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PAWEŁ RUTKOWSKI[1*], DARIUSZ KATA[1], JOANNA MASTALSKA-POPŁAWSKA[1], JERZY LIS[1], MAGDALENA SZUMERA[1]

THERMOPHYSICAL PROPERTIES OF LOW VISCOSITY EPOXY RESIN WITH THE ADDITION OF BORON PHASES FOR DUAL-USE MILITARY AND CIVILIAN APPLICATIONS

The study presents a comprehensive analysis of low-viscosity resin composites with boron carbide (BC) and hexagonal boron nitride (BN) additions to modify their rheological, elastic, heat-transfer, and thermal-stability properties. The analyses being conducted are related to a specific dual application, rapidly produced through a simple mixing process. The main purpose of their use is to dissipate the energy of moving vehicles and the heat transferred to the material. They can also be used, because of the low viscosity, in various other applications, ranging from filling hard-to-reach areas, to bonding layers or impregnating materials such as ballistic fabrics. Various thermal analysis techniques, such as thermogravimetry, differential scanning calorimetry, laser flash analysis and dynamic mechanical analysis were used to assess their properties. Modulus values of up to 5.5 GPa were obtained at a frequency of 20 Hz and a temperature of –60°C, compared to 4.0 GPa for the pure resin. A temperature of 50°C was selected as the upper limit, where a value of 1.7 GPa was obtained for a 10 vol.% BCBN blend, compared to 1.2 GPa for the pure resin. Materials with thermal conductivity nearly three times higher than that of pure resin have been obtained. These findings suggest that incorporating boron-based ceramic fillers enables effective tuning of both the thermomechanical performance and the heat-transfer characteristics of low-viscosity epoxy systems. Such behaviour indicates their potential for use in multifunctional structures that require simultaneous mechanical stability and enhanced thermal management.

Keywords: Epoxy resin 652; boron carbide; hexagonal boron nitride; thermophysical properties

1. Introduction

Epoxy resins are versatile thermosetting polymers widely used for their superior adhesion, durability, chemical resistance, and structural strength. They are primarily utilized in adhesives, high-performance coatings, electronics encapsulation, and industrial composite materials (e.g., aerospace/marine parts). They can form a durable bond with a wide range of substrates, including wood, metal, glass, and concrete, making them excellent adhesives and coatings. Other advantages include low shrinkage, typically up to 2% upon curing, which minimizes internal stress. They can also withstand high temperatures and maintain their stability under harsh environmental conditions. But they have drawbacks, most notably health risks from toxic fumes and skin sensitization. They are also high-cost, time-consuming to cure (often taking days), and highly sensitive to temperature and humidity. Furthermore, epoxy typically yellows over time when exposed to UV light and requires precise, skilled application to avoid flaws such as bubbles or incomplete curing [1-6]. From a materials science perspective, the performance of epoxy systems is strongly governed by their cross-linked network architecture and the resulting limitations in thermal transport, which is typically dominated by phonon scattering within the amorphous polymer matrix. Consequently, the intrinsic thermal conductivity of unmodified epoxy resins remains low, which restricts their application in systems requiring efficient heat dissipation.

This article examines the effect of boron carbide (B_4C), boron nitride (h-BN/hBN) and their mixtures on improving thermal and mechanical properties of epoxy resins. Boron carbide is an extremely hard, low-density technical ceramic – ranked third behind diamond and cubic boron nitride – with a Vickers hardness of ~30 GPa, high melting point (2450°C), and often called "black diamond". It is essential for ballistic armor, resistant materials, and nuclear control rods [7-15]. Hexagonal boron nitride is a synthetic, white, lubricating powder often called "white graphite" due to its layered, graphitic structure. Composed of boron and nitrogen, it is highly valued for being an electrical insulator with high thermal conductivity, extreme chemical

[1] AGH UNIVERSITY OF KRAKOW, FACULTY OF MATERIALS SCIENCE AND CERAMICS, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

* Corresponding author: pawelr@agh.edu.pl

inertness, and thermal stability up to about 1000°C. It is widely used in high-temperature electronics, lubricants, and polymers [16-21]. h-BN enhances thermal conductivity while maintaining electrical insulation. B_4C primarily improves stiffness and radiation shielding. Their combined effect depends on dispersion, interfacial interactions, and percolation. Common composites including B_4C-hBN often use h-BN to reduce friction or to act as a sintering aid to enhance toughness. Hexagonal boron nitride (h-BN) can be formed on the surface through high-temperature (850 °C) nitrogen ion implantation, thereby reducing the coefficient of friction. Composite materials of B_4C-hBN are produced by adding h-BN to B_4C powder to improve fracture toughness and friction properties. Due to these properties, such composite materials can be used in applications requiring high temperatures, extreme wear resistance and good heat dissipation [22-26]. However, most studies focus on fully ceramic systems or metal matrix composites. In contrast, significantly fewer reports address the behavior of B_4C-hBN hybrid systems dispersed within polymer matrices, particularly in the context of low-viscosity resins intended for processing-intensive applications.

This article characterizes a wide range of thermal and thermomechanical properties of Epidian 652 epoxy resin with boron carbide and hexagonal boron nitride phases, as well as their mixtures at up to 20 vol.%. The literature lacks a comprehensive approach to B_4C-hBN systems as additives to epoxy resins. The described research results can be used to implement these systems as lightweight composite layers in materials with high thermal and mechanical resistance and high neutron absorption capacity. There is limited systematic data correlating filler content, rheological behavior during processing, and the resulting thermophysical performance, all of which are critical parameters for scalable manufacturing and application-oriented design.

The study aims to conduct a comprehensive analysis of the rheological and thermophysical properties of materials based on low-viscosity resin containing particles of boron carbide, hexagonal boron nitride, and specific mixtures of these two boron-based phases-mixtures that are rarely encountered, and certainly not in these quantities. Such resin additives could be used in hybrid processes involving neutrons and gamma radiation [27-32], which may have protective applications in civil engineering and in the manufacture of armor or other components in the defense industry [33,34]. Adding BN is very important in corrosion applications [35]. It is equally important to analyze the rheological properties of the produced suspensions to determine their suitability for easily casting various shapes, coating surfaces, or impregnating hard-to-reach areas or fabrics used in both the civilian and defense markets. Here, the addition of hexagonal boron nitride – commonly known as white graphite – plays a very important role. Reducing the coefficient of friction could be highly significant for the production of ballistic shields, both in the outer layers and interlayers, to alter the trajectory of an incoming projectile relative to the shield. In the production of ballistic armor, the bonding of individual layers is of great importance, as the properties of the adhesive affect the stability of the armor, energy dissipation during vehicle movement due to vibration under various temperature conditions, and heat dissipation (also for camouflage purposes). Therefore, data from dilatometric tests, dynamic mechanical analysis conducted at various temperatures and frequencies, and heat transport studies are essential. Due to varying atmospheric conditions, DMA data for dual-use materials were obtained at both –60°C and 50°C. The study also included a thermal stability analysis of the materials under conditions with and without air exposure, and thus for materials intended for interlayer bonds and topcoats. The above studies were conducted on low-viscosity resin containing 2.5, 5, 10, and 20 vol.% boron carbide particles, hexagonal boron nitride, and new materials with a 50/50 volume ratio of the two phases. Such an approach enables a direct assessment of structure-property relationships across a wide compositional range, which is essential for identifying optimal formulations that balance processability with functional performance.

