of carbon nano-materials. The carbon nanofibers grown at 500 °C were of solid graphite structure, and those grown at 600 °C and 700 °C were of hollow graphite structure [9]. Koopman et al. explored the compression of glass micro balloons and observed a clear correlation between the diameter to failure load and diameter to fracture energy [10]. Mohammed Imran et al. studied the variable weight percentage of HGM in epoxy composites made by the sonication method and reported that the compressive strength declined when the HGM weight percentage increased and the storage modulus increased [11]. Rahaman et al. investigated the glass fiber-reinforced laminated epoxy carbon nano tube composites and discovered that the addition of multi-walled carbon nano tubes significantly enhanced the composite’s flexural modulus, flexural strength, and modulus of storage [12]. Ho Sung Kim et al. examined the impact and fracture properties on the HGM/epoxy composites and observed that the HGM did not enhance the fracture toughness, impact force, and specific flexural strength while the flexural modulus was increased [13]. An investigation of the dielectric properties of HGM/epoxy composites was conducted by Yung et al., observing that as the HGM content increased, the dielectric constant, dielectric loss, and thermal conductivity were reduced. With an increase in HGM content, the thermal expansion coefficient and glass transition temperature improved [14]. Swetha et al. performed an experiment to study the mechanical characteristics of HGM/epoxy composites and observed that the modulus and strength decreased with increasing HGM volume percent but improved with increasing microsphere wall thickness [15]. Yingjie Qiao et al. studied the compression and thermal characteristics of the HGM/epoxy composites, observing that the density, compressive modulus, compressive strength, and thermal conduction property of the composites decreased as the HGM volume percentage increased [16]. Mohammed Imran et al. studied the characteristics of HGM and CNT reinforced epoxy composites and observed that the compressive strength increased up to 5 weight percentage of HGM and decreased thereafter. The modulus of storage of the composites rose as HGM concentration increased [17]. Ronald et al. analyzed the water immersion properties of the carbon nanofiber reinforced epoxy composites with glass micro balloons and found that the compression modulus was not affected but decreased the compression strength [18]. Tien et al. investigated the influence of volume percentage and wall thickness of glass micro balloon reinforced epoxy matrix syntactic foams. According to their findings, the glass transition temperature rose as the volume percentage increased and was not affected by wall thickness, whereas thermal stability increased with increased wall thickness and was not affected by volume fraction [19]. CNT and graphene fillers in reinforced polymer nanocomposites were studied by Garima Mittal et al. They determined that increasing the filler loading reduced the electrical and mechanical characteristics of the material, owing to particle agglomeration. Additionally, CNT-based composites had lower load transfer and electrical conductivity than graphene-based composites [20]. Nishant Shirodkar et al. studied the graphene/epoxy nano-composites and observed that small quantity addition of graphene powder and proper mixing had an effect on the polymer’s mechanical characteristics [21]. Dong Ho Kang et al. explored the influence of HGM on the single-walled carbon nano tube-loaded polypropylene composites, observing that 1–7 weight percentage
of HGM showed better performance [22]. Xin Zhao et al. examined the mechanical characteristics of graphene-based polyvinyl alcohol composites, finding that the mechanical characteristics were optimum at 1.8 volume percentage of graphene [23]. Mohammad A. Rafiee et al. investigated the mechanical characteristics of epoxy nanocomposite reinforced with graphene as well as single-walled and multi-walled carbon nano tubes, observing that the graphene performed better than graphene CNT additives [24]. Shao-Yun Fu et al. observed that the toughness and strength of particulate polymer matrix composites were influenced by particle/matrix adhesion, particle size, and particle content, while composite stiffness was found to be determined by particle content rather than particle/matrix adhesion [25]. Very few studies are available on the comparative studies on the influence of CNT and graphene nano fillers on thermal and mechanical characteristics of HGM reinforced epoxy composites [26,27].

This work aimed to examine the comparative effect of CNT and graphene nano fillers on thermal and mechanical properties with varying weight percentages of HGM reinforced epoxy composites. Epoxies are used as structural adhesives and matrix materials because they are inexpensive, easy to fabricate, have high specific strength, and provide thermal and electrical insulation. HGM is an emerging material that influences the properties even for small concentrations and is preferred where there is a need to combine high Young’s modulus with low density. CNTs are important fillers due to their nanoscale dimensions and exceptional mechanical, thermal, and electrical properties. Another excellent filler material is graphene, a carbon allotrope made of a monolayer of carbon atoms organized in a 2D (two-dimensional) hexagonal lattice nanostructure with one atom forming each vertex. It has a high surface area and robust mechanical and electrochemical properties used in composites, electronics, energy, and biomedical fields.

