INVESTIGATION OF THE THERMAL CONDUCTIVITY OF HEXAGONAL BORON NITRIDE EPOXY COMPOSITES

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Abstract

The subject of this study is to investigate the thermal conductivity of hexagonal boron nitride epoxy micro composites and whether it is affected by application of different dispersion techniques or sedimentation effects and by attributed effects regarding the condition of the thermal filler material. Specimens with filler content up to 50 wt.-% of the composite were prepared and analysed using several experimental methods for the examination of dispersion state, particle size distribution, sedimentation behaviour and thermal diffusivity measurement. The results show a discernable but small influence of the dispersion technique on the thermal conductivity, unless the thermally conductive fillers are damaged in the dispersion process. A more pronounced influence on thermal conductivity arises from effects associated with sedimentation and particle orientation in particular.

1. Introduction

Polymer composites with remarkable thermal conductivity are of increasing interest for many applications in electronics, aerospace, polymer processing and others for thermal management purposes. Greater power and load increases heat generation and may lead to material degradation which is why excess heat has necessarily to be dissipated via thermally conductive materials [1]. Especially for electronic encapsulation electrical insulation of the material is also often required. A common approach to increase the thermal conductivity and to retain the electrical insulation is the incorporation of thermally conductive ceramic fillers like hexagonal boron nitride (hBN) into the polymer matrix [2].

Especially in particle modified polymer composites there are many parameters which may influence the thermal conductivity of the composite like the filler content, the filler geometry and size distribution, the filler orientation, the filler network formation and others [3, 4]. Usually many of those parameters are difficult to adjust or to maintain and moreover may be influenced by the applied processing techniques. Hence it is important to understand how primarily different dispersion techniques affect the particle conditions and how this influences the thermal conductivity of the composite. Therefor, this study investigates the influence of several basic dispersion methods on the dispersion state, the particle size distribution and additional effects like filler sedimentation with regard to thermal conductivity of hBN modified polymer composites.

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2. Materials and experimental methods

2.1. Materials and sample preparation

The investigated composites consist of hBN micro particles embedded in an epoxy matrix, which was the resin RIMR 135 and the hardener RIMH 137 from Hexion Inc. [5]. The hBN filler material was HeBoFill 501 with a mean particle size of d_{50} = 45 µm supplied by Henze BNP AG [6]. The particles' structure is highly anisotropic and they possess an in-plane thermal conductivity up to two orders of magnitude greater than in perpendicular direction, depending on the degree of crystallinity [7, 8]. This circumstance is helpful to evaluate particle orientation effects in the composite. Specimens with 0, 1, 10, 25 and 50 wt.-% hBN content were prepared. The fillers and matrix were mixed and the hBN particles were then dispersed by one of various dispersion techniques (manual dispersion: MD, different dissolvers: DS 1 - 4, sonotrode: Son, three-roll-mill with different gaps: 3RM). Small samples were taken from each mixture for light microscopy and viscosity measurements. The hardener was added and the whole mixture was then stirred for 10 minutes and degassed at 5 mbar. The compound was poured into a mould as shown in Fig. 1 and then cured for 48 hours at 30 °C and post cured for 15 hours at 80 °C. The geometry of the mould allowed the hBN fillers to settle in a considerable manner during cure. This yielded in a gradient in hBN content from the top to the middle to the bottom of the mould. Three specimens were cut out of the three areas of the cured composites for density, specific heat capacity and thermal conductivity measurement. The specimens for thermal conductivity measurement were polished and coated with a thin graphite layer to eliminate reflection of the xenon flash lamp.