2. Materials and methods

The epoxy resin composites with boron-based ceramic particles were composed of Epoxy Epidian 652 resin (density of 1.1 g/cm^3; coded as E652) of Sarzyna Chemical, boron carbide grade HD 15 – A product of H.C. Starck (particle size of 0.6-0.9 μm, density of 2.51 g/cm^3, purity of 98.0 %, BET surface area of 15.4 m^2/g) and hexagonal boron nitride BO-502 of Atlantic Equipment Engineers (particle size of 2-3 μm, density of 2.25 g/cm^3, purity of 99.9 %, BET surface area of 10.41 m^2/g; AEE, USA, Bergenfiels). The resin to IDA hardener ratio was A:B=100:50. The composite sets were prepared at the specified volume fractions and their coding is presented in TABLE 1. To cast composites, the A component of epoxy Epidian 652 resin was mixed with boron carbide, hexagonal boron nitride or with a 50 vol.%/50 vol.% mixture of these powders using a dissolver of Pendraulik-Teja, model Yellow 075. The mixing process took 60 min at 300 rpm, and then the IDA hardener was added for the next 2 min at 300 rpm before the casting process. In the case of 20 vol.% hexagonal boron nitride, the resin behaved like a paste, making a casting process impossible. Before the casting process, slurries without hardener were rheologically analyzed by the Physica MCR-301 rheometer of Anton Paar. The viscosity was measured over time at a constant shear rate of 100 1/s using a parallel-plate system (PP 25) with a 0.3 mm gap. The measurement was made at 25°C, and the results are presented in Fig. 1. Viscosity of pure Epidian 652 resin is approximately 0.72 Pa·s. Analyzing the effect of the addition of both powders on the viscosity of mixtures with a single additive, it was noted that the B_4C (BC) samples were more viscous than the h-BN (BN) samples, but the differences were small. A noticeable difference is at the 20 vol%, where the viscosity of the h-BN resin is almost twice as high (about 50 Pa·s) compared to the viscosity of the B_4C mixture (about 26 Pa·s). The viscosity of mixtures containing both ceramic powders is similar to that of resins with only B_4C. Generally, grain size of ceramic particles has a significant impact on the viscosity of epoxy resin, follow-

ing the principle that smaller particles increase viscosity, while larger particles decrease it, assuming the same volumetric loading. Smaller particles have a higher specific surface area with higher surface energy, creating more particle-particle interactions and increased resistance to flow. Therefore, with small fractions of individual powders, up to 5 vol.%, suspensions with B_4C are characterized by higher viscosity (smaller grain size and higher specific surface area). However, as the powder content increases, its shape also begins to affect viscosity. B_4C is characterized by an irregular shape, while hBN has a typical lamellar structure. The boron carbide the powder morphology will have an influence on viscosity in case of higher its concentration due to the change of degree of particle sphericity [36]. Flat particles have high aspect ratios, meaning they can easily align parallel to the direction of flow (shear). This situation can work for low its concentrations, at higher amounts of boron nitride flat structures the agglomeration is very common in literature [37]. Agglomerated particles trap large amounts of resin in their internal structures, effectively decreasing the "free" liquid available in the slurry and significantly raising the viscosity. Higher surface energy of flat structures results, at its high loading, in higher viscosity.

Afterwards, ceramic dispersions prepared in this way were poured into a 2.9 cm × 19.3 cm × 0.32 cm silicon mold and left there for 14 days due to supplier recommendations.

TABLE 1

Material coding and composite compositions

Material	Resin	B_4C	h-BN
	vol.%	vol.%	vol.%
E652 (reference)	100	0	0
E652_2.5BC	97.5	2.5	0
E652_5BC	95	5	0
E652_10BC	90	10	0
E652_20BC	80	20	0
E652_2.5BN	97.5	0	2.5
E652_5BN	95	0	5
E652_10BN	90	0	10
E652_20BN	—	—	—
E652_2.5BCBN	97.5	1.25	1.25
E652_5BCBN	95	2.5	2.5
E652_10BCBN	90	5	5
E652_20BCBN	80	10	10

The prepared composites were cut into samples for various investigations starting from fracture analysis by Apreo2 (ThermoFisher Scientific) scanning electron microscope with the use of a LVD detector. Before the examination, the materials were PVD coated with graphite. In the next step, materials were subjected to thermal analysis in a nitrogen atmosphere for use as an interlayer in ballistic shields and in a synthetic air atmosphere for use as a surface layer in ballistic shields. Thermal analysis investigations were examined by STA 449 F3 Jupiter apparatus of Netzsch (Germany, Selb) with use of DSC-TG sample carrier. The results were described with the use of Proteus 8.0.3 software. Aluminum pans with a lid were used for investigations in nitrogen flow up to 600°C and in aluminum crucibles with a lid in air flow conditions up to 800°C. For both cases, the sample mass was around 7 mg and gases flowed with a set of 50 mL·min^{-1} of purging and 20 mL·min^{-1} of protective. All DSC-TG analyses were performed with 10°C·min^{-1} heating rate.

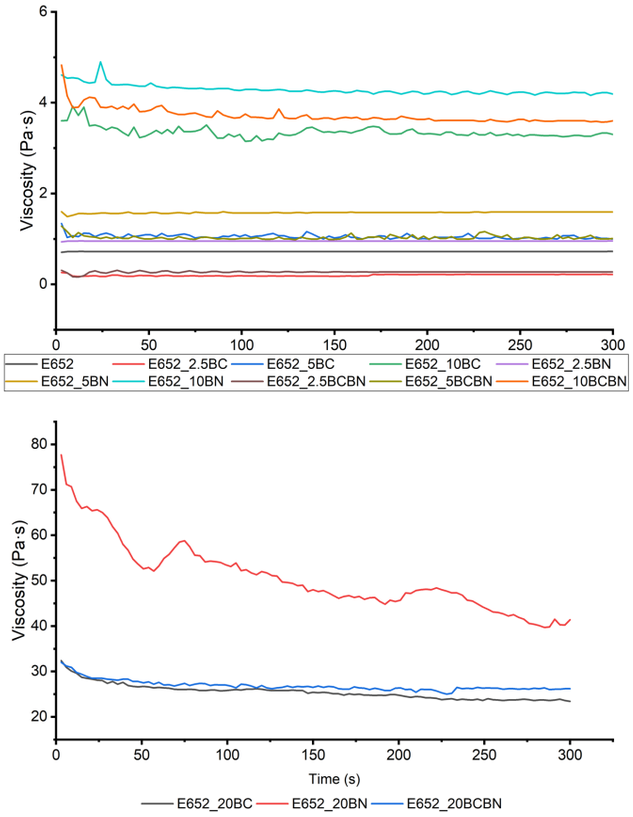

Fig. 1. Rheology analysis of resin slurries

Due to material vibration and working condition, for example, for military applications on the battlefield, the elastic properties were determined in a wide range from –60 to 100°C. These tests on prepared composites were performed using dynamic mechanical analysis (DMA) on a Netzsch (Germany, Selb) DMA 242E Artemis apparatus equipped with Proteus 8.0.3 software. Due to the possible application the 2×17 mm holder for dual cantilever bending was applied. The analysis was made in a nitrogen flow of 50 mL · min^{-1} of purging gas and 50 mL · min^{-1} of protective gas. The other process conditions were as follows: 3°C · min^{-1} heating rate, 20 μm amplitude, and frequency of 1, 5, 10 and 20 Hz.