Composites were prepared using varying amounts of hollow glass micro balloons (0, 2, 4, 6, 8, and 10 wt %) in epoxy matrix by using open mold casting. The novel aspects of the present study include (a) use of hollow glass micro balloons, CNT, and graphene for developing polymer composites; (b) the effect of varying hollow glass micro balloons on the mechanical and thermal properties; and (c) structure-property correlations for varying amounts of filler content.

2. Experimental Work

2.1. Materials

Araldite LY 556 Epoxy resin and Aradur HY 951 hardener were procured from Huntsman Advanced Materials India Private Limited, Mumbai, India. Cured epoxy resin and hardener has a density of 1.19 g/cm³, tensile strength of 52 MPa, tensile modulus of 2800 MPa, elongation at break of 11%, shear modulus of 1230 MPa, Shore D hardness of 85, and glass transition temperature of 67 °C. Hollow glass microspheres with trade name MicroLite GM 20 made of soda-lime borosilicate glass were procured from Petra Buildcare Products, Bhavnagar, Gujarat, India. Hollow glass microspheres have a particle size of 2–13 µm, true density of 0.18–0.22 g/cm³, and thermal conductivity of 0.0521 W/mK at 20 °C. Carbon nano tube and graphene were obtained from Sigma-Aldrich Chemicals Private Limited, Bangalore, India. Carbon nano tubes (CNTs) are the allotrope of carbon and are cylindrical in shape with an average particle size of <50 nm, tube length of 5 to 30 nanometer, true density of 2.26 g/cm³, and specific surface area of 50 to 500 m²/g. Graphene, a promising carbon nanomaterial, has an atomically thin single-layer structure. Surface area of graphene > 500 m²/g and electrical conductivity of graphene ≥ 1000 S/m.

2.2. Specimen Preparation

The composites were prepared using the open mold casting process. Composites with hollow glass microspheres in varying content (2, 4, 6, 8, and 10 wt %) were prepared by thoroughly mixing with epoxy resin (Araldite LY556) and finally with the hardener (Aradur HY 951) in the resin: hardener ratio of 100:10 by weight. The prepared mixture was poured into two sets of molds, first with dimensions of 110 mm diameter with 5 mm
thickness, and second with $180 \times 180 \times 6$ mm. Molds were applied with releasing agent before pouring of the mixture and cured at the atmospheric condition for 24 h. The samples removed from the mold were marked and cured in a hot air oven at $70 \, ^\circ C$ for 4 h. For comparative studies, a similar procedure was repeated for the fabrication of hollow glass microsphere-filled epoxy composites with varying weight percentages (2%, 4%, 6%, 8%, and 10%) and CNTs (constant 0.5% by weight) and graphene (constant 0.5% by weight) separately. The disc-shaped specimens from the first mold were used for thermal properties, while the specimens marked and cut from plate-shaped composites were used for evaluating mechanical properties. Figure 1 shows the flow diagram of composite fabrication. Figure 2a,b shows the photographs of dies used for sample preparation of mechanical and thermal properties respectively. Figure 3 shows the photographs of specimens of (i) tensile, (ii) flexural, (iii) impact and (iv) thermal conductivity. Figure 3a shows the specimens of Hollow Glass Microspheres reinforced Epoxy (HGM/E) composites. Figure 3b shows the specimens of Hollow Glass Microspheres and Carbon Nano Tubes reinforced Epoxy (HGM/CNT/E) composites. Figure 3c shows the specimens of Hollow Glass Microspheres and Graphene reinforced Epoxy (HGM/G/E) composites.

![Flow diagram of composite fabrication](image1)

**Figure 1.** Flow diagram of composite fabrication.

![Photographs of dies used for sample preparation](image2)

**Figure 2.** Photographs of dies used for sample preparation: (a) mechanical and (b) thermal.
2.3. Tensile, Flexural, Impact, and Thermal Conductivity

