THERMALLY CONDUCTIVE & FLAME RETARDANT EPOXY-GF NOVOLAC PREPREGS FOR PCBs – CORRELATION OF THE FILLER NETWORK MORPHOLOGY WITH FINAL PROPERTIES

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Abstract
Within the scope of this research, thermally conductive and flame retardant Epoxy Novolac formulations, as polymer composites and their GF-reinforced prepregs, were investigated, by correlating the 3-D conductive filler network formation with the resulting macro-scale thermal properties. With this, the thermal properties of these highly filled resin formulations and especially, the influence of particle platelet size (aspect ratio) on filtration during processing is correlated. The flame retardancy is investigated with Cone Calorimetry. SEM micrographs of the laminate cross-sections show the filler distribution in the fiber-reinforced matrices and also highlight the fiber wetting. The overall impregnation quality and the formation of pores due to filler agglomeration or entrapped air is detected via FVC content and Ultrasound C-Scans, respectively. Finally, the overall laminates quality is detected with ultrasound C-scans. The results show that the thermal conductivity and its resulting 3-D filler network is strongly dependent on filler content, filler nature and its particle size distribution. With increasing filler content and filler aspect ratio, the effect on thermal properties and filtration is more evident. Moreover, the hybrid combination of *hexagonal* BN (*h*-BN) and Boehmite fillers have a strong effect on the network formation during processing, resulting in enhanced thermal properties. Taking into consideration the cost factor, the through-plane (*z*-direction) heat dissipation and the flame retardancy can be tailored by optimizing the size, aspect ratio/geometry and nature of the fillers.

1. Introduction

Current technological trends in electronics towards miniaturization, higher service temperatures and dense switching powers have opened up critical thermal management issues. Early material failure due to the low heat spreading often occurs as delamination in the interlayer between the polymeric matrix (insulator) and the metallic-based assembly parts (highly thermally conductive). In order to overcome this issue of insufficient heat spreading, the advantageous properties of an Epoxy Novolac polymer matrix, i.e. its high T_g, are combined with the inorganic fillers *hexagonal* Boron Nitride (*h*-BN) and Boehmite to increase the overall thermal properties, i.e. thermal conductivity and flame retardancy, respectively.

In literature, it is well known that adding ceramic fillers (i.e. AlN, BN or Silica) with high intrinsic thermal conductivity increase the overall Epoxy resins' thermal transport behavior [1,2]. Many studies show that the filler size [3–9] , geometry [4,6,10], concentration [3–9] and the fillers aspect ratio play a crucial role for the 3-D network formation of the fillers in order to build up a continuous channel for heat passing through. Moreover, the thermal conductivity can be further enhanced by the combination of two fillers of different sizes [9,10] and/or of different nature [5,11].

On prepreg scale, it is of strong scientific interest to study the structure property relationship between glass fibre-reinforcement on morphological network formation and final properties, especially in highly-filled Epoxy composites. However, not much literature can be found on the relevance of processing, filtration effects and the overall laminates' properties. [12] In addition, compared to current industrial standard solvent-based impregnation, this technical-scale impregnation route is completely solvent-free. As the fillers increase the resins' viscosity tremendously, it is important to find the perfect interaction between the preparation of the formulation, i.e. mixing parameters, filler content and their filler combinations, and finally the processing parameters, e.g. film coating speed, temperature at the coating unit or at the heating table in the B-Staging unit itself. Therefore this study aims to scientifically understand the effect of glass-fibers on the processing of resin formulations with high filler content of platelet shaped fillers. Furthermore, this study aims to correlate the effect of the micro-scale morphology with the final thermal properties, i.e. thermal conductivity, T_g and flame retardancy.

2. Experimental Section

2.1. Materials and Preparation of filled Prepreg-based EP-Novolac-GF Laminate

A multifunctional Epoxy Novolac resin, D.E.N.™ 438 (from OLIN) with an epoxy equivalent of 176 - 181 g/eq was used as a high T_g reference matrix resin which was cured with Diethymethylbenzenediamine (XB3473), supplied by Huntsman Advanced Chemicals (Basel, Switzerland), in the stoichiometric ratio of 100 : 24.1. As a flame retardant, Boehmite, (platelet shape), supplied by Nabaltec AG with a density of 3.07 g/cm^3 and a D_{50} of 2 μm, was used. Two *hexagonal* Boron Nitride (BN) types, purchased from Henze BNP with a D_{50} of 2 μm and 12 μm, were used. All BN types are of platelet shape and have an average filler density between 2.27 and 2.35 g/cm^3. The glass fabric, with an aerial weight of 25 g/m^2 was purchased from PD Interglas Technologies GmbH.