Other very important property for material application is linear thermal expansion (CTE), thermal diffusivity and thermal conductivity. The CTE was determined by DIL 402C dilatometer of the Netzsch company with alumina sample holder and pushrod. The tests were made on 25 mm length samples under following conditions: 15 cN load, 1°C · min^{-1} heating rate, and 70 mL · min^{-1} nitrogen flow. Before the measurement alumina standard was used for calibration, and calibration correction for the measurement was performed according to ASTM E 228 with use of Netzsch Proteus 8.0.3 software. In order to deter-

mine thermal conductivity, thermal diffusivity and specific heat capacity were measure by the use of laser flash analysis method by LFA 427 apparatus of Netzsch. The test was made in static air conditions at room temperature (RT). The graphite-coated samples were 10 mm – 10 mm square shape and had 2-2.5 mm thickness, and were analyzed in alumina square sample holder (centring cone) with SiC cap. For the measurements, the following conditions were used: InSb detector, voltage 500 V, and pulse of 0.6 ms. Exactly the same conditions were used for Pyroceram 9606 reference material to determine, with use of Proteus Netzsch LFA Analysis 8.0.3 version software, specific heat capacity and finally thermal conductivity of prepared materials.

3. Results and discussion

In order to evaluate the casting process of slurries containing boron-containing particles and to subsequently analyze their thermophysical properties, SEM observations of material fractures were conducted, as shown in Figs. 2-5.

Compared to the fracture surface of the pure resin (Fig. 5c), the composites exhibit a finer fracture morphology (Fig. 2), which becomes more pronounced with increasing boron carbide content and improved particle dispersion. This observation indicates a modification of the fracture mechanism rather than a direct change in the cross-linking process. The presence of well-dispersed inorganic particles may influence crack propagation paths and local stress distribution, thereby contributing to the observed changes in thermophysical properties discussed in subsequent sections.

In the case of a resin additive consisting solely of h-BN (BN) particles, Fig. 3, it was observed that, in addition to a finely divided microstructure and dispersed fine BN platelets, agglomerates are also formed, which may negatively affect the achievement of the highest thermophysical properties. However, their presence may improve the lubricating properties of the materials. A very similar situation occurs in a system containing a mixture of the inorganic phases B_4C and h-BN (Fig. 4), where the presence of boron nitride agglomerates, in addition to well-dispersed boron carbide, can, for example, results in only

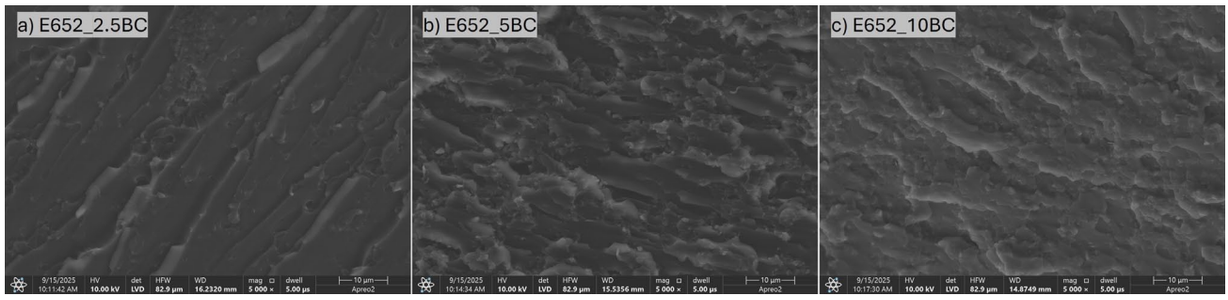

Fig. 2. SEM observations of fractures of composites containing B_4C, 10 μm scale bar

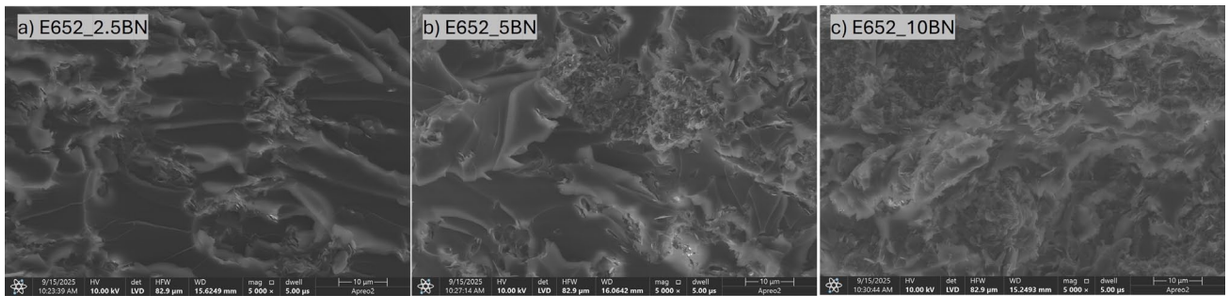

Fig. 3. SEM observations of fractures of composites containing h-BN, 10 μm scale bar

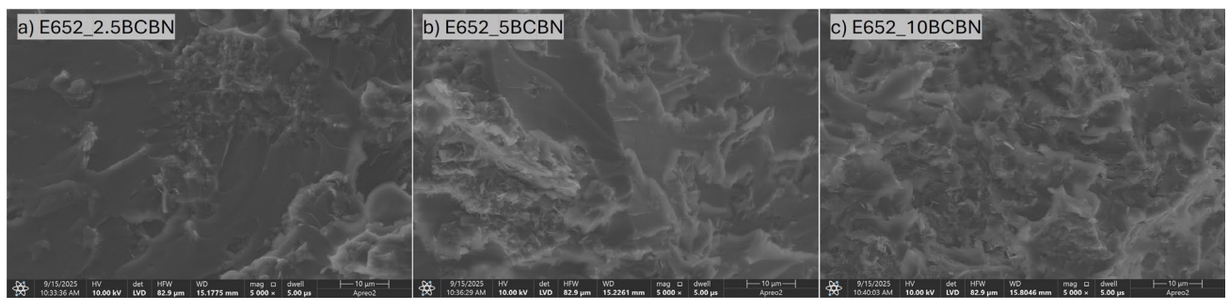

Fig. 4. SEM observations of fractures of composites containing B_4C and h-BN, 10 μm scale bar

