KSÜ Mühendislik Bilimleri Dergisi, 27(4),2024
Derleme Makalesi

KSU J EngSci, 27(4), 2024
Review Article

Kahramanmaras Sutcu Imam University
Journal of Engineering Sciences

Geliş Tarihi : 13.06.2024
Kabul Tarihi : 19.07.2024

Received Date : 13.06.2024
Accepted Date : 19.07.2024

ENHANCING THERMAL PROPERTIES OF FIBER-REINFORCED POLYMER COMPOSITES TO BE USED IN BATTERY CASINGS: A REVIEW

BATARYA MUHAFAZLARINDA KULLANILABİLEN ELYAF TAKVİYELİ POLİMER KOMPOZİTLERİN ISIL ÖZELLİKLERİNİN İYİLEŞTİRİLMESİ HAKKINDA BİR DERLEME

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ABSTRACT

Fiber-reinforced polymer composites, particularly those reinforced with carbon fiber, hold significant promise for use in battery casings. Since the performance of the batteries of electric and hybrid vehicles is highly dependent on the operating temperature, the thermal management system of the battery pack is essential. For this thermal management to be efficient, the battery enclosure must have sufficient thermal conductivity and thermal diffusivity values. However, most of the fiber-reinforced polymer composite materials have poor thermal properties. Thus, it is necessary to increase the thermal conductivity and thermal diffusivity values of such materials. In this paper, studies that have succeeded in increasing the thermal properties of fiber-reinforced polymer composites by applying different methods have been examined. The methods and obtained results are reviewed and discussed. Also, some suggestions are given to the potential applicators. Therefore, the most applicable methods, to enhance the thermal properties of the composite battery cases, can be determined and compared with one another.

Keywords: Composites, thermal conductivity, thermal diffusivity, battery case

ÖZET

Fiber takviyeli polimer kompozitler, özellikle karbon fiber ile güçlendirilmiş olanlar, batarya muhafazalarında kullanım için umut vaat etmektedir. Elektrikli ve hibrit araçların bataryalarının performansı büyük ölçüde çalışma sıcaklığına bağlı olduğundan, batarya paketinin termal olarak yönetilmesi zorunludur. Bu termal yönetimin verimli olabilmesi için batarya muhafazasının yeterli termal iletkenlik ve termal difüzivite değerlerine sahip olması gerekir. Ancak, elyaf takviyeli polimer kompozit malzemelerin çoğu zayıf termal özelliklere sahiptir. Bu nedenle, bu tür malzemelerin ısıl iletkenlik ve ısıl yayılım değerlerinin artırılması gerekmektedir. Bu makalede, farklı yöntemler uygulayarak elyaf takviyeli polimer kompozitlerin ısıl özelliklerini arttırmayı başaran çalışmalar incelenmiştir. Yöntemler ve elde edilen sonuçlar gözden geçirilmiş ve tartışılmıştır. Ayrıca, potansiyel uygulayıcılara bazı önerilerde bulunulmuştur. Böylece, batarya kutularının ısıl özelliklerini geliştirmek için en uygulanabilir yöntemler belirlenip birbiriyle karşılaştırılabilecektir.

Anahtar Kelimeler: Kompozitler, ısıl iletkenlik, ısıl yayınım, batarya kutusu

To Cite: GÖKCİLER, O.C., & GEREN, N., (2024). ENHANCING THERMAL PROPERTIES OF FIBER-REINFORCED POLYMER COMPOSITES TO BE USED IN BATTERY CASINGS: A REVİEW. *Kahramanmaras Sutcu Imam University Journal of Engineering Sciences*, 27(4), 1633-1646.

INTRODUCTION

The use of fiber-reinforced polymer composites (FRPC) is increasing, almost in every sector. Due to, their high strength and high elastic modulus combined with their low weight, FRPCs are widely used in the automotive, marine, aircraft, defence, energy industries, and sports equipment (Şen et al., 2010). In particular, carbon fiber reinforced polymer (CFRP) composites have been increasingly used in recent years due to their high modulus of elasticity (E) / density (ρ) and strength (σ) / density (ρ) ratios. In order to better understand the advantages of such materials over conventional materials, the material selection chart that is prepared by Michael F. Ashby is given in Figure 1. The high specific strength and high specific modulus of the CFRP composites can be observed in the next figure.

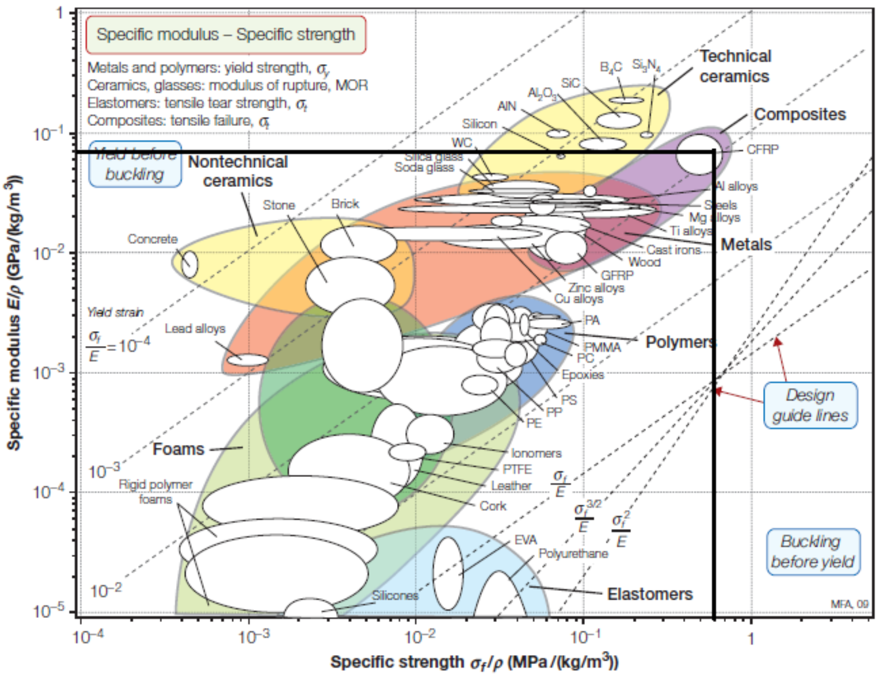


Figure 1. Specific Modulus-Specific Strength Chart (Ashby, 2011)

