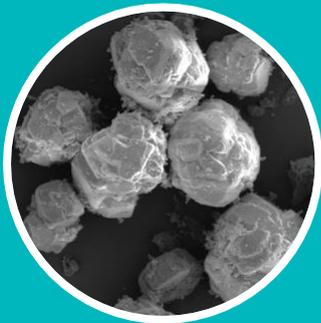


APYRAL® HC

Optimized Flame Retardant Filler for Thermal Conductive Applications

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25 µm

APYRAL® HC 500

Since decades thermal conductivity in polymers is already an important parameter for Thermal Interphase Materials (TIM) in electronic applications. However, with the global activities of the automotive industry to change from classic combustion engines to electric drive units, the thermal conductivity of polymer compounds and composites has certainly reached a new momentum.

With the help of optimized APYRAL® HC fillers, formulators obtain a toolbox to reach required thermal conductivity levels in an easy way.

This paper deals with the use of aluminium hydroxide and aluminium oxide and their pros and cons for thermal conductivity applications.

▪ **Product properties**

- Optimized particle size distribution
- Unique morphology
- High packaging density
- Improved sedimentation stability
- Low hardness and abrasion
- Low cost in comparison to high performance fillers
- Very low density

▪ **Compound properties**

- Extremely low viscosity
- Extremely high filler loads
- Good dispensing properties
- High flame retardancy
- Good thermal conductivity (isotropic)
- Good value
- Very low density & weight

1. Introduction

The automotive industry goes through a revolutionary change from combustion engines to electrical drive units. Safe rapid charging technologies and longevity are indispensable for a broad consumer acceptance of Electrical Vehicles (EV). An efficient thermal management system is a technological prerequisite to make this happen. The major components which need consideration are the electrical motor, the power electronics (e.g. inverter and converters) and last but not least the lithium-ion battery (LiB).

The thermal conductivity (TC) of the components forming the battery case, the gap fillers in the battery stacks, various adhesives and gaskets as well as the motor coil encapsulation and many other components require very different solutions based on existing and even on totally new designed polymer compounds.



Figure 1. LiB as central part of modern EV.

Probably the most important component of a modern electric vehicle is the LiB itself (s. Figure 1). To keep it from overheating during fast charging the heat has to be conducted out of the battery stacks through the battery enclosure to an external (active) cooling system. Here the **adhesive** attaching the stacks to the enclosure and especially the **gap filler** between the single stacks of the battery module (s. Figure 2) play key roles

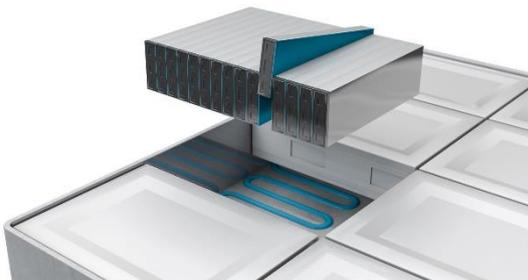


Figure 2. Adhesive and gap filler in a lithium-ion battery.

For **gap fillers** usually a thermal conductivity of **2.5 – 3 W/mK** is demanded, which requires filling levels often significantly above 80 wt.-%.

While gap fillers and classic thermal interface materials (TIM) in the electronic industry are used in scale of some grams per unit, a modern LiB requires kilograms of a gap filler. In this regard, easy and fast dispensing plays a critical role to enable short assembly times.

Nabaltec AG has developed high performance fillers based on aluminium-tri-hydroxide (ATH) – **APYRAL® HC**. Their optimized particle size distributions simultaneously allow high packaging densities (resulting in high TC values) and extremely low viscosity levels.

This paper shall concentrate on the advantages when using Nabaltec AG's aluminium hydroxide based fillers optimized for liquid dispensing applications, like cast resins potting & encapsulating and especially modern gap fillers for EV-batteries.

2. Parameters influencing thermal conductivity

When trying to improve the TC of a polymer compound a set of parameters of the compound ingredients have to be considered. Figure 3 gives a simple overview on these parameters.