To investigate the mechanical behavior of composites, we conducted tensile, impact, and flexural tests on all the specimens. The specimens for these tests were cut from the composites molded in the form of a plate. Tensile tests were performed on specimens of 165 × 12.7 × 3 mm with a gauge length of 115 mm conforming to ASTM D638 standard. Shimadzu (AG-50kNISD MS, Kyoto, Japan) universal testing machine was employed to conduct tensile tests at a 50 mm/min cross-head speed. The dog bone-shaped specimen was clamped between the cross heads and loaded using the moving cross head until the maximum load was reached. From the observed load and elongation values, we calculated the tensile properties. Flexural tests were performed on specimens of size 127 × 12.7 × 3 mm as per ASTM D790 standards. Three-point bending flexural test was carried out on an Instron (3382, Boston, MA, USA) universal testing machine with 2.6 mm/min cross-head speed for 130 mm span length. The specimen was kept between supports and loaded using the moving cross-head until the yield was reached. From the observed load and deflection values, we calculated the flexural properties. Impact tests were performed on specimens of size 63.5 × 12.7 × 3 mm with a V-notch as per ASTM D256 standards. Izod impact test with 2.54 mm "V" notch depth and 45° notch angle was performed on a Tinius Olsen (IT 504, Horsham, PA, USA) impact testing machine. The notched specimen was fixed vertically in the impact testing machine vice and broken with a swinging pendulum. The amount of energy absorbed by the material during the breaking process was directly noted from the machine. To study the thermal behavior, we performed the thermal conductivity test on disc-shaped specimens of sizes of 110 mm diameter with 5 mm thickness using Lee’s disc apparatus. The specimen was kept on the horizontally suspended disc, and steam was passed into the steam chamber placed on the specimen until the temperatures in the chamber and the disc were steady. The temperatures of the steam chamber and disc were noted. Then, the specimen was removed, and the steam chamber was placed directly on the disc. The disc was heated at 5 °C above the temperature of the disc. The steam chamber was removed, and the disc alone was allowed to cool. The temperature of the disc while cooling was noted at regular intervals. A graph

\[
\rho^{th} = \rho_f V_f + \rho_m V_m
\]

where
\(\rho^{th}\) — theoretical density;
\(\rho_f\) — density of filler;
\(V_f\) — filler volume fraction;
\(\rho_m\) — density of matrix;
\(V_m\) — matrix volume fraction.

Additionally, the experimental density \(\rho^{exp}\) is determined using the Archimedes principle by measuring mass of samples in air and water. Estimation of the void content \(\varnothing_V\) is accomplished by comparing experimental and theoretical density values and is denoted by

\[
\varnothing_V = \frac{(\rho^{th} - \rho^{exp})}{\rho^{exp}}
\]

where
\(\varnothing_V\) — void content;
\(\rho^{th}, \rho^{exp}\) — theoretical and experimental density values, respectively.

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2.4. Scanning Electron Microscopy

Structure-property correlations of flexural fracture surfaces were carried out using scanning electron microscopy. A field emission scanning electron microscope (FESEM) FEI, Quanta 200 was employed for imaging the surfaces. The fractured portion of the specimens was cut to a height of 10 mm without disturbing the fractured surface. Gold palladium electroplating was used to coat fractured surfaces to prevent electron charging. The coated samples were attached to a stub by double-sided electrically conductive adhesive carbon tape. An accelerating voltage of 10 kV power supply was used for imaging the specimens.

3. Results and Discussion

3.1. Density

Method of fabrication, uniform dispersion of constituents in the epoxy matrix, and lower void content significantly influenced the mechanical behavior of composites. Experimentally measured densities of different composites are depicted in Figure 4. Further, void content estimations, as well as theoretical and experimental density, are reported in Table 1. Experimental density values were lower than theoretical density values due to the entrapment of air in the composite encountered during fabrication. However, it was evident that the densities of all the composites declined with increasing hollow glass microballoon content. Hollow glass microballoons have an average density of 200 kg/m³, which is lower than neat epoxy by roughly six times. These microballoons, apart from possessing low density, are also hollow in nature; thereby, more space is utilized by the fillers in the composite. As a result, all the composites revealed a decrease in density values as the HGM content increased. Similar trends can be observed in [14,28–30]. Furthermore, HGM/E composites revealed lower density as compared with HGM/CNT/E and HGM/G/E. Further, the void content estimations indicated that observed values were minimal and can be neglected. The minute variations noticed in the standard deviations affirmed the consistency achieved in the fabrication of samples.
affirmed the consistency achieved in the fabrication of samples. From possessing low density, are also hollow in nature; thereby, more space is utilized by the minute variations noticed in the standard deviations. Theoretical density values were lower than experimental densities of different composites. It was evident that the densities of all the composites declined with increasing hollow glass microballoon content. Hollow glass microballoons have an average density of 200 kg/m³, which is lower than neat epoxy by roughly six times. These microballoons, apart from possessing low density, are also hollow in nature; thereby, more space is utilized by the minute variations noticed in the standard deviations.