In addition to the above-mentioned areas of use, another area where CFRP materials can be used is in the battery case of electric vehicles (EVs) and hybrid vehicles (HVs). In terms of specific energy absorption (amount of energy per unit mass), CFRP composites have superior collision energy absorption capability as well as low weight compared to metallic materials such as steel and aluminium. Due to these advantageous properties, CFRP materials have become the preferred choice for battery cases in the past decade, such as in the BMW i3 electric vehicle (Pety et al., 2017).

Another advantage of forming the battery case of an EV or HV from CFRP is the property of electromagnetic interference (EMI) (Luo & Chung, 1999). Since the battery pack is located under the driver and the passengers, it is very advantageous if the battery housing has electromagnetic interference properties, such as CFRP composite. Also, the danger of the thermal runaway fire is another issue that cannot be ignored in battery package technology. When this issue is considered, the superior thermal runaway performance of such composites, than aluminium and steel, makes them a greater candidate as the battery casing material (E-mobility, 2024).

Besides the highly advantageous properties mentioned above, the thermal conductivity and thermal diffusivity of CFRP composites are very low. In order to use CFRP composites efficiently in battery casing, it is necessary to increase these unfavourable thermal values by making various modifications to the CPRP material. Because, despite the advantages of lithium-ion (Li-ion) batteries, which are widely used in electric vehicles, such as long life, reliability, high energy density, wide voltage window, fast charge/discharge rates, relatively wide operating temperature range, and practical battery pack design, the optimum operating temperature energy efficiency is between 10 °C and 40 °C (Biswas et al., 2022; H. Lee et al., 2019; F. Zheng, et al., 2017). In addition, when electric vehicles are operated in very cold or very hot climatic conditions, or when one or more of the batteries in the battery pack are damaged, the pack must be thermally managed.

In order to increase the thermal conductivity of the CFRP battery case, Chan et al. produced CFRP composites to be used as high-energy storage devices and improved the conductivity of the polymer structure by mixing nano-particles such as gold and graphene oxide into the epoxy matrix material at a rate of 1 wt% (Chan et al., 2019). The high cost of this study should be emphasized. Because the materials such as, gold and graphene oxide are used as the nano-filler material. The superior thermal conductivity of these two filler materials cannot be discussed. However, their high costs make this approach less attractive. As a different approach that aims to improve the thermal management of the battery pack, Pety et al. designed a sandwich structure by placing the battery cells between micro-vascular carbon/epoxy plates and thus achieved both volume and weight gain (Pety et al., 2017). In this study, the coolant fluid flows within the micro-vascular channels that are embedded within the CFRP composite layers without any additional piping. Thus, the handicaps that are related with additional piping systems such as; extra weight, extra maintenance cost, increased failure possibility, and more material consumption can be ignored.

As mentioned above, the usage of FRPC materials, including battery case technology, is increasing, but their low thermal conductivity and low thermal diffusivity values limit their usage. For example, the thermal conductivity of glass fiber-reinforced polymer composites, which are widely used in almost every sector, is 0.20-0.25 W/mK (AYGÜN, 2020). Also, the thermal conductivity of CFRP composites measured at room temperature is approximately 0.630 W/mK, and the thermal diffusivity is 0.485 mm^2/s (Thermtest Instruments, 2020). As can be seen, even though carbon fiber is used as fiber reinforcement material with a thermal conductivity value of up to 800 W/mK, the composite material has shown almost insulating properties (X. Zhang et al., 2000).

This low thermal conductivity and thermal diffusivity of CFRP composites is mainly due to the insulating properties of the polymers used as matrix material. It is seen in Table 1, how low the thermal conductivity and thermal diffusivity of the polymers used as matrix materials in FRPCs are when they are used in pure form. For this reason, the majority of the studies carried out to increase the thermal conductivity are studies aimed at increasing the thermal conductivity of the matrix material.

Table 1. Thermal Conductivity And Thermal Diffusivity Values Of Some Matrix Polymers (Takezawa et al., 2003; Tavman, 2015)

Polymer Matrix	Thermal Conductivity (W/mK)	Thermal Diffusivity (mm^2/s)
Low density polythene	0.28-0.32	1.70×10^{-7}
High density polythene	0.38-0.58	2.73×10^{-7}
Epoxy resin	0.17-0.21	1.57×10^{-7}
Polypropylene	0.18-0.24	0.96×10^{-7}
Poly Vinyl Chloride	0.16-0.20	1.225×10^{-7}

In order to increase the thermal conductivity and thermal diffusivity of the polymer matrix, the nano and micro-sized fillers are added within the polymer matrix. These conductive fillers, used in various studies, can be graphene, carbon-fiber, ceramic or metal alloys (Han & Fina, 2011). Each type of filler has its advantages and disadvantages. For example, metals such as, gold and copper have very high thermal conductivity. However, most of the metals significantly, increase the weight of the polymer matrix material.