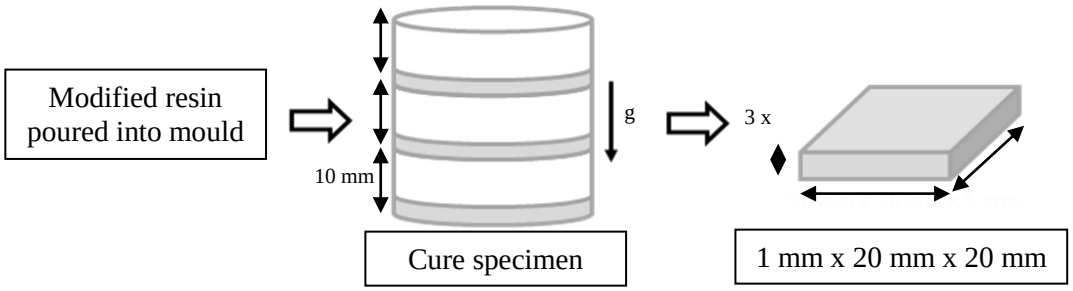

Figure 1. Process of specimen preparation with defined geometries for sedimentation of fillers and for measurement of thermal conductivity.

2.2. Assessment of dispersion state

To analyse the dispersion state of the hBN particles in the epoxy matrix, light micrographs were taken for each specimen and compared for each dispersion method. For that reason the micrographs were first converted into a binary image where black areas represent particle elements and white areas represent matrix elements. With the binary images the degree of homogeneity and the degree of dispersion or agglomeration can be calculated. Therefor a grid was applied to the image which divided it into several sectors. For each sector of the image the relation of black elements to all elements of the sector was calculated with MATLAB from The MathWorks Inc. The arithmetic mean μ of all sectors divided by the standard deviation σ then gave information about the spatial distribution of the particles in the matrix and defined the degree of homogeneity. Agglomerates in the sectors were counted to estimate the degree of agglomeration of the particles. For each specimen five images were analysed to calculate both indices to compensate for the deviation of the samples.

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2.3. Measurement of particle size distribution

The dispersion micrographs were also used to calculate the size distribution of the hBN particles in the matrix. In conjunction with the degree of agglomeration the degree of dispersion can be assessed. The diameter of all particles was measured by ImageJ. Hereby the cumulative distribution of the size of all particles in the micrograph can be calculated. To measure the cumulative distribution of the untreated particles, a laser diffractometer (LS 13 320 Laser Diffraction Particle Size Analyser from Beckman Coulter Inc.) was used as well as for the analysis of the particle size distribution in several samples after cure when sedimentation of the particles occured. For that reason the particles were reclaimed by combustion of the epoxy matrix at 700 °C in oxygen rich atmosphere in a furnace. In addition possible damaging of the particles during dispersion was investigated by means of scanning electron microscopy (Zeiss LEO 1530 Gemini from Carl Zeiss Inc).

2.4. Analysis of particle sedimentation behaviour

To determine the actual volume and weight fraction of hBN in all specimens, the density of these specimens was measured and then their filler content was calculated. The filler content was then used to analyse particle sedimentation behaviour. Micrographs of the cross-sections of all specimens were prepared to get additional information about the sedimentation behavior of the fillers as a function of settle height and to analyse volume fraction, particle orientation and network in the specimens as well as their dispersion state.

2.5. Determination of thermal conductivity

Thermal diffusivity a was measured through the xenon flash diffusivity method (XFA 600 from Linseis Messgeräte GmbH) in vacuum atmosphere. The measurements were performed at 25 °C, 40 °C and 60 °C. The density ρ of all specimens was determined as described in section 2.4 and the specific heat capacity c_p of the specimens was measured using differential scanning calorimetry on a NETZSCH DSC 204 F1 Phoenix. The thermal conductivity λ was then calculated according to equation 1:

$$\lambda(T) = c_p(T) \cdot \rho(T) \cdot a(T) \quad (1)$$

3. Results und discussion

3.1. Dispersion state

The dispersion state of the hBN particles in the matrix was judged according to their degree of homogeneity and their degree of agglomeration. Fig. 2 shows both calculated parameters and their standard deviations for samples with 1 wt.-% hBN in epoxy resin and for different dispersion techniques. A high value represents a high degree of homogeneity and a high degree of agglomeration, respectively. Therefore, for a good dispersion quality a high degree of homogeneity and a low degree of agglomeration are essential. Fig. 2a) depicts that the manual dispersion, the dispersion using the dissolvers 1 and 4 and the three-roll-mill using gaps with 75 µm/50 µm for three mill cycles result in the best degrees of homogeneity, followed by dissolver 3 and the sonotrode. Three-roll-mill cycles with other gaps result in lower degrees of homogeneity. Fig. 2b) shows that the lowest degree of agglomeration is achieved by several three-roll-mill processes followed up by the sonication technique. The highest degree of agglomeration remains by use of manual dispersion followed by dispersion using the dissolvers. The results show also that methods providing a good agitation of the mixture reach a higher degree of homogeneity while techniques with higher energy input reach a lower degree of agglomeration. Particularly for the three-roll-mill processes it was observed that the degree

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of homogeneity tends to lower from the first mill step to the third mill step giving rise to the assumption of separation effects on larger particles in the milling process.