The prepreg production was carried out on a technical-scale EHA Composites Machinery. The resin formulation was prepared as following: To ensure even wetting and filler dispersion, the resin and the fillers were mixed at 200-250 rpm for 4 min so that the generated shear forces help in complete wetting of the fillers. Later, the mixing speed was lowered to 180 rpm for about 15 min. After this, the hardener was incorporated, and the mixing speed was further lowered to 110 rpm to avoid excess generation of air inclusions. This formulation was then poured in the coating head unit of the prepreg production line which was maintained at a temperature of 80 ⁰C to avoid early gelation.
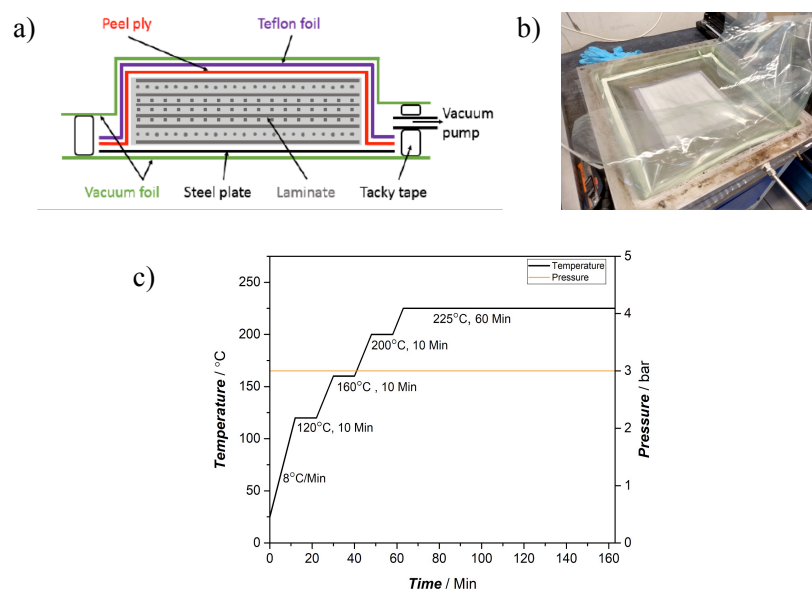
Figure 1. a) Schematic set-up of the hand-lay up (side view), b) and on the right the top view of the autoclave set-up and c) temperature/pressure curing profile for the production of GF-laminates.

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The uncured resin was then film coated on a siliconized release paper using the direct coating method. The prepreg was cut into 200 x 200 mm^2 single layers and were stacked up by hand lay-up on a steel plate (Figure 1a + b) and cured in an autoclave set-up according to the curing cycle in Figure 1 under vacuum (< 25 mbar). The detailed temperature-pressure profile can be seen in Figure 1c).

2.2. Characterization Methods

Thermal conductivity measurements were carried out in through-plane direction at 25°C using a heat flow meter FOX50 from TA Instruments (New Castle, United States) according to ASTM C518 in specimens with the diameter of 60 mm and a thickness of 3 mm.

Dynamic mechanical thermal analysis (DMTA) was performed at a heating rate of 3 K/min from 30 °C- 280 °C in torsional mode at a deformation of 0.1% and an applied frequency of 1 Hz using the ARES RDA III from Rheometrics Scientific (Germany). The specimens had a rectangular geometry in a size of 50 x 10 x 3 mm^3 according to the standard DIN EN ISO 6721-7. The glass transition temperature was evaluated by the maximum of the tan δ curve.

A *Cone Calorimeter*, iCONE™ FTT (UK) was used to evaluate the flame retardancy and other important fire properties, i.e. t_{ig} (time to ignition), TSR (total smoke release) and HRR (heat release rate). The samples, with a geometry of 100 x 100 x 3mm^3, were measured in a horizontal set-up with an applied heat flux of 35 kW/m^2. The FIGRA value is calculated by dividing PHRR with the time to PHRR (tPHRR), which indicates the fire growth rate. 2 samples of each composition were conditioned and tested. All results are averaged.

Non-destructive ultrasound testing was performed by using HFUS 2400 (Air Tech) test machine in order to access the overall laminates quality. The tests were done in distilled water at room temperature. A pulse echo with a velocity of 2900 m/s was applied. C-Scans were then used to study the possible inhomogenities (pore formation, entrapped air, defects) within the laminate.

