Role of the Interface in Improving Surface Degradation Properties of Epoxy Nanocomposites

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It is widely accepted that the interface between polymer and filler particles plays a major role in modifying composite properties, both electrical and otherwise. In this work, we examine the role of the interface in affecting a particular electrical characteristic of the nanocomposite, viz. its resistance to surface degradation. Dielectric materials with improved resistance to surface discharges would help in ensuring better performance and greater reliability of apparatus in service. This paper takes a comprehensive look at the recent work by the authors in this area, and tries to understand the role of the interface in this context. Two essential features emerge. Increase in the interfacial zone at the expense of the bulk polymer imparts better degradation resistant properties to the composite specimen and tailoring of the chemical bond structure at the interface leads to further improvement.

Key words: *Epoxy nanocomposite, surface degradation, pre-processing, GPS, interfacial polymer*

1.0 INTRODUCTION

In recent years, polymer composites with metal-oxide fillers have attracted great interest, both in industry and academia. Inclusion of a small fraction of nanofillers can have a major impact on electrical properties such as breakdown strength, degradation resistance to surface discharges and voltage endurance. While it is not clearly understood by the research community how the incorporation of nanoparticles affect the polymer matrix structure and the composite behaviour, it is widely accepted that the interface between polymer and filler particles plays a major role in modifying the composite properties, both electrical and otherwise. In this context, we examine the role of the interface in affecting a particular electrical characteristic of the composite, namely, its resistance to surface degradation.

During normal operation or under fault conditions, insulating materials within electrical apparatus may be exposed to surface discharges, e.g. partial discharges from neighbouring sites in the dielectric assembly. These discharges impinge on the dielectric material causing erosion and material degradation and could ultimately lead to dielectric failure. Dielectric materials with improved resistance to surface discharges would help in ensuring better performance and greater reliability of the apparatus in service. This paper takes a comprehensive look at the recent work by the authors [1, 2] in this area, and the understanding gained thereof.

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2.0 INTERFACIAL POLYMERS

One of the salient features of nanoparticles is that their use converts a bulk matrix into an interfacial material. For a given volume fraction of filler material, smaller the size of the particles, smaller is the interparticle distance, scaling as a factor of the radius. Additionally, smaller the particle size, greater is the area of what constitutes the interfacial zone, scaling as a factor of (radius of the nanoparticle)$^{-1}$. Thus, a very large percentage of the bulk polymer now takes on the properties of an interfacial polymer. The properties of the polymer in the interfacial regions are often widely different from that of the bulk material.

In this work [1], it was observed that the use of nanosized Al_2O_3 particles (rather than microsized particles of the same material) in epoxy resin results in considerable improvement in its resistance to degradation when exposed to surface discharges. Surface discharge studies were conducted on epoxy and composite specimens using an IEC-(b) electrode system. This system consists of a rod-plane electrode assembly as shown in Fig. 1.
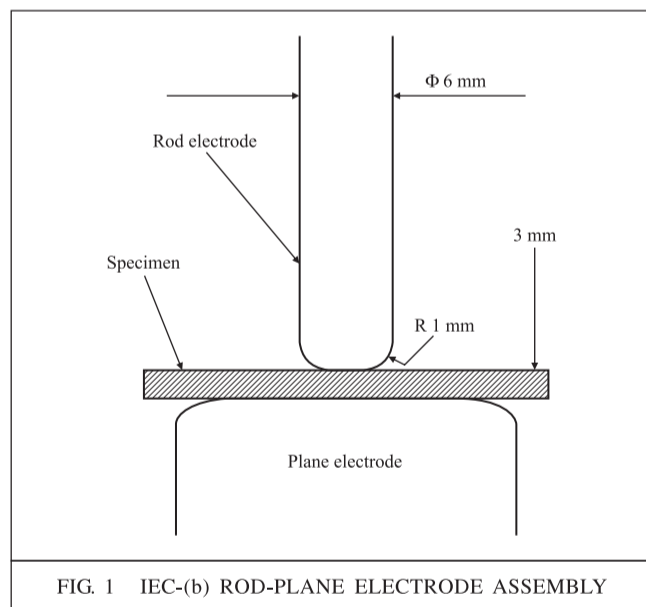