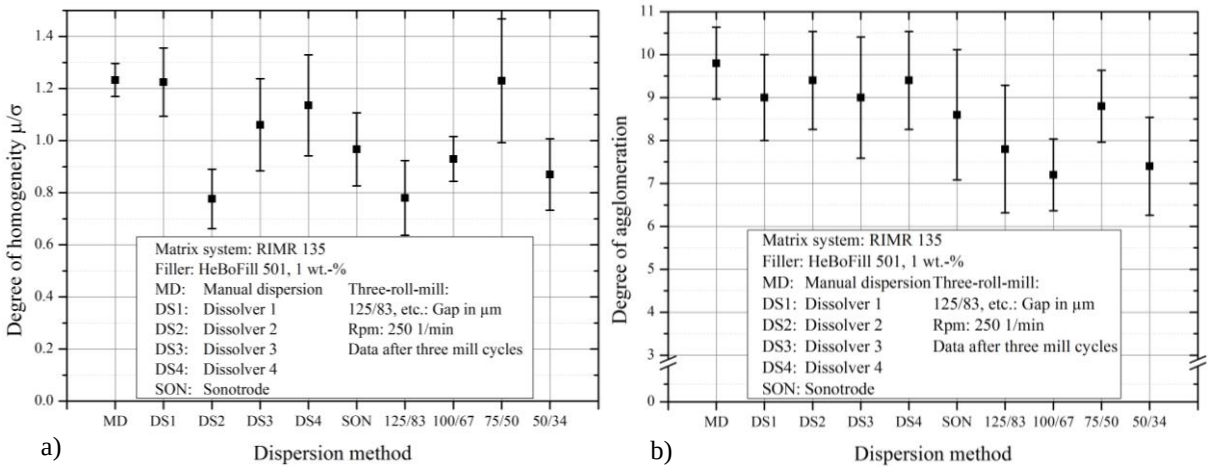

Figure 2. Degrees of a) homogeneity and b) agglomeration of 1 wt.-% hBN particles in samples prepared by use of different dispersion techniques.

3.2. Particle size distribution

To assure that during the dispersion process no particle grinding or separation take place, which would alter particle size distribution and therefore distort the evaluation of the dispersion state, the actual particle distribution after the dispersion process was measured. Furthermore and according to [9, 10] a decreasing primary particle size would decrease the possible thermal conductivity due to an increase in the particle surface and therefore in the total thermal resistance area. Accordingly the particle size distribution is displayed in Fig. 3 for the several dispersion techniques to evaluate detrimental change of particle size and to support the selection of a ‘mild’ dispersion method.