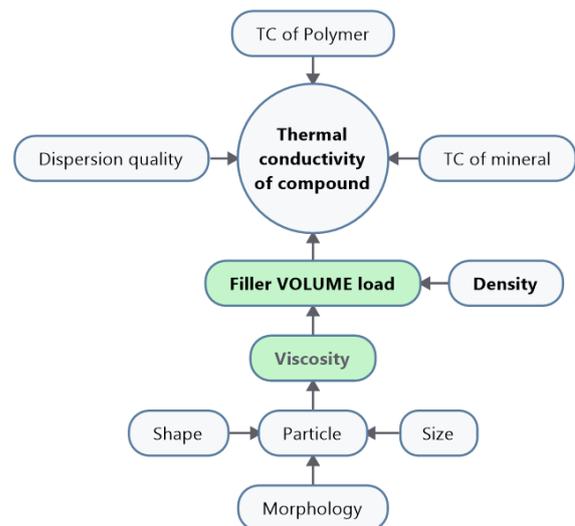


Figure 3. Important parameters to influence the thermal conductivity of a polymer compound.

First and foremost, one usually considers the **thermal conductivity of the resin and of the mineral filler**. The TC of most resins is very low, consequently TC of the mineral filler is in the focus. Naturally the formulator seeks fillers

with high intrinsic TC values, like boron nitride (BN), aluminium nitride (AlN), alumina (Al₂O₃, AO) or magnesia (MgO). For an overview of selected mineral fillers for polymer applications including their TC values please compare Table 1. However this paper shall demonstrate that **a high intrinsic TC of the filler is not a necessity**. A high filler loading can be more important, which the following chapters shall demonstrate.

2.1. Filler load

When filling a compound one quickly realizes that **filler loading level** is a very crucial parameter. This is understandable as one tries to replace as much of the insulating polymer by the better conducting mineral. With low loading levels the TC is affected only little, while with increasing load the incremental increase of TC becomes bigger. Such an effect is well known when trying to increase the electrical conductivity (EC). Only when the particles start to touch each other, the conductivity rises strongly. This point is called the **percolation threshold**, see Figure 4. For EC this point is very sharp, while for TC the steepness of the slope changes more slowly. But both parameters, TC and EC, have in common that a minimum filling level is required to gain an adequate level of conductivity. The percolation threshold explains why it is better to plot the TC versus **volume based filling level** (vol.-%) rather than filler loading based on weight percent (wt.-%).

Ultimately, the formulator has to gain as **high filling levels** as possible. These levels may be limited by mechanical properties and processing factors during compounding. Such an important factor is the **viscosity performance** of the filler, as a low viscosity is crucial to gain high filler loadings.

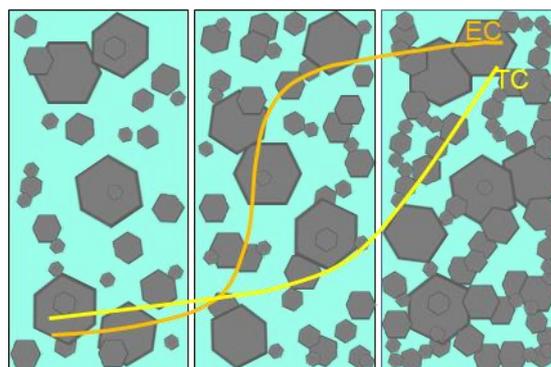


Figure 4. Percolation threshold for the electrical (EC) and thermal conductivity (TC) of a compound.

2.2. Viscosity

As indicated above the viscosity effect of the filler cannot be underestimated. Actually this is the dominating factor to obtain high filling levels necessary for high TC values. The upper graph in Figure 5 shows the influence of the filler loading to the resulting viscosity increase of an unfilled unsaturated polyester resin (UP) by various mineral fillers. The fillers have been dispersed by a high speed dissolver into the resin, which featured a low viscosity of about 0.9 Pa*s only. Step by step the filling level was increased until the **maximum filling level** with a visible good dispersion was reached (indicated by the sign **STOP** in Figure 5).

Subsequently after dispersion each resin compound was measured in a rotational rheometer. The viscosity value was determined at a shear rate of 10⁻⁵ at 22 °C. The plotted relative viscosity represents the quotient of the viscosity of the filled resin to the viscosity of the neat, unfilled resin at same measuring conditions. After measuring the viscosity, the compounds have been cured and the specimens were polished to obtain a plain surface necessary for measuring the thermal conductivity by Hot Disk method at 22 °C, according to ISO 22007-2. The resulting TC of these cured compounds are plotted in the lower graph of Figure 5.