There are many studies on FRPC materials containing metal fillers, but such fillers are generally not preferred, because they increase the weight of the material even though their electrical conductivity is high (Kumlutaş et al., 2002). On the other hand, ceramics such as aluminium nitride (AlN), boron nitride (BN), and silicon carbide (SiC) have a wide range of applications due to their high thermal conductivity, low weight, and electrical resistance (Ishida et al., 2005).

The most common and advantageous filler types are carbon-based fillings which show high thermal conductivity and low weight. In particular, graphene fillers are highly favoured due to their high thermal conductivity, accessibility, and relatively low price (Tu & Ye, 2009). Thermal conductivity and thermal diffusivity values of widely used conductive filling types are given in Table 2.

The direction in which thermal conductivity and thermal diffusivity are improved is very important in terms of using the material in the correct application. In most of the studies, thermal conductivity and thermal diffusivity have been investigated in two directions, through the thickness direction (Zhang et al., 2019) and the in-plane direction (Yu et al., 2017). The direction, in which the thermal improvement will be made, depends on the field of use. While some studies focus on improving thermal properties in one direction only, there are also studies in the literature that provide thermal improvement in both directions.

Table 2. Thermal Conductivity And Thermal Diffusivity Values Of Some Filling Materials Used In FRPC At 25 °C (Martin-Gallego et al., 2011; Tavman, 2015)

Filler Type	Thermal Conductivity (W/mK)	Thermal Diffusivity(mm^2/s)
Carbon (amorphous)	6 - 174	216.5 $x10^{-6}$
Carbon nano-tube	2000-5000	30 x 10^{-2}
Graphene	5300	80-90
Gold	345	1.27 x 10^{-4}
Copper	483	1.11 x 10^{-4}
Aluminium	204	8.42 x 10^{-5}
Zinc	116	4 x 10^{-5}

This paper presents the methods and results of various studies that aim to increase the thermal conductivity and thermal diffusivity of FRPC materials to be used in battery packs of EVs and HVs. Studies with similar approaches are examined under the same topic and the results, advantages, and disadvantages of the studies are presented. The discussions and comparisons of these studies are given in the following sections. Comparisons and proper selections can be made due to this paper with respect to the application and availability of the materials.

THE USE NANO AND MICRO PARTICLE FILLERS

The most widely used method to increase thermal conductivity and thermal diffusivity in FRPC materials is to apply high thermal conductivity fillers in nano-micro sizes into the matrix material or on the surface of the fabric. These fillers are applied randomly regardless of their positions. By applying the fillers into the polymer matrix material or on the fabric surface, a heat transfer path is created in which heat transfer can take place quickly and efficiently. Thus, the thermal properties of the material are improved. These studies differ according to the type, geometry, size, and application method of the filling material. For example; Zheng et al. (2019) aimed to increase the thermal conductivity of FRPC material by applying copper (Cu) and hexagonal-boron nitride (hBN) particles to the surface of carbon fiber fabric by using the electrophoretic deposition method (Figure 2). Some copper-coated carbon fabric samples used in this study were subjected to heat treatment in an electric furnace at temperatures of 300 °C, 400 °C, and 500 °C to remove the oxidation risk and any impurities in the coating. In order to make comparisons, thermal measurements of carbon fiber epoxy composite (CFEC) materials that have undergone different treatments, as well as an untreated CFEC sample used as a reference sample, were also performed. In addition, a tensile test was applied to the treated samples and the reference sample to observe whether the electrophoretic deposition method has an effect on the mechanical properties of the material. As a result; it is reported that this method increases the thermal conductivity and thermal diffusivity of CFECs, the thermal conductivity increases as the deposition process increases, and the heat treatment applied before the deposition process and the increase in the heat treatment temperature, positively affect the thermal conductivity of the material. However, a decrease in the tensile strength of the samples subjected to electrophoretic deposition was detected. Table 3 and Table 4 were prepared in order to observe the results more clearly.

As can be seen from Table 4, a higher amount of filler provides greater thermal conductivity in both directions. However, it must be remembered that the metal fillers such as Cu and BN greatly increase the weight of the structure. Therefore the optimum amount of filler material should be applied to the structure. Also, the time of the electrophoretic deposition and the temperature of the heat treatment process positively affect the thermal conductivity in both directions.

In another study by Lee et al. (2019), it was aimed to increase the thermal conductivity in the thickness direction by placing inorganic crystals between the layers of FRPC. For this purpose, aluminium (Al), magnesium (Mg), and copper (Cu) crystals were used to create a heat transfer path between the FRPC layers (Figure 3). The thermal conductivity increased as a result of placing inorganic crystals in different ratios between the layers. The highest thermal conductivity value measured throughout the thickness was obtained with the use of magnesium with a weight ratio of 0.01 wt% with an increase of 87%. In addition, the effect of inorganic crystals on the flexural strength of the material was measured by a three-point bending test and it was observed that the presence of these crystals increased the flexural strength. Although this method does not increase the thermal conductivity at a high rate, it is an important candidate in the literature with its easy applicability and positive effect on flexural strength. In addition, these types of metal fillers such as Al, Mg and Cu have relatively lower price than other fillers like graphene or gold. This feature can be emphasized as another important advantage of this method, particularly for the appliers who are searching for a cheap solution.