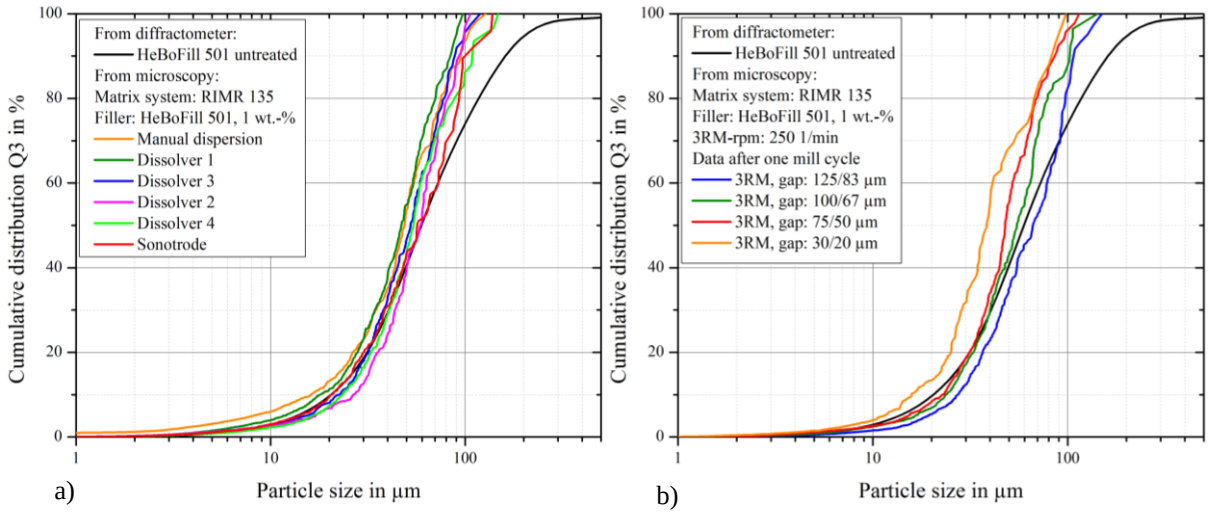

Figure 3. Cumulative distribution of hBN particle size directly after application of various dispersion techniques and measured by optical microscopy.

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The untreated filler material, as it's particle size distribution is shown in Fig. 3, contained some large agglomerates. In principle all dispersion techniques were effective in breaking agglomerates down to primary particle size level when compared to the data of the manufacturer. Apart from that there were only small differences in the particle size distribution obtained from the light micrographs for most dispersion techniques. Apparently no extensive damaging of the hBN particles took place. Only for the three-roll-mill dispersion method a shift in particle size down to smaller diameters was observed when the mill gap size was decreased from 100 µm/67 µm down to 75 µm/50 µm and lower. This indicates that the use of smaller gaps for the three-roll-mill dispersion process to increase the degree of homogeneity and to lower the amount of agglomerates also leads to filler separation or damage. To clarify whether the particles were damaged during the dispersion process, several samples with particles retrieved from the composite via combustion of the epoxy matrix were examined by means of scanning electron microscopy. The results for the different dispersion methods in Fig. 4 are compared to untreated hBN particles. It can be observed that manual dispersion and dispersion using the dissolver do not lead to notable damage of the primary particles. In contrast the red arrows in Figs. 4d) for sonication and 4e) for three-roll-milling show observable debonding of multiple hBN layers of the filler and extensive damage induced through folding of the particles, respectively. Obviously high local energy input during the dispersion process may lead to damaging of the primary particles.