Table 1. Important powder parameters of common thermal conductive fillers:

Name, abbreviation	Formula	T _{decomp} [°C]	TC [W/mK]	Density [g/cm ³]	Mohs hardness
APYRAL® HC, Aluminium hydroxide, ATH	Al(OH) ₃	200	20 - 25	2.4	3
APYRAL® AOH, Boehmite, AOH	AlOOH	340	2.3	3.0	3 - 4
NABALOX® HC, Alumina, AO	Al ₂ O ₃	>> polymer	20 - 40	3.9	9
Magnesium hydroxide, MDH	Mg(OH) ₂	320	10	2.4	3
Magnesia	MgO	>> polymer	40 - 60	3.6	6
Hexagonal Boron nitride	BN	>> polymer	15 - 400	2.2	1
Aluminium nitride	AlN	>> polymer	180 - 220	3.2	9
Silica	SiO ₂	>> polymer	1 - 12	2.2 - 2.6	6 - 7
Calcium carbonate	CaCO ₃	>> polymer	4 - 6	2.7	3
Polymers	-	> 350	0.2 - 0.5	-	-

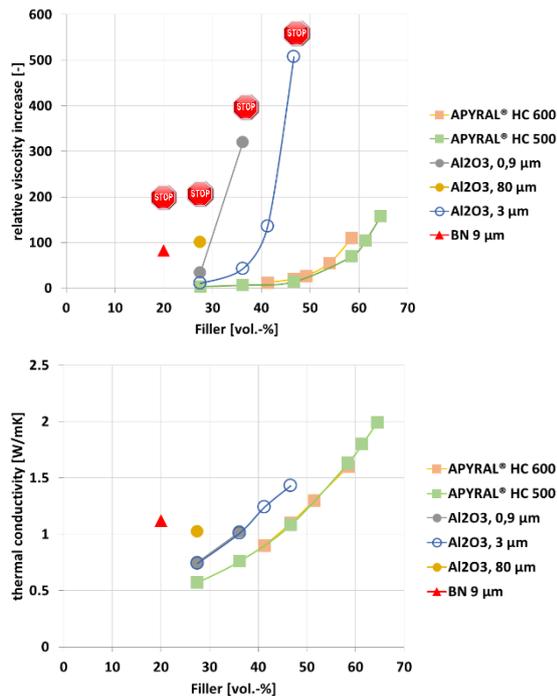


Figure 5. Relative viscosity of **APYRAL® HC** in comparison to calcined Al₂O₃, and BN in UP resin at shear rate 10⁻⁵ at 22 °C (above) and the corresponding TC values (Hot Disk method) after curing (below).

Similarly to the conductivity, the viscosity is rising strongly with increasing filler loads. However, the rheological performance of BN and alumina is lacking far behind the one of optimized **APYRAL® HC**. These discrepancies can be explained when considering the differences in particle size and morphology of the individual minerals, displayed in Figure 6.

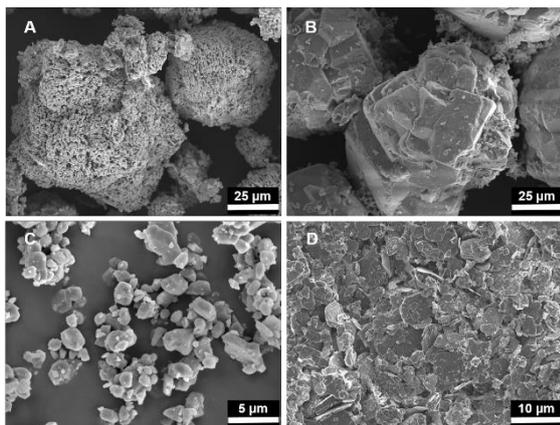


Figure 6. SEM-images of calcined alumina (80 μm, A), **APYRAL® HC 500** (B), calcined alumina (3 μm, C), and BN (9 μm, D).

2.3. Particle size

Very often formulators seek for fillers with big particle size as they expect to gain not only

lower viscosity enabling higher filling level, but also higher TC levels in comparison to small particles. In theory this is truly the case when one compares particles of the same chemistry and morphology which feature low porosity. However this is not easy to obtain in every kind of mineral.

For example, **APYRAL® HC** and the coarse calcined alumina have similar particle size, but their viscosity is very different. **APYRAL® HC** (Figure 6, B) consists of single grown, compact crystals, while the coarse alumina (Figure 6, A) is revealed as a hard agglomerate of small primary crystals with many internal macro pores. This raises oil absorption and viscosity. Thus, only one filling level could be obtained no higher filling was possible, limiting the obtainable TC.