Scanning electron microscopic (SEM) measurements were obtained on a Zeiss Leo 1530 instrument operating at 3 keV. Samples were cut, embedded, polished and then platin-sputtered.

3. Results & Discussion
3.1 Morphological studies of the produced highly-filled GF laminates – *Quality Assurance , T_g and Fibre Volume Content*

The mixing of the highly-filled formulations were optimized already in the composite stage (without GF) towards mixing speed and time. This was done accordingly with respect to the additive dispersion which was studied via SEM. This knowledge was then directly transferred to the prepreg processing. The influence of prepreg processing on the stability of the filler dispersion without sedimentation of the hybrid combination of BN 12 µm and Boehmite 2 µm (ratio 3:1) at a total filler concentration of 20 vol % was studied using optical microscopy. Figure 2 shows the *in-situ* dispersion study of the hybrid formulation (a) directly after mixing with a static mixer and before pouring into the coating unit and (b) after doctor-blading the thin composite film on the silanized paper during processing. Although the filler content is high (20 vol %), the fillers are well dispersed without any visible agglomeration.

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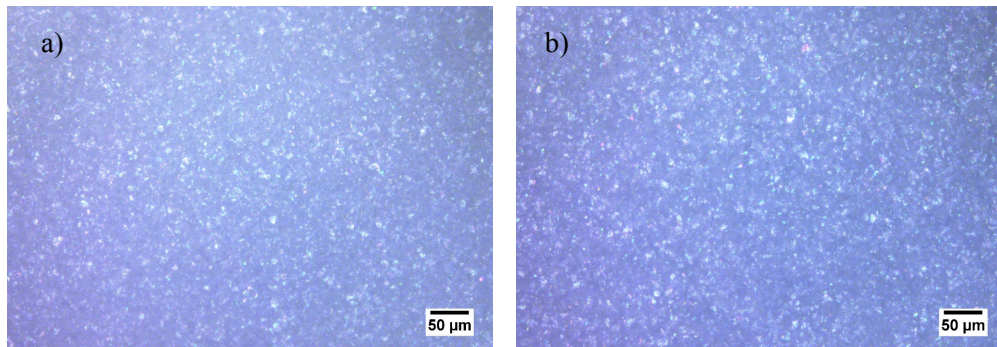
Figure 2. In-*situ* dispersion studies of 20 vol % hybrid formulation at two different stages during prepreg processing (Magnification: 20x): a) after mixture preparation and b) after film-casting during prepreg production.

Table 1 shows the measured glass transition temperatures (T_g) of each laminate and their corresponding fibre volume content. The T_g was not influenced by the addition of fillers. However, with the incorporation of BN only, the T_g increased, whereas with the incorporation of Boehmite, the T_g decreased slightly. This might be due to the interaction between the surface-silanized GF and the functional groups attached to the edges of the BN fillers.

Table 1. Summarized properties of the produced laminates at 20 vol % filler content.

Specimen Type	T_g (°C)	FVC (vol %)
Neat EP-Novolac	235.4	19.0
EP + BN 2μm	236.8	20.3
EP + BN 12μm	237.7	20.5
EP + BT 2μm	235.7	22.8
EP + BN 12μm + BT 2μm	232.3	21.1

As the resin content is high, especially in the reference laminate, a certain resin flow is induced by the pressure leading to an uneven surface. However, the C-scan images of the filled laminates show more even results in comparison to the unfilled laminate, indicating the addition of fillers help lowering the resin flow. Exemplarily, only the C-scan and optical micrograph of the hybrid, BN and Boehmite filled laminate is shown in Figure 3.
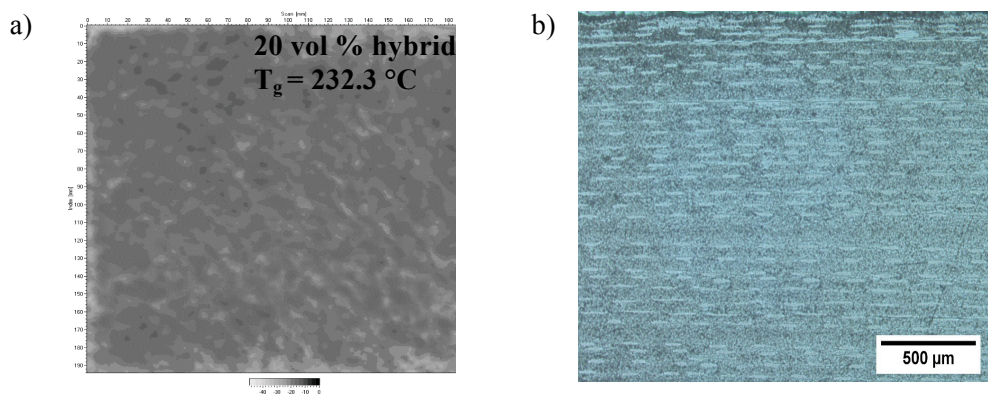
Figure 3. Exemplary C-scan image (a) and the optical micrograph of the laminate cross section (b) at 2.5x magnification for the 20 vol.% hybrid laminate.