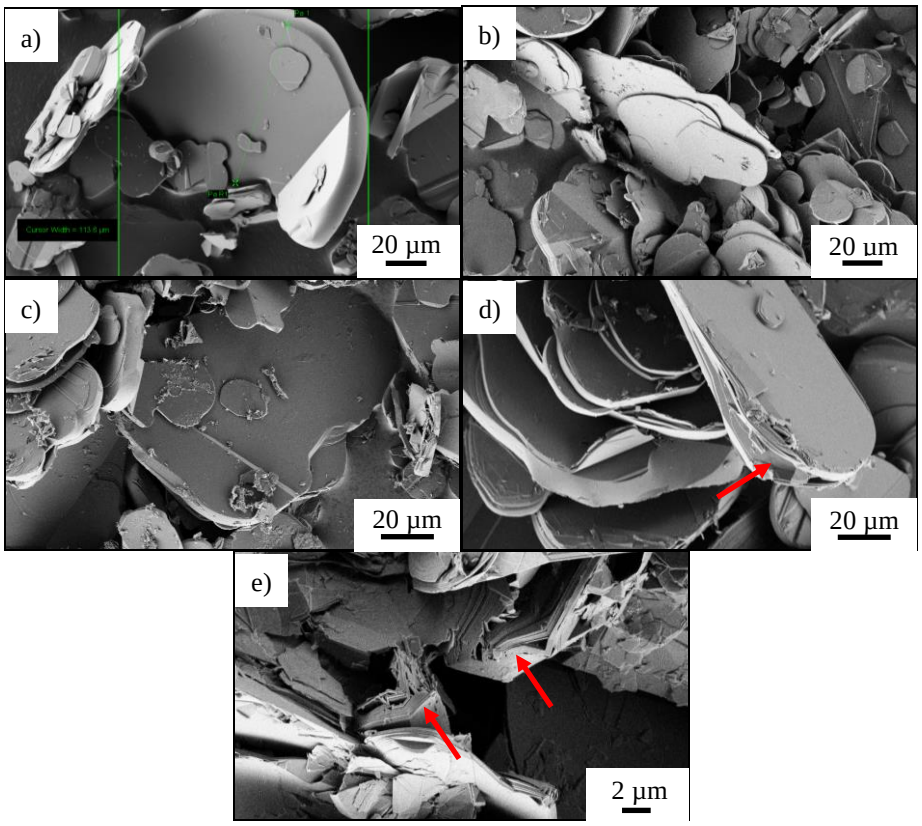

Figure 4. Scanning electron micrographs of hBN particles treated with different dispersion methods: a) untreated hBN particles b) manual dispersion c) dissolver 1 d) sonotrode e) three-roll-mill 100/67.

3.3. Particle sedimentation behaviour

To investigate the sedimentation behaviour of the hBN micro fillers during cure, the density of all specimens for thermal conductivity measurement was measured and calculated by means of Archimedes principle. With regard to the density of the epoxy matrix and the filler material the actual hBN volume content and weight content of all specimens were calculated. This enabled an overview

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of the actual filler content of all specimens after sedimentation of the fillers dependent on their former position in the mould. Most specimens were affected by a significant degree of filler sedimentation and the lower specimens have a much higher filler content than those specimens above. It appears that the maximum filler content which can be achieved by sedimentation is limited. In fact the specimens from the bottom of the mould have a comparable filler content with a deviation of 2 wt.-% for each individual dispersion method, regardless of the former filler contents of for example 10 wt.-% or 25 wt.-% before sedimentation. In addition all the top and middle specimens with 25 wt.-% former filler content have a comparable filler content of 25 wt.-% after sedimentation. Sedimentation is therefore the more mitigated the higher the particle content is, which is due to the increasing viscosity of the mixture with increasing particle content.

Micrographs of the cross section of different specimens show that the particles do not form a dense packing at the bottom of the mould but a regular interlaced network. In any case and regardless of the applied dispersion method, the former degree of dispersion is neutralised and superposed by the sedimentation effects. Where sedimentation leads to a high filler content, the particles are automatically evenly distributed.