Table 1. Density and void content estimation of specimens.

| Specimen Designation | Material Composition HGM/CNT/E (Weight %) | Theoretical Density \( \rho^t \) (kg/m³) | Experimental Density \( \rho^{exp} \) (kg/m³) | Void Content \( \phi_V \) |
|----------------------|--------------------------------------------|---------------------------------|-----------------------------|----------------|
| 2HGM/E               | 2:0:0.98                                   | 1172.160                        | 1165.300 ± 25.637          | 0.588          |
| 4HGM/E               | 4:0:0.96                                   | 1152.320                        | 1146.450 ± 25.222          | 0.512          |
| 6HGM/E               | 6:0:0.94                                   | 1132.480                        | 1124.600 ± 24.741          | 0.700          |
| 8HGM/E               | 8:0:0.92                                   | 1112.640                        | 1104.540 ± 24.300          | 0.733          |
| 10HGM/E              | 10:0:0.90                                  | 1092.800                        | 1084.440 ± 23.858          | 0.770          |
| 2HGM/CNT/E           | 2:0.5:0.97.5                               | 1276.700                        | 1265.420 ± 27.839          | 0.891          |
| 4HGM/CNT/E           | 4:0.5:0.95.5                               | 1256.860                        | 1245.650 ± 27.404          | 0.899          |
| 6HGM/CNT/E           | 6:0.5:0.93.5                               | 1237.020                        | 1228.250 ± 27.022          | 0.714          |
| 8HGM/CNT/E           | 8:0.5:0.91.5                               | 1217.180                        | 1207.320 ± 26.561          | 0.816          |
| 10HGM/CNT/E          | 10:0.5:0.89.5                              | 1197.340                        | 1190.350 ± 26.188          | 0.587          |
| 2HGM/G/E             | 2:0:0.97.5                                 | 1279.200                        | 1270.230 ± 27.945          | 0.706          |
| 4HGM/G/E             | 4:0:0.95.5                                 | 1259.360                        | 1248.630 ± 27.470          | 0.859          |
| 6HGM/G/E             | 6:0:0.93.5                                 | 1239.520                        | 1228.450 ± 27.026          | 0.901          |
| 8HGM/G/E             | 8:0:0.91.5                                 | 1219.680                        | 1208.660 ± 26.591          | 0.911          |
| 10HGM/G/E            | 10:0:0.89.5                                | 1199.840                        | 1188.450 ± 26.146          | 0.958          |

3.2. Tensile Strength and Modulus

The response of composites to resist applied forces in tension is vital since it provides information the materials to resist when forces are applied in tension. Determining the tensile properties is crucial because it provides information concerning various tensile properties (elastic limit, tensile strength, modulus of elasticity, etc.). Tensile properties vary for every composite, and thereby tensile tests are performed to understand the behavior of different composites [31]. Tensile strength and modulus of HGM/E, HGM/CNT/E, and HGM/G/E composites are depicted in Figure 5. The tensile strengths of different HGM composites are presented in Figure 5a. It is noticed that when the amount of HGM in the composites increased, the tensile strength of the composites fell. This was because tensile strength is governed by bonding strength, effective load transfer, particle size, and particle-loading, primarily adhesion between particles and matrix [25,32–34]. As the particle loading rose, the compatibility between the matrix and particles was lost due to insufficient matrix material to cover the particles, and load transfer decreased, resulting in the reduction of tensile strength. Comparing the tensile strength of HGM/E, HGM/CNT/E, and HGM/G/E composites, we found that the effect of additional reinforcements (carbon nano tubes and graphene) did not yield a significant change in the strength of the composites.
Tensile modulus of HGM/E, HGM/CNT/E, and HGM/G/E composites are shown in Figure 5b. Contrary to the strength values, tensile modulus of all the composites depicted increasing trends with an increase in volume fraction of hollow glass microballoons. It is noted that the tensile modulus increased with an increase in reinforcing particle loading. This was because modulus depends on particle loading and not on particle/matrix adhesion, since the particles have a higher modulus than the matrix. Moreover, when the particles are nano-sized with a larger surface area, a nano effect is created that greatly enhances the stiffness. Comparing the tensile modulus of HGM/E, HGM/CNT/E, and HGM/G/E composites, we found that the addition of graphene resulted in the highest modulus yield when compared to carbon nano tubes, owing to their intrinsic mechanical characteristics and the strong interfacial bonding, which results in an improved interfacial stress transfer efficiency [35–37].

![Figure 5a](image1.png)  
**Figure 5a.** Tensile modulus of composites.

