Tape casting of UV-curable aluminium nitride-based slurries

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Abstract:

Aluminium nitride (AlN) is one of the materials used for the preparation of substrates for electronic circuits. Such substrates can be prepared via tape casting method. Until now, only non-aqueous and aqueous tape casting was developed and studied for AlN. In this work, the development of UV-curable tape casting for AlN, including the use of photopolymerisable binder, is shown. Two different dispersing agents, BYK-W 9010 and glycerol trioleate, were used to stabilize and homogenize AlN dispersions. In order to modify the powder surface, a pre-treatment step was used, where the powder was first mixed with the dispersing agent in an azeotropic solvent mixture, followed by the evaporation of the solvents and the redispersing of the pre-conditioned powder into the reactive binder. The effective concentration of the dispersants, the impact of the solid loading on the viscosity and slurry behaviour, as well as the effect of the powder pre-conditioning, were studied by means of rheological measurements. Green tapes were optimised by evaluating the effect of the casting gap and the photo- and co-initiator

concentrations. Finally, FTIR measurements were used to estimate the polymer conversion degree as a function of exposure time for the green tapes.

Keywords:

aluminium nitride, reactive binders, tape casting, UV-curing

1. Introduction

In recent years, AlN has gained the interest of many manufacturers in the area of substrates for high-density integrated circuit packages. The densities of circuit packages are often limited by thermal dissipation, therefore they require high thermally conductive substrates. AlN is able to provide the needed thermal conductivity and, together with the many attractive properties, such as low thermal expansion coefficient (close to that of silicon), low dielectric constant and low electrical conductivity, makes it a better choice for fabrication of the substrates for electronics than the commonly used Al_2O_3 [1–3]. Additionally, AlN is a promising candidate for the manufacturing of heat exchangers.

Tape casting is a commonly used method for the preparation of ceramic substrates for electronics. It is the most efficient and reliable method of producing thin and flat ceramic green sheets. Those thin ceramic sheets might be subsequently stacked together and laminated to fabricate multilayer structures for different application.

When compared to other production methods, tape casting can ensure high green bodies densities and good production efficiency [4–6].

Slurries that are used for tape casting have to fulfil several requirements such as high ratio between the ceramic powder and the organic additives, low viscosity, high stability and high homogeneity. The first stage of tape casting is dispersing the powder in a sol-

vent via dispersing agents. This influences the properties of the green tapes and the sintered ceramics, including density and microstructure homogeneity [4].

Tape casting technique involving the use of solvents requires a thermal drying stage, during which solvents are evaporated. This stage is crucial, as it affects the quality of the final tape. A possible alternative to this is tape casting based on UV-curable systems [5,7]. This innovative process uses a reactive binder, which polymerises when irradiated by UV-light. The ceramic powder is dispersed in the binder, along with a photoinitiator. When the UV-light is applied, the photopolymerisation reaction is initiated and creates a ceramic powder particle entrapping matrix. The use of solvents is no longer necessary, therefore the drying step can be omitted. This, in turn, allows to retain the entire amount of the tape cast slurry within the green tape, as well as to avoid high shrinkage and crack formation that may occur during thermal drying. Additionally, UV-curing is time efficient, because the solidification can be performed after casting and results in high density green bodies. However, the amount of binder used in UV-curable systems is significantly higher than in solvent-borne systems. A comparison between the two systems is given in the work of Chartier et al. [5].

Wet processing of AlN with H₂O carries the risk of hydrolysis of the particles' surface, which results in powder oxidation and the production of ammonia. It is therefore, advised to substitute H₂O with non-aqueous media for wet processing of AlN [8].

Despite this, both, non-aqueous and aqueous tape casting processes have been developed for AlN [2,3,6,8–12]. Depending on the chosen system, different strategies of dispersion preparation are applied.

Chartier et al. [2], as well as Descamps et al. [9], dispersed AlN powder in 66/34 vol% of butan-2-ol/ethanol solvent mixture. Both groups used phosphate ester as the dispers-

ing agent. After dispersing the powder, the binder and the plasticizers were added to the slurry. Esposito et al. [8] prepared a slurry by mixing Y_2O_3 (sintering aid) together with glyceryl trioleate, as the dispersant. For the solvent, a 85/15 wt% of toluene/isopropanol mixture was used. Then, the other slurry components were added and the addition of each of them was followed by a mixing stage. Next, the prepared slurry was outgassed, in order to eliminate air bubbles which may affect the quality of the cast tapes.