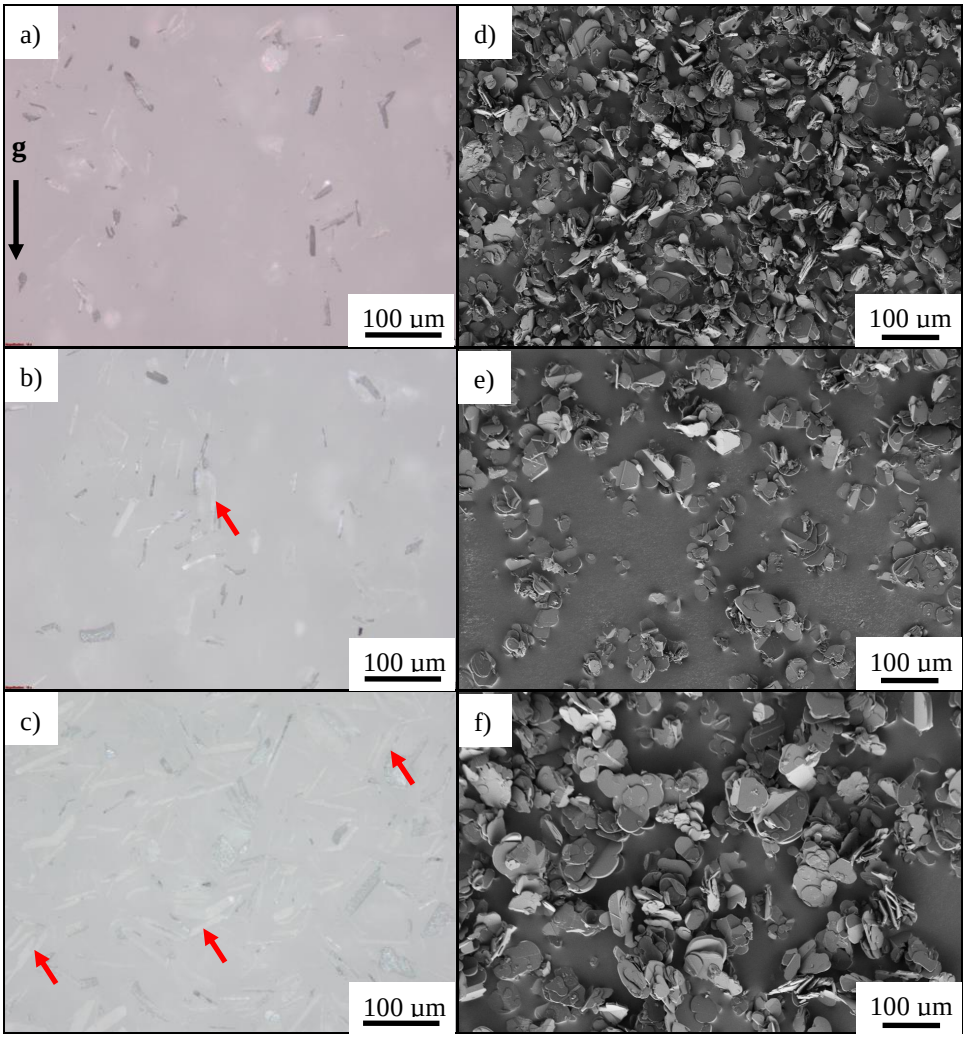

Figure 5. Cross section (a, b, c) and scanning electron micrographs (d, e, f) of hBN particles in epoxy matrix [g = gravity]: a) and d) top position, b) and e) middle position, c) and f) bottom position.

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Fig. 5 shows some cross-section and scanning electron micrographs of the same specimens and their fillers from a set with former filler content of 10 wt.-% and now a different filler content from top to bottom position, respectively. The cross-section micrographs give further information about the packing and orientation of the hBN particles during sedimentation. The specimens from the top and the middle position (Figs. 5a and 5b) show a state where further sedimentation was prohibited due to gelation and cure of the epoxy matrix and not due to the bottom of the mould. It can be seen that the particles tend to turn into vertical position for sedimentation movement to minimize the flow resistance in the resin. Especially Fig. 5b depicts that the majority of the particles is oriented vertically which contributed to the thermal conductivity in thickness direction due to the high anisotropy of the hBN particles. In contrast, with a higher particle content and when the particles approached the bottom of the mould, their orientation was more horizontal. When the particle content is increased, more particles tend to form clusters with a certain orientation as indicated by the red arrows in Figs. 5b and 5 c, which was also observed by [7]. Figs 5 d, e and f show that particle size tended to increase due to sedimentation when the top and middle positions of specimens are compared to the bottom position.

3.4 Thermal conductivity

To evaluate whether the aforementioned results have an effect on the thermal conductivity of the hBN micro composites, the thermal conductivity of all specimens was measured. In Fig. 6 thermal conductivity is plotted against the actual filler content for different dispersion methods and specimen positions. Thermal conductivity shows a slight progressive increase with increasing hBN filler fraction. At a filler content of approximately 40 wt.-% the thermal conductivity of the composite reached 500 % of the thermal conductivity of the neat resin. Besides the higher filler content at the bottom of the mould those specimens also exhibit a better particle network compared to specimens with lower filler content. Nevertheless this did not lead to a strong progressive increase of thermal conductivity due to the change in particle orientation from vertical to horizontal caused by sedimentation effects and the high anisotropy of the hBN particles. Therefore, it can be stated that not only the particle network density but also the particle orientation had an important influence on the thermal conductivity as also mentioned in [7]. Specimens with a high amount of vertically oriented fillers possess a higher thermal conductivity for a certain filler content. In general those specimen with particles dispersed by sonication or dissolver show the least scattering in thermal conductivity. They posses also higher thermal conductivity than specimens prepared by hand dispersion. The considerable scattering of the specimens prepared by three-roll milling dispersion is unexplained at this point.

