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Ceramic suspension optimization using factorial design of experiments

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Abstract

The influence of organic phases (binder and two plasticizers) on ZnO slip viscosity and the properties of green tape were studied using design of experiments (DOE). Analysis of the results show no significant influence of the three components on slip viscosity and green tape density, but joint influence of two factors—binder polyvinyl butyral (PVB) and plasticizer polyethylene glycol (PEG)—is significant on green tape adhesion to the substrate tape of casting machine.

Keywords: Adhesion; Design of experiments; Suspensions; Tape casting; ZnO

1. Introduction

Ceramic tape casting and green sheet lamination technologies have been used in the production of multilayer chip varistors. The varistor composition is based on fine-grained high purity ZnO with addition of other oxide Bi_2O_3, MnO_2, Co_3O_4, Sb_2O_3, whereas a ceramic slurry for tape casting consists of these oxides, solvent (water or organic liquid), dispersant, binder and plasticizer.[1]

The role of dispersant, binder and plasticizers in tape casting processing is well studied and documented.[2,3] However, for each particular system the amount of all additives has to be carefully optimized with respect to slip viscosity and green tape properties.

To understand how organic additives influence on tape characteristics and to optimize the components in organic suspension a series of experiments should be used. Design of experiments (DOE) is one method that has proven to be very efficient in distinguishing major and minor contribution of factors on product studied.[4,5]

The purpose of design of experiments is to discover the critical variables, which influence the final product, their effects on variability and their respective settings.

The variables that we observe how influence on some characteristics of the product are referred as factors and the characteristics that we measure are referred to as response. The factors may be either quantitative, having numerical value or qualitative, having position value.

A design of experiments is the most economical and most accurate method for performing process optimization. A designed experiment will accelerate the learning of the interrelationships of the process variables, determine what variables are critical to the process and determine at what levels these variables are critical to the process. The design of experiments was used by authors[4,5,8] to investigate the influence of process parameters or different materials used in hybrid circuits production and Taguchi method[6,7] in processing of ceramic components. We have used, in this article, the design of experiments because this method is much more sensitive on two or three factor interaction, which we have observed how influence on green tape characteristics.

A system similar to those reported in literature[9,10] was used for processing of ZnO based suspension. The system is based on solvent toluene/isopropyl alcohol/methyl ethyl keton (MEK), oleic acid as a dispersant, binder polyvinyl butyral (PVB) and two plasticizers polyethylene glycol (PEG) and di (2-ethylhexyl) phthalate (DEHP).

The influence of three factors; binder and two plasticizers on the ZnO suspension viscosity and green sheet characteristics was analyzed using factorial design of

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experiments and from the results obtained the suspension composition was optimized. The difficulty in the optimization of the suspension composition was more expressive because ZnO grains were whisker shaped instead of spherical grains.

2. Experimental

Ceramic slurries were made from ZnO WSE1203 with mean particle diameter of 1.2 μm (grains like whiskers with aspect ratio 1:8) and organic components; solvent toluene/isopropyl alcohol/methylethyl ketone, oleic acid (Merck) as dispersant, polyvinylbutyral (PVB) from Monsanto as binder and the plasticizers polyethylene glycol (PEG) from Merck and di (2-ethylhexyl) phthalate (DEHP) from Riedel de Haen.

Each run of the suspensions was prepared in three steps. In the first one the powder is immersed in the solvent and the dispersant is mixed in. When a homogeneous mixture is obtained and particles are appropriately repelled, the plasticizers and binder are added as the second and third step. The order of addition of the components is critical; the dispersing agent must be added before the other organic compounds to prevent competitive adsorption onto the particle surface.[3]

In the first phase ZnO powder, solvent and dispersant were homogenized in a planetary mill for 2 h, after that in the second phase, binder and plasticizer PEG were added and homogenized for another 4 h. The order of addition of each component influences dispersion of particles in the slip and, thereby, slip viscosity. In the third phase, the plasticizer DEHP and remaining part of the solvent were added and the slip was homogenized during the night.

The optimal concentration of dispersant was determined from the minimum in slip viscosity vs. dispergant concentration curve and concentration of ZnO powder in the homogenized slip was 55 wt.% (16 vol%.).

Viscosity measurements were performed using Haake VT500 viscometer.

Preliminary experiments on the slip viscosity and adherence of green tape to a casting carrier film were conducted to determine the minimum and maximum concentrations of PVB, DEHP and PEG. The criterion for the minimum and maximum concentrations was a slip viscosity at about 1 Pa s, which from our experience is an adequate viscosity for tape casting with a suspension prepared from a ZnO powder of rounded 1 μm particles. The second criterion was the easy release of the green tape from the carrier substrate.