Most authors mixed all slurry components one after another, whereas in the case of aqueous tape casting, the authors first coated the surface of the AlN powder with a surface-active agent to prevent the powder hydrolysis. Liu et al. [6] prepared AlN ceramics via aqueous tape casting. To prevent hydrolysis they treated the surface of AlN with a surface-active agent, namely 4 wt% phosphoric acid and 4 wt% aluminium dihydrogen phosphate. They performed the surface treatment by mixing for 24h in alcohol then rinsing (repeated for 10 times) the powder with alcohol to remove any residual surface-active agents. Then the surface-modified powder was dried in a vacuum furnace at 60 C°. Next, the powder was dispersed in distilled water, together with a sintering aid, mixed for 12h in order to prepare the dispersion for tape casting.

The aim of this study was to develop AlN-based slurries using a UV-curable binder as dispersing medium for tape casting. The surface treatment of the AlN powder, based on existing literature data, was carried out by coating the dispersing agents in an azeotropic mixture of solvents, which is referred to as pre-treatment. It was shown by Moreno et al. [13], that the selected dispersing agents (glyceryl trioleate, BYK-W 9010) show the best dispersability in an azeotropic mixture of methylethylketone (MEK) and ethanol (EtOH). Pre-treatment stage was followed by drying the powder under vacuum and re-dispersing it in a photopolymerisable binder. The influences of the two different dis-

persing agents, pre-treatment and solid contents were investigated via rheological measurements. Finally, the green tapes were evaluated by measuring the degree of polymerization using Fourier Transformed Infrared Spectroscopy (FTIR).

2. Experimental procedure

2.1. Raw materials

The AlN powder Grade B ($BET = 1.85\text{m}^2/\text{g}$) from H.C. Starck (Germany) was used as the main component. BYK-W 9010 (BYK; a phosphoric acid ester of a monofunctional carboxylic acid, 100% active substance, $M_w \approx 1000\text{ g}\cdot\text{mol}^{-1}$, chain length 5-10 nm) from BYK Additives & Instruments (Germany) and glycerol trioleate (GTO; 65% active substance) from Sigma Aldrich (Switzerland) were used as the two different dispersing agents. 1,6-hexanediol diacrylate (HDDA), Miramer M200 from Rahn AG (Switzerland) was used as the photocurable binder. It is a liquid difunctional monomer with a viscosity of 0.005-0.015 Pa·s at 25°C and a refractive index of 1.455. Genocure ITX (isopropylthioxanthone) from Rahn AG (Switzerland) and N,N,N',N'-tetramethylethylenediamine from Sigma Aldrich (Germany) were used as the photoinitiator and co-initiator, respectively. The molecular structures of the reactive binder and both initiators are shown in Figure 1.

2.2. Processing and shaping

2.2.1. Powder pre-treatment and preparation of reactive slurry

In order to coat the powder surface with the dispersing agent, a so called pre-treatment stage was applied. The AlN powder was treated with a dispersant and was ballmilled for 24h in an azeotropic mixture of MEK (66 vol%) and absolute EtOH (34 vol%).

Ballmilling was performed in a PET bottle with the grinding medium being 3 mm zirconia balls. The coated powder was dried in a Rotavapor R-134 from Büchi, Switzerland and redispersed in the photopolymerisable binder by milling in a planetary ball mill PM 400 from Retsch®, Germany (3mm zirconia grinding medium, zirconia-lined milling vessel). That step was combined with mixing the slurry with the photo- and the co-initiator. Next, the slurry was placed under vacuum for 30 minutes to remove any residual air bubbles.