Table 3. Sample Names And Characteristics (Zheng et al., 2019)

Sample Names	Time of the Electrophoretic Deposition (h)	Temperature of the Heat Treatment Process (°C)
CF	-	-
BCC1	1	-
BCC1.5	1.5	-
BCC2	2	-
BCC3	3	-
BCC_300	3	300
BCC_400	3	400
BCC_500	3	500

Table 4. Thermal Conductivity Of The Specimens (Zheng et al., 2019)

Specimen	hBN/Cu Coating(vol %)	Through Plane Thermal Conductivity (W/m.K)	In-plane Thermal Conductivity(W/m.K)
Epoxy/CF	-	0.68 ± 0.01	4.18 ± 0.03
Epoxy /BCC1	9.59	1.24 ± 0.01	4.90 ± 0.02
Epoxy /BCC1.5	12.42	1.44 ± 0.01	5.02 ± 0.03
Epoxy /BCC2	14.09	1.68 ± 0.02	5.15 ± 0.03
Epoxy /BCC3	18.34	1.95 ± 0.03	5.48 ± 0.03
Epoxy /BCC_300	18.32	1.98 ± 0.02	5.61 ± 0.03
Epoxy /BCC_400	15.56	2.14 ± 0.03	5.77 ± 0.03
Epoxy /BCC_500	11.86	2.16 ± 0.03	6.14 ± 0.03

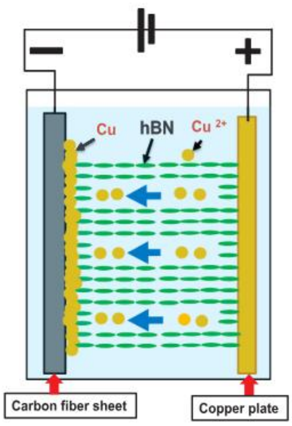


Figure 2. Schematic View Of The Electrophoretic Deposition Method (Zheng et al., 2019)

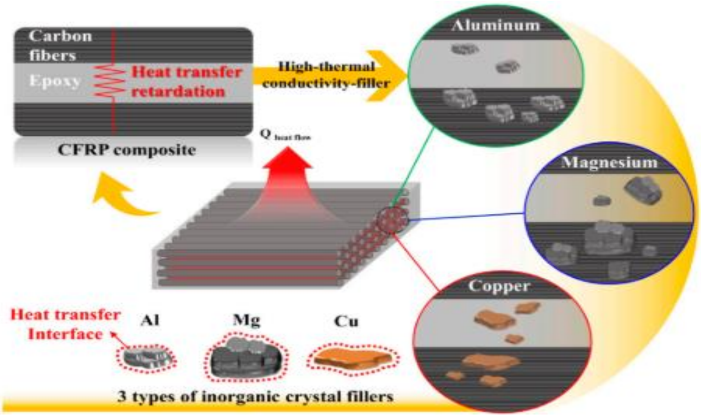


Figure 3. Schematic Representation Of The Study By Lee et al. (2019)

Another study, by Barani et al. (2020), aimed to increase the thermal conductivity and thermal diffusivity of epoxy, directly, by adding graphene and copper nano-particle fillers to epoxy at different ratios. This type of filling is called binary filler, and a relatively high thermal conductivity value of 13.5 ± 1.6 W / mK can be obtained when using 40% graphene and 35% copper in weight ratio. In addition to the successfully increased thermal conductivity, the thermal diffusivity of the FRPC material has also increased significantly. This study stands out in the literature, with its high thermal conductivity value, its positive effect on thermal diffusivity, and its relatively easy applicability.

In another research, Yan et al. (2019), aimed to increase thermal conductivity by mixing micro-Al_2O_3, silicon-based nano-particles (SiO_2), and carbon nano-tube fillers into epoxy resin at different ratios.

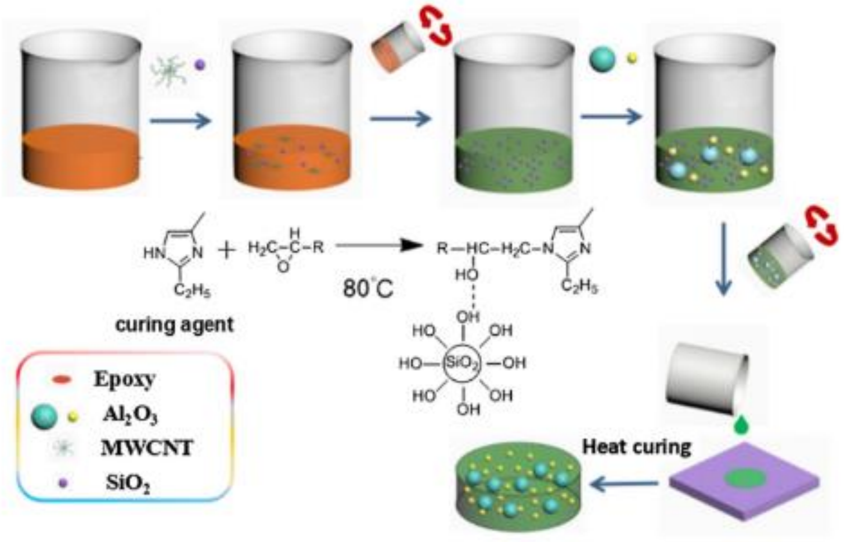


Figure 4. Schematic Representation Of The Mixing Process In The Study By Yan et al. (2019)

Enhanced Thermal Stability by using Nano /Micro Fillers

In some studies, micro/nano particle fillers directly mixed into epoxy. It has been observed that in addition to thermal conductivity and thermal diffusivity, thermal stability has also been improved. For example; In a study carried out by Uzay (2022a), cubic boron-nitride (c-BN) nano-particles were dispersed into epoxy at different ratios to increase the tensile and impact strength of the composite structure. During this study, it was found that the presence of c-BN particle fillers increased the glass transition temperature by 16.09% to 21.14% and accordingly improved the thermal stability of the composite material. Another study performed by Uzay et al. (2022) aimed to reinforce the epoxy polymer matrix by adding carbon nano-tubes (CNTs) doped with graphene nano-platelets (Gr) to epoxy polymers. In addition to ascension in the micro-hardness of the structure increased thermal stability and high enthalpy values were obtained according to thermal analyses. The effects of nano-fillers on the thermal properties of epoxy composites with micro-Al_2O_3 particles are investigated by Gao & Zhao (2014). In this study, specially synthesized nano-fillers and micro-Al_2O_3 particles were utilized as thermally conductive fillers in the epoxy composite to achieve improved thermal properties. In addition to improved thermal conductivity, the density of epoxy composites with the synthesized nano-fillers was decreased and the corresponding thermal stability was enhanced.