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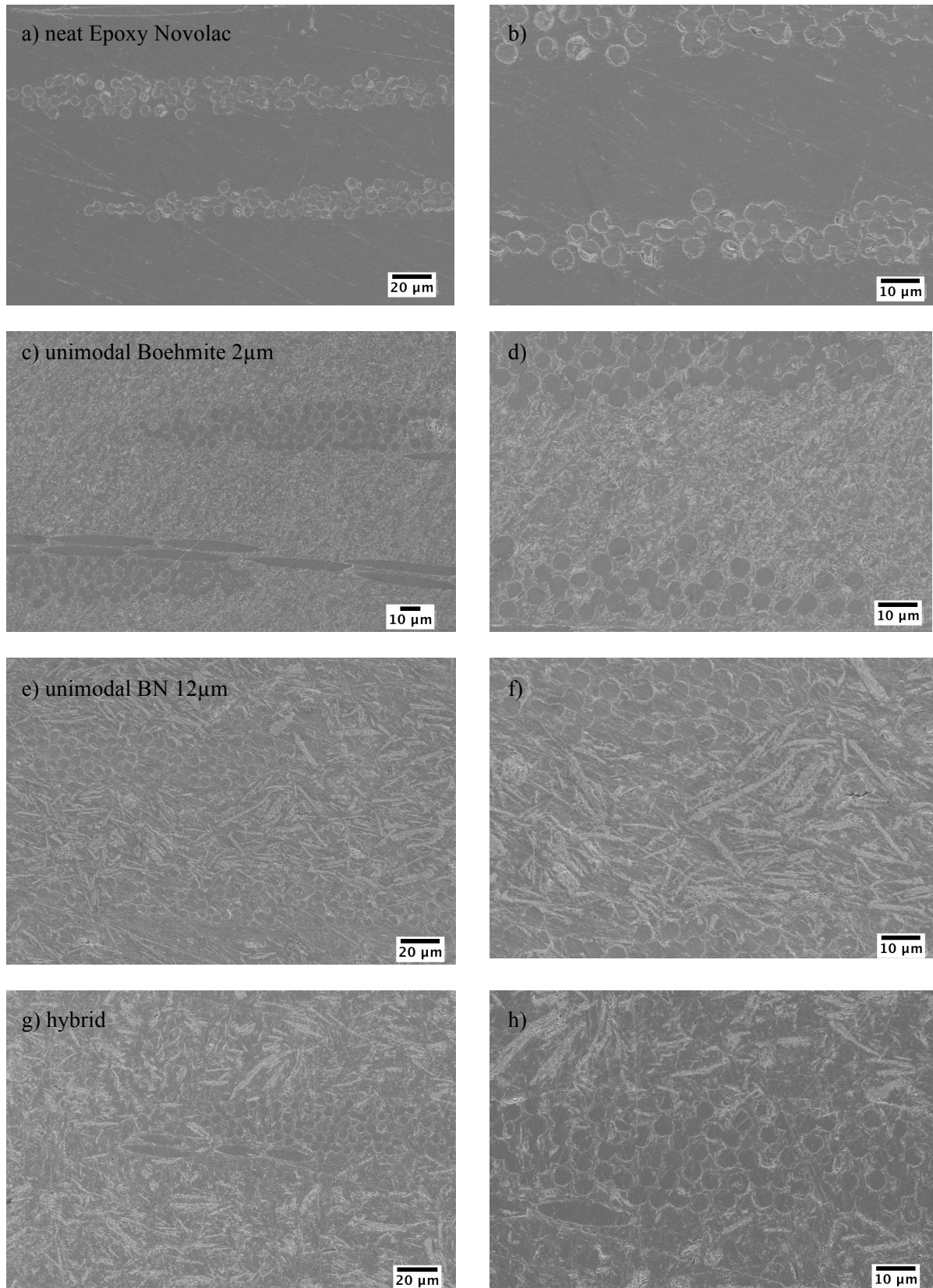
Figure 4. Cross-sectional SEM micrographs of the produced highly-filled Epoxy GF laminates (20 vol %). a + b) neat Epoxy Novolac, c + d) unimodal Boehmite (2µm platelet-size), e + f) unimodal BN (12µm platelet size) and g + h) hybrid filled laminate. Left Columns are at 500x magification, right columns at 1000x magnification.