2.2.2. Preparation of the green tapes

The outgassed slurry was deposited on a polyester film, the carrier, (Mitsubishi GmbH, HostophanRN) and spread using a doctor blade via a laboratory tape caster. The tape casting was performed at room temperature, with a casting speed of 0.005 ms^{-1} . The cast tapes were cured by exposing them to UV-irradiation and applying a continuous flow of nitrogen gas. Curing under an inert gas atmosphere was applied to reduce the effect of oxygen inhibition. Eight 3W LED bulbs from Shenzhen Fedy Technology Co. LTD, China with a wavelength of 365 nm were used as the source of the UV-irradiation. The curing equipment was a self-made polyethylene box, where the UV-bulbs are located on the top and the tapes were placed on the bottom. A laboratory power supply was used to generate the current necessary to run the bulbs. Measurements of the exposure intensity were done using FieldMaxII-TO from Coherent (USA). Exposure intensity was measured in three different locations inside the polyethylene box resulting in an average value of $487 \pm 43 \text{ } \mu\text{W}\cdot\text{cm}^{-2}$. The scheme of the process, from slurry preparation to green tape production, is shown in Figure 2.

The influence of the photo- and co-initiator concentrations, casting gap, and solid contents on the quality and exposure time of the produced green tapes were evaluated by a series of experiments. The applied casting gaps were 100 μm and 200 μm . Two ratio variations were used for the photo- and co-initiator slurry additives, i.e. 1:2 and 2:1, respectively. The concentrations were based on the binder weight.

3. Characterisation techniques

3.1. Slurry characterisation

Rheological measurements of AlN based slurries were performed using a Modular Compact Rheometer MCR 302 from Anton Paar (Germany) and a coaxial cylinder measuring system CC27-SN36412, in order to investigate the optimal dispersing agent concentration, the influence of powder pre-treatment and the solid load.

Slurries containing different concentrations of each dispersing agents were made using pre-treated powder redispersed in HDDA. The concentrations of the dispersant were determined in respect to the powder weight and correspond to the dispersant solution, not the active substance. The investigated slurries contained 40 vol% of AlN powder and the following dispersant concentrations: 0.2; 0.8; 1.0; 2.0wt% and 0.2; 0.5; 1.0; 2.0wt% of BYK and GTO, respectively. After establishing the optimal dispersant concentration, the effect of the pre-treatment stage was investigated. The slurries were prepared by adding 40 vol% of either the pre-treated or non-coated powder, the dispersant and HDDA and mixing the components together. Next, dispersions containing different solid contents, in the range of 40 vol% - 60 vol%, were analysed. Slurries for rheological measurements were mixed in the planetary ball mill for 30 minutes at 100 rpm and the tests were performed using the following program: increasing the logarithmic ramp for

shear rates between 0.01 and 200 s⁻¹ and decreasing the logarithmic ramp for shear rates between 200 and 10 s⁻¹.

Static Light Scattering measurements were done using LS 13 320 from Beckman Coulter (Germany) in order to determine particle size distribution (PSD) of the non-treated and pre-treated powder with each dispersing agent. The measurements were performed in isopropanol for slurry samples containing 30 vol% of AlN powder and dispersing agents, which were collected directly from the mixture prepared for the AlN pre-treatment, after 24h mixture mixing. AlN with no surface modification was mixed directly in isopropanol.

3.2. Tapes characterisation

The thickness of the green tapes after curing under UV-light was measured. The applying casting gap was 100 µm and 200 µm casting gaps and the slurry containing 40 vol% of AlN and each dispersing agents. Thickness of a tape was measured three times and an average was calculated.

Additionally, the green tapes were characterised by determining the degree of polymer conversion as a function of exposure time, based on FTIR measurements. FTIR was performed using a Tensor 27 spectrometer from Bruker (Germany) with an attenuated total reflection (ATR) component. Both, the top and bottom surfaces of the tapes were investigated by placing them on the ATR diamond and pressing with a sample holder. Each spectrum, with a resolution of 4cm⁻¹, is an approximation of 32 scans. The OPUS software was used to apply baseline corrections to each spectrum, which was further used to calculate the conversion degree. Each spectrum was normalized and the calculations were based on the areas under the graph assigned to the two carbon – carbon dou-

ble bonds of the acrylate structure (C=C stretching and C=C twisting, in the regions of 1600-1660cm⁻¹ and 1350-1430cm⁻¹, respectively) and the carbonyl group (C=O stretching was assigned to the peak at 1720cm⁻¹), which served as the reference bond. The conversion degree was calculated according to a formula proposed by Wu and Halloran [14], shown by Equation 1.

