Epoxy-Boehmite Nanocomposites as New Insulating Materials

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ABSTRACT: The results of a comparative analysis performed on specimens of nanostructured epoxy resins obtained by different boehmite filler concentrations are reported in this paper. The specimens were prepared by dispersion of boehmite nanoparticles into a cycloaliphatic epoxy resin cross linked under UV. Photopolymerization process was followed by RT-FTIR and the properties of uv-cured films investigated. Dielectric properties, in particular space charge accumulation, are measured as a function of nanofiller content. Results indicate that space charge build up and charge mobility are affected largely by filler content. Concentrations of nanofiller of 5–7 wt % show significant decrease of the space charge with respect to the base-epoxy resin and an increased mobility of negative carriers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2541–2546, 2009

Key words: electrical properties of nanocomposites; space charge accumulation; electric strength measurements; UV curing

INTRODUCTION

Polymer nanocomposites have drawn considerable attention, in recent years, due to improvements in various properties including scratch resistance, abrasion resistance, heat stability, and other mechanical properties.[1–3] The use of inorganic particles in the nanoscale range is particularly attractive with the aim of improving the properties of the polymers by controlling the degree of interaction between the polymer and the nanofiller.[4] Several good review articles have been written on the synthesis, characterization and applications of the polymeric nanocomposites.[5,6]

Recently much attention has also been devoted on the use of inorganic nanofiller with the aim of improving electrical insulating properties of either of thermoplastic or thermoset polymeric matrices.[7–9] It has been demonstrated that nanostructured polymeric materials show interesting modification of electrical properties that could affect positively insulation systems. In particular, an increase of electric strength and voltage endurance or a decrease of

space charge accumulation can be achieved by addition of a small percentage of nanofillers, e.g., layered silicates or inorganic oxides.[10,11] It must be remembered that space charge accumulation in the insulation bulk is a big concern particularly for high-voltage DC applications, producing localized electric field enhancement which can lead to electric overstress and, thus, to premature insulation breakdown. In addition, improved electric strength and voltage/thermal endurance would be beneficial particularly for those insulation systems subject to large electro-thermal stress, such as accessories in cables or rotating machine windings.

Within this framework it could be interesting manufacturing epoxy-based nanocomposites for insulating materials obtained via UV-induced polymerization, with the aim of improving electric properties, e.g., reducing space charge accumulation.

UV-curing technique is getting an increasing importance in the field of coatings due to its peculiar characteristics.[12] In fact, it induces polymer formation with a fast transformation of liquid monomer into a solid film with tailored physical-chemical and mechanical properties. It can be considered an environmental friendly technique, due to the solvent free process, and it is usually carried out at room temperature, therefore guarantees the saving of energy. Furthermore, the cationic photopolymerization process of epoxy systems present some advantages

compared to the radical one[13]: lack of inhibition by oxygen, low shrinkage, good adhesion, and mechanical properties of cured films.

The aim of this article is to investigate the preparation and characterization of UV-cured epoxy-based nanocomposites containing boehmite filler. The UV-curing process was studied by means of real-time-FTIR and the thermal and viscoelastic properties of the cured networks were evaluated. The investigation of the electrical properties of nanocomposites was studied through space charge and electric strength measurements, comparing the behavior of unfilled and filled materials.

EXPERIMENTAL

Materials

3,4-Epoxycyclohexylmethyl-3′,4′-epoxycyclohexane-carboxylate was purchased from Aldrich (**CE**) and used as epoxy resin. Boehmite (Disperal 40®, was supplied by Sasol, aggregation particle size 50 μm, surface area BET 100 m^2/g) was used as filler in the range between 1 and 7 wt % with respect to the epoxy resin. Triphenylsulphonium hexafluoroantimonate (UVI 6976) was supplied from Dow and used as cationic photoinitiator: it is in solution with propylene carbonate (50% w/w) and it was added to the curable mixtures at a concentration equal to 2% (wt/wt) of actual photoinitiator.

Sample preparation and characterization

Composites were prepared by mixing CE with boehmite filler in the range between 1 and 7 wt %. The filler was previously subjected to a drying treatment at 80°C under vacuum before adding it to the epoxy resin. The mixtures were ultrasonificated for 30 min and the cationic photoinitiator added at 2 wt %. The obtained mixtures were photocured by means of Fusion UV lamp with an intensity on the surface of the sample of 200 mW/cm^2 and a speed belt of 6 m/min.

The kinetics of the photopolymerization were determined by real-time FTIR spectroscopy, employing a Thermo-Nicolet 5700 instrument. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes *in situ* the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in the absorbance of the epoxy ring in the region 760–780 cm^{-1}. This band was normalized to the carbonyl C=O signal, centered at 1700 cm^{-1}. A medium pres-

sure mercury lamp, equipped with an optical wave-guide, was used to induce the photopolymerization (light intensity on the surface of the sample of about 30 mW/cm^2): all the conversion curves summarized and compared in one figure were performed on the same day and under the same conditions, thus good reproducibility was obtained.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765–84.

Dynamic-mechanical thermal analyzes (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration. The samples were 4 × 1 cm with a thickness of 200 μm.

Samples were prepared for TEM observation by Ar$^+$ ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300 keV transmission electron microscope (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph program. The TEM observations were always performed using a very low electron flux to avoid any structural modification of the sample induced by the electron beam.

Electrical measurements consisted of AC electric strength and space charge measurements. The former were performed on a sample of five specimens for each material by increasing the voltage applied to the specimens with a given ramp (20 kV/min) and measuring the breakdown electric field. Data were processed, then, through the Weibull probability distribution, obtaining the values of α and β which correspond to the breakdown field at 63.2% probability and the shape coefficient (inversely proportional to standard deviation), respectively.[14]

Space charge measurements were carried out at 10 and 20 kV/mm through the pulsed electroacoustic (PEA) technique which allows to obtain a bi-dimensional pattern of the charge density in the insulation bulk. An electric pulse (10 ns width) was applied to the specimen together with the DC poling voltage. The pulse generates an impulsive electric field inside the specimen which exerts a force on any charge present in the insulation whose amplitude is proportional to the net local charge.[15] A pressure wave profile, having the shape of the original charge profile, is produced from the interaction between the electrical force and the material structure and propagates through the insulation at the sound velocity. A piezoelectric transducer, located under the ground electrode, generates a voltage signal (PEA output signal) proportional to the pressure wave propagating through it. The voltage signal is then amplified by two large-band amplifiers, and sent to an acquisition system.
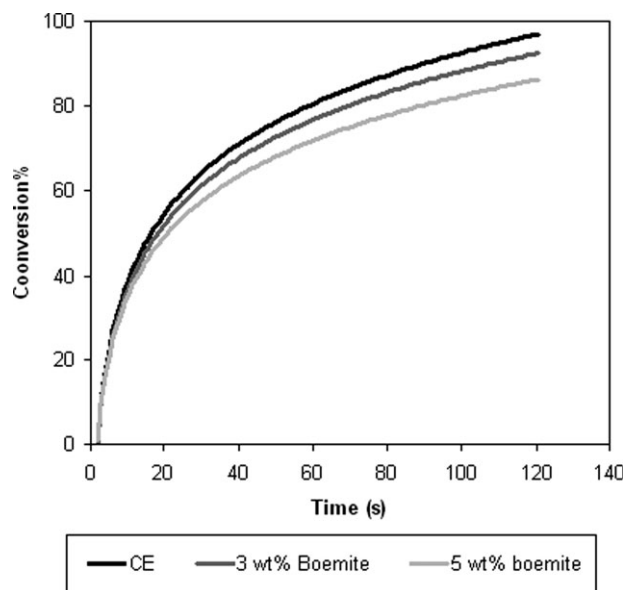
Figure 1 Real-time FTIR conversion curves for CE unloaded resin and in the presence of increasing boehmite content.

PEA tests were performed at room temperature and consisted of a polarization phase lasting 10,000 s, followed by a depolarization phase (volt-off) where the specimen is short-circuited and grounded for 3600 s.