From an SEM analysis and granulometric measurements we determined that a new lot of ZnO grains were not round but like whiskers, and the grain surface was smaller than in the suspensions which we have studied before. In the first phase of the experiments, to determine the low and high margins for PVB, PEG and DEHP concentration, we prepared a suspension with concentrations of PVB up to 9 wt.% and as low as 6 wt.%, and the results of the suspension–viscosity measurements were out of tolerances. After tape casting, the adhesion of the tape to the casting machine was to great, it was impossible to release the tape from the machine. Using the same method we also selected the minimum and maximum concentration levels for PEG and DEHP. The low and high concentration levels of the PVB binder and the PEG and DEHP plasticizers were selected for a suspension viscosity at 0.8–1.3 Pa s, but the release of the cast tape from the machine was not very good. To optimize the composition of the organic suspension with whisker-like ZnO grains to obtain a good flexible tape we used Design Expert software for the suspension-preparation experiments with three factors (PVB, PEG, DEHP) and two levels of concentration in order to analyze their influence on the suspension and tape characteristics.

After having determined minimum and maximum concentration for binder and plasticizers (levels) a test matrix, usually an orthogonal array was generated and "runs" were conducted for the different combinations of input factors.

Depending on number of factors selected and levels for each factor, using the Design Expert software a 2^n number of experiments that must be investigated ($2=$ number of levels, $n=$ number of factors) was statistically ordered.[11] In our case with three factors (PVB, PEG and DEHP), and two levels (maximum and minimum of concentration of each factor), 8 run of experiments must be performed.

Table 1 presents 8 runs of experiments, statistically chosen with Design Expert software for three factors with two levels.

The viscosity measurement of slip given in Table 1, adhesion of green tape to tape carrier, and specific density of the green tapes were used as characteristics, which in the design of experiments are selected as responses.

Table 1
Eight runs selected with Design Expert with three factors and three responses

	Responses					
Run	Factor A: PVB (wt.%)	Factor B: PEG (wt.%)	Factor C: DEHP (wt.%)	Viscosity (Pa s)	Adhesion (mark)	Tape green density (g/cm^3) (mean value)
1	7.40	3.60	6.00	0.8	2	2.4
2	7.40	3.60	5.50	0.9	3	2.3
3	7.00	3.60	5.50	0.8	4	2.5
4	7.00	3.60	6.00	0.8	4	2.5
5	7.40	3.00	5.50	1.2	4	2.4
6	7.40	3.00	6.00	1.3	4	2.3
7	7.00	3.00	6.00	0.8	3	2.5
8	7.00	3.00	5.50	1	2	2.4

The viscosities of all suspensions prepared with ZnO powder with PVB, PEG and DEHP concentration given in Table 1 was measured immediately after suspension preparation. After tape casting on the polyester tape carrier of tape casting machine and drying, the tape was separated from the tape carrier. Adhesion was characterized by visual inspection, giving the mark 1 when it was impossible to release the tape from a tape carrier and 5 to the tape that is easily removed.

The tapes green density was measured on three samples from the same tape with volume and weight measurements and mean value of three measurements was calculated.

Each of the runs was repeated, in first series of runs fresh organic components were used and in second series six months old chemicals.

The results obtained with Design Expert analysis are similar for both series when viscosity, adhesion or green density are used as response. The results given in Table 1 are for the second series of run.

The influence of the main factors PVB, PEG and DEHP separately on three responses; viscosity, adhesion, and green density of tape were observed. The influence of two factors AB, AC and BC and three factors ABC together was also analyzed using the Design Expert software.

The results of the analysis were given in a half-normal probability graph as the percentage probability (y-axis) of the occurrence of effects given in the x-axis. The percentage of the probability P is given as the area under the curve of the percentage occurrence versus effects. If the P was plotted against x, a sigmoid cumulative normal curve was obtained and when the normal probability paper was used, with adjusted x and y-axis, the P versus x plot is shown as a straight line.

3. Results and discussion

The results of the analysis of the main effect of parameters A, B, C separately, two AB, AC or BC and three effects ABC together on the slip and green tape characteristics are given as normal probability plots, when the slip viscosity (Fig. 1), tape adhesion (Fig. 2) and green density (Fig. 3) of tapes were observed as responses.

The results given in Figs. 1–3 show the significant effect of the main factors A, B and C and combined factors AB, AC and BC and the three factors ABC together, on slip viscosity, adhesion and the green density of the tape.

As we can see from Fig. 1, all the effects are distributed according to the normal distribution (all measured effects fall on a straight line). There is no significant effect of the observed factors on the suspension viscosity for the concentration of binder and plasticizers given in Table 1.

