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New low-voltage varistor composites

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New varistor-type polymer composites for low-voltage application have been developed. The filler is made of commercially available doped ZnO-varistor powder. The polycrystalline filler particles act as varistors due to their typical grain-boundary structure. The presented varistor composite materials show very low values for the breakdown field strength down to 200 V mm^{-1}, as compared with already existing varistor-type composites, and fairly high α-values in the range of 10.

1. Introduction

In the past, interest has grown in multifunctional materials. One class of such new materials is composites consisting of a polymeric matrix and filler particles with tailored properties. Such a material combines the flexibility, cheapness and easy processability of polymeric materials with desired additional functionality, such as, for example, high conductivity and polarizability for screening, non-linear dielectric properties, toughness, piezoactivity for mechanical positioning and pressure sensing [1–6].

Carbon black or metal-filled polymers show a positive temperature coefficient (PTC) of electrical resistivity [1]. Therefore, they are widely used as self-limiting heating tapes and circuit-protecting devices [2, 7].

Even more challenging is to go one step further and use fillers, which possess (for more functionality) an additional electrical non-linearity. Such materials with at least two functionalities, for example a varistor-like behaviour and the PTC effect, have been described before [3]. These already introduced varistor composites show a fairly high breakdown field, E_B, of about 500 V mm^{-1} and values of the non-linearity, α, of electrical conductivity between 5 and 10.

In the present paper, a newly developed varistor-type polymer composite is described which shows a low breakdown field strength and a fairly high non-linearity of electrical conductivity. In order to characterize this material, temperature-dependent I–V measurements have been performed on the composite material with a polyethylene matrix containing 20–50 vol% ceramic varistor filler.

2. Experimental procedure

The varistor filler has been prepared by sintering of a spray-dried powder of a low-voltage varistor material (Type D70, Merck, Germany). Fig. 1 shows a scanning electron micrograph of spray-dried raw varistor powder (not sintered). A typical varistor particle which is produced by sintering of the loose spray-dried powder with its structure is seen in Fig. 2a. It has a nearly spherical shape, can be hollow or compact, and shows certain domains separated by grain boundaries.

The size, number of grain boundaries per particle, and thus the electrical properties of the filler material can be adjusted by controlling the sintering conditions and the doping of the varistor material [8]. A more homogeneous particle distribution has been achieved by sieving the varistor material before and after sintering to sizes between 60 and 160 μm. In order to check the sintering conditions, varistor tablets pressed at a pressure of 100 MPa have been sintered together with loose varistor particles. Fig. 3 shows a scanning electron micrograph of such a varistor ceramic.

For the polymer matrix, a high-density polyethylene (Lupolen 5231HX from BASF, $T_m = 134\,^{\circ}\mathrm{C}$) has been chosen. The compounding of the varistor material (filler content 20–50 vol%) together with the polyethylene, was performed within 10 min by utilizing a Brabender Plasticorder at a temperature of 190 °C. Afterwards the composite was pressed at 145 °C and 11 MPa to produce 2 mm thick plates.

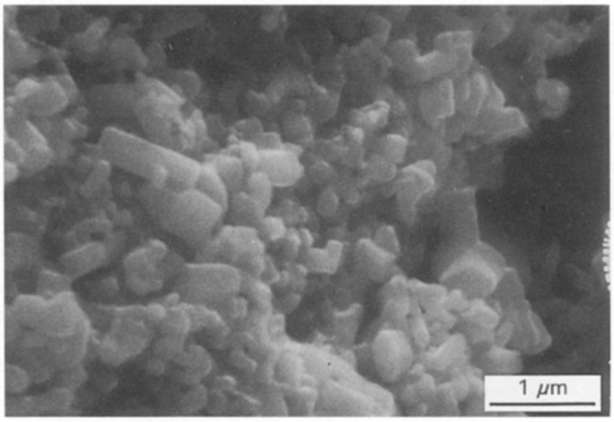

Figure 1 Scanning electron micrograph of spray-dried varistor powder as delivered from Merck Company, Germany.