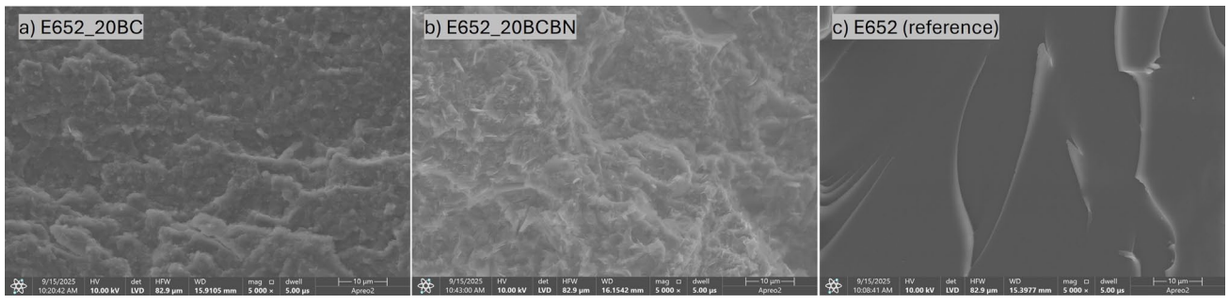

Fig. 5. SEM observations of fractures of E652 resin and composites B_4C and B_4C+h-BN, 10 μm scale bar

a slight difference in the heat transfer parameters between the E652_BN and E652_BCBN composites.

Fig. 5 indicates that composites containing 20 vol.% of BC and BCBN exhibit relatively homogeneous microstructures, except for the non-processable E652_20BN composition. This suggests that the applied preparation method enables effective particle distribution even at high filler contents. However, direct conclusions regarding application performance require further validation under relevant service conditions.

Due to their dual-use applications – such as in the operational conditions of projectiles equipped with an ignition element – the composite materials obtained in this way require an analysis of their thermal stability both in a nitrogen flow environment for the interlayer bonding of ballistic shields and in an air flow environment for the applied surface layers. Therefore, the results of the thermal analysis tests, conducted in both gases, are illustrated in the graphs in Figs. 6-17.

Thermal analysis indicates that the modified resin systems remain stable up to approximately 320°C, as evidenced by the onset of significant mass loss and the corresponding DSC response (Fig. 6 and Fig. 7). The addition of boron carbide reduces the apparent rate of mass loss, which is reflected in the slope of the TG curves and the intensity of the DTG peaks. This behavior is primarily associated with the increasing inorganic fraction rather than a direct stabilization of the polymer matrix. As the boron carbide content increases, the mass loss during resin decomposition decreases, which is consistent with the weight fraction of boron carbide particles when converted from volume fractions. This reduction in mass loss may contribute to improved structural retention at elevated temperatures. The presence of ceramic particles also modifies heat and mass transport within the material by altering diffusion pathways.

By analyzing the thermal analysis curves for the boron nitride additive and given the heat transport anisotropy characteristics of this phase, one can attempt to explain the increased exothermic effect observed for 2.5% BN – Figs. 8 and 9. When the sample contains a small amount of well-dispersed, flat h-BN particles (Fig. 3a), heating the system results in faster temperature equalization throughout the sample volume, leading to a more intense decomposition of the organic material. This is also reflected in the more negative values of the DTG curve compared to those of the resin. Larger amounts of introduced h-BN particles, including those observed in the microstructure images of agglomerates of this phase (Fig. 3b and c), result in a decrease in the DTG derivative values and a change in the slope of the TG curve during decomposition (the smallest slopes for E652_10BN). The presence of agglomerates may limit the rate of resin decomposition due to slower heat transfer in porous aggregates.

The behavior of E652_BCBN systems shows broadly similar trends to those observed for single-phase fillers (Figs. 10 and 11). For a 5 vol.% addition, the magnitude of the exothermic effect is comparable to or slightly higher than that of the pure resin. At higher filler contents (10 and 20 vol.%), the exothermic peak becomes broader and less intense. This change is likely related to the increasing fraction of inorganic phases and the