FIG. 1   IEC-(b) ROD-PLANE ELECTRODE ASSEMBLY

The surface roughness profiles of each epoxy composite specimen were obtained using a computer-controlled Laser Surface Profilometer, before the test and after every three hours. The total volume of eroded material was calculated from the depth profiles. The degraded surfaces of epoxy composites were examined with high-resolution online camera, Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

Fig. 2 shows a plot of the volumes of material removed from each specimen as a function of the exposure time. The neat epoxy sample shows the maximum amount of degradation right from the outset. Specimens with equal volume fractions of nanosized Al_2O_3 and TiO_2 fillers show that the eroded volumes for both nanofilled specimens are significantly lower than that of epoxy. The microfilled Al_2O_3 specimen shows the least degradation in the initial hours; however, at the end of eighteen hours, the largest amount of material is eroded from the neat epoxy specimen, followed by the microfilled Al_2O_3 specimen. The nanofilled specimens suffer lower amounts of material erosion.
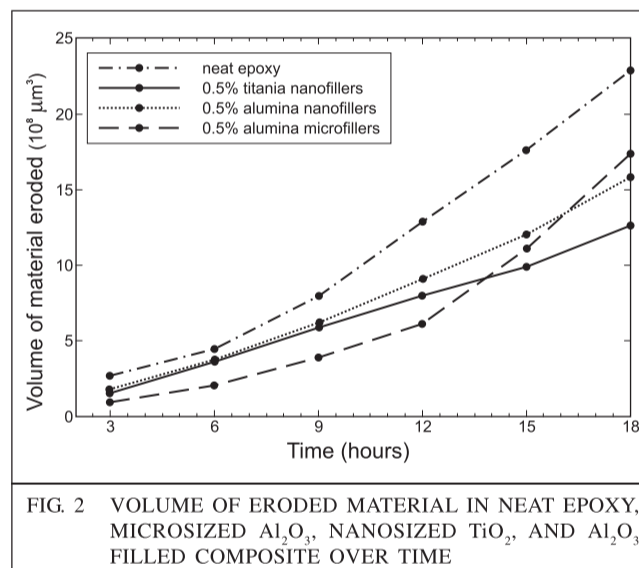

FIG. 2   VOLUME OF ERODED MATERIAL IN NEAT EPOXY, MICROSIZED Al_2O_3, NANOSIZED TiO_2, AND Al_2O_3 FILLED COMPOSITE OVER TIME

The above results clearly show that incorporating nanoparticles in the bulk matrix significantly improves resistance to surface erosion.

In the light of this finding, the authors proposed a possible mechanism of surface degradation in particle-reinforced epoxy, which could explain the observed improvement. Neat epoxy, in the absence of reinforcements in the bulk matrix, gets eroded fast. However, the metal-oxide particles act as reinforcements in the bulk matrix.

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When exposed to discharges, the particles do not get dislodged easily. Additionally, possible phase changes in the particle-epoxy interface region make the volume of material in this region resistant to degradation.

Initially, the epoxy present between nanoparticles begin to get eroded, and very fine degradation channels are formed, as shown in Stage-1 of Fig. 3. With further exposure to discharge, the channels get deeper and wider; however growth of the channel in any direction is arrested when it encounters a nanoparticle, so that the channels are contained in the inter-particle regions. As the channel grows deeper, nanoparticles emerge from the volume of the material, and degradation is arrested. This is shown in Stage-2. The erosion channel sizes are determined by the combined sizes of the particles and the interface region surrounding each particle. Degradation thus proceeds by erosion of only the inter-particle epoxy, and over time, many more metal-oxide particles are exposed. These particles continue to sit on the surfaces, while epoxy layers get depleted.
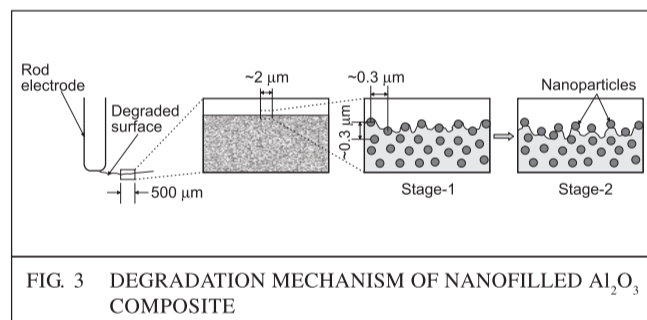
the rod electrode, after six, twelve and eighteen hours of degradation respectively. Fig. 4A shows the three-dimensional (3D) topographic image of a similarly degraded epoxy surface after six hours of degradation. Particles are visible on the surfaces of the degraded nanocomposite, while none are visible on the epoxy surface. A comparative study of Figs. 4B to 4D, shows clearly that an increased number of metal-oxide particles are exposed with time on the degraded surfaces. This provides credence to the proposed theory that interfacial zones and nanoparticles are resistant to degradation.
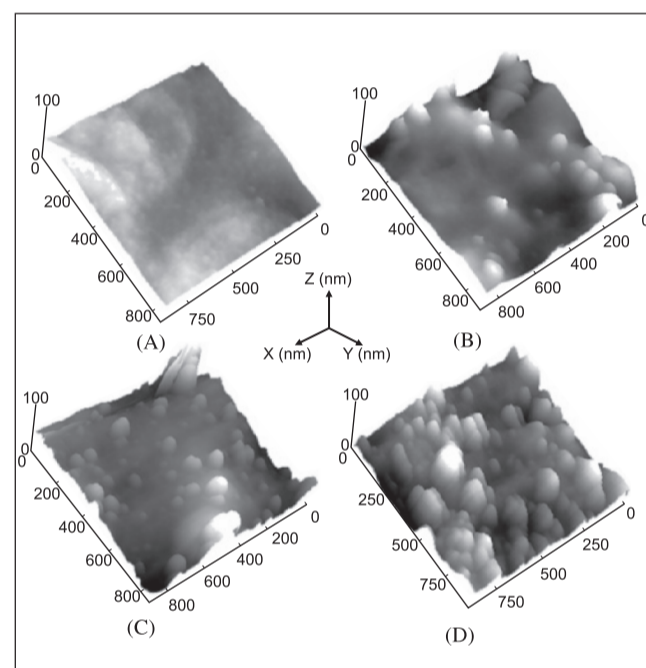

FIG. 4 AFM IMAGES OF A 900 nm × 900 nm SURFACE (2 mm FROM THE ELECTRODE EDGE) OF (A) NEAT EPOXY AFTER 6 HOURS OF DEGRADATION AND Al_2O_3 FILLED NANOCOMPOSITE AFTER (B) 6 HOURS (C) 12 HOURS (D) 18 HOURS OF DEGRADATION

FIG. 3 DEGRADATION MECHANISM OF NANOFILLED Al_2O_3 COMPOSITE

Nanocomposites thus have overwhelmingly larger interface regions which resist erosion. Corroboration for the above proposed mechanism was found in EDX analysis, which showed increase in metal (Al or Ti) content in the surface material with degradation.

Further, Figs. 4B to 4D show the Atomic Force Microscopy (AFM) images of a small surface (900nm × 900nm) of an alumina filled nanocomposite, 2 mm away from the edge of

3.0 CHEMICAL BONDING AT THE INTERFACE

The above work brings out that the principal characteristic that the nanodielectric lies in its increased interfacial area. Another factor that greatly influences the behaviour of the nanocomposite is the chemical structure at the interfaces. The authors found direct evidence [2] that tailoring the chemical bonding at the epoxy-particle interface directly influences composite properties.

In order to investigate this effect, the as-received particles were pre-treated before use in composite preparation. The following techniques were used.

- Heating the particles before use.

- Functionalising with GPS (3-glycidoxy-propyltrimethoxysilane) before use.

- Functionalising with GPS after heating

The processing techniques for various specimens used in the tests are described in [2].