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The morphology of each laminate cross-section can be seen in Figure 4. The incorporation of Boehmite to the reference (neat Epoxy Novolac) shows that the small platelets are well distributed and also infiltrate the GF (Fig. 4c + d). The larger-sized BN shows (Fig. 4e + f), although having anisotropic filler geometry, an isotropic orientation in all 3 directions throughout the laminate volume. In addition, in agreement with the high filler content, the fillers tend to touch each other at their edges forming a constant pathway in the z-direction. The hybrid combination of BN and Boehmite shows, a similar morphology. The larger-sized BN are randomly oriented without confined direction and are well dispersed. The smaller-sized Boehmite attach close to the BN particles and in addition, infiltrate the GF and also fill the gap between the low thermally conductive GF, low thermally conductive resin matrix and the highly thermally conductive BN particles.

3.3 Thermal Properties

3.3.1 Characterization of the *through*-thickness Thermal Conductivity – *Correlation between highly-filled Composites and their GF reinforced laminates*

Figure 5a) shows the thermal conductivity of the resin composites without the GF. The thermal conductivity (TC) can be enhanced with increasing the concentration of each filler. The slope of the curve of the plotted thermal conductivities in Fig. 5a) is the lowest for Boehmite. The BN filled systems result in higher TC values due to their higher intrinsic TC. However, combining BT and BN, the TC is even further increased at the highest concentration of 20 vol % of total filler content.

The impregnation of a GF with these formulations results in comparable TC values (Fig. 5b). The thermal conductivity of the neat, unfilled laminate is the lowest with 0,19 W/mK. The incorporation of Boehmite, a filler with a rather low intrinsic thermal conductivity, increases the conductivity up to 90 % (0,36 W/mK). The unimodal BN filled laminates result in higher values, due to the higher intrinsic thermal conductivity of these ceramic fillers. Also, there is a clear size-effect visible. The 12 µm-size BN lead to a higher TC value compared to the 2 µm-size, 0,54 W/mK and 0,43 W/mK, respectively. This implies that increasing the platelet size and aspect ratio of BN has a positive impact on the thermal conductivity resulting in less phonon scattering effects by BN 12µm. However, the combination of both fillers, results in the highest value of 0,56 W/mK indicating a synergistic effect. This is due to the fact, that the larger sized-BN fillers (12 µm) are well distributed with an isotropic orientation and the 2 µm-sized Boehmite platelets filling the gaps not only between the BN platelets, but also infiltrate the GF, thus bridging the low TC of the matrix and the GF (Figure 4).
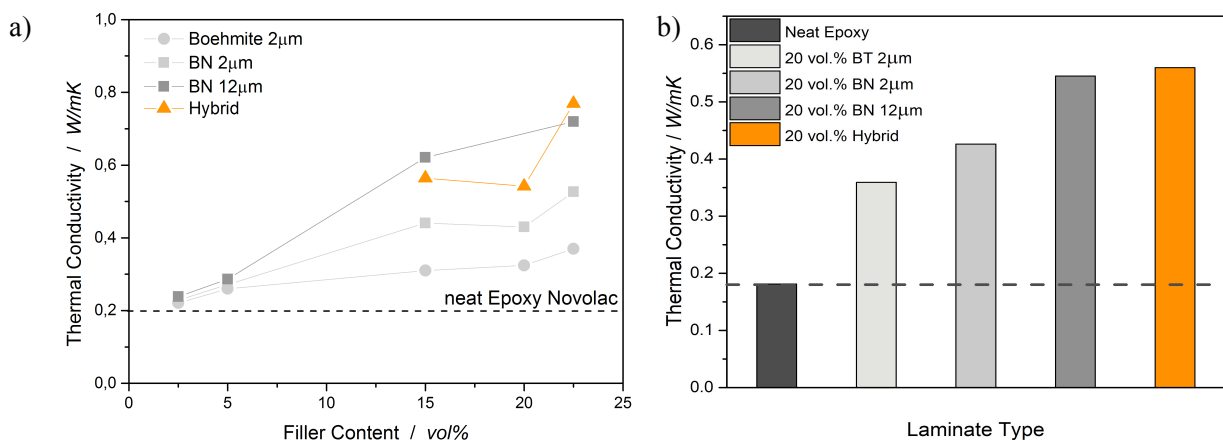

Figure 5. Comparison of the thermal conductivity of highly-filled resin composites (a) and of the highly-filled laminates (b), both based on the same formulations.