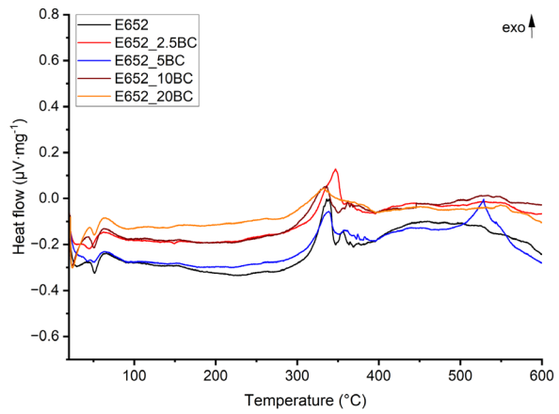

Fig. 6. DSC of E652 with B_4C (BC) in N_2 flow

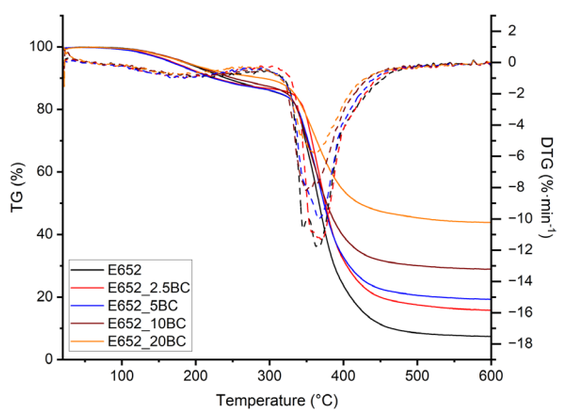

Fig. 7. TG-DTG of E652 with B_4C (BC) in N_2 flow

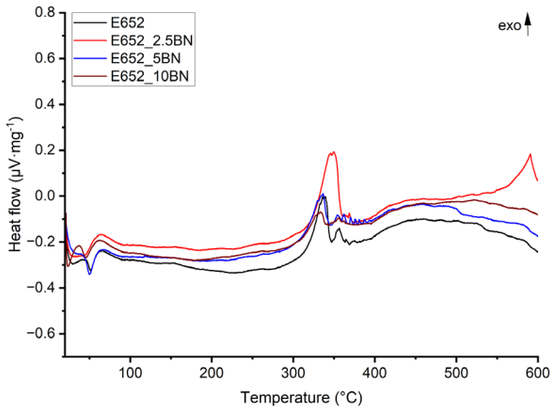

Fig. 8. DSC of E652 with h-BN (BN) in N_2 flow

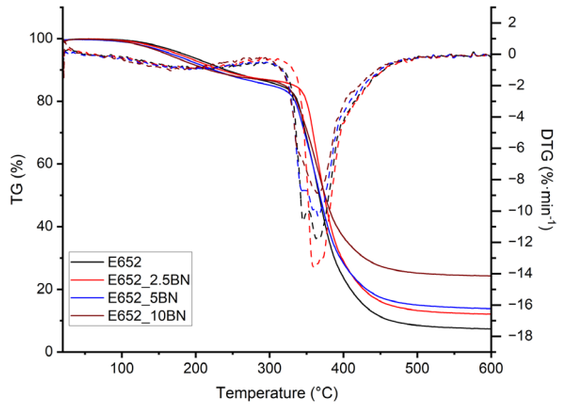

Fig. 9. TG-DTG of E652 with h-BN (BN) in N_2 flow

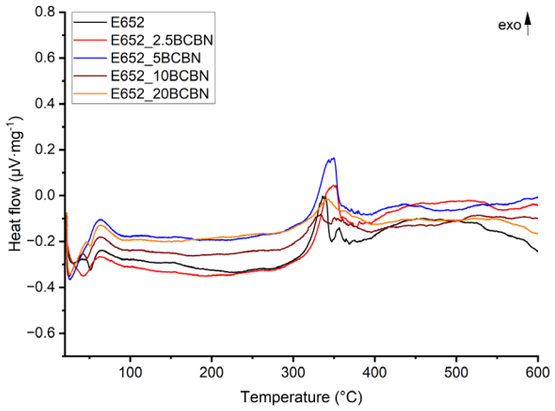

Fig. 10. DSC of E652 with B_4C/h-BN (BCBN) in N_2 flow

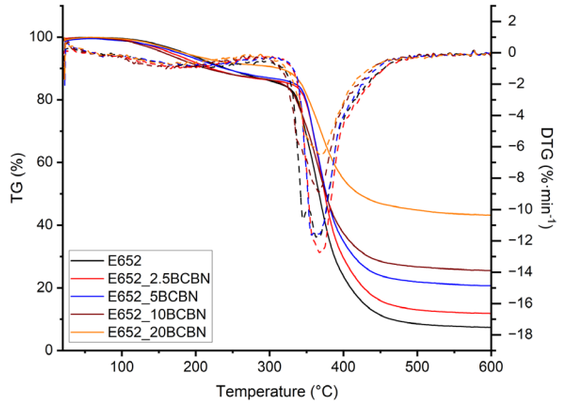

Fig. 11. TG-DTG of E652 with B_4C/h-BN (BCBN) in N_2 flow

resulting modification of the composite structure. As in other systems, the overall mass loss decreases with increasing ceramic content, consistent with an increasing fraction of the thermally stable inorganic phase.

When epoxy-based composites are used as surface layers, they may be exposed to elevated temperatures in air. Under such conditions, the oxidation behavior of boron carbide becomes relevant. An increase in mass above approximately 600°C observed in TG/DTG curves (Fig. 13) is consistent with oxidation of boron carbide [38], leading to the formation of boron oxide and gaseous products. This effect becomes more pronounced with increasing B_4C content. At temperatures around 650°C, the organic matrix is largely decomposed, and the remaining mass is primarily associated with inorganic components. The reduced rate of mass loss with increasing filler content is consistent with the higher fraction of thermally stable phases. Analysis of DSC curves for E652_BC systems (Fig. 12) shows that, at higher filler concentrations, the exothermic peak associated with resin decomposition around 350°C becomes less distinct, while a secondary exothermic effect appears near 600°C. This second effect may be associated with oxidation reactions and/or secondary degradation of carbonaceous residues formed during resin decomposition. At approximately 600°C, a decrease in mass is still observed (Fig. 13), which is consistent with ongoing reactions involving residual organic species or fine fractions of boron carbide.

Boron nitride itself is stable in air up to a temperature of 1000°C; therefore, the main factors influencing its stability may be heat transfer within the material and changes in the pathways of oxygen diffusion. In the case of this additive, the changes observed in the figure are negligible, and this additive causes only a slight shift in the temperature and intensity of the effects on the DSC curve. In contrast to the addition of boron carbide alone (Figs. 12 and 13), in this case, no secondary exothermic effect (associated with the oxidation of fine B_4C particles) is observed; instead, the only reaction is that of oxygen with carbon at a temperature of approximately 500-550°C, the residue left after the decomposition of the resin (Fig. 14). The relatively small changes in the thermal response suggest that h-BN acts primarily as an inert phase under these conditions, exerting limited influence on the polymer matrix's decomposition pathway.

When B4C and h-BN are added to the resin (Figs. 16 and 17), the thermal analysis curves are qualitatively similar to those for E652_BC composites (Figs. 12 and 13). What is interesting is that, in a mixture of boron carbide and boron nitride, a second broad exothermic peak is visible at 600°C for compositions with higher boron carbide content, which indicates the