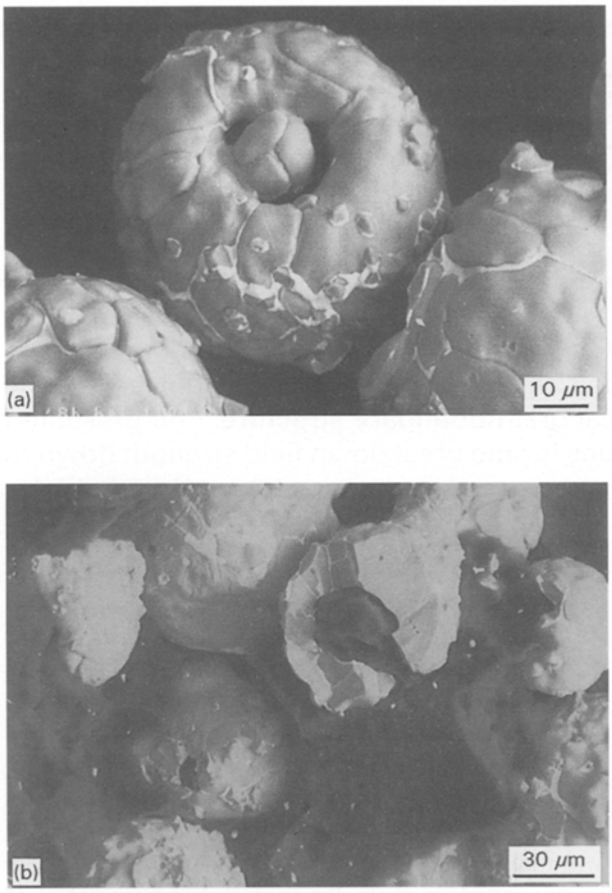

Figure 2 Scanning electron micrographs of (a) a varistor filler particle, (b) a varistor composite with 50 vol% filler content.

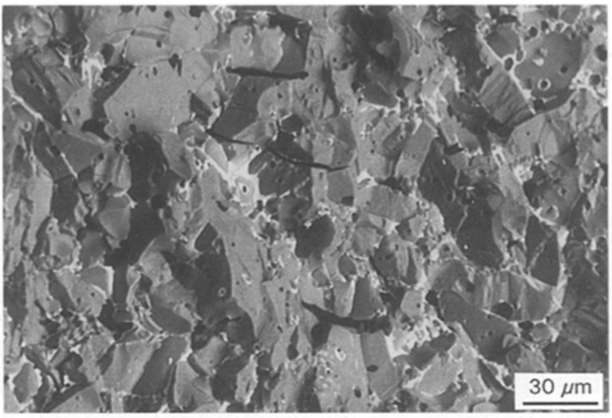

Figure 3 Scanning electron micrograph of a varistor ceramic sintered at 1100 °C for 8 h pressed to a pellet at a pressure of 100 MPa.

3. Results and discussion

In Fig. 2b, a scanning electron micrograph is shown for a 50 vol% varistor composite. For the electrical contacts, either thin gold layers were deposited by evaporation, or colloidal graphite (GRAPHIT 33, Kontakt Chemie, Rastatt, Germany) was sprayed on to the composite surface.

Fig. 4 compares the j–E characteristics at $T = 25$ °C of a ceramic varistor tablet, a sample made from loose sintered varistor particles only, and of a varistor composite with 50 vol% filler content. The ohmic $j(E)$ behaviour at low voltage changes to a highly non-linear relationship for higher electrical fields ($E > E_B$: breakdown field strength is defined at $j = 1\ \mu\text{A cm}^{-2}$). The relation can be approximated by Equation 1 with α as the non-linearity coefficient, j, the current density and E, the electrical field strength. A detailed summary of numerical results of all investigated materials is given in Table I

$$j \sim E^{\alpha} \qquad (1)$$

The j–E characteristics of loose sintered varistor material show a lower α, a higher E_B and an increased leakage current compared with the varistor ceramic.