In the last article to be analysed under this sub-topic; the effects of magnesium oxide (MgO) micro-particles on the mechanical and thermal properties of laminated carbon fiber-reinforced polymer composites are investigated by Uzay (2022b). In this study, the polymer epoxy matrix was modified with 0% (pure), 2 wt%, and 4 wt% Magnesium oxide (MgO) fillers. Then the laminar composites were manufactured with the vacuum bag method. The entire manufacturing scheme is given in Figure 5. The thermal performance of the polymer composites with and without MgO additives was analysed comparatively by performing the thermo-gravimetric analysis (TGA) and differential scanning calorimeter (DSC). The TGA and DSC instruments revealed that the decomposition temperatures increased and curing behaviours improved depending on the MgO content. As can be seen from all these studies under this sub-topic, not only thermal conductivity and thermal diffusivity but also the thermal stability of the FRPCs can be improved by using micro/nano-sized fillers. This enhanced thermal stability emphasized the positive effects of the micro/nano-fillers on the thermal properties of the FRPCs.

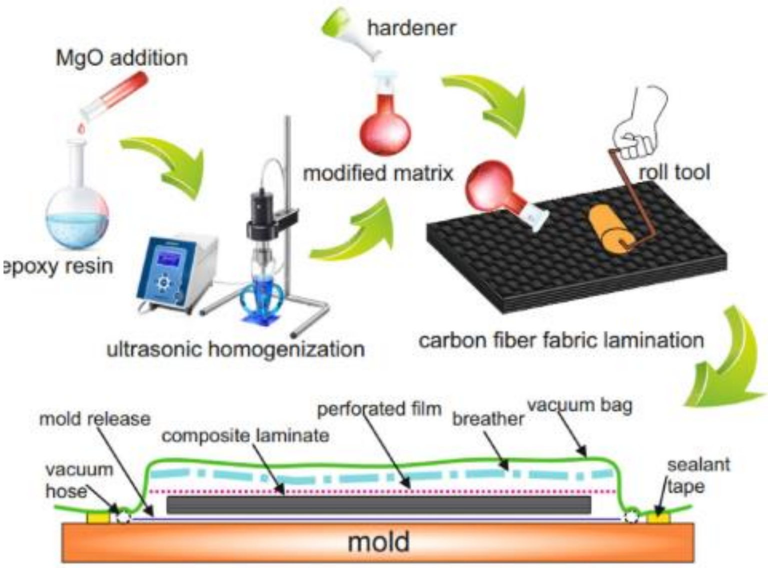


Figure 5. Schematic View Of The MgO Filled Laminar Fiber Reinforced Polymer Composite Manufacturing (Uzay, 2022b)

THE USE OF 3D STRUCTURES

In many studies to increase the thermal conductivity of FRPC materials, structures where heat transfer can take place efficiently are added to the composite material. These structures are usually created in the through-thickness direction. These three-dimensional structures are formed from materials with high thermal conductivity, then added to the matrix material or woven between the fibers in different forms.

For example; Ouyang et al. aimed to increase the thermal conductivity both through the thickness and through the plane by weaving high conductivity Cu and graphene films (HOGF) into the material (Figure-6) (Ouyang et al., 2022). AF represents the adhesive film in the next figure. In addition, the effect of these thermal films on the interlayer shear strength was also investigated. The results of 49.19 W/mK using graphene film with a volume fraction of 1.97% and 21.45 W/mK using copper film with a volume fraction of 1.74% are the highest values obtained in this study. These thermal conductivity values are 11029% and 4753% higher than the thermal conductivity of a standard CFRP material, respectively, and these results demonstrate the success of the study. However, the presence of these thermal films reduced the interlayer shear strength by 13-19%.

