Nano-Composite Dielectrics: The Dielectric Nature of the Nano-Particle Environment

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Keywords : nanometric polymer composites, interfaces, double layers, dielectric permittivity, electrical conduction and breakdown

There is increasing interest in using polymeric nanocomposites as materials with exceptional dielectric or insulating properties. However the factors which lead to these improvements are still to be determined precisely. In this paper attention is focussed on the local dielectric environment of the nanometric filler particle in the polymer matrix and particularly on the interface between the filler particle and the polymer matrix. It is emphasised that this interface is itself a distinct phase with nanometric proportions which can be comparable with the particle size and is likely to control the dielectric features of the composite

Using a simple geometric argument based on a cubic close-packed array it is shown how the concentration and nanometric size of the particle can lead to the interface becoming the dominant phase in the composite. For example it is estimated that for a typical composite dielectric of TiO_2 filler particles in an epoxy resin, the interfaces will interfere and possibly interconnect for spherical particles of 20 nm radius at concentrations greater than 25%. If the particles are spheroidal and particularly if oblate (disc-like) the interfaces are shown to become even more significant. In addition, for the latter, the interface volume and surface can become very much greater than that for spherical particles; the volume even becoming greater than the matrix volume.

The forces defining the interface between particle and polymer are considered. Two interesting features, which influence the dielectric properties, are emphasised. The first is the Stern-Gouy-Chapman double layer of interfacial electrical charges, which will always be present in practical cases, and the second is the influence of this on the polymer network immediately adjacent to the particle. The polymer chains become restricted there and less flexible and therefore less polarizable. The interaction between particles in close proximity both in the final composite and during a mobile forming phase now depends on the complex interaction of these interfaces. This affects both the mechanical and electrical properties of the composite. Particular attention is given to the latter.

The interface becomes a phase in its own right with its own permittivity characteristics, thus turning an apparent two-phase dielectric into a three-phase one. This upsets the ability to tailor the permittivity of the composite to particular design characteristics. The presence of the interface as a dielectric of finite extent rather than a dimensionless boundary becomes

prominent in the frequency characteristics of the composite. The finite interface model can be usefully applied to more complex composites such as filler particles consisting of metal-coated glass bubbles. In such cases, since the lateral properties of the polarizable conduction path in the metal coating around the bubble is considered to be important, the presence of several interfaces in this system in parallel with the coating can become important.

The contribution of interface properties is also shown to be important in determining the insulating properties of composites intended as insulators. Separate leakage conduction paths will exist through the bulk polymer matrix and via the interfaces. The two paths become distinct and largely separate because charge trapping state energies are different in the two phases because of differences in the local polarizability of the polymer which determines the charge trap energy. The paths will be percolative in form and dependent on the filler particle size and geometry. Whether one or the other is a preferred conduction path depends again on the particle size, shape and concentration and on interface dimensions

The presence of the particle matrix and the attendant interfaces as a finite phase with particular conduction characteristics will also have a marked influence on the manner of the electrical breakdown of the composite in high fields. The breakdown process is likely to be electro-mechanical in nature tending to open cracks in the polymer structure. Initially these will be broken into discrete micrometric lengths encouraged by the disposition of filler particles and the surrounding interfaces. Each such length could give rise initially to a confined breakdown and subsequent partial discharge without propagating further. The independent nature of these breakdown events will delay the overall macroscopic failure of the composite considerably and give the composite improved insulating endurance.

Since particle interfaces have such a central role in determining the characteristics of dielectric and insulating composites it is suggested that detailed studies should be made of their properties. The investigation of the electrical characteristics of single nanometric particle-polymer interfaces in detail using modern nanometric surface scanning techniques should be possible. At present there is a dearth of information on the physics and chemistry of these interfaces. Intelligent design of electrical properties will depend in particular on an understanding of processes at the nano and sub-nanometric level.

Nano-Composite Dielectrics: The Dielectric Nature of the Nano-Particle Environment

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The evident influence of the reduction in particle size to nanometric dimensions on many properties of polymeric dielectric composites emphasises the role of the filler particle-matrix interface. The interfacial environment itself, which is also of nanometric dimensions, can be dominant in determining the properties of the composite. Employing a cubic close-packed array of particles with appropriate interfaces to the polymer as a simple representation of a composite many of the features can be effectively demonstrated and used to model dielectric permittivity, electrical conduction and breakdown in polymeric composites.

Keywords : nanometric polymer composites, interfaces, double layers, dielectric permittivity, electrical conduction and breakdown

1. Introduction

The concepts of nano-technology are having far-reaching application throughout science and engineering. The review by Frechette et al⁽¹⁾ sets out a panorama encompassing the biological as well as the inanimate sciences and extending from quantum to classical concepts. At the same time it seeks to highlight the so-called nano-dielectric entity within this framework.