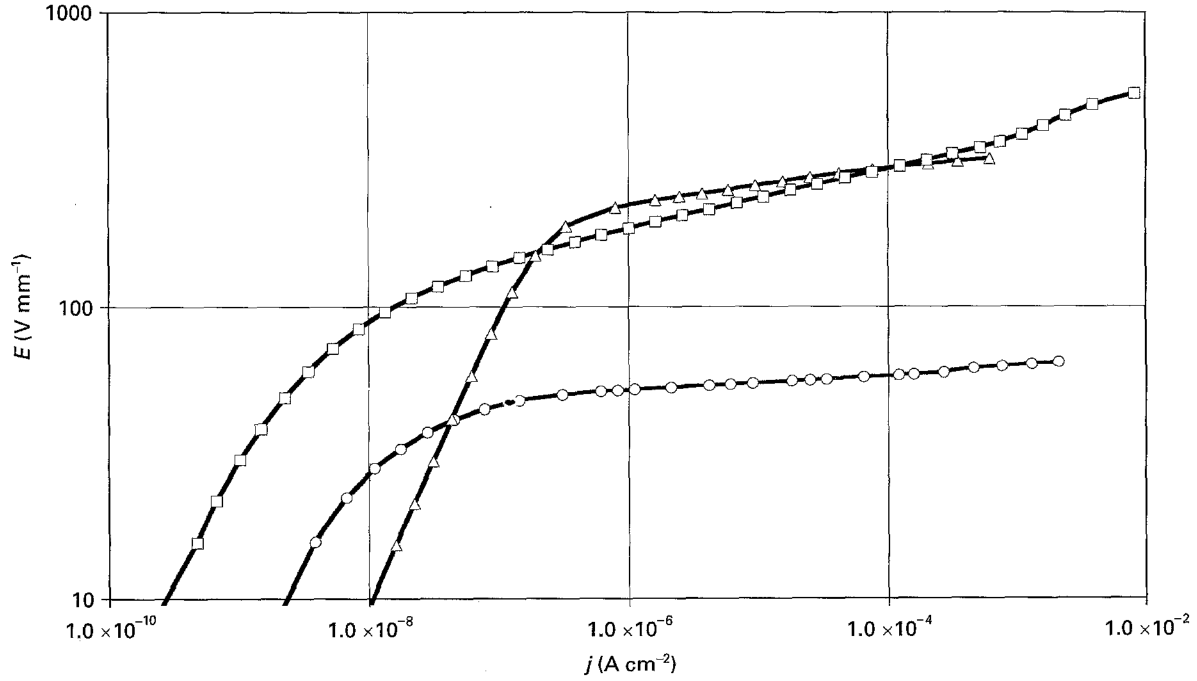

Figure 4 j–E characteristics at $T = 25$ °C of (○) a ceramic varistor tablet, (△) loose sintered varistor particles and (□) a varistor composite with 50 vol% varistor filler.

TABLE I The breakdown field, E_B, the non-linearity, α, and the specific resistivity, ρ, at low electrical field strength of the investigated materials

Material	E_B (V mm^{-1})^a	α at E_B	ρ (Ω cm) at 0.1 E_B
ceramic varistor (T = 25 °C)	60	35	5.0×10^{10}
sintered varistor particles (T = 25 °C)	200	17	1.0×10^{10}
PE + 20% varistor (T = 25 °C)	600–800	9	1.0×10^{14}
PE + 20% varistor (T = 135 °C)	–	≈ 1	1.0×10^{14}
PE + 35% varistor (T = 25 °C)	200	9	7.0×10^{11}
PE + 35% varistor (T = 120 °C)	220	6	3.0×10^{10}
PE + 35% varistor (T = 135 °C)	350	17	8.0×10^{13}
PE + 45% varistor (T = 25 °C)	180	9	4.5×10^{10}
PE + 50% varistor (T = 25 °C)	190	9	4.0×10^{11}
PE + 50% varistor (T = 80 °C)	120	8	3.0×10^{9}
PE + 50% varistor (T = 100 °C)	120	7	2.5×10^{9}
PE + 50% varistor (T = 135 °C)	380	6.4	5.0×10^{11}

^{a} E_B is taken at a current density of 1 μA cm^{-2}.