To estimate space charge accumulation, the space charge density (in absolute value) accumulated in the insulation bulk can be calculated from the detected profiles according to the following equation,[16]:

$$Q(t) = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} \left| \rho(x,t) \right| dx \qquad (1)$$

where x_1 and x_2 are the electrode positions, and $\rho(x)$ is the space charge density profile measured at time t.

An important parameter is the maximum stored charge density, Q_{max}, which is evaluated by eq. (1) at the beginning of the depolarization phase ($t = 2s$ after voltage-off). Moreover, the depolarization characteristic can be obtained drawing the absolute stored charge density $Q(t)$ in relative value of Q_{max}, at different depolarization times.[16] This plot can provide important pieces of information regarding dynamics of charge mobility in the insulation.

RESULTS AND DISCUSSION

UV curing process

The starting point of this investigation was the evaluation of the effect of the presence of boehmite in the UV-curing process of a commercially available epoxy resin. The epoxy group conversion was followed by means of real-time FTIR investigation.

The conversion curves as a function of irradiation time for the unloaded CE resin and in the presence of increasing amount of boehmite, in the range between 1 and 5 wt %, are reported in Figure 1. While the slope of the curves gives an indication of the rate of polymerization, the plateau value gives the final conversion.

Polymerization for the pristine CE resin is quite rapid since the first step, and an almost complete epoxy group conversion was achieved after one minute of irradiation. By increasing the filler content in the photocurable formulation a slight decrease on epoxy group conversion is induced. It is possible to explain this behavior taking into account that by increasing the filler content an increase on viscosity is achieved, with an important decrease on the reactive species mobility and therefore, on percentage of epoxy group conversion. Furthermore it was shown by TEM analysis (see below) that the nanofiller have a tendency to form micron-size clusters ranging between 30 and 40 μm. This aggregation could produce a scattering effect and light absorption that will hinder the light transmission into the filled resin. A similar behavior was previously found in literature.[17]

Nevertheless, up to a content of 5 wt % of boehmite in the photocurable formulation it is possible to reach a high conversion in a short irradiation time.

The cured films were characterized by a high gel content values (always above 98%, see Table I) indicating the absence of soluble oligomeric species. These results show that by means of UV-curing it is possible to achieve highly crosslinked boehmite-epoxy composites.

Thermal and viscoelastic properties of cured films

Dynamic-mechanical thermal analysis (DMTA) was carried out on cured films. DMTA allows the evaluation for the elastic and viscous components of the modulus of the material, in a large temperature interval. Therefore, this technique gives a complete characterization of the thermal and viscoelastic properties of the material.

The storage modulus (E') and the dissipation factor (tan δ curves), as a function of temperature, are shown in Figure 2(A,B) respectively. The glass transition temperature, T_g, is defined as the maximum of tan δ curves, and the values are reported in Table I.

TABLE I
Properties of UV Cured Films

Sample	Gel content (%)	T_g DMTA (°C)
Pure CE	99	200
CE + 1 wt % filler	98	200
CE + 3 wt % filler	98	228
CE + 5 wt % filler	98	241
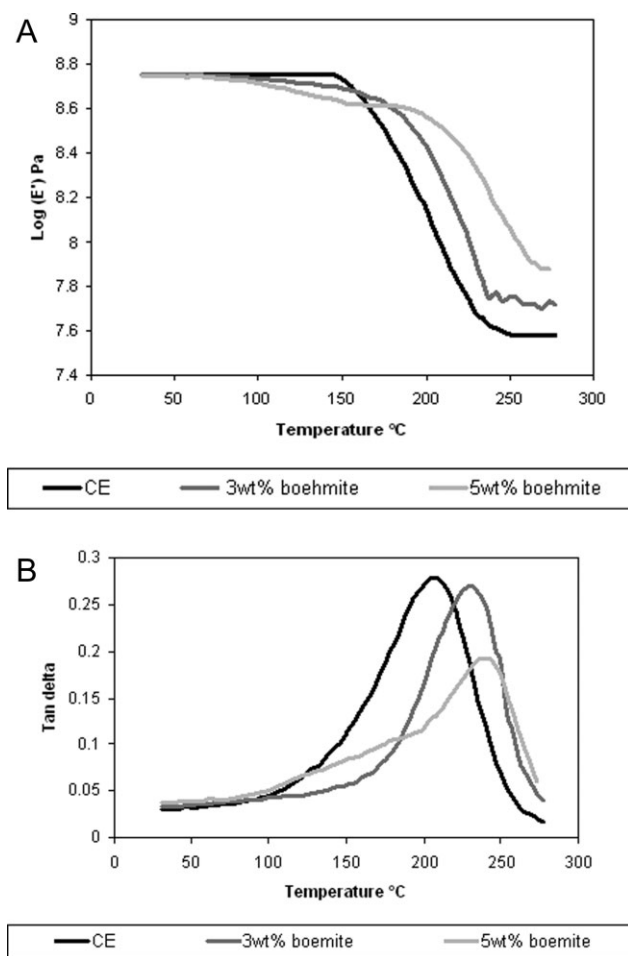
Figure 2 (A) DMTA modulus E' curves for uv-cured films containing increasing amount of Boehmite (B) DMTA tan delta curves for uv-cured films containing increasing amount of Bohemite.

From DMTA curves it is possible to observe that by increasing filler content in the photocurable formulation a shift of tan δ peak towards higher temperature is achieved and a higher storage modulus is evident in the rubbery region. Also a broadening of damping peak amplitude is evident in the presence of the higher filler concentration.

It was previously discussed that RT-FTIR showed a decrease of epoxy group conversion by increasing boehmite content in the photocurable formulations. The decrease on epoxy group conversion should be accompanied with a decrease of crosslink density and therefore to a flexibilization of the cured network with a decrease on T_g values.

We have observed an opposite behavior, with an increase on T_g and E' values by increasing the boehmite content in the photocurable formulations. This could be attributed to a predominant hindering effect of the nanofiller on polymer chains motions, which is expected to enhance the network rigidity.

Furthermore, the filler can decrease the free-volume of the polymer network with a further increase on T_g values. These effects are predominant with respect to the flexibilization effect induced by the lowering of epoxy group conversion.

TEM analysis on UV cured films

The morphology of the uv-cured composites was investigated by means of TEM analysis. The TEM analysis were performed on cured film containing 5 wt % of the nanofiller. The bright field TEM picture is reported in Figure 3. Some small aggregates of boehmite of around 100–200 nm are evident together with some bigger aggregates, from 30 to 60 µm; nevertheless larger macroscopic aggregation was avoided during polymerization. Taking into account the strong tendency of these particles to form large aggregate size, the obtained result is particularly interesting and show the possibility to obtain nano-micro epoxy-based composites. The hindering of large filler aggregation could be due to the rapid initiation and kinetic associated with photopolymerization technique, which allow the medium to be quickly solidified around the filler dispersion. In this way it was possible to reduce large macroscopic agglomeration tendency of boehmite nanoparticles.

Electrical properties of UV cured films

AC electric strength results are reported in the Figure 4. As can be observed, the 63.2th percentile, α,
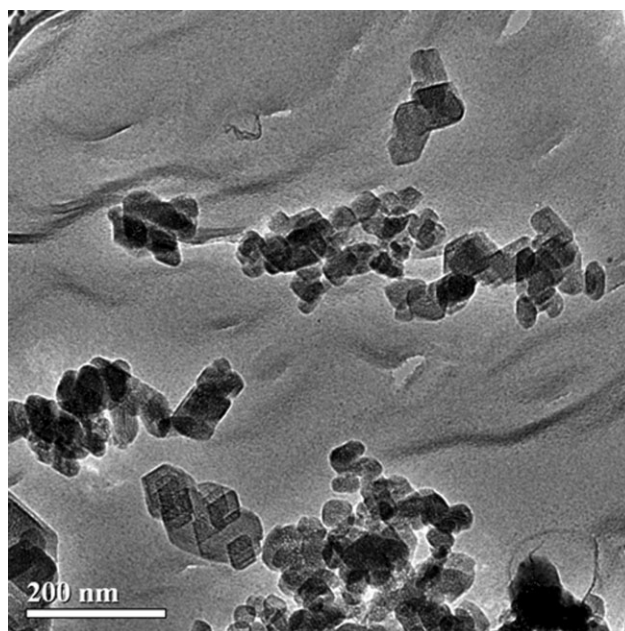
Figure 3 Bright field TEM micrograph for CE photocured film containing 5 wt % of Boehmite.
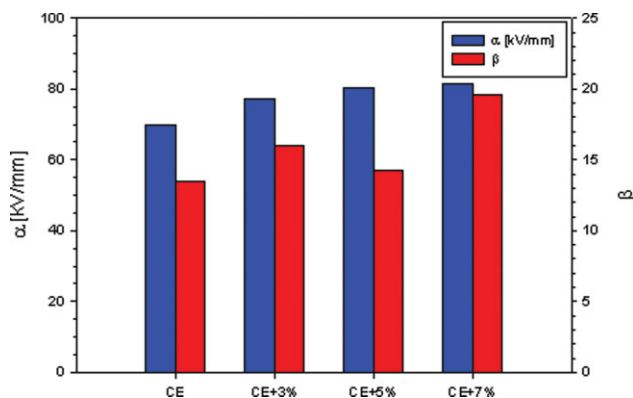
Figure 4 Electric strength (α and β value of the Weibull distribution) measured on base-epoxy and nanofilled specimens (from 3 to 7% in weight). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Maximum stored charge density for the nano-filled and base materials calculated from space charge measurement profiles at 10 and 20 kV/mm (from 3 to 7% in weight). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increases slightly with nanofiller content, the same occurs for the specimen homogeneity measured by the β parameter. For instance, the increase in the electric strength is about 16% for the specimen containing the 7 wt % of the nanofiller with respect to the base-epoxy resin.

Among electrical properties, nanostructuration appeared to affect more effectively space charge accumulation under DC voltage. Space charge patterns were obtained at 20 kV/mm for the unfilled and for the nanofilled epoxy resin containing 7 wt % of boehmite.

It was shown that, in the unfilled resin a large amount of charge is injected from both electrodes forming two homocharge (charge having the same polarity of the closer electrode) distributions. The nanostructured material, on the contrary, showed a significantly reduced amount of charge in the insulation bulk. It is noteworthy that an heterocharge (charge having opposite polarity with respect to the closer electrode) formation was observed in this case.

A quantification of space charge accumulation is provided by the average stored charge density calculated by means of eq. (1) at the beginning of depolarization period, which is reported in Figure 5 for PEA tests at 10 and 20 kV/mm. As can be observed a significant reduction of maximum accumulated charge is shown by materials containing 5–7 wt % of nanofiller with respect to the pristine epoxy resin. A concentration of 3 wt %, on the contrary, is not able to improve the performance of the material as regards space charge accumulation.

Charge dynamics comparison between the unfilled-epoxy resin and the 7 wt % nanofilled material is provided by the depolarization characteristics of Figure 6. We can see that after 10s from short-circuiting the pristine material and that containing 7 wt % of
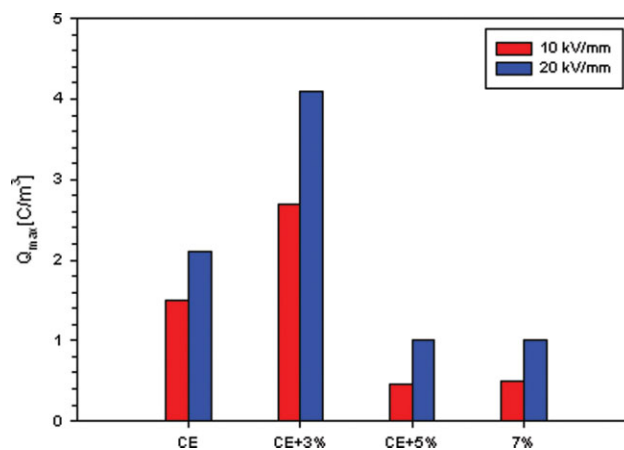
nanofiller still retains the 85% and 65% of the initial charge, respectively.

The results above presented on space charge accumulation properties lead to the following considerations.

First of all, the smaller charge accumulation shown by the nanostructured materials is a proof that the addition of nanofillers is able to change the chemical/physical structure of the base material as regards charge trap distribution and/or trap depth. The material having a nanofiller content ranging between 5 and 7 wt % shows, in fact, halving of charge accumulation at both 10 and 20 kV/mm with respect to the pure epoxy material. This could mean that nanostructuration may reduce the number of deep traps and/or increase the traps having a smaller depth (shallow traps), which allow less charge to accumulate in the insulation bulk.
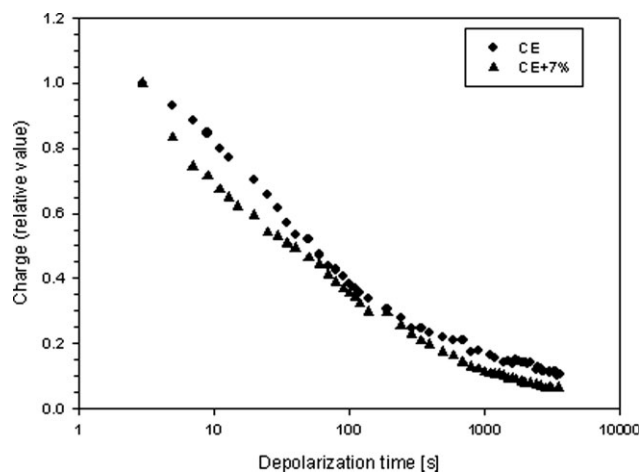
Figure 6 Depolarization characteristics obtained on base and nanofilled (7 wt %) epoxy resin after polarization at 20 kV/mm.

Moreover, the increase of shallow trap distribution in the nanostructured materials can provide a larger mobility of accumulated charge which can be released by the material more quickly, as confirmed by the depolarization characteristics of Figure 6.

It is noteworthy that charge mobility can affect also the nature of charge accumulation in the material, e.g., homocharge or heterocharge. In the base resin, in fact, a large amount of charge is injected from the electrodes and trapped in the material forming an homocharge distribution close to the injecting electrodes. In the 7 wt %-nanofilled material, on the contrary, injected charge, trapped in shallower traps, has faster dynamic with respect to the base material. In this case, charge can travel across the insulation thickness as a "charge packet" and trap close to the opposite electrode, which acts as a partially-blocking electrode, forming an heterocharge distribution. This phenomenon was observed recently also on PE-based materials for high-voltage cables.[18]

CONCLUSIONS

Boehmite nanoparticles were dispersed, by ultrasonification, in an epoxy resin in the range between 1 and 5 wt %. The formulation was cured by means of UV light, in the presence of a suitable cationic photoinitiator. The photopolymerization process was investigated by means of RT-FTIR, showing a slight decrease on epoxy group conversion by increasing boehmite content in the photocurbale formulation. Nevertheless the cured films were characterized by a high gel content values (always above 98%) indicating the absence of soluble oligomeric species.

An increase of T_g values was observed for films containing boehmite. This could be due to a good dispersion of the filler within the polymeric network that can hinders the segmental motion of the polymeric chains and decrease the free-volume. These effects are predominant with respect to the flexibilization effect induced by the lowering of epoxy group conversion.

TEM analysis showed boehmite aggregates ranging from 100 to 200 nm up to 30–40 μm. Larger particles aggregates was avoided, allowing a certain degree of nanostructuration of the samples, probably because of the fast uv-induced polymerization process.

The addition of inorganic nanofiller, e.g., boehmite, is able to improve significantly electrical properties of epoxy resin, particularly space charge accumulation. This phenomenon occurs in almost all the polymers due to the huge amount of available localized state, particularly located in the amorphous region, in which electronic (or ionic) charge can be trapped even for a long time, depending on the trap depth. The presence of nanofiller can change radically the morphology and microstructure of the base insulating material and, thus, trap depth of original localized state, likely decreasing deeper traps and increasing the availability of shallow traps. This lead to smaller charge accumulation shown by the nanostructured material and an high charge dynamic of which high-voltage applications can benefit in terms of better endurance and reliability.

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