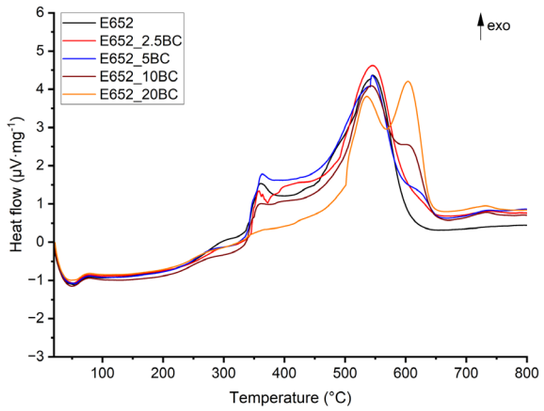

Fig. 12. DSC of E652 with B_4C (BC) in air flow

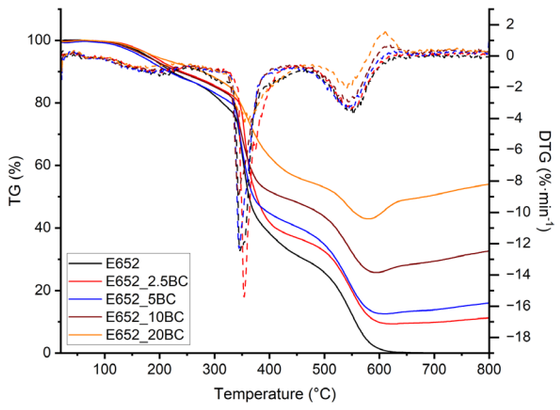

Fig. 13. TG-DTG of E652 with B_4C (BC) in air flow

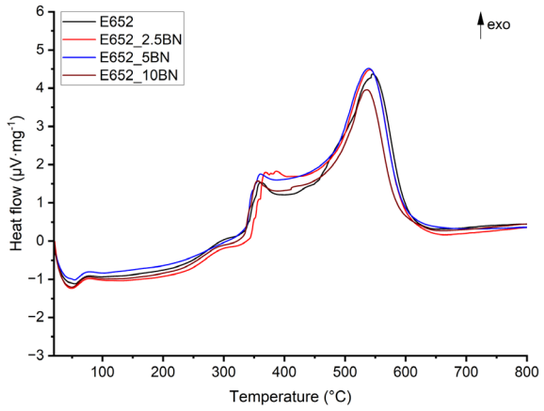

Fig. 14. DSC of E652 with h-BN (BN) in air flow

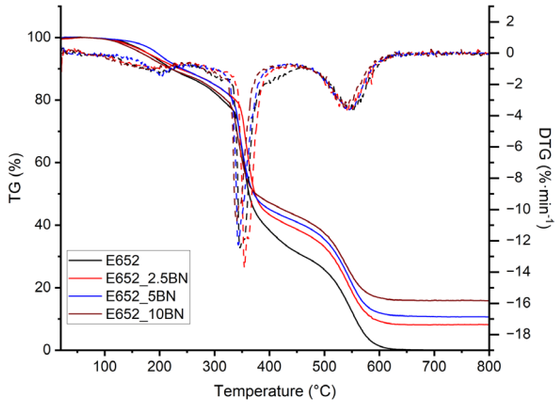

Fig. 15. TG-DTG of E652 with h-BN (BN) in air flow

dominant contribution of B_4C in this temperature range. In this case as well, oxidation of boron carbide particles occurs, accompanied by an increase in mass at temperatures above 650°C. The magnitude of the mass increase tends to increase with boron carbide content in the composite.

Given the potential use of these materials in civil engineering structures as well as in vehicle components or personal protective equipment – where materials must be tested for system vibration under both positive and negative temperature conditions – tests were conducted using dynamic mechanical analysis.

The test results regarding changes in the storage modulus and loss tangent are shown in Fig. 18. The results indicate that at subzero temperatures, a 20% boron carbide content has the greatest effect on increasing the storage modulus, and this type of material has a value of approximately 5,400 MPa. In the case of the BC-containing system, a 2.5% addition has almost no effect. The remaining compositions in the E652-BC system achieve intermediate values. In the case of hexagonal boron nitride, even the smallest amounts of inorganic particles introduced result in a significant increase in the material's stiffness.

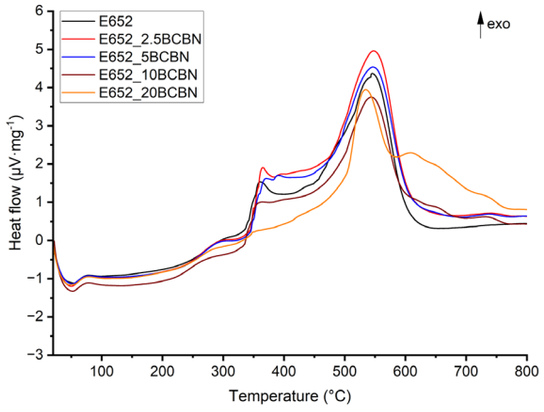

Fig. 16. DSC of E652 with B_4C/h-BN (BCBN) in air flow

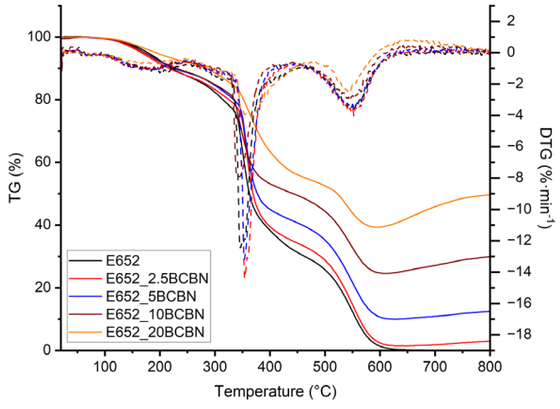

Fig. 17. TG-DTG of E652 with B_4C/h-BN (BCBN) in air flow

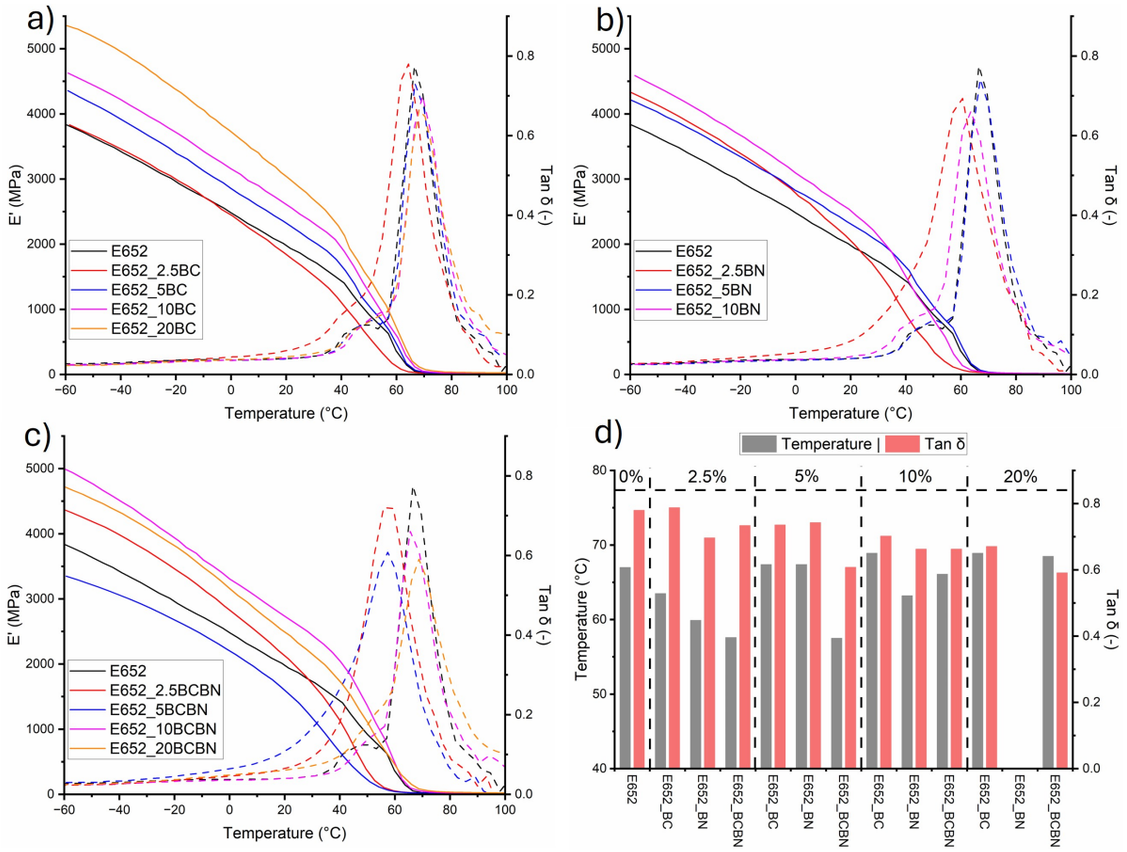

Fig. 18. DMA results of storage modulus (E') and damping factor (tan δ) of composite at 1 Hz; bar chart is for RT