The results given in Fig. 2 show that the influence of two factors together AB (binder PVB and plasticizer

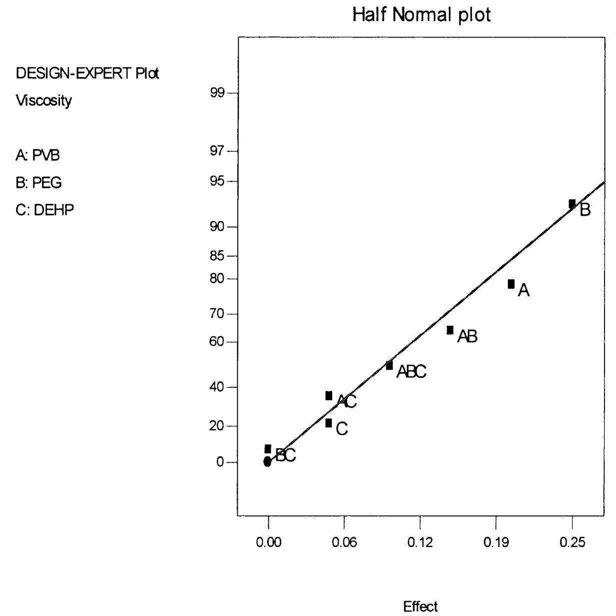

Fig. 1. Half-normal probability plot for slips with viscosity as the response.

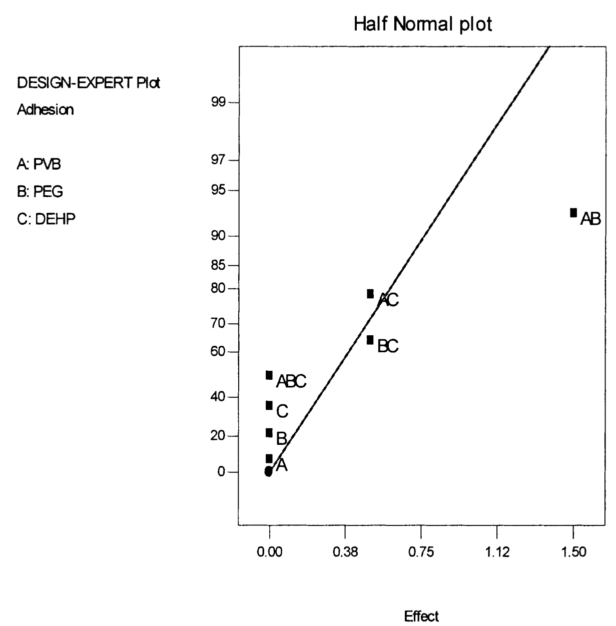

Fig. 2. Half-normal probability plot for slips with adhesion as the response.

PEG) are significant for tape adhesion to the Mylar tape of the machine. (all measured effects are fitted on a straight line except for the effect of two factors AB together).

The measured effects of the main factors A, B, C and the two factors together AC and AB shown in Fig. 2 is difficult to fit to a cumulative normal distribution presented as a straight line. In other words all the main effects A, B, C are 0 and the effect of the two factors AC, BC are about 0.45 and according to Design Expert the curve

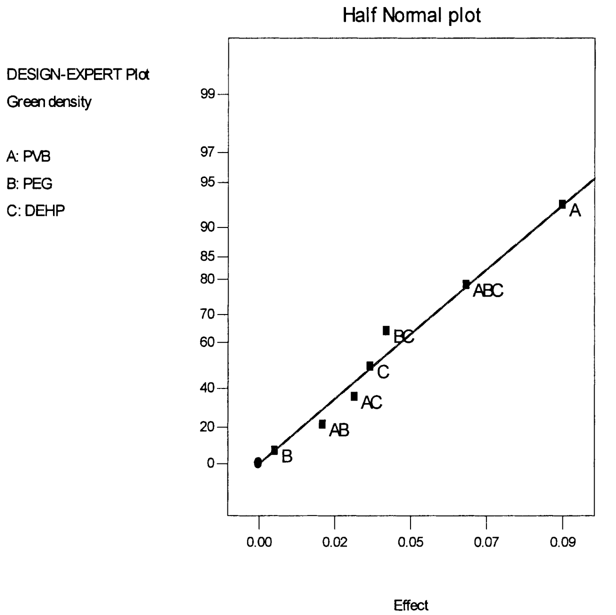

Fig. 3. Half-normal probability plot of slips with green density as the response.

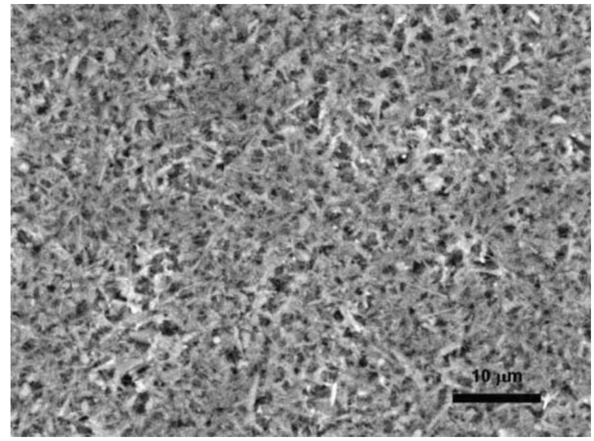

Fig. 4. SEM microstructure of top surface of green tape from "run" 2 (magnification bar is 10 µm).