Dielectric entities of nanometric dimension are being considered in the two main branches of electrical engineering. In the communication and related industries there is an insistent demand for smaller and smaller device elements to operate in the micro-chip circuit environment. The need for high permittivity gate elements and low permittivity inter-connections on a nanometric scale offers considerable scientific and technical challenge. In the electrical power industry the drive is different. Dielectric materials are employed on a micrometric or greater level and certainly not on a nanometric scale. Yet there is a growing belief that the incorporation of nano-particles within a microscopic dielectric matrix to form a so-called nano-composite will bring benefit in one form or another, perhaps in terms of mechanical or thermal properties or more directly that the insulating properties of the composite will be superior to those of the matrix. The review by Tanaka et al⁽²⁾ focusses attention on polymer nano-composite dielectrics; macroscopic polymer matrices in which are dispersed nanometric size filler particles. It is clear however that much is not understood about the manner in which nano-particles influence the permittivity, loss, conductivity, space-charge and electric strength of these composites. Although many of the conclusions of this review appear to suggest conflict over the mechanisms involved, there is a general consensus of opinion that nano-composites offer a route to insulation with much improved characteristics.

In the following attention will be focussed on the dielectric environment of the nano-particles (the filler of a conventional composite) in a polymeric matrix and the physico-chemical factors which determine it. Related treatments have been given earlier⁽³⁾⁽⁴⁾. To begin, a number of simple features of the mensuration associated with the nano-filler-matrix situation which are not

immediately intuitive but which contribute directly to determining the properties of the nano-composite will be described. Several authors such as Tanaka et al⁽⁵⁾ have made similar points.

2. The Ideal Composite

An idealised version of a composite would be a uniform dispersion of spherical filler particles of radius r in a homogenous isotropic matrix. In a conventional composite r is likely to be of micrometric dimension but in a nano-composite it will be some three orders of magnitude less. If M_f and M_m are, respectively, the masses of filler and matrix in the composite and assuming initially that mixing does not affect the particle or matrix structures then the mass of filler particles per volume of composite

is $M_f \left(\frac{M_f}{\rho_f} + \frac{M_m}{\rho_m} \right)^{-1}$ where ρ_f and ρ_m are the densities of filler

particles and the matrix. If the filler particle has radius r then the number of particles per unit volume of matrix, assuming a cubic

close-packed structure, will be $M_f \left[\frac{4\pi}{3} \rho_f r^3 \left(\frac{M_f}{\rho_f} + \frac{M_m}{\rho_m} \right)^{-1} \right]$. The

minimum distance d in the matrix between the particles can be expressed as

$$d = r \left\{ \left[\frac{4\pi}{3} \left(1 + \frac{M_m \rho_f}{M_f \rho_m} \right) \right]^{\frac{1}{3}} - 2 \right\} \dots\dots\dots (1)$$

It is customary to express the composition of the composite in terms of F , the weight % of filler, which as a fraction, is $M_f (M_f + M_m)^{-1}$ and Eq. (1) can be written as

$$d = r \left\{ \left[\frac{4\pi}{3} \left(1 + \frac{1-F}{F} \frac{\rho_f}{\rho_m} \right) \right]^{\frac{1}{3}} - 2 \right\} \dots\dots\dots (2)$$

d depends not only on particle size but also on filler concentration and the relative density of filler and matrix. It is instructive to consider the situation for representative but typical composites. Figure 1 shows d for a range of nanometric spherical filler particles as a function of filler concentration F in a matrix of density 1400 kgm^{-3} which might be typical of a polymeric resin. Densities of 2000, 4000 and 17000 kgm^{-3} have been chosen for the

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Fig. 1. Minimum distance d between spherical filler particles in a cubic close-packed array as a function of filler concentration F for a range of particle radii r . The polymer matrix density is assumed to be 1400 kg m^{-3} and the filler particle densities 2000 , 4000 and 17000 kg m^{-3} . The corresponding density ratios ρ_f/ρ_m are (a) 1.43 , (b) 2.86 and (c) 12.1 . A plausible range of interface thickness 2δ is indicated in (b).

particles corresponding approximately to those of aluminium silicate clay, titanium dioxide and gold.

As might be expected the inter-particle separation decreases with increasing particle concentration but it does so rapidly and at low concentrations when the radius is small. For example Fig. 1(b), roughly approximating to a titanium oxide filler in resin shows that for a particle radius of 10 nm and a $5 \text{ wt } \%$ concentration, the inter-particle separation d is 59 nm but it decreases to 15 nm , less than the particle diameter when the concentration is $40 \text{ wt } \%$, and the composite becomes nano-structured. Particles of $1 \mu\text{m}$ radius at the same $\text{wt } \%$ produce a conventional composite.