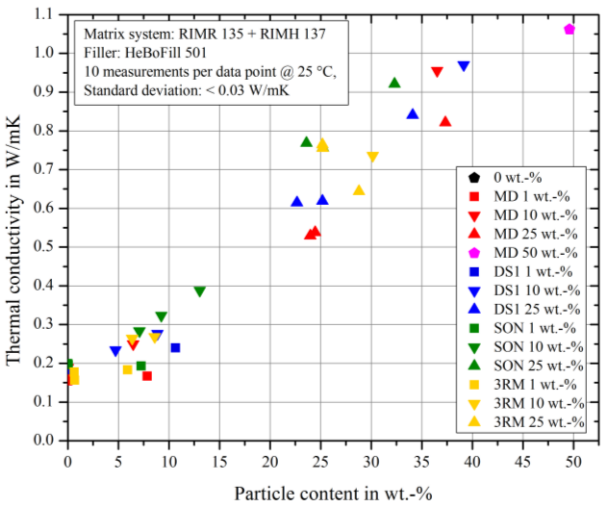

Figure 6. Thermal conductivity of hBN epoxy composites vs. hBN content for different dispersion techniques.

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4. Conclusions

The presented study shows the effects of different dispersion techniques, the subsequent effects of the dispersion process on the filler material and effects based on filler sedimentation on the thermal conductivity of hBN epoxy micro composites. It is shown that the relevance of the dispersion technique is discernible but low for micro-sized fillers and high filler contents, unless the particles get damaged by the dispersion process. Therefore it is recommended to choose a dispersion technique (e.g. dissolvers) which supports a good homogeneity of the particles and is also time and cost efficient. Effects like filler sedimentation and filler orientation show a more pronounced influence on the thermal conductivity of anisotropic filler composites.

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References

[1] W. Zhou, S. Qi, Q. An, H. Zhao, and N. Liu. Thermal conductivity of boron nitride reinforced polyethylene composites. *Materials Research Bulletin,* 42:1863-1873, 2007.

[2] I. A. Tsekmes, R. Kochetov, P.H.F. Morshuis, J.J. Smit. Thermal Conductivity of Polymeric Composites: A Review. *2013 IEEE International Conference on Solid Dielectrics, Bologna, Italy,* June 30 – July 4 2013.

[3] W. Übler. *Erhöhung der thermischen Leitfähigkeit elektrisch isolierender Polymerwerkstoffe.* Technische Fakultät der Universität Erlangen-Nürnberg, 2002.

[4] X. Huang. P. Jiang, and T. Tanaka. A review of dielectric polymer composites with high thermal conductivity. *IEEE Electrical Insulation Magazine,* 27:8-16, 2011.

[5] Momentive, Hexion Specialty Chemicals: Technical Information EPIKOTE Resin MGS RIMR 135 and EPIKURE Curing Agent MGS RIMH 134 - RIMH 137, Hexion Specialty Chemicals (Ed.), Stuttgart, 2009.

[6] Henze Boron Nitride Products: Product Information HeBoFill 501 Boron Nitride Powder, Henze BNP AG (Ed.), Lauben, 2014.

[7] R.F. Hill, and P.H. Supancic. Thermal Conductivity of Platelet-Filled Polymer Composites. *Journal of the American Ceramic Society*, 85: 851-857, 2002.

[8] S.G. Mosanenzadeh, and H.E. Naguib. Effect of filler arrangement and networking of hexagonal boron nitride on the conductivity of new thermal management polymeric composites. *Composites Part B: Engineering,* 85:24-30, 2016.

[9] C. Nan, R. Birringer, D.R. Clarke, and H. Gleiter. Effective thermal conductivity of particulate composites with interfacial thermal resistance. *Journal of Applied Physics,* 81:6692-6699, 1997.

[10] D.P.H. Hasselman, and K.Y. Donaldson. Effect of reinforcement particle size on the thermal conductivity of a particulate-silicon carbide-reinforced aluminum matrix composite. *Communications of the American Ceramic Society,* 75:3137-3140, 1992.

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