$$\alpha(t) = \frac{\left[\frac{A_{1620}+A_{1410}}{A_{1750}} \right]_0 - \left[\frac{A_{1620}+A_{1410}}{A_{1750}} \right]_t}{\left[\frac{A_{1620}+A_{1410}}{A_{1750}} \right]_0} \cdot 100 \% \quad (1)$$

Additionally, in order to determine the processing reproducibility, FTIR measurements and conversion degrees calculations were repeated for the new series of samples cast by using 100 µm and 200 µm gap and following exposure times 2; 4; 6; and 8 minutes.

4. Results and discussion

4.1. The influence of used dispersing agents and concentrations

The effectiveness of the two selected dispersants, i.e. BYK-W 9010 and GTO, was evaluated by means of rheological measurements. Figure 3 depicts the viscosity values of the slurries containing 40 vol% of AlN powder and different concentrations of the dispersing agents at the shear rate equal 25 s⁻¹. It can be seen that, in both cases, the AlN-based slurries exhibit an initial drop in viscosity where a minimum was registered at concentrations equal 1 wt% and 0.5 wt% for BYK and GTO, respectively. The amount of BYK required to reach the minimum point is twice the amount when compared to GTO. Additionally, the change in viscosity is smoother and the minimum point is at a higher viscosity value in the case of GTO, whereas for BYK the change is more pronounced and the minimum point is lower, as well as the overall viscosity values.

Concentrations of 1 wt% for BYK and 0.5 wt% for GTO correspond to an effective concentration of the dispersants and to the best state of dispersion. Lower concentrations of dispersing agent do not provide saturation adsorption, leading to a continuous decrease in viscosity. On the other hand, an excess of the dispersing agent may have an opposite effect, i.e. an increase in the slurry viscosity due to interactions between the molecules of the dispersant [15]. In other studies, where phosphate ester was used for AlN [9]; yttria stabilized zirconia [15] and alumina [5], an increase in viscosity when exceeding the optimum dispersing agent concentration was also observed.

In this work, it was observed that the use of GTO results in higher viscosities than when using phosphate ester. Similar results were observed in a work on alumina [13], where the effect of phosphate ester, GTO and some other dispersing agents were studied. According to Moreno et al. [13], the effectiveness of phosphate ester is higher than GTO, due to its dissociation. H_3O^+ ions are released into the solvent and the particles start to be positively charged and attract the anionic end of the phosphate ester. Therefore, the combination of particle charge repulsion and the steric repulsion of the polymeric chains generates an electrosterical stabilization [9,13].

Figure 4 depicts PSD of non-treated and treated with AlN powder each dispersing agent and Table 1 collects the measurements statistics. It can be seen that both dispersing agents shift the PSD into the lower size range in comparison to the not-treated powder. The optimised concentrations of the dispersing agents, corresponding to the lowest viscosity values, were applied for further rheological tests, as well as for slurry preparation for the tape casting procedure.

4.2. The effects of the pre-treatment process

In order to confirm that the pre-treatment of AlN had a beneficial influence on the viscosities of the AlN slurries and dispersion homogeneity, viscosities of the slips containing already pre-treated powder and non-pretreated powder were compared. Figure 5 shows the results of the measurements.

The viscosity of the suspensions containing BYK initially decreases and at the shear rate of ca. 5 s^{-1} , it starts to gradually increase again. This means that initially, a shear thinning behaviour occurs, which later transforms into weak shear thickening behaviour. The slurries containing GTO only exhibit shear thinning behaviour. Both dispersing agents lower the viscosity values of the pre-treated powders. Therefore, it can be expected that pre-treatment improves the stability and homogenisation of the suspensions of the photocurable binder. Additionally, the use of GTO reduces the thixotropy.

The pre-treatment allows the dispersing agent to more effectively adsorb on the surface of AlN particles. Additionally, it may result in avoiding competition which can appear between the adsorption of the dispersing agent on the particles surface as well as of the other compounds [16].

4.3. Effect of the solid load on the viscosity

The use of surfactants allows to increase the solid loading to levels which are necessary for the processing and subsequent sintering, i.e. above 40 vol% [17]. Therefore, an attempt was made to increase the powder concentration in the slips containing HDDA.