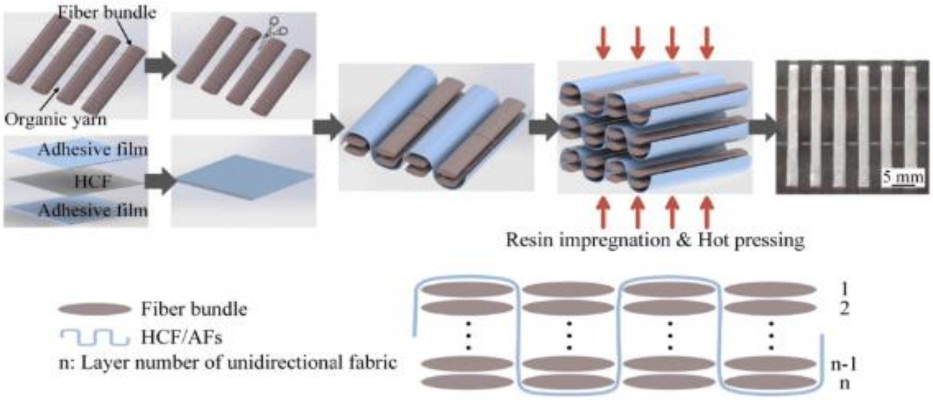
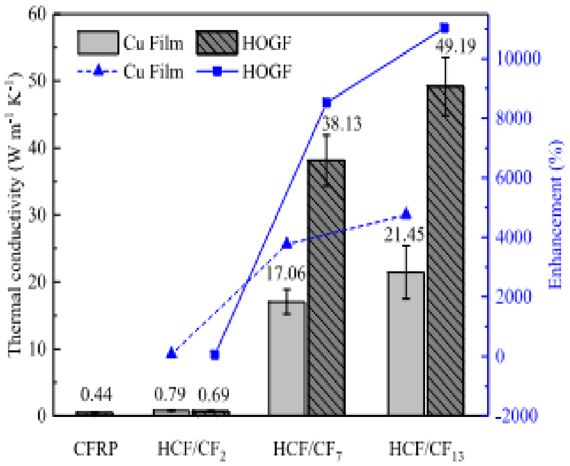
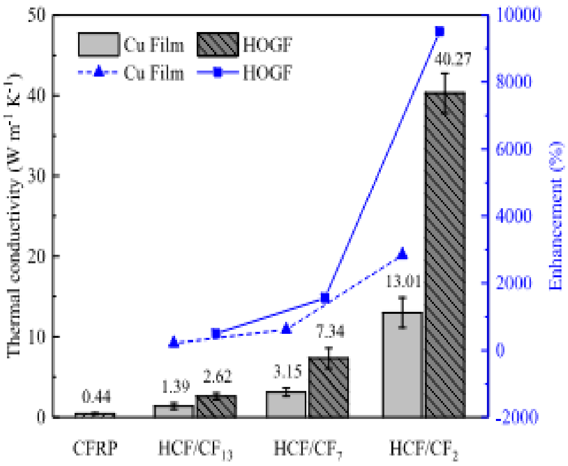


Figure 6. Schematic Representation Of The Study By Ouyang et al. (2022)

In another finding obtained in this study, it was determined that the thermal conductivity increased along the thickness but decreased along the plane as the number of curls (waves) of the thermal film between the fibers increased. Thermal conductivity graphs obtained for different samples are shown in Figure 7 for a better explanation of the obtained results. When these results are examined; CFRP is carbon fiber reinforced polymer, HCF is Highly Conductive Film and CF is the carbon fiber fabric, and the expression HCF/KF$_n$, n, represents the number of layers of carbon fiber woven with each film. Therefore, a higher 'n' indicates that the thermal film has more curl. As can be seen from the results, the thermal conductivity of the material increases, significantly, as the 'n' value increases. However, it should be emphasized that the construction of such a composite is very hard to apply and requires skilled operators and sensible manufacturing machines. Although the thermal conductivity is considerably improved, the applicator should consider this disadvantage.



(a)



(b)

Figure 7. Results Of The Study By Ouyang et al. (2022) **a.** Thermal Conductivity Values Measured Through-Thickness **b.** In-plane Directions

As another example, in the study performed by Yu et al. (2016) a three-dimensional structure was created to increase the thermal conductivity of FRPC material through the thickness, where heat conduction can efficiently take place. Copper z-fillers and aluminium foil materials were used for this process (Figure 8). Due to this process, the thermal conductivity value in the thickness direction increased by 12 times. The diameters of the copper z-fillers were selected as 2, 4, and 6 mm and the highest thermal conductivity value of 7.6 W/mK was obtained when z-fillers with a diameter of 2 mm were used. In addition, a tensile test was applied to the specimens to understand the effect of copper z-fillers on the mechanical properties of the composite material. It was observed that the z-fillers negatively affected the tensile strength and Modulus of Elasticity of the material. The main reason for this is that the copper fillers added to the structure cause twisting of the adjacent fibers. Although the thermal conductivity is considerably improved, the noticeable decrease in mechanical properties is a major handicap of this study.

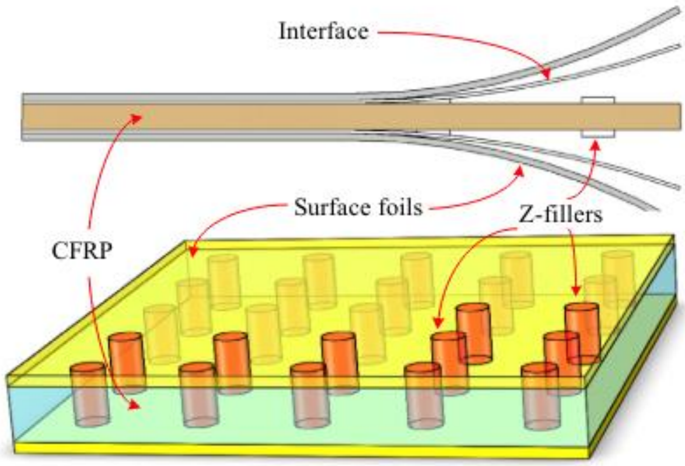


Figure 8. Schematic Representation Of Specimens Produced In The Study By Yu et al. (2016)

In another study examined under this topic, Schuster et al. (2008), aimed to increase the thermal conductivity of FRPC material both analytically and experimentally. It was aimed to increase the thermal conductivity of FRPC material with fibers with high thermal conductivity value, especially copper, weaved through the thickness. During this study, it was observed that the thermal conductivity increased as the number of conductive fibers increased, up to a value of 6.7 W/mK. Although a significant increase in thermal conductivity is achieved, it is quite difficult to construct such a composite, which is schematically shown in Figure 9.