The sintering of the loose varistor particles creates smaller grains compared to the varistor ceramic, as can be seen from the scanning electron micrographs in Figs 1 and 2a. This change in internal structure can be associated with a higher breakdown field compared to the varistor ceramic. The enhanced leakage current of the loose sintered material may be caused by water contamination located at the grain boundaries. It can also be due to a creepage current of the test apparatus, because the powder could not be measured using a guard ring shielding.

A comparison of the results of the composite and the loose sintered varistor powder shows, surprisingly, nearly equal E_B, but a smaller α for the former. The coincidence of E_B is an indication that no additional polymer layers exist between the varistor particles, even at a filling level of 50 vol%. The different α values can be explained by different contact pressure between the particles.

Fig. 5 shows the j–E characteristics of varistor composites for variable filler content at T = 25 °C. Depending on the filler content, E_B varies between 200 and 800 V mm^{-1} as listed in Table I. All composites show similar non-linearity with $\alpha \approx 9$ according to Equation 1. The varistor composite with only 20 vol% filler content has a much lower overall conductivity and increased E_B because the filler fraction is below the percolation threshold. For a higher amount of filling, the j–E characteristics become very similar. The E_B of about 200 V mm^{-1} of the 35–50 vol% filled composites is remarkably low compared to recently published data of varistor composites [3], and is even very close to E_B values of commercially available pure varistor ceramic material [9, 10].

At the high-field end of the j–E graphs, a slight up-turn is visible. This increased resistance may be caused by the separation of the varistor particles in the composite due to the thermal expansion of the polyethylene, driven by the internally generated heat at the varistor particle contact points. To demonstrate this limiting effect, j–E characteristics of a varistor composite with 50 vol% filler content are shown in Fig. 6 for different temperatures. The increased low-field conductivity at T = 80 and 100 °C, respectively, of two orders of magnitude is largely due to the NTC effect of the still touching semiconducting varistor