These simple arguments become significant when account is taken of the nature of the particle-polymer matrix contacts. A contact will result in an interface (sometimes called an interphase or interaction zone) through which there is a gradual change of properties from those of the particle to those of the surrounding matrix. The physico-chemical nature of the interface will be considered in more detail in Section 3 but here it is considered uniform around the particle and extending a distance δ from it. Generally δ will be a few nanometres in extent but when the matrix is polymeric, as will be discussed later, δ may be as much

Fig. 2. Interface to particle volume ratio R_{ip} as a function of δ/r for various aspect ratios c/a of spheroidal particles where c is the semi-axis and a is the radius of rotation; $c/a = 1$ for spherical particles

as 40 nm . In this situation, as can be seen in Fig. 1, it can be comparable with the inter-particle spacing d and thus a major feature extending throughout the inter-particle space for a range of particle sizes and concentrations. For example, in the case of 20 nm particles with a density ratio 2.86 the inter-particle distance becomes entirely bridged by the interface at concentrations above about $25 \text{ wt } \%$. Even for 10 nm radius particles, an interface of only 2 nm becomes a significant part of the inter-particle space for concentrations above $40 \text{ wt } \%$.

It is equally instructive to consider the volume occupied by the interface. This volume, expressed as a proportion of filler particle volume, is shown as R_{ip} in Fig. 2 (aspect ratio 1) as a function of the ratio δ/r (interface thickness to particle radius). When δ/r reaches about 26% the interface volume exceeds the particle volume and becomes increasingly significant as δ/r exceeds that value. Thus the particle-matrix contact can lead to the generation of a new and possibly dominant phase with properties likely to be different from either particle or matrix. The interface volume grows at the expense of the matrix. The ratio of the two can be expressed as

$$R_{im} = \frac{F}{1-F} \frac{\rho_m}{\rho_f} R_{ip}.$$

In practice it is unlikely that the filler particles will be truly spherical. The possible geometries will extend from needle (carbon nanotube) to disc-like (clay platelet) forms. In these circumstances it is not possible to specify an inter-particle spacing since specific particle orientation and preferred packing will occur determined by local force fields. It is possible, however, to determine the particle surface area and the effect of interface layers in these cases and to compare them with those for spherical particles. Consider the particle to be spheroidal with a semi-axis of rotation c , radius of rotation a and mass equivalent to that of a spherical particle of radius r so that $a^2c = r^3$. The particle is prolate (needle-like) when the aspect ratio c/a is >1 and oblate (disc-like) when <1 . Figure 3 shows how S the relative surface area of the spheroid with respect to that of the sphere of equal mass changes as the aspect ratio changes. The oblate case in particular shows that a very marked increase in area occurs as the disc-like form appropriate for example to exfoliated clay is approached.

It is also possible to determine the interface to particle volume ratio R_{ip} for various aspect ratios in terms of δ/r as shown in Fig. 2.

Fig. 3. Spheroid to spherical surface area ratio S for particles of equal mass as a function of the aspect ratio c/a

The interface volume becomes increasingly dominant as the aspect ratio departs from unity for both prolate and oblate spheroids even when δ/r is small. Generation of interface volume will normally be at the expense of the polymeric matrix but the ratio of interface to matrix volume R_{im} has a hypothetical upper limit of unity. The

corresponding limit to R_{ip} is then $\frac{1-F}{F} \frac{\rho_f}{\rho_m}$.

For a 25 wt % of filler for which ρ_f/ρ_m is 2.86 (Fig. 1) the limiting R_{ip} is 8.6. While this would not be attained for spherical particles unless the interface ratio δ/r was in excess of 1.1, (Fig. 2), it would easily be reached for δ/r equal to 0.08 for disc-like particles with an aspect ratio of 0.1. Thus when spheroidal filler particles are employed, conditions where the interface properties will dominate over those of the matrix can easily occur and will control the composite performance. At the extreme aspect ratios associated with carbon nanotube or exfoliated silicate platelets, packing congestion will encourage correlated orientation and local domain textures. The simple geometric analysis above highlights the weakness of employing particle size and concentration alone in comparing composite performance. It is significant that the much-investigated composites based on carbon nanotubes or exfoliated clays with large aspect ratios are extreme examples of this situation. These features justify the expectation that interfacial properties will be a key factor in composite performance.

The topological similarities between the polymer nano-composites, semi-crystalline polymers such as polyethylene, block co-polymers and liquid crystal polymers should be noted at this point. Consideration of semi-crystalline polymers such as polyethylene as matrix polymer composites with crystalline lamellae as filler interspersed with amorphous polymer as matrix is likely to provide refreshing ideas about their mechