Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Ceramics International 34 (2008) 131–136
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

A varistor–polymer composite with nonlinear electrical-thermal switching properties

Chiung-Chih Lin [a], Woei-Shyong Lee [b,*], Chang-Chun Sun [c], Wen-Hwa Whu [a]

[a] *Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University, Ta-Hsi, Taoyuan, 33509 Taiwan, ROC*
[b] *Mackay Medicine, Nursing and Management College, Taipei, 112 Taiwan, ROC*
[c] *Department of Electronic Engineering, Lee-Ming Institute of Technology, Tai-Shan, Taipei, 243 Taiwan, ROC*

Received 10 March 2006; received in revised form 4 August 2006; accepted 22 September 2006
Available online 22 November 2006

Abstract

We studied the dependence of the *E–J* characteristics on the sintering conditions in varistor fillers, the filler content in the polymer matrix and for different polymers and suggest a possible nonlinear electrical-thermal switching mechanism. The nonlinear coefficient and breakdown field of a sample with 100 vol.% varistor fillers sintered at 950 °C for 5 h were 12.24 and 135 V/mm, separately. A decrease in the amount of filler content in polymeric matrix or using a fortified polymer improved the electrical properties by increasing the breakdown field to the 263–964 V/mm range and decreasing the leakage current density in the 1.06×10^{-5} to 1.13×10^{-10} A/cm^2 range. This varistor–polymer composite can exhibit two nonlinearities in electrical conductivity. In the conducting state above the varistor filler breakdown, the polymer matrix reduces the conductivity, if a critical temperature is reached. Thereby the over voltage is limited by the fillers (i.e. varistor effect) and the over current is limited by the polymer matrix (i.e. positive temperature coefficient effect).

Keywords: B. Composite; Nonlinear electrical-thermal switching

1. Introduction

Many researches have been devoted to the electrical characteristics of metal–polymer composites [1–4]. Carbon black and metal powders, e.g. Al, Ag and Ni, have been used as fillers. However, the composite properties of electrically nonlinear particles dispersed in an insulating matrix have received little attention in the literatures [5–8]. A conspicuous reason for this study is the widely used applications for these composites in current-limiting resetable switches, controlling electrical fields and limiting dangerous over voltages. Doped zinc oxide varistor materials are the most common choice today for lightening impulse protection or other forms of electrical discharges. When varistor powders are used as fillers in an insulating polymer matrix, they can impart strong electrical nonlinearity directly to the composite. In general, at critical filler content the varistor fillers are well separated and the composite is insulating. The filler resistance is only slightly higher than that of the polymer. The nonlinear conductivity is initially dominated by the effective grain boundaries of these fillers. The conductivity increases rapidly as more percolation paths form until the breakdown field is reached. Considerable polymer expansion then occurs, leading to rapidly increasing resistance when the temperature increases towards the melting point. The common understanding of the nonlinear electrical-thermal switching and device operation is based on the coupling of nonlinear electricity, Joule heating and positive thermal resistance coefficient (PTRC) in the composites [9]. This allows us to combine the nonlinear electrical behavior needed with polymer processing properties to control a high field or electrostatic discharge protection for electronics.

2. Experimental

In this study, we combined sol–gel and standard ceramic processing to produce fine varistor powders as functional fillers. The first steps in producing functional fillers (varistor powders) are similar to the processes developed by Duran et al. [10]. The

---

* Corresponding author. Tel.: +886 2 2858 4180; fax: +886 2 2858 4183.
E-mail address: wslee@mkc.edu.tw (W.-S. Lee).

0272-8842/$32.00 © 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.09.018

precursor powders obtained from spray drying are composed of zinc oxide, boundary formers ($Bi_2O_3 + Sb_2O_3$) and conductivity enhancers (CoO + MnO) [11–15]. The agglomerate can have diameters of 0.1–1 μm. The precursor powers are sintered between 850 and 1100 °C for 5 h into varistor powders. The varistor powder morphology with a number of grain boundaries was observed by scanning electron microscopy (SEM). The number of grain boundaries and the electrical properties of each filer particle can be adjusted over a large range by adjusting the composition and sintering conditions. The shape of the filler is almost spherical. The varistor agglomerates were selected as varistor fillers by sieving with the filler particle sizes between 0.1 and 1 μm. These fillers can be compact or dispersed depending on the processing conditions.

Thermoset and thermoplastic polymers have been used as an insulating matrix. We used epoxy (Echo chemical Co. Ltd.), which has a low viscosity (2250 cps/25 °C) at room temperature. The varistor powder was mixed with epoxy and degassed using a three roll miller (EXAKT 120E-450). The composite composed of 45.01 vol.% filler was cured at 110 °C for 10 min. Linear low density polyethylene (melting temperature $T_m = 122$ °C, melt flow index = 2 g/10 min), low density polyethylene (melting temperature $T_m = 111$ °C, melt flow index = 0.923 g/10 min) and high density polyethylene (melting temperature $T_m = 131$ °C, melt flow index = 0.04 g/10 min) were compounded in a double-cone mixer (Chin Yi machinery Co. Ltd.) for 30–60 min separately. The filler content varied from 14.1 to 100 vol.%. The sample with 100 vol.% filler content (i.e. varistor composed of varistor agglomerates) was pressed into a disc of 10 mm in diameter and 1 mm in thickness at a pressure of 80 MPa and other samples with 14.1–45.01 vol.% were hot pressed into discs of 10 mm in diameter and 1–1.5 mm in thickness at a pressure of 30 MPa. Each sample was then coated with silver paint on both sides for electrical contacts in the current–voltage (*I*–*V*) measurement. The *I*–*V* characteristics of varistor agglomerates were estimated by measuring the sample with 100 vol.% filler content. And the electrical properties of all samples were measured by an electrometer (Keithley 237). The breakdown field (E_B) was measured at a current density of 1 mA/cm^2. The nonlinear coefficient (α) of the breakdown field was estimated for the current density ranges from 0.5 to 5 mA/cm^2 using the equation $J = KE^{\alpha}$, where K is a material constant. The leakage current density was defined as the current density at $0.8E_B$. In situ infrared (IR) thermal imaging (SC2000, FLIR) connected with electrometer (Keithley 237), as shown in Fig. 1, was used to monitor the macroscopic electrical-thermal switching of the varistor–polymer composite.

3. Results and discussion

The typical morphology of the functional filler sintered at 950 °C for 5 h is shown in Fig. 2. The figure shows the zinc oxide grains. The lighter areas are the grain boundaries that produce the varistor effects.

Fig. 3 shows a comparison of the current density (*J*)–electric field (*E*) characteristic of a varistor composed of varistor powders and a ceramic varistor material. The ceramic was sintered under the same conditions as the varistor powders. In the case of a varistor composed of varistor powders, the leakage current density increases and the breakdown field decreases

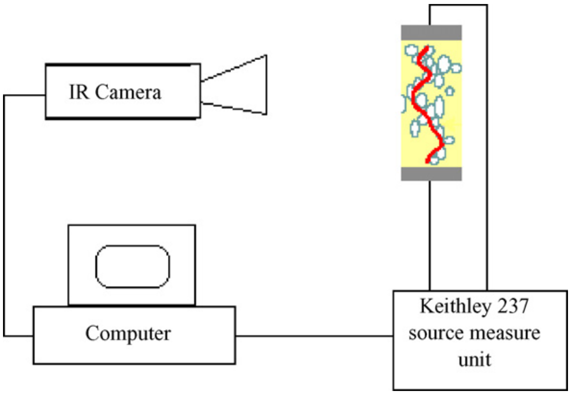

Fig. 1. Schematic diagram of the in situ IR imaging system and the *I*–*V* measurement system.

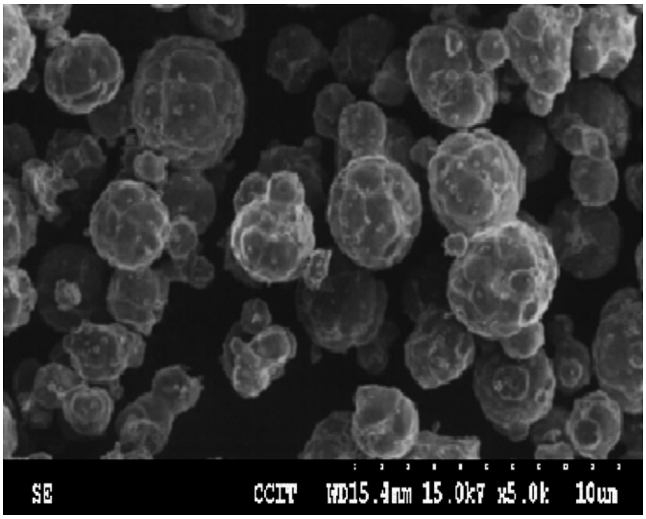

Fig. 2. ZnO-based varistor filler sintered at 950 °C for 5 h.

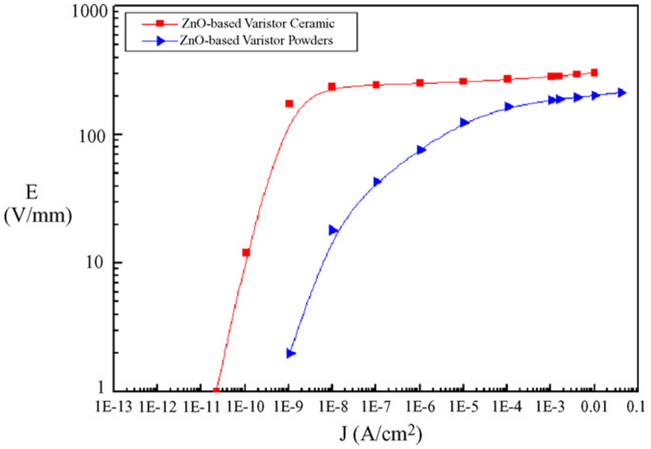

Fig. 3. *J*(*E*) characteristics of ZnO varistor and varistor filler sintered at 950 °C for 5 h.

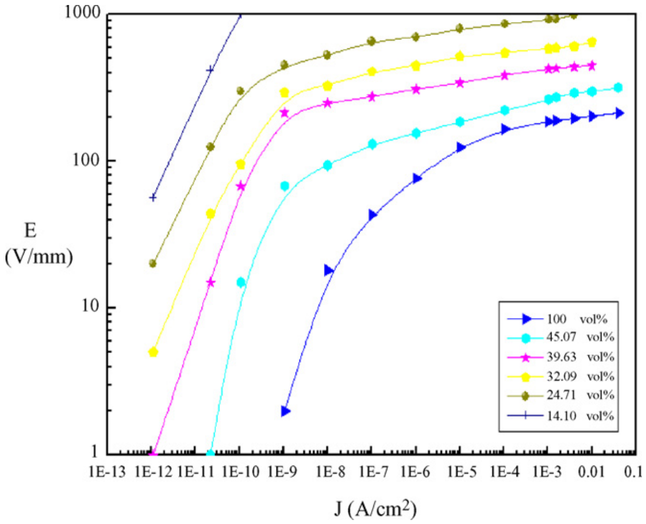

Fig. 4. $J(E)$ characteristics of LLDPE polymer composite varistors under different filler contents. The filler sintering condition was 950 °C, 5 h.

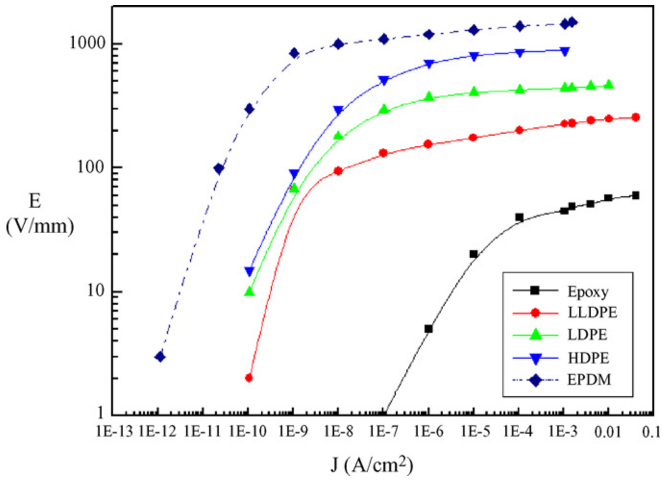

Fig. 5. $J(E)$ characteristics of polymer composite varistors each under a different polymer matrix, LLDPE, LDPE, HPDE and EPDM, respectively. The filler content was 45.07 vol.% and sintered at 950 °C, 5 h. The dashed line is obtained from Ref. [17].

compared to the ceramic varistor. The breakdown field decrease is attributed to the lower density. The inhomogeneous contact explains the shift in the leakage current density. Although the nonlinear property of a varistor composed of varistor powders seems not good enough, these varistor powders exhibit a confirmed varistor effect. Consequently, the desired characteristics are sensitive to the powder preparation conditions.

Because polymer material has great potential for future applications, LLDPE was used as an insulating matrix material in the following experiments. We varied the amount of the functional filler in these experiments. Fig. 4 shows the breakdown field–current density (E–J) characteristic dependence on the filler fraction. Increasing filler content leakage current density leads to decrease breakdown field. This is due to the lower contact resistivity of the fillers in LLDPE. The changes in breakdown fields and nonlinearity coefficients are listed in Table 1. The other thing that we have seen is an effect from the polymer matrix. In the past, one always assumed that the polymer matrix was just a binder that would not have any other effects, however, there are some specific effects. We have looked at epoxy, low density polyethylene, high density polyethylene, EPDM, etc. from many experiments and found a difference in the material response as a function of the polymer materials as shown in Fig. 5 [16]. For example, the breakdown field in the same filler fraction is higher than that in a comparable epoxy sample. This is due to the higher contact resistivity of the fillers in LDPE compared to epoxy. The epoxy matrix shrinks during curing and thus brings the fillers into more intimate contact than the LDPE matrix. It can be expected that an even stronger reduction in the current could be realized if the insulating polymer matrix is fortified, e.g. by cross-linking or adding another insulating polymer with a higher melting point. The changes between these polymers are just as considerable as those achieved by changing the sintering conditions. By combining filler preparation and percolation effects, composites with a wide range of electrical properties can be produced [17].

Table 1
The electrical characteristics of polymer composite varistors with different filler contents

Weight ratio	Volume content (vol.%)	Nonlinear coefficient (α)	Breakdown field, E_B (V/mm)	Leakage current density (A/cm^2)
1:1	14.10	[a]	[a]	[a]
2:1	24.71	32	924	1.13E−10
3:1	32.99	31	589	2.53E−09
4:1	39.63	22	427	1.72E−08
5:1	45.01	18	263	1.06E−05

The densities of filler and LLDPE are 5.606 and 0.92 g/cm^3, separately.

[a] The value cannot be measured by the voltage-limit (1 kV) of Keithley 237 I–V electrometer.

Polyethylene is known to have strong thermal expansion close to the melting point which can be used to produce PTCR effects. In combination with varistor fillers the two effects can be combined to form a nonlinear electrical-thermal switching

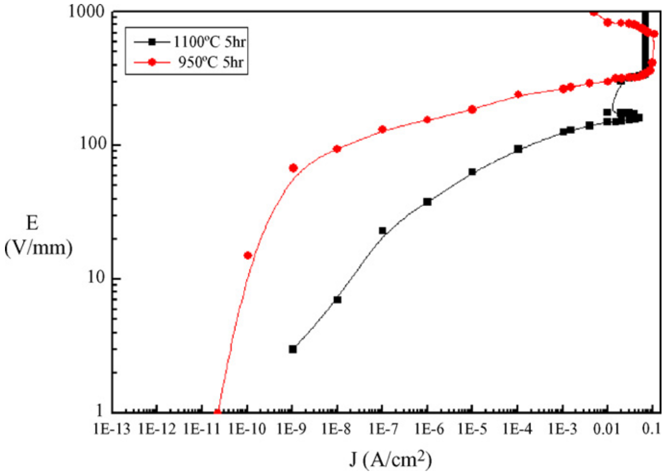

Fig. 6. $J(E)$ characteristics of LDPE polymer composite varistors composed of 45.01 vol.% fillers. The filler sintering conditions were 950 and 1100 °C, 5 h.

device. The basic manifestation of the macroscopic electrical-thermal effect is that applying a voltage beyond some threshold value yields a large increase in the macroscopic resistance. This effect is exhibited in Fig. 6 by the electric field–current density characteristics of a self-protecting device made of a varistor–LDPE composite. These curves are achieved by changing the sintering conditions in Fig. 6. Fig. 7 shows the electrical-thermal dependence of this composite for an example using 45.01 vol.% varistor filler in an epoxy matrix. The high-current paths are visualized by the increase in temperature caused by Joule heating. In the nonlinear regime (B), the current increases exponentially and is then limited to a certain value in the upturn regime (C). The nonlinear phenomenon can be explained by the semiconducting behavior of the varistor filler. As expected from semiconductor physics, resistivity depends exponentially on temperature. Starting around 100 °C the epoxy matrix expands strongly due to the melting of crystalline areas. This leads to a separation of the varistor fillers and then increasing resistivity. This is known as the electrical-thermal switching effect. Thus the nonlinear electricity determined by the quality of effective grain boundaries of the varistor fillers dominate the overall behavior only as long as the micro-contact resistances are smaller than the filler resistance. The resistance effects are always accompanied by losses in the form of heat. The PTCR effects can be used to limit the dissipated energy because the melting polymer does not allow a further increase in the electrical field. Little information is available on microscopic filler contacts in composites, in particular about the possible

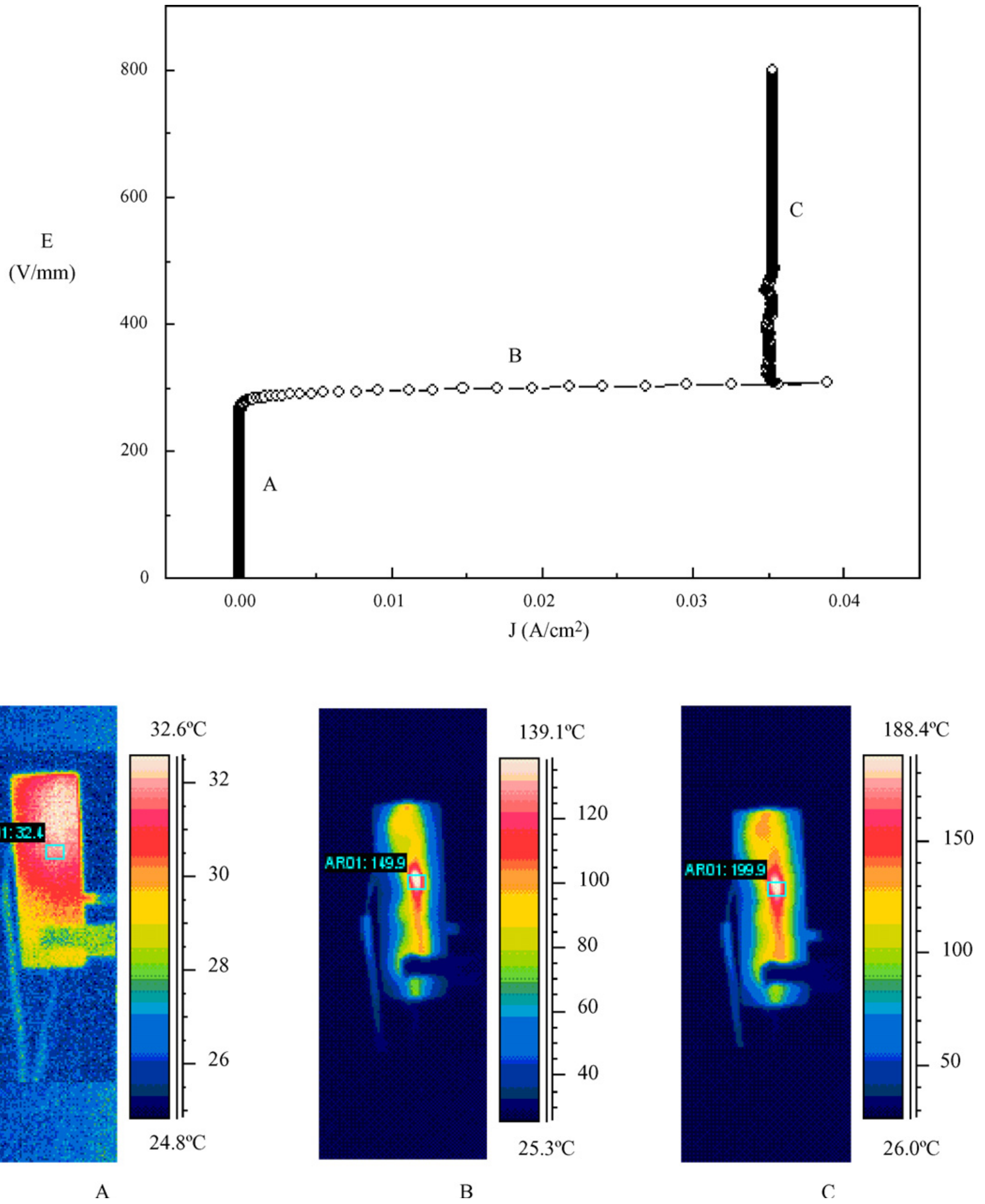

Fig. 7. Composite nonlinear electrical-thermal dependence of the epoxy polymer composite varistors composed of 45.01 vol.% fillers. The fillers were sintered at 1100 °C for 5 h and the composite was cured at 120 °C for 10 min. A is prebreakdown region with very low current; B is nonlinear region with high-current paths which can be visualized by the increase in temperature caused by Joule heating; C is upturn region with limited current which is controlled by the melting point of epoxy.

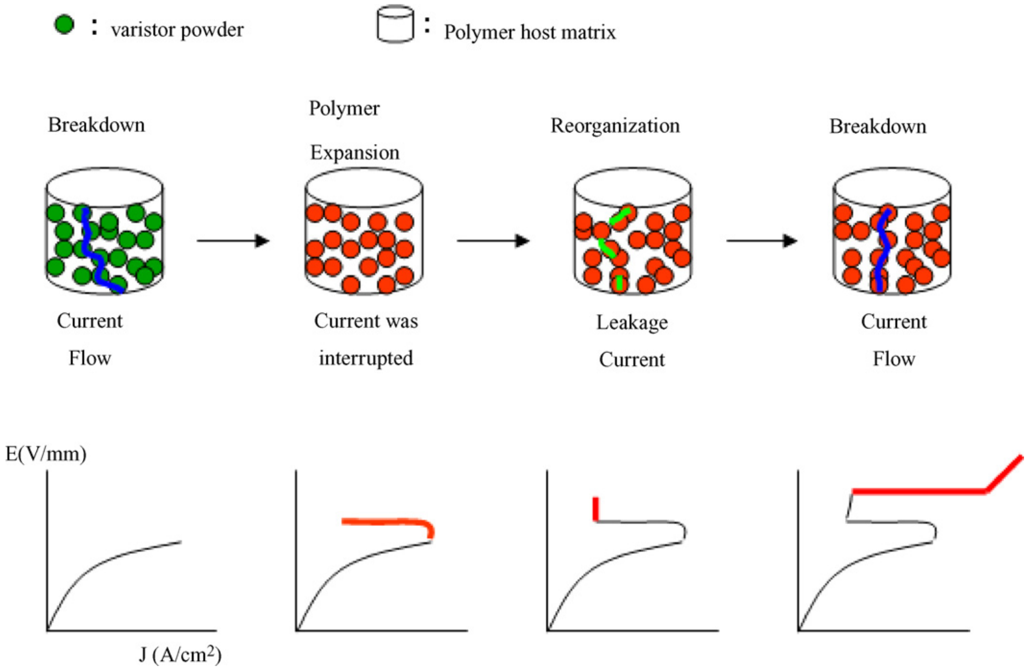

Fig. 8. The evolution of $J(E)$ characteristics change with the varistor–polymer composite interior structures.

presence of very thin insulating polymeric layers penetrating the contact areas. If these interfacial layers are present with a thickness large enough to suppress tunneling, they add a high contact resistance and strongly affect the composite characteristics.

The results described above are accounted for by the competition between the melting and tunneling contacts. When the applied field is larger than the breakdown field and melting does not occur, there is a relatively wide distribution of current paths, i.e. the nonlinear effect. On the other hand, when the applied field is further increased and local melting occurs, the melting eliminates a portion of the connections and creates new tunneling paths at the same time. Thus, we can use Fig. 6 and previous literatures [5,6] to suggest that the nonlinear electrical-thermal switching mechanism as illustrated in Fig. 8.

By careful optimization of the varistor filler properties, the micro-contacts and processing, a varistor–polymer composite with highly nonlinear electrical-thermal switching properties can be realized. This new approach could open new possibilities in over voltage protection and electric field control. Such a composite is needed at the edge of the semiconducting cable screen near the cable end, where high electrical fields must be limited to avoid flashovers or damage to the cable.

4. Conclusions

We have shown that polymer composites containing varistor fillers exhibit nonlinear electrical-thermal switching properties. Above the breakdown field, the nonlinear effect dominates and then melting takes place. Using the PTCR and varistor effects in one material, the composite becomes multifunctional. They can act as varistors due to the nonlinear electricity of the effective grain boundaries inside each individual filler, and as PTCR due to micro-contact separation from the insulating polymer matrix expansion. This composite can be tuned to specific applications [8] by adjusting the matrix, the formulation and the sintering conditions for the varistor fillers.

References

[1] V.G. Shevchenko, A.T. Ponomarenko, C. Klason, Strain sensitive polymer composite material, Smart Mater. Struct. 4 (1995) 31–35.
[2] M.B. Heaney, Resistance-expansion-temperature behavior of a disordered conductor–insulator composite, Appl. Phys. Lett. 69 (17) (1996) 2602–2604.
[3] D. Bloor, K. Donnelly, P.J. Hands, P. Laughlin, D. Lussey, A metal–polymer composite with unusual properties, J. Phys. D: Appl. Phys. 38 (2005) 2851–2860.
[4] R. Strumpler, J. Glatz-Reichenbach, Conducting polymer composites, J. Electroceram. 3 (4) (1999) 329–346.
[5] R. Strumpler, P. Kluge-Weiss, F. Greuter, Smart varistor composites, Adv. Sci. Technol. 10 (1995) 15–22.
[6] F. Greuter, R. Strumpler, US Patent 5,858,533 (1999).
[7] R. Strumpler, J. Glatz-Reichenbach, ABB Corporate Research, Smart polymer composite thermistor, Mater. Res. Soc. Symp. Proc. 600 (1) (2000) 293–298.
[8] F. Greuter, M. Siegrist, P. Kluge-Weiss, R. Kessler, L. Donzel, R. Loitzl, H.J. Gramespacher, Microvaristors: functional fillers for novel electroceramic composites, J. Electroceram. 13 (2004) 739–744.
[9] D. Azulay, M. Eylon, O. Eshkenazi, D. Toker, M. Balberg, N. Shimoni, O. Millo, I. Balberg, Electrical-thermal switching in carbon–black–polymer composites as a local effect, Phys. Rev. Lett. 90 (23) (2003) 236601–236604.
[10] P. Duran, F. Capel, J. Tartaj, C. Moure, Low-temperature fully dense and electrical properties of doped-ZnO varistors by a polymerized complex method, J. Eur. Ceram. Soc. 22 (2002) 67–77.
[11] R.J. Lauf, W.D. Bond, Fabrication of high-field zinc oxide varistors by sol–gel processing, Ceram. Bull. 63 (1984) 278–281.
[12] R.G. Dosch, B.A. Tuttle, R.A. Brooks, Chemical preparation and properties of high-field zinc oxide varistors, J. Mater. Res. 1 (1986) 90–99.
[13] A. Banerjee, T.R. Ramamohan, M.J. Patni, Smart technique for fabrication of zinc oxide varistor, Mater. Res. Bull. 36 (2001) 1259–1267.

[14] J. Wu, C. Xie, Z. Bai, Preparation of ZnO–glass varistor from tetrapod ZnO nano-powders, Mater. Sci. Eng. B 95 (2002) 157–161.
[15] P.Q. Mantas, J.L. Baptista, The barrier height formation in ZnO varistors, J. Eur. Ceram. Soc. 15 (1995) 605–615.
[16] M.W. Ellsworth, Organic/inorganic hybrid materials, in: Proceedings of a Workshop Sponsored by the Division of Polymer Chemistry, American Chemical Society, Sonoma, California, 2001.
[17] D.S. McLachlan, M. Blaszkiewicz, R.E. Newham, Electrical resistivity of composites, J. Am. Ceram. Soc. 73 (1990) 2187–2203.