In case of calcined alumina the optimum viscosity is gained when the primary particles (Figure 6, C) are set free by gentle grinding without further destroying them. This is usually the case at mean particle sizes between 1 and 10 μm, depending on the calcination state. When grinding is enforced to smaller particle sizes, then the primary particles are destroyed and more micropores generated which leads to high oil absorption and viscosity (s. Al₂O₃, 0.9 μm in Figure 5). However, even alumina in ideal primary crystals state do not feature the viscosity performance of the unique crystals of **APYRAL® HC**.

2.4. Particle shape

The distinct platy nature of the BN crystals (Figure 6, D) lead to very strong shear thinning effect in fluids.



Figure 7. Aborted experiment trying to disperse 27 vol.-% of BN in UP-resin. All material clogs to the wall while the dissolver blade (not shown) is mixing only air.

In the reported experiments a filler load of 20 vol.-% BN could be generated only, leading to a low TC level. When trying to disperse a higher

loading of 27 vol.-%, the BN could not be dispersed. During addition of the filler the compound was clogging at the wall of the container, a region of low shear where the viscosity is several orders of magnitude higher than in the near of the dispersion blade (high shear region).

This makes the dispersion of platy BN very difficult and leads to low to moderate filling levels only. The high intrinsic TC level of this mineral could not be fully utilized as the rheology was limiting the filler loading.

Another aspect influenced by the particle shape is the 3-dimensional flux of the conducted heat. Ideally the heat shall be conducted in equal measure in all dimensions (**isotropy**) and not directed in one direction only (**anisotropy**).

The graphite-like molecular structure of BN does not only lead to a platy shape, but also to the fact that within the plates the heat is conducted much faster in plane than through plane. Thus, BN has a strong intrinsic anisotropy in its particles. However, due to the rheological properties plates often align into the same direction during flow, e.g. during injection molding. Therefore in a lot of applications where BN is utilized as a filler, a strong anisotropy of TC in the final component needs to be considered.

To check for anisotropy a simple experiment was made. The two specimens from the viscosity/TC-experiment described above were cut into stripes, each stripe turned by 90 degrees and glued together with same uncured resin compound. The TC of these specimens was measured again after hardening and polishing of the former cut stripes.

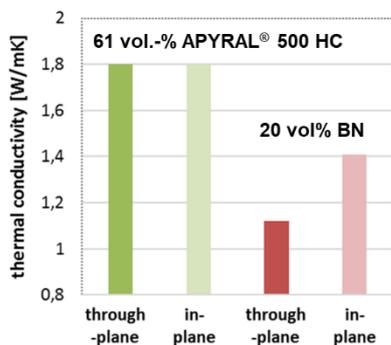


Figure 8. Thermal conductivity of an UP resin filled with BN or APYRAL® 500 HC, measured in- and through-plane.

Although the original specimen have been prepared by a simple casting, which should not

evoke a high degree of alignment of the BN particles, a significant higher in-plane-TC could be determined for the BN compound (see Figure 8). Other than for BN, absolutely no difference of TC whether measured in plane or through plane, was observed for APYRAL® HC. This is confirming the expected isotropy of ATH, demonstrating that HC parts made by APYRAL® HC filled resins are free from geometrical design restrictions.

2.5. Density (specific gravity)

Considering the model of touching particles to generate a high TC it is better to plot the TC versus **volume based** filling level rather than filler loading based on weight percent. Therefore the density (specific gravity) of the filler plays an important role. Low density fillers will gain a higher volume loading at the same loading level by weight.

APYRAL® HC exhibits a very low density (2.4 g/ml). This is a very important point when calculating the mass based formulation cost versus the volume based application cost, where a certain volume has to be filled.

Finally, using APYRAL® HC with its unique rheological properties allows highest filler loadings resulting in **even higher TC levels in comparison to calcined alumina or even BN**.

The obtained TC of the maximum filling levels of the UP compounds are plotted in Figure 9 in two ways, by volume fraction (vol.-%) and weight fraction (wt.-%) of the same compound.

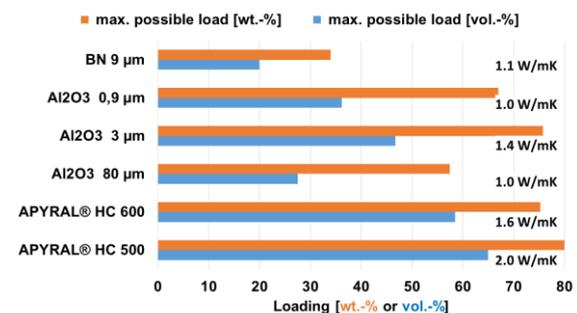


Figure 9. TC of APYRAL® HC in comparison to calcined alumina, and BN in UP-resin at 22 °C (Hot Disk method).