The dynamic mechanical analysis results (Fig. 18, TABLES 2 and 3) provide insight into the effect of ceramic fillers on the thermomechanical response of the epoxy-based composites over a wide temperature and frequency range. The storage modulus (E') increases with increasing boron carbide content, particularly at subzero temperatures, where the highest values are observed for the 20 vol.% BC system (approximately 5400 MPa at –60°C and 20 Hz). This behavior reflects the high stiffness of the ceramic phase and its ability to restrict the mobility of polymer chains within the cross-linked epoxy network. At low filler contents (2.5 vol.% BC), the effect on the storage modulus is minimal, which suggests that the concentration of inorganic particles is insufficient to significantly alter the load transfer mechanisms within the composite. As the filler content increases, a more pronounced reinforcement effect is observed, consistent with increased stiffness contribution of the dispersed phase. This trend is consistent across the analyzed frequency range, although higher frequencies generally lead to increased modulus values due to reduced time available for molecular relaxation processes. In the case of hexagonal boron nitride, even low filler contents result in a noticeable increase in stiffness at subzero temperatures. This may be related to the presence of plate-like particles that limit the segmental mobility of the polymer chains. However, at elevated temperatures (e.g. 50°C), the reinforcing effect is less pronounced compared to boron carbide, which may reflect differences in particle morphology. The hybrid BCBN systems exhibit intermediate behavior, combining features of both filler types. At higher filler contents (10-20 vol.%), these systems show a significant increase in storage modulus, although not always exceeding the values observed for pure B_4C-filled composites. This suggests that the reinforcing effect is influenced by the relative content of the filler phases. Analysis of the loss tangent (tanδ) and peak-temperature values (TABLE 2) indicates that the glass-transition region shifts toward higher temperatures with increasing frequency, which is consistent with the viscoelastic nature of the epoxy network. At the same time, the decrease in tan δ values with increasing filler content, particularly for B_4C-rich systems, suggests reduced energy dissipation and restricted molecular mobility within the polymer network. The loss tangent is an indicator of damping capacity of vibrations transferred to the material during work.

The DMA results demonstrate that incorporating boron-based ceramic fillers modifies the thermomechanical properties of the composites. The observed trends indicate that the balance between stiffness and damping behavior can be modified by adjusting both the type and content of the filler phase.

In order to fit adhesives to other materials it is necessary to control thermal expansion of the material in correlation with their thermal analysis and dynamic mechanical behavior. The results shown in the figure indicate that for most of the tested materials, the linear thermal expansion is in the range of 0.84-0.97% in comparison to 0.86% for resin. The greatest values 0.97% are for up to 5% of B_4C additive and for 10% of h-BN, which may be

TABLE 2

Peak temperature and damping factor values in function of applied frequency

Material	Temperature, (°C)				tanδ, (-)			
	1 Hz	5 Hz	10 Hz	20 Hz	1 Hz	5 Hz	10 Hz	20 Hz
E652	67.0	70.3	71.9	74.6	0.780	0.876	0.894	0.927
E652_2.5BC	63.5	67.5	69.6	72.2	0.788	0.856	0.881	0.905
E652_5BC	67.4	70.9	72.5	75.1	0.736	0.836	0.863	0.881
E652_10BC	68.9	72.4	74.2	76.4	0.702	0.797	0.819	0.840
E652_20BC	68.9	72.1	74.1	76.5	0.671	0.732	0.750	0.767
E652_2.5BN	59.9	64.1	66.8	69.4	0.697	0.697	0.772	0.811
E652_5BN	67.4	70.8	73.0	75.0	0.743	0.846	0.871	0.896
E652_10BN	63.2	67.2	69.0	71.5	0.663	0.764	0.796	0.825
E652_2.5BCBN	57.6	61.7	63.4	66.3	0.734	0.817	0.850	0.881
E652_5BCBN	57.5	61.3	63.2	66.5	0.608	0.690	0.724	0.761
E652_10BCBN	66.1	69.6	71.3	73.9	0.663	0.764	0.788	0.818
E652_20BCBN	68.5	72.0	73.8	76.2	0.591	0.656	0.675	0.695

TABLE 3

Storage modulus values as a function of temperature and applied frequency

Material	*E′* at –60°C, (MPa)				*E′* at 50°C, (MPa)			
	1 Hz	5 Hz	10 Hz	20 Hz	1 Hz	5 Hz	10 Hz	20 Hz
E652	3838	3912	3942	3980	921	1070	1135	1189
E652_2.5BC	3857	3916	3939	3964	571	727	798	879
E652_5BC	4374	4443	4482	4517	1050	1226	1325	1377
E652_10BC	4643	4716	4750	4783	1265	1424	1505	1608
E652_20BC	5359	5435	5472	5500	1479	1682	1775	1875
E652_2.5BN	4337	4398	4427	4460	358	517	615	727
E652_5BN	4217	4286	4327	4358	1047	1206	1269	1343
E652_10BN	4621	4697	4737	4769	850	1014	1081	1175
E652_2.5BCBN	4372	4428	4450	4474	356	581	674	785
E652_5BCBN	3356	3400	3421	3443	222	336	404	470
E652_10BCBN	4998	5088	5126	5165	1358	1558	1629	1757
E652_20BCBN	4724	4792	4823	4865	1111	1308	1391	1475

related to structural heterogeneity and the presence of agglomerates, as observed in SEM analysis. The lowest were recorded for 20% of boron carbide (low thermal expansion of B_4C and percolation threshold) and or 20% BCBN additive – decline to 0.74% and the higher fraction of rigid inorganic phases. For the produced materials, mean linear thermal expansion, in 20-80°C range, is between 141 up to $162 \cdot 10^{-6}$ K^{-1}. The lowest values are for 20% of BC and BCBN reaching even $123 \cdot 10^{-6}$ K^{-1}. The thermal conductivity data reported in this paper agree with the literature [39].

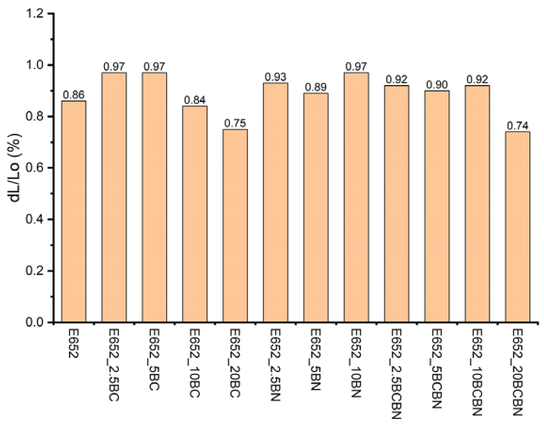

Fig. 19. Linear thermal expansion of composites determined at 80°C

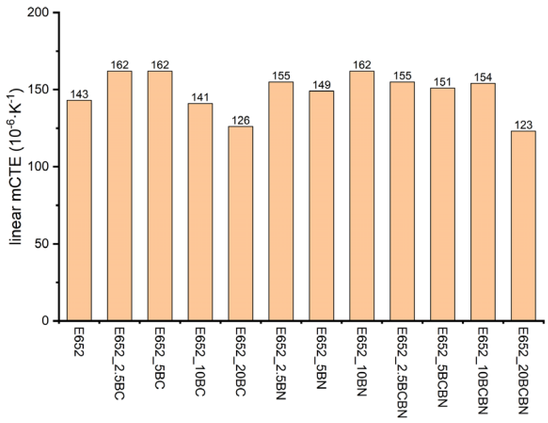

Fig. 20. Mean linear thermal expansion coefficient of composites determined in 20-80°C temperature range