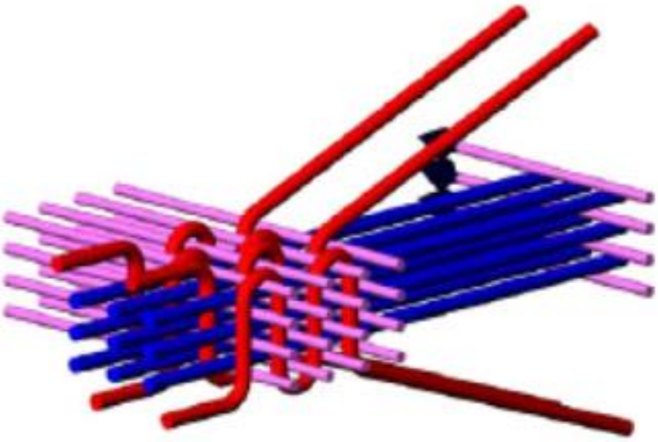


Figure 9. Schematic Representation Of The Composite Structure (Schuster et al., 2008)

In addition to the three-dimensional structures created to increase the thermal conductivity of the FRPC material described above, some studies in the literature have focused on increasing the thermal conductivity of the polymer matrix material directly by creating three-dimensional structures in the polymer. In a study conducted for this purpose, a continuous structure was formed in the polymer matrix by using materials with high thermal conductivity such as graphene, carbon nano-tubes, boron nitride, or metal (Zhang et al., 2020).

As another example; In the study by Ye et al. (2018), it was reported that the thermal conductivity of epoxy increased by 891% by forming a three-dimensional diamond structure into the epoxy matrix. As a result of this study, the thermal conductivity value of epoxy increased up to 2.28 W/mK when the three-dimensional structure was used at 1.2 wt%. Significant improvement has been achieved in this study. However, the high cost of diamonds creates a major disadvantage to the application of this approach. In another study by An et al. (2018), aiming to increase the thermal conductivity of epoxy polymer by using a three-dimensional structure, the thermal conductivity was increased to a very high value of 35.5 W/mK by using 35 wt% of three-dimensional graphene structure. This high increase of 16805% in thermal conductivity makes this study one of the highlights. The same graphene structure, when used at 0.92% by volume, Lian et al. (2016), obtained a thermal conductivity increase of

1231%. It is also possible to create these three-dimensional structures by combining two different materials. For example; An et al. (2018), succeeded in increasing the thermal conductivity value of epoxy polymer material up to 11.01 W / mK with the three-dimensional structure formed by using graphene and boron nitride (BN) at 44 wt%. In another study by Tian et al. (2018), using only a three-dimensional BN structure, it was reported that the thermal conductivity of epoxy polymer material increased by 2780%. A thermal conductivity value of 5.19 W/mK was obtained with 24.4 wt% BN.

As can be seen, when graphene is used in the formation of a three-dimensional structure, the thermal conductivity increases at a high rate. Although so far, only studies using epoxy as the matrix material have been mentioned, significant increases in thermal conductivity and thermal diffusivity values have been observed in studies where three-dimensional graphene structure is formed in polyamide material or in the phase change materials (PCM) (Loeblein et al., 2015; Yang et al., 2018; Yang et al., 2016).

Different types of materials have been considered and reviewed, in several studies that are used to improve the thermal properties of the FRPCs. When all of the studies are considered, graphene shows higher improvements than other candidates.

THE USE OF CHEMICAL METHODS

Other types of methods of increasing the thermal conductivity of FRPC materials that can be used in the battery case of the EVs and HVs are examined under the main topic of 'chemical methods'. When other methods are considered, chemical methods, which are more difficult to apply and have relatively lower efficiency, are not preferred as much as other methods due to these disadvantages. Although such methods are not used as frequently as nano-micro fillers and three-dimensional structures, they are encountered in some studies of the literature.

For example, in a study by Liang et al. (2013), it was aimed to increase thermal conductivity by forming carbon nano-fibers (CNF) directly on the carbon-fiber fabric, using the chemical vapour deposition method (Çoşğun et al., 2021). In addition, as another approach in this study, the thermal conductivity value was measured by mixing CNF fillers directly into epoxy resin. According to the maximum results obtained, an increase of 30% in the thermal conductivity in the thickness direction was obtained when CNFs formed directly on the carbon-fiber fabric were used, and an increase of 10% in the thickness direction was obtained when CNF fillers were mixed into the epoxy resin. In addition, the presence of CNF fillers did not show an improvement in thermal conductivity along the plane, while CNFs formed directly on the carbon-fiber fabric caused an increase in thermal conductivity both in-thickness and along the plane. However, the increase in thermal conductivity is lower than both the studies conducted with nano-micro fillers and the studies conducted by forming three-dimensional structures. The image of the CNF structures on the fibers was imaged by scanning electron microscopy (SEM) and the detailed image of the CNF was imaged by transmission electron microscopy (TEM) (Figure 10).

In the second and final study to be analysed under this main topic is the one presented by Yu et al. (2021). They presented an environmentally friendly, low-cost, and highly efficient method to improve the thermal conductivity of carboxylated acrylonitrile-butadiene rubber (XNBR) matrix by non-covalent-modification-of-boron-nitride (BN) using tannic acid (TA) chemistry. The best result obtained as a result of the study was the value of 0.42 W/mK obtained by using 30% BN-TA-XNBR by volume. This value corresponds to 260% of the thermal conductivity value of pure XNBR with a thermal conductivity of 0.16 W/mK. The fact that this study is environmentally friendly and cost-effective compared to others, has enabled it to be included in this paper.