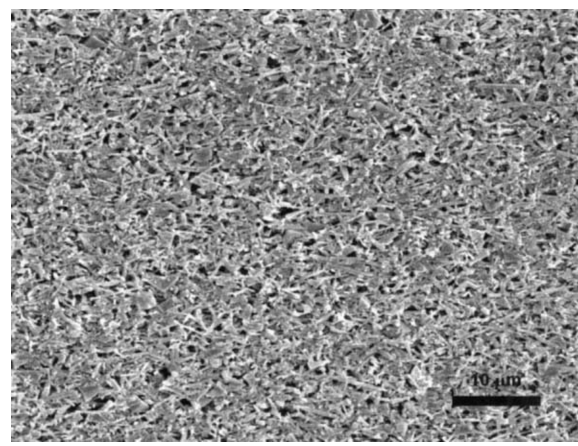

Fig. 5. SEM microstructure of top surface of green tape from "run" 7 (magnification bar is 10 µm).

must be fitted through the small effects. In this case it is not possible to have all the points of the small effects on the line. It is important for the conclusion that the influence of both factors together, AB has a significantly larger effect on the tape adhesion than the other factors (1.5), and that this point is the most distant from the fitted curve of the normal distribution.

The results given in Fig. 3 show that there is no significant effect of the factors on green tape density (all measured effects fall on a straight line).

From our results using Design Expert analysis, given in Table 1 we can see that the easiest separation of ceramic tape from tape carrier is obtained when slip was prepared with 7.0 wt.% of PVB and 3.6 wt.% of PEG, or 7.4 wt.% of PVB and 3.0 wt.% of PEG (both factors influence!). We can only speculate that with this concentration of organic components in the slip, the best plasticizers/binder ratio is obtained so that cohesion between particles after drying in the tape is the highest.

The green density varies from 2.3 to 2.5 g/cm^3, although there is no systematic influence of three factors on density measured. In the selected range of minimum and maximum concentrations of binder and plasticizers the influence on green tape density is inside the measurement error.

The SEM analysis of upper surface of green tape casted with slip with PVB, PEG and PHE concentration given in Table 1 as run 2 are given in Fig. 4 and as run 7 are given in Fig. 5. The results are in good agreement with the density, showing porous tape for run 2 and denser one for run 7.

In the literature[12–14] was reported about influence of plasticizer/binder ratio on easy separation from tape carrier and on mechanical properties of sintered tape.

The authors[12] reported that Al_2O_3 green tape obtained by casting organic suspension show a reaction between the ceramic sheet and the tape carrier due to aggressive binders.

The study of authors[13,14] show that the plasticizer contents corresponding to an organic volume near to the maximum filling of the tape porosity give a correct compromise between mechanical strength and elongation of the tape. On the other hand, increase of binder content for a fixed plasticizer amount, induced the increase of the rupture strength of the tape up to a certain amount of binder. For binder concentration corresponding to organic volumes higher than the porous volume, an important diminution of this characteristic appeared.

In our preliminary experiments we have excluded the influence of tape carrier material on green tape adhesion, for tape casting we have used polyester material with silicon protection and we have prepared the same organic suspension with ZnO spherical grains with easy separation from this tape carrier.

To further optimize the adhesion of green tape to tape carrier, one can optimize the ratio of PVB and PEG according to results given in Table 1, preparing slip with low PVB concentration level and higher PEG concentration than in presented experiments. Another solution is to prepare suspension with higher PVB concentration level and lower PEG concentration than in our experiments.

4. Conclusion

- The results of Design Expert analysis on ZnO slip viscosity and green tape characteristics, that there is no significant effect of binder PVB and plasticizers PEG and DEHP, or two or three factors effect on slip viscosity or green tape density. For selected concentrations of PVB, PEG and DEHP the influence on slip viscosity and green tape density is inside the measured error.
- The joint influence of two factors: binder PVB and plasticizer PEG on a tape adhesion were found. The better release of tape from tape carrier of casting machine was obtained with both 7.0 wt.% of PVB and 3.6 wt.% of PEG, or 7.4 wt.% of PVB and 3.0 wt.% of PEG in the slip composition.
- The SEM analysis of top surface of green tape with high value of measured green density show also microstructure with dense packed particles.
- To obtain very easy separation of green tape from the tape carrier is necessary to optimize PEG concentration using minimum and maximum value of binder.

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