For slurries containing BYK, the solid content was gradually increased from 40 vol%, to 45; 50; 55; and 60 vol% (Figure 6a). As expected, the increase in solid content increased the slurry viscosity. Additionally, higher solid concentrations resulted in a stronger shear thickening behaviour. The highest possible solid content in this study was

60 vol%. This amount of powder resulted in a very strong shear thickening behaviour, hence the slurry could not be investigated via the coaxial cylinder measuring system. Similarly, for slurries containing GTO, the viscosity also increased with the increase in solid loading. Nevertheless, shear thickening behaviour was not observed and the highest reachable solid load was approx. 50 vol% of powder. Further solid load increasing up to 55 vol% resulted in obtaining an inhomogeneous paste, lacking flowability.

The range of the viscosity values, which are suitable for tape casting can be found to be approx. 0.8 Pa·s 1.2 Pa·s [5]. Taking this into consideration, the slurries stabilised by BYK are too liquid for tape casting, with exception of the slurry containing 55 vol% of AlN. However, that slip exhibits a shear thickening behaviour which in general is not a desirable phenomenon for tape casting. On the other hand, among suspensions containing GTO (Figure 6b), only the slurry containing 40 vol% of solid fits into the given viscosity range, whereas slurries with higher solid contents are too viscous. Nevertheless, solid concentration in the range of 40 vol% to 45 vol% could fit into the suitable viscosity range. The advantage of slurries dispersed by GTO is that they exhibit a shear thinning behaviour, which is favourable for tape casting.

The shear thickening phenomenon is not a desirable rheological behaviour for tape casting as it does not ensure low viscosity at a rather high shear rate (doctor blade movement), and a high viscosity after blade passing. Therefore, good homogeneity and accuracy of the green tape dimensions can not be ensured, as well as avoiding ceramic particles settling in the cast tape. Nevertheless, the phenomenon should not be a problem for systems undergoing photopolymerisation, as the tape is exposed to UV-radiation directly after casting, therefore leading to an instant hardening of the tape [5,7].

4.4. Tape casting and photopolymerisation

The slurry containing 40 vol% of AlN powder and 1 wt% of BYK was studied. Ratios of 1:2 and 2:1 of photoinitiator and co-initiator concentrations were applied to the system. The 1:2 ratio resulted in shorter exposure times, as more free radicals were formed to initialise a polymerisation reaction, whereas the 2:1 ratio resulted in longer exposure times.

Independently from the initiator concentrations, the tapes cast using the 200 μm gap required longer exposure times than those cast at 100 μm , by visual observation. In general, in the case of the thicker layers, a higher energy dose is required to cure the tape, meaning that at a given exposure intensity polymerisation reaction takes longer time. High concentrations of the photoinitiator cause high absorption of the incident light in the upper film layers. Therefore, the intensity of the incident light in the bottom layers is reduced and the polymerisation does not occur uniformly [7,18].

Additionally, depending on the applied casting gap, the quality of the UV-cured tapes varied. For a casting gap of 100 μm , the surface of the cured tapes was smooth, whereas tapes cast using a casting gap of 200 μm exhibited wrinkles on the surface after the UV-curing process (Figure 7). The wrinkling phenomenon was especially prominent for the concentration ratios of 1:2 of initiators. The ratio of 2:1 resulted in the reduction of the wrinkling on tapes cast with a casting gap of 200 μm . Therefore, the ratio of 2:1 (1 wt% : 0.5wt%) of photo- and co-initiator was applied in all further experiments.

The structure of tapes containing 40 vol% of AlN powder seemed to be two-layered. It was possible to distinguish the layers with the naked eye on the fracture surface once the tapes were removed from the carrier. The layers were prone to delamination when

removing the tape from the carrier. This phenomenon is most likely attributed to uneven polymerisation throughout the entire tape thickness. Additionally, the green tapes were characterized by warpage after releasing them from the carrier, which might be related to the polymerisation shrinkage of the acrylate binder.