**Figure 5.** Tensile (a) modulus and (b) strength of composites.

### 3.3. Flexural Strength and Modulus

Composites’ ability to withstand bending deflection when subjected to various loads is termed as flexural strength. Composites designed for many products and applications require retention of flexural properties [38]. Figure 6a displays the flexural strength of HGM/E, HGM/CNT/E, and HGM/G/E composites. The strength of all the composites revealed trends similar to tensile behavior, wherein HGM/G/E depicted higher strength as compared with HGM/CNT/E and HGM/E. However, the strength of all the composites decreased with a rise in hollow glass microballoon content. Flexural modulus of HGM/E,
HGM/CNT/E, and HGM/G/E composites are shown in Figure 6b. Modulus of all the composites depicts increasing trends with an increase in hollow glass microballoon content. A significant rise in modulus was seen with HGM/G/E composites, owing to an exceptionally high aspect ratio and higher modulus of graphene particles that assist in good load transfer from the matrix to reinforcements, thereby enhancing the overall modulus [39]. Similar trends were reported by [40–42].

![Figure 6](image)

**Figure 6.** Flexural (a) strength and (b) modulus of composites.

### 3.4. Impact Strength

Composites' response to sudden impact loads is the crucial property required for most of the envisaged applications. Comparison of impact strength of HGM/E, HGM/CNT/E, and HGM/G/E composites is depicted in Figure 7. With the increase in HGM content, the impact strength of the composites decreased for all the composites. This was due to the fact that the increase of hard reinforcing particles increased brittleness and clustering and hence decreased the impact strength at higher particle loading.
Thermal conductivity is an important property of composites designed for thermal applications. Low thermal conductivity of hollow glass microballoons and high aspect ratio of CNTs and graphene are beneficial in effectively building thermal networks [43]. Figure 8 compares the thermal conductivities of the HGM/E, HGM/CNT/E, and HGM/G/E composites. The thermal conductivity of all composites decreased with increasing HGM content. However, HGM/E composites revealed the lowest thermal conductivity as compared with HGM/CNT/E and HGM/G/E composites. The low thermal conductivity of HGM/E composites was mainly attributed to the ability of hollow glass microballoons to absorb moisture effectively. However, with the addition of CNT and graphene in the HGM/epoxy composites, the thermal conductivity increased by up to 4% by weight. This was because the thermal conductivity of graphene and CNT are higher than the thermal conductivity of HGM.

The present work effectively demonstrates the development of three different types of composites, namely, HGM/E, HGM/CNT/E, and HGM/G/E, with a purpose to widen the material options available for polymer-based composites. All the composites revealed good flexural properties and thermal conductivity with moderate impact strength. These composites can be utilized as core for preparation of sandwich composites and targeted for thermal applications. The composites can also be used in the fabrication of casing for energy storage devices and electronic equipment requiring dissipation of heat developed due to the chemical reaction or operation of electronic devices to the surrounding.

3.6. Micrography

Figure 9a–e shows the scanning electron microscopy images of flexural fractured surfaces of HGM/CNT/E composites with varying content of HGM from 0 to 10 wt %. It is evident from the micrographs that there was good dispersion of the reinforcing particles in the epoxy matrix. Further, it was also observed that clustering took place at the higher loading of HGM particles. Nevertheless, as the HGM content increased, survival of hollow particles also increased, and thereby there was an increase in the modulus of the composites at increasing HGM content. Under flexural loading, both compressive and tensile stresses...
were developed in the composites. Striation marks can be seen on all the specimens, irrespective of HGM content; however, the magnitude of striations decreased with higher HGM content. As a result, the modulus of composites showed an increasing trend.

![Figure 8. Thermal conductivity of composites.](image)

![Figure 9. Cont.](image)
Figure 9. SEM micrographs of flexural fractured surfaces of (a) neat epoxy, (b) 2HGM/CNT/E, (c) 4HGM/CNT/E, (d) 6HGM/CNT/E, (e) 8HGM/CNT/E, and (f) 10HGM/CNT/E composite specimens.

4. Conclusions

- Fabrication and testing of thermal and mechanical properties of HGM/E, HGM/CNT/E, and HGM/G/E composites were carried out successfully.
- Tensile and flexural modulus rose with an increment in particle loading.
- Mechanical characteristics of HGM/G/E composites were found to be higher than HGM/CNT/E composites.
- The thermal conductivity of the composites reduced with the increment in weight percentage of HGM, while it increased with the rise of graphene in comparison with CNT.
- Uniform distribution of the reinforcing particles in the epoxy matrix was observed from SEM images.
- Comparing HGM/E, HGM/CNT/E, and HGM/G/E composites with varying weight percentages of HGM ranging from 0 to 10%, we found HGM/G/E composites with 10% of HGM and 0.5% of graphene by weight in epoxy matrix to be the optimum.
- The composites can be used in the fabrication of casing for energy storage devices and electronic equipment requiring dissipation of heat developed due to the chemical reaction or operation of electronic devices to the surrounding.

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