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3.3.2 Characterization of the Flame Retardant Effect via Cone Calorimetry

Table 2 shows the results of the Cone Calorimetric test of the laminates. The neat, unfilled GF-laminate shows the shortest time to ignition and the highest PHRR also resulting in the highest FIGRA value. With the incorporation of Boehmite, being a flame retardant, the t_{ig} is slightly increased but mainly the PHRR is affected. Boehmite is stable up to 350°C and then decomposes in a two-step reaction to form Al_2O_3 barrier on top of the burning sample. In the first reaction step, the system is cooled down by released water molecules in the gas-phase, and then the ceramic barrier is formed both leading to a low PHRR. BN, in unimodal distribution, shows its major effect in increasing the t_{ig}, due to the better intrinsic ability of thermal transport, i.e. the higher intrinsic thermal conductivity and higher thermal stability (> 1200°C). However, the PHRR is comparable to the neat laminate. The size of the BN platelets shows that the smaller BN is more efficient. The combination of both fillers, Boehmite and BN 12 respectively, results in the highest T_{ig} and highest t(PHRR) indicating a synergistic effect of simultaneously increasing the t_{ig} and lowering the PHRR.

Table 2. Combustion and flame retardant behaviour comparison of the filled EP Novolac laminates (heat flux of $35kW/m^2$).

Composition	t_{ig} (s)	*t (PHRR)* (s)	*PHRR* / (kW/m^2)	*THE* / (MJ/m^2)	*TSR* / (m^2/m^2)	*FIGRA* (kW/m^2s)
neat EP Novolac	88	105	686,3	48,42	1850,3	6,54
EP + BN 2µm	135	145	588,1	51,37	2028,9	4,05
EP + BN 12µm	130	162	655,6	49,4	1919,1	4,03
EP + BT 2µm	111	145	383,9	49,5	1656,8	2,64
EP + BT 2µm + BN 12µm	136	180	593,2	48	1870,5	3,29
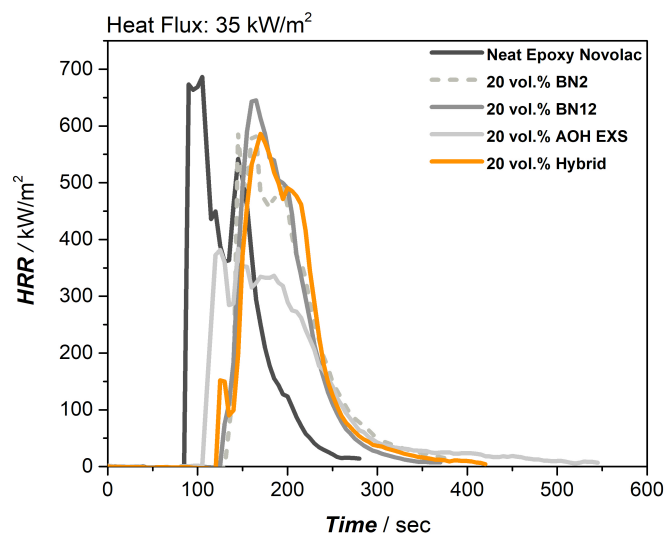
Figure 6: Heat Release rate (HRR) in dependency of time for different laminate systems measured at $35 kW/m^2$ heat flux in a cone calorimeter

4. Conclusions

In this study, highly-filled multifunctional Epoxy Novolac laminates were produced via a solvent-free production route. Moreover, synergistic effects between BN and Boehmite were studied by focusing on thermal conductivity and flame retardancy with both properties being enhanced. Although the filler

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content is high, the fillers showed a good dispersion before and after processing with no agglomeration or sedimentation. Although, the fillers are platelet-shaped, the filler orientation showed a high degree of randomness. The laminate production, done via an autoclave set-up, did not induce an anisotropic filler orientation nor filtration. Moreover, the addition of these fillers did not influence the T_g negatively with the fiber-volume content kept contant.

Acknowledgments

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