Tape casting the slip containing 55 vol% of AlN powder and 1 wt% of BYK was also performed in order to determine if the shear thickening behaviour would hinder the casting process. Despite the unfavourable behaviour, tape casting was possible as the thickening of the slurry under the applied shear rate did not prove to be an obstacle. However, the slurry tended to flow after the doctor blade passed and, therefore, did not preserve the dimensions defined by the doctor blade, both for 100 μm and 200 μm casting gaps. Regarding the polymerisation process, 55 vol% of powder required longer exposure times. Moreover, higher solid concentrations, resulted in less warpage of the green tapes. Nevertheless, the wrinkling phenomenon was not eliminated when a casting gap of 200 μm was applied.

The reasons of wrinkling phenomenon can be found in uneven polymerisation throughout the tape thickness and the polymerization shrinkage of the HDDA. The top surface of the tape shows faster crosslinking than the lower layers, therefore, it starts to shrink over the still-liquid lower layers. Additionally, applying of the inert atmosphere during photopolymerisation contributes to wrinkling formation. It reduces the oxygen inhibition and increases reaction rates differences for the top and the bottom layers [19].

Dispersions containing 40 vol% of AlN powder and 0.5 wt% of GTO also exhibited the wrinkling phenomenon, when applying a 200 μm casting gap. In the case of the tapes cast from this particular slurry, the tapes preserved their shape after the passing of the doctor blade.

For the green tape thickness measurements, the tapes exposed to UV-light for 6 min and 8 min were chosen, as these exposure times resulted in the tapes removable from the carrier. In the Table 2 are given the average values of measured thicknesses. Casting applying 100 μm and 200 μm casting gap resulted in the tapes' thickness lower and higher than the applied gap, respectively. The decrease in thickness is a result of the polymerisation volume shrinkage of HDDA, which according to the literature is ca. 19 % [20]. The increase in the thickness is assigned to the wrinkles formation. Therefore, the values collected in the Table 2 may be misleading.

Additionally, depending on the dispersing agent being used, dispersions exhibited different tape carrier wetting behaviour. When using BYK, it was possible to cast tapes only on a silicon-uncoated side of the polyester carrier. Applying GTO allowed to cast tapes both, on silicon-uncoated and silicon-coated side of the polyester carrier.

4.5. Conversion degree estimation

The effect of the casting gap on the degree of polymerisation conversion was investigated. For this purpose, slurry containing 40 vol% of AlN powder and 1 wt% of BYK was analysed. Figure 8 shows the results of the conversion calculations. The applied gap of 100 μm resulted in a significant increase in conversion degree after 4 min of curing for the top surface and 6 min for the bottom surface. The highest conversion degrees were obtained after 10 min of curing, when the plateau-like region starts, and are approx. 76% and 42% for the top and bottom surfaces, respectively. Thicker tapes start to show conversion already at an exposure time of 2 min, whereas the thinner tapes did not show any polymerisation after this exposure time. Thicker tapes required shorter exposure

times to reach the plateau-like region, 8 min for the top surface (76%), and 6 min for the bottom surface (35%).

In all cases, there was an initial rapid conversion degree increase until reaching the plateau-like region, at a particular exposure time, where polymerisation never reaches 100%. This can be related to the so called *gel point*, at which the mobility of the monomers starts to be inhibited by newly polymerized chains. Therefore, monomers are not free to move any longer and do not show the ability to further polymerize [14].

The wrinkling phenomenon could have affected the accuracy of the FTIR measurements and, therefore, the results of conversion degree calculations of the tapes cast using a 200 μm gap.

Regarding the suspension containing 40 vol% of AlN powder and 1 wt% of GTO, the conversion degrees are depicted in Figure 9. The highest conversion degree (approx. 82%) is obtained after 10 min of exposure for the top surface, when the plateau-like region starts. In the case of the bottom surface, the plateau-like region was not achieved as the conversion was still ongoing and a final value of 52% was calculated. Tapes containing GTO exhibit slightly higher conversion degree than those with BYK.