Fig. 5 shows a plot of the volumes of material removed from each specimen (normalised with respect to the volume of material removed in neat epoxy specimen after three hours of degradation) as a function of the exposure time. The specimens that were used for the surface discharge tests were (A) neat epoxy, and composite with fillers (B) as-received Al_2O_3 platelets (C) functionalised Al_2O_3 platelets (D) as-received spherical Al_2O_3 nanoparticles (E) functionalised spherical Al_2O_3 nanoparticles (F) heated spherical Al_2O_3 nanoparticles (G) spherical Al_2O_3 nanoparticles functionalised after heating. It was observed from Fig. 5 that the composite made with neat epoxy degrades the most. A considerable amount of reduction in surface degradation was found when as-received alumina platelets were used as reinforcement of epoxy composites, even more so when platelets functionalised with GPS were used. Epoxy composites containing as-received spherical nanoparticles showed lower degradation rates than specimens with either as-received or functionalised platelets. Functionalising the spherical particles with GPS was found to further improve degradation properties of composites even better than the as-received spherical nanoparticles. Much lower degradation rates were obtained when as-received spherical nanoparticles were heated before use. Finally, best results were achieved when the spherical nanoparticles were heated first and then functionalised with GPS after being heated.
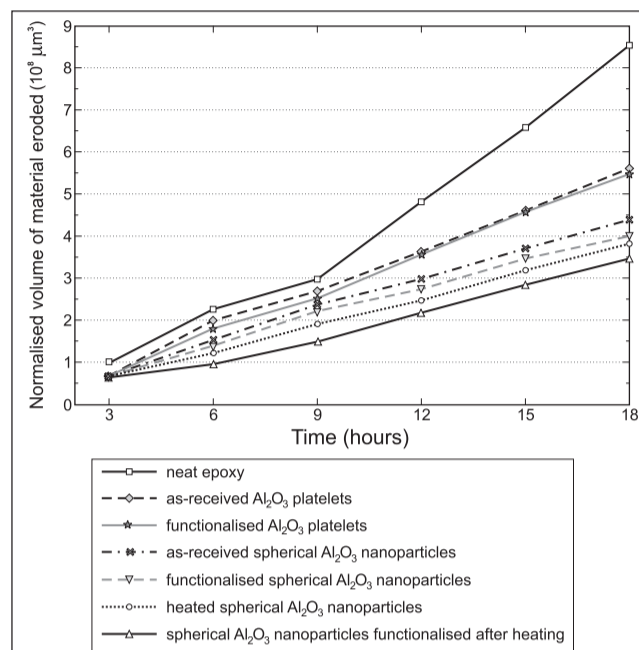

FIG. 5 VOLUME OF ERODED MATERIAL (NORMALISED WITH RESPECT TO VOLUME OF MATERIAL REMOVED FROM NEAT EPOXY SPECIMEN AFTER 3 HOURS OF DEGRADATION) IN—
(A) NEAT EPOXY RESIN AND COMPOSITES WITH FILLERS (B) AS-RECEIVED Al_2O_3 PLATELETS (C) FUNCTIONALISED Al_2O_3 PLATELETS (D) AS-RECEIVED SPHERICAL Al_2O_3 NANOPARTICLES (E) FUNCTIONALISED SPHERICAL Al_2O_3 NANOPARTICLES (F) HEATED SPHERICAL Al_2O_3 NANOPARTICLES (G) SPHERICAL Al_2O_3 NANOPARTICLES FUNCTIONALISED AFTER FIRST HEATING

It can therefore be inferred that heating as well as functionalising nanoparticles with GPS helps in enhancing the resistance of the nanocomposite to degradation due to surface discharges.

Pre-processing the nanoparticles essentially changes the chemical nature of the interface, and the manner in which the filler particles incorporate themselves within the polymer network. Fourier Transform Infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy were utilised to investigate these chemical interactions.

In general, metal oxide nanoparticles contain a large number of surface hydroxyl groups [3-5]. The hydroxyl groups on the surface of the nanoparticles are hydrogen bonded with each other and with absorbed water molecules [3-7]. This prevents the formation of any chemical bonds between the particles and the epoxy

molecules. Heating the particles to 200°C liberates the surface hydroxyl groups from the absorbed water molecules. This leads to an increase in the number of free surface hydroxyl groups, and therefore allows hydrogen-bonding interactions between particles and the epoxy resin. The enhancement in the surface degradation properties of the composite having heated nanoparticles could be interpreted as the consequence of formation of a strong interfacial region in between the heated particles and polymer matrix.