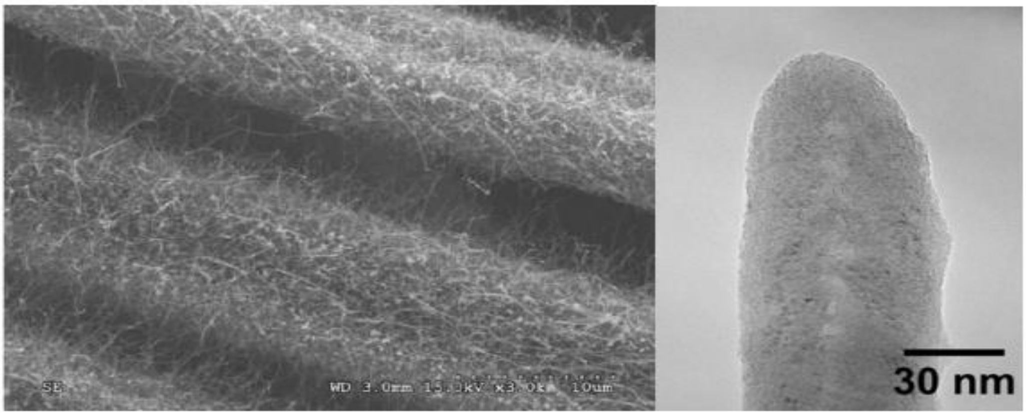


Figure 10. a. SEM Image Of CNF Structures On Fibres **b.** TEM Image Of CNF Structures (Liang et al., 2013)

DISCUSSION

The methods for enhancing the thermal properties of FRPCs that can be integrated into the battery enclosures of the EVs/HVs are reviewed and proposed in this paper. The methods that are based on similar approaches are categorized under the same topic. In this section all methods will be generally discussed and compared with each other.

Nano-micro fillers found to stand out with their superior features. Due to their properties of; relatively low cost, easy applicability, and the availability of the filler materials. Such fillers also provided a significant increase in the thermal conductivity of the composites. These studies, which do not require an advanced production method and high cost, are the first methods that come to mind in many studies aiming to increase thermal conductivity. In addition, nano and micro fillers are suggested to the appliers who are willing to increase the thermal properties of the FRPC materials easily, quickly, and without any high cost. A study that is examined under the topic of nano/micro fillers, stands out due to obtained high thermal conductivity (Barani et al., 2020). They used copper-graphene filler materials called binary fillers and obtained significant thermal conductivity improvement. The value of 13.5 ± 1.6 W/mK obtained in this study is considerably higher than other studies involving nano-micro particle fillers. This study emphasizes the importance of the usage of binary filler structures to enhance the thermal properties of the FRPCs.

In the studies aiming to increase thermal conductivity, many of the studies with the best results were grouped under the title of three-dimensional structures. In all of the studies that are examined under the title of nano-micro fillers, the fillers were applied randomly into the matrix material or on the fabric surface, regardless of their position. On the other hand, since the three-dimensional structures are not applied randomly, but to create a path where heat transfer can take place efficiently, the thermal conductivity values obtained are higher than the studies under the other topics. The construction of the 3D structures creates a heat transfer path within the composite. Due to this pathway, the heat can flow efficiently within the composite layers and the insulation property of the polymer matrix is no longer a problem for thermal applications. Since the created heat transfer path is not random, such methods can be used in special applications. For instance, the thermal properties of only one part of the composite material can be improved while the rest can be kept. In recent years, three-dimensional conductive structures have been formed using graphene fibers. In addition to the thermal conductivity of graphene of 5300 W/mK, their low-density values of 230 kg/m^3 when used in fiber form, make these materials the first candidate that comes to mind in the creation of conductive three-dimensional structures (Martin-Gallego et al., 2011; Venkateshalu & Grace, 2020). In particular, the study by An et al. (2018), which succeeded in increasing the thermal conductivity by 16805% by using the three-dimensional graphene structure by 35% by weight of the matrix, shows how much such three-dimensional structures can increase the thermal conductivity.

The studies analysed under the chemical methods are the least preferred methods to increase the thermal properties of the composites. Because they require advanced chemical technology, are difficult to apply, and have relatively less effect on thermal conductivity. However, they offer a more environmentally friendly perspective compared to other methods.

As can be seen from most of the studies, graphene is the first candidate that comes to mind when the enhancement of the thermal properties of the FRPCs is the issue. If the cost matters and the very high thermal conductivity values are not necessary, metal fillers such as Cu, Al, and Mg, should be used. However, this paper is focused on the FRPCs that have the potential to be used in the battery enclosures the weight of the filler material becomes a very important aspect. Because the increase in any weight of the EV/HV increases power consumption and reduces the range and performance of the batteries. Thus, metal fillers are not the right answer for increasing the thermal properties of the FRCPs that are used in the battery case. The applicator or the manufacturer should consider every aspect from cost, weight, availability, and applicability while selecting the proper method to improve the thermal properties of such composites

CONCLUSION

The use of EVs and HVs is increasing day by day. Due to this increase, efficient use of vehicle batteries is very important. In this article, the advantages of using FRPC materials in battery case designs are discussed. In addition, the low thermal conductivity and thermal diffusivity properties of FRPCs, which are a major disadvantage of FRPCs, are mentioned. It is stated that these thermal properties limit the use of such materials and these properties should be improved in order to use such composites in the battery casings of EVs and HVs.

The studies under the same main topics in this article are based on similar methods. Each study has its own advantages and disadvantages. Which method to choose may differ according to the field application.

The main purpose of this article is to present the promising studies that have succeeded in increasing the thermal properties (thermal conductivity, thermal diffusivity and thermal stability) of FRPC materials with different methods and to provide a comparison with each other by gathering the numerical data they have obtained under a single framework.

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