Again one can see the strong effect of the low density of APYRAL® HC: The alumina with best viscosity features (3 µm) can be filled up to 76 wt.-% but results in a lower TC than APYRAL® HC 600 which reaches only 75 wt.-% loading.

The higher TC value can only be explained when taking the volume based filling level into account, displayed as blue bars. When utilizing **APYRAL® HC 500** with its outstanding viscosity performance an even higher volume loading and a TC of 2 W/mK can be obtained.

The unique properties of **APYRAL® HC 500** were demonstrated in several resins with varying viscosity and intrinsic TC levels. The results are displayed in Figure 10. Depending on the viscosity level and the mechanical properties (e.g. cross linking degree) of the resin, different loadings and TC levels close to 3 W/mK can be gained. This makes **APYRAL® HC 500 and 600** ideal candidates for modern TIM and especially gap fillers for EV batteries.

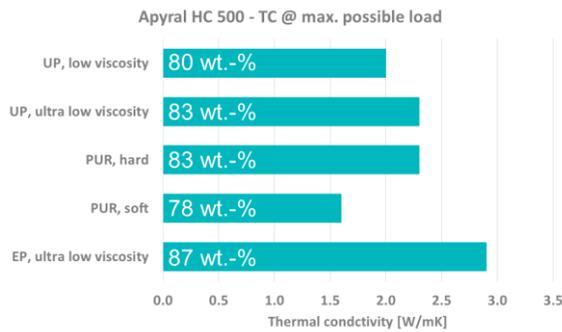


Figure 10. Thermal conductivity of selected resins of various chemistry and cross linking density filled with **APYRAL® 500 HC** to the maximum possible load.

3. Additional application parameters

3.1. Abrasion

HC compounds used in EV parts, especially gap fillers for LiB packs and modules, are to be consumed in big volumes so far not known from TIM in classical electronic applications, In large scale industrial applications **abrasion** and wear of tools during production and dispensing of HC compounds becomes an extremely important quality and cost factor.

Because of Mohs hardness 9 (practically only diamond is harder) Al_2O_3 particles are excellent abrasive materials - and it is known that abrasiveness increases strongly with particle size. This is another reason why it is not a good idea to use big alumina particles at high loadings. Materials with low Mohs hardness and low abrasion, like **APYRAL® HC** (Mohs 3) are to be preferred.

In Figure 11 the color of a PU resin compound filled with **APYRAL® HC 500**, a fine and a

coarse spherical alumina is shown. The differences of abrasion from a common high speed dissolver disk during a 10 minute dispersion are very obvious. Practically no abrasion occurs when utilizing **APYRAL® HC**, while Alumina will always cause extra cost due to abrasion.

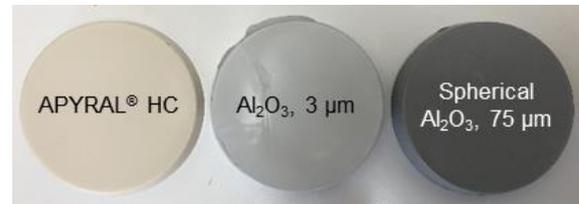


Figure 11. Color change of a PUR compound due to abrasion from dissolver disk when utilizing Al_2O_3 .

3.2. Flame retardancy

Likewise other electric components, LiBs belong to the safety sensitive components of an EV. Such components need to fulfil fire safety requirements. While final standardization is still in progress, materials in use are commonly requested to fulfill flame retardancy classification according to the UL 94V0 (similar to E&E applications).

Even when using BN or alumina at high filling levels which fulfil the required 3 W/mK, an UL94 V0 classification is not easy to achieve. Therefore additional flame retardants have to be used, which lead to higher cost and even higher viscosity.

This is not the case with **APYRAL® HC** as it is based solely on ATH, a well-known mineral flame retardant. In many resins a UL94 V0 classification is already achieved with filler loadings of 60 – 65 wt.-%. When it is used at loadings enabling 2.5 - 3 W/mK reported above, often very stringent flame retardancy classifications like e.g. lined out in EN 45545 (European railway standard) can be achieved.

Such highly filled glass fiber reinforced plastics (e.g. SMC / BMC) are already in use, when such severe flame retardancy classifications are required. This additional feature may play an important role when using glass fiber reinforced battery housings in an EV.

Hence **APYRAL® HC** is not only a filler enabling required thermal conductivity but features also excellently as flame retardant and smoke suppressor, enabling additional value and performance for a broad use in EV applications.