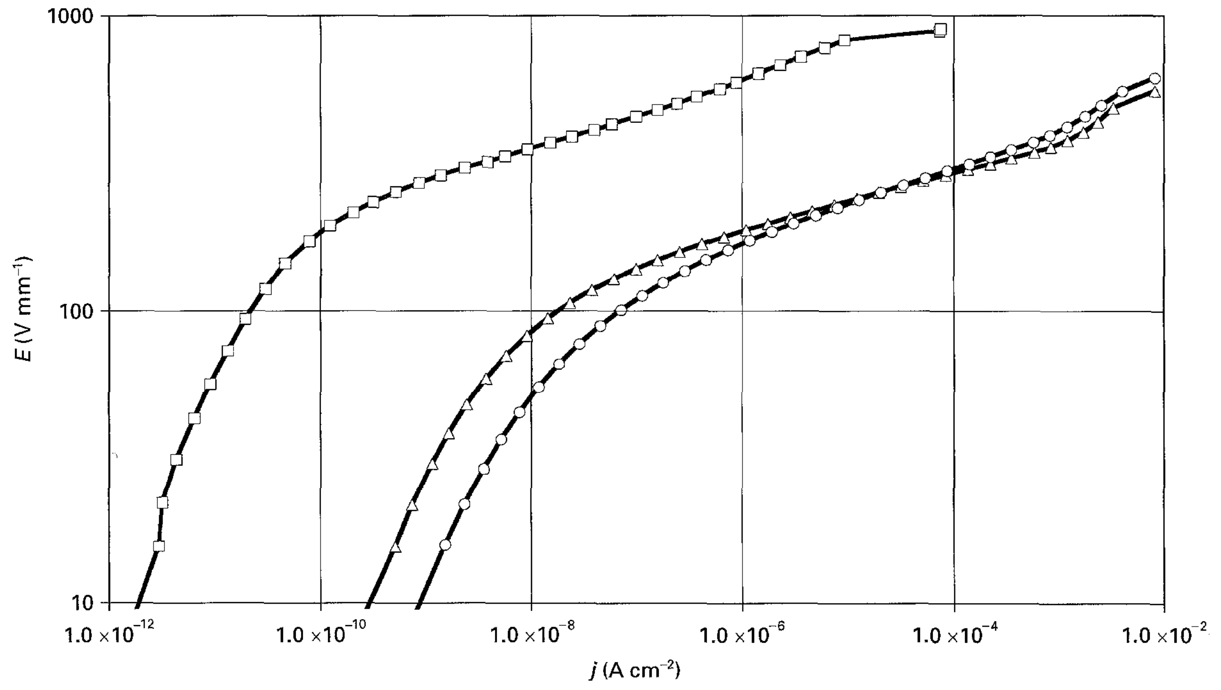

Figure 5 j–E characteristics at T = 25 °C of varistor composites with (□) 20, (△) 35 and (○) 45 vol% varistor filler.

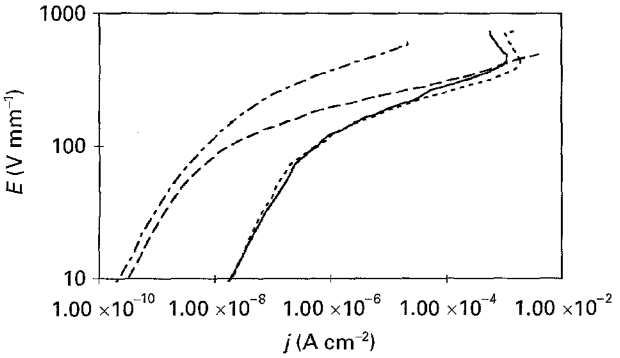

Figure 6 The j–E characteristics of a varistor composite with 50 vol% filler content at different ambient temperatures: (— —) 25 °C, (- - -) 80 °C, (———) 100 °C and (— - —) 135 °C. For the measurement which is taken at $T = 25°$ C, no current reduction is seen, whereas for elevated temperatures, a limitation and even a strong reduction of the current density is visible with increasing applied electrical field strength.

particles. At higher fields and current densities, current restriction is seen, very pronounced at the upper end with a power loss of about 3.5 W cm^{-3} at $T = 100$ °C and even 7 W cm^{-3} at $T = 80$ °C, respectively. This generated power heats up the material remarkably. Of course, at higher ambient temperature, less current density is necessary in order to get the composite into the limiting state. A further increase of the ambient temperature to $T = 135$ °C leads to a strong overall current reduction. This is very visible from the shift to lower current densities of the entire $j(E)$ characteristic taken at 135 °C (Fig. 6). Both the behaviour at $T = 80$ or 100 °C (which is still below T_m of the polyethylene) and at $T = 135$ °C (which is at T_m of the polyethylene) are driven by the thermal expansion of the polymer.

4. Conclusion

New varistor-type polymer composites for low-voltage applications have been developed. The material shows very low breakdown field strengths below 200 Vmm^{-1} with a non-linearity of $\alpha \approx 10$. Thus this composite material seems to be a promising candidate for new low-voltage applications, e.g. for integrated transient suppression or field grading in bushings and cable termination. It combines the advantages of polymer processing with the strong non-linear conductivity of ceramic varistor material. The j–E characteristics show current limitation for $E > E_B$, in particular at elevated ambient temperature, which is associated with the thermal expansion of the polymer matrix and the separation of the percolating varistor particles.

Acknowledgements

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