Processing reproducibility showed that tapes cast by using 100 μm and 200 μm gap and exposed for 2 min to the UV-light exhibited some polymerization only on the top surfaces (the bottom surfaces remained liquid). This was not the case before, especially for the thinner tapes. Figures 8 and 9 also depict the conversion degree calculation repetition values. The measurements repetition revealed that conversion degree varies for different sample batches. However, in all cases, conversion degree is characterised by the same trend, the longer exposure time the higher conversion degree. Additionally, con-

trary to the expectations, the top and bottom surfaces of the thicker tapes show higher conversion than thinner ones.

Lower conversion degrees on the bottom surfaces are mainly influenced by tape thickness. The polymerisation degree slows when “travelling” through the tape, as the photon concentration decreases in relation to the distance. Therefore, a lower conversion degree on the bottom of the tape is achieved [5]. Additionally, higher conversion degrees for the top surfaces of the tapes correspond to the fact that the UV-radiation source was placed above the tapes. Therefore, the photons had to penetrate through the tape thickness to reach the bottom of the tape. These results are in good agreement with the observations from casting experiments.

5. Conclusions

The study has shown that thin AlN tapes can be produced via UV-curable tape casting. The proposed powder pre-treatment was proven to be beneficial as it improves the rheological behaviour of the slurries. The effective concentrations of BYK and GTO dispersants were found to be 1 wt% and 0.5 wt%, respectively. BYK proved to be a more effective dispersing agent than GTO, as it resulted in significantly lower viscosity values. This, in turn, allowed to increase the solid contents up to 55 vol% of AlN powder. However, this concentrated slurry resulted in a shear thickening behaviour. The slurries containing GTO as the dispersing agent were found to be more suitable for tape casting, as they are characterized by a shear thinning behaviour, which is favourable for the tape casting process. Moreover, the viscosity values are within the favourable range for tape casting. Additionally, GTO as dispersant allowed casting tapes on the silicon-coated and uncoated side of the polyester carrier.

The quality of the cast tapes depends on the applied casting gap and the tapes possessing the highest quality were achieved at a gap of 100 μm . Nevertheless, it may be beneficial to improve the quality of thicker tapes by eliminating of the wrinkling phenomenon. The results of FTIR with the ATM component were sufficient in evaluating the conversion degrees of the green tapes. It was shown that the curing behaviour is similar for both dispersants and the top surfaces reach higher conversion degrees than the bottom surfaces. Comparing the tapes with different thicknesses revealed that thicker tapes are characterized by shorter exposure times to reach the plateau-like region and higher conversion degrees. Additionally, the conversion degree calculations showed that the process and FTIR measurements reproducibility are limited.

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Declarations of interest:

none.

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Fig 1 Molecular structure of a) 1,6-hexanediol diacrylate (HDDA); b) isopropylthioxanthone; c) N,N,N',N'-tetramethylethylenediamine, d) glycerol trioleate (GTO)

Fig 2 Scheme of the process

Fig 3 Evolution of AlN slurries viscosity as a function of dispersant concentration: a) BYK, b) GTO, at a shear rate of 25 s^{-1}

Fig 4 Particle size distribution of AlN with and without dispersing agents (in isopropanol)

Fig 5 Effect of the powder pre-treatment on viscosity: a) with BYK; b) with GTO

Fig 6 Effect of the solid load on the dispersions viscosity; a) slurries with BYK, b) slurries with GTO

Fig 7 Surface of the tapes cast with casting gap of: a) $100 \mu\text{m}$; b) $200 \mu\text{m}$

Fig 8 Conversion degree for the tapes with BYK cast with the casting gap of a) $100 \mu\text{m}$; b) $200 \mu\text{m}$

Fig 9 Conversion degree for the tapes with GTO cast with the casting gap of $100 \mu\text{m}$

Table 1 Particle size distribution statistics

Material	$d_{10} [\mu\text{m}]$	$d_{50} [\mu\text{m}]$	$d_{90} [\mu\text{m}]$
AlN	1.96	4.02	7.33
AlN + 1 wt% BYK	1.16	3.03	5.93
AlN + 0.5wt% GTO	1.28	3.08	6.00

Table 2 Green tapes' thickness

Dispersing agent	Exposure time [min]	Casting gap [μm]	Average thickness [μm]
BYK	6	100	73 ± 2
	8	100	72 ± 3
	6	200	215 ± 10
	8	200	218 ± 16
GTO	6	100	67 ± 7
	8	100	84 ± 5