In the case of functionalised nanoparticles, a covalent bond is formed between the epoxy particles and the epoxy. Fig. 6 shows FTIR spectrum of the GPS-functionalised spherical Al_2O_3 nanoparticles. The broad peak at 1118cm^{-1} is mostly the result of the formation of a Si-O-Al bond with slight indications of other bonds such as Si-O-H and Si-O-Si [4]. Thus, covalent bonding has been formed between the silane and alumina nanoparticles.
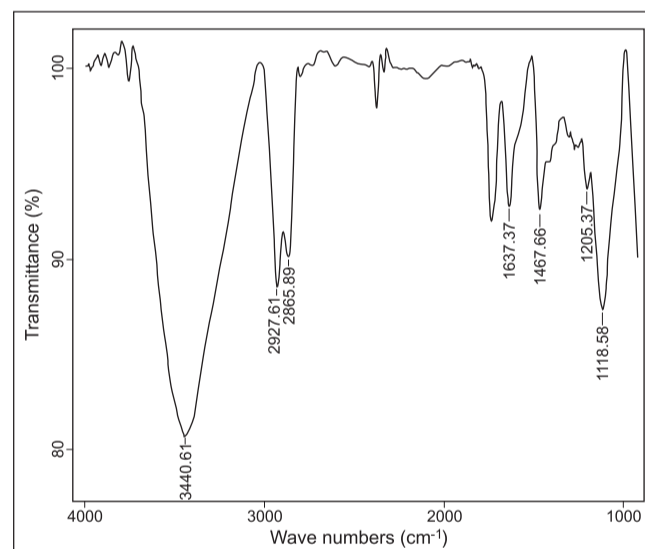

FIG. 6   FTIR SPECTRUM OF GPS FUNCTIONALISED NANOPARTICLES. THE PEAK AT

I.   3440.61cm^{-1} CORRESPONDS TO O-H GROUP STRETCHING VIBRATION (COMBINATION OF O-H GROUP FROM HYDROLYSED SILANE, SURFACE HYDROXYL GROUPS OF THE NANOPARTICLES, AND HYDROXYL GROUPS OF ABSORBED WATER MOLECULES).

II.   1248.07cm^{-1} CORRESPONDS TO EPOXIDE RING VIBRATION.

III.   1118.58cm^{-1} BROAD PEAK CORRESPONDS TO ASYMMETRICAL Si-O STRETCH (Si-O STRETCH FROM Si-O-H, Si-O-Al AND Si-O-Si).

After the bond formation between nanoparticles and GPS, the epoxide group on other side of the GPS molecule would participate in cross-linking with epoxy (on addition of hardener). This makes a continuous network of nanocomposites with the formation of strong covalent bonds between nanoparticles, GPS and epoxy matrix. In the case of heated nanoparticles, the number of free hydroxyl groups is more and so a larger number of Al-O-Si bonds are formed. Thus, the particles functionalised with GPS after heating produce stronger bonds with GPS, and therefore with epoxy.

It would essentially appear that greater the strength of the bond between filler particles and the polymer matrix, more will be the resistance of the composite to the degradation process due to slowing down of the process of material removal. The strength of the bond increases from van der Waals and hydrogen bond to ionic bond to covalent bond. Thus, the nature of the bond has a considerable effect on the amount of change observed in the bulk property.

4.0   CONCLUSIONS

The work described here brings out two essential features of the contribution of the interface to bulk property change. Increase in the interfacial zone at the expense of the bulk polymer imparts better degradation resistance to the composite specimen. Tailoring of the chemical bond structure at the interface leads to further improvement. There are certainly other ways in which the interface plays a dominant role, which have not been touched upon here. However, it might undoubtedly be said that a very close scrutiny of the interfacial polymer is essential to further advancement in the area of nanodielectrics.

5.0   ACKNOWLEDGEMENT

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