Figs. 21 and 22 show the effects of boron carbide, boron nitride, and their mixtures on diffusivity and thermal conductivity. The measurements showed that the addition of ceramic particles significantly increases both the thermal diffusivity and thermal conductivity, with values reaching up to 0.3 $mm^2 \cdot s^{-1}$ compared to 0.11 $mm^2 \cdot s^{-1}$ for the resin alone. This change generally correlates with an increase in the amount of the modifier applied. In the case of boron carbide, this increase is noticeable at concentrations above 5% by volume. In the case of h-BN (BN) or a mixture of 50% by volume B_4C and 50% by volume h-BN (BCBN), even 2.5% by volume results in observable changes. The addition of h-BN or its mixtures with boron carbide yields thermal diffusivity values higher than those of B_4C-containing systems. However, the highest values are achieved for composites containing 20 vol.% of boron carbide/h-BN mixture (0.3 $mm^2 \cdot s^{-1}$). This behavior suggests that particle packing density and the formation of effective heat-transfer pathways play a dominant role in these systems. With regard thermal conductivity (Fig. 22), it is influenced by factors such as specific heat capacity and the distribution of inorganic particles. A decrease in thermal conductivity is observed with a 2.5% boron carbide addition, or is comparable to that observed with the smallest amount of BCBN added to the mixture. Higher boron carbide (BC) contents, both in the form of a single inorganic phase and as an additive to the mixture, result in a significant increase in thermal conductivity compared to the resin and the resin with boron carbide. The presence of h-BN agglomerates, as observed in SEM analysis, may introduce interfacial thermal resistance and disrupt continuous heat-conducting pathways, thereby limiting the effective utilization of the intrinsically high thermal conductivity of h-BN. Consequently, despite its favorable intrinsic properties, the overall enhancement in thermal conductivity remains constrained by microstructural heterogeneity. Removing the h-BN agglomerates from the material would allow for higher values to be achieved; however, in the planned applications, it may be difficult to employ a more complex preparation process. In the present study, the highest thermal conductivity is achieved for the composite containing 20 vol.% of the BCBN mixture (0.54 $W \cdot m^{-1} \cdot K^{-1}$), compared to 0.19 $W \cdot m^{-1} \cdot K^{-1}$ for the neat resin, indicating the formation of partially effective thermally conductive networks within the composite structure. The thermal conductivity data reported in this paper agree with the literature [40-42].

4. Conclusions

The present study demonstrates that incorporating boron-based ceramic fillers (B4C, h-BN, and their mixtures) significantly influences the microstructure and functional properties of low-viscosity epoxy resin systems. SEM observations confirm refinement of fracture morphology, indicating altered crack propagation mechanisms, although h-BN-containing systems exhibit agglomeration, which introduces microstructural heterogeneity and limits the efficiency of property enhancement. The addition of ceramic phases leads to a substantial increase in thermal diffusivity and thermal conductivity. The highest thermal diffusivity (0.3 $mm^2 \cdot s^{-1}$) was obtained for composites with 20 vol.% B_4C/hBN mixture (BCBN), reflecting the dominant role of particle packing density and the formation of continuous heat-transfer pathways that facilitate phonon transport. The maximum thermal conductivity (0.54 $W \cdot m^{-1} \cdot K^{-1}$) was achieved in the BCBN system, corresponding to nearly a threefold improvement over the neat resin, constrained by interfacial thermal resistance and the presence of h-BN agglomerates, which disrupt effective thermal transport. Thermal analysis confirms improved thermal stability of the modified systems, particularly in B_4C-containing composites, which reduced the rate of mass loss and delayed degradation indicate a barrier effect and restricted diffusion of volatile decomposition products and contribute to enhanced high-temperature performance. Dynamic mechanical analysis reveals a consistent increase in storage modulus with increasing filler content, exceeding 5 GPa at subzero temperatures in B_4C-reinforced systems, accompanied by reduced damping, which reflects constrained segmental mobility and enhanced load transfer at the filler-matrix interface. The incorporation of ceramic fillers also reduces the coefficient of thermal expansion, especially at higher filler contents (for example from $143 \cdot 10^{-6} \cdot K^{-1}$ for pure resin to $126 \cdot 10^{-6} \cdot K^{-1}$ for sample with 20 vol.% of B_4C),

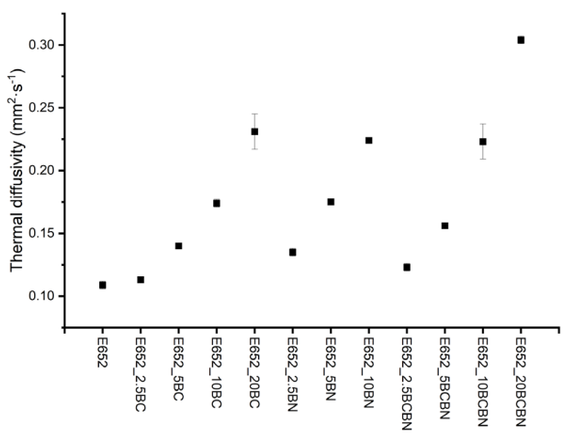

Fig. 21. Thermal diffusivity of composites at RT

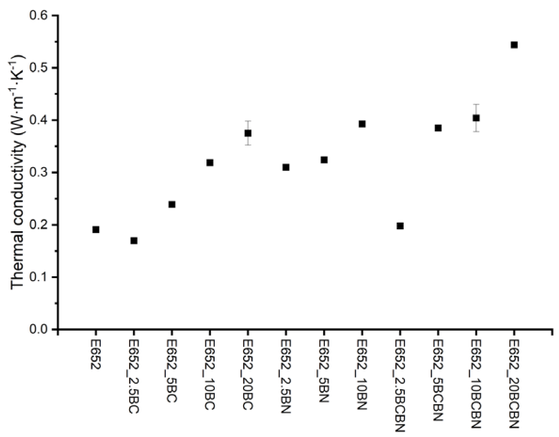

Fig. 22. Thermal conductivity of composites at RT

which is attributed to the low intrinsic expansivity of the ceramic phases and the mechanical constraint imposed on the polymer network. The results confirm that boron-based fillers enable effective modification of thermophysical and mechanical properties of epoxy systems, with performance governed by filler type, content, and dispersion state, while the developed methodology has also been applied in ongoing research on polyurethane adhesives for wooden structures, supporting the development of materials with improved thermomechanical performance (project no. 2021/43/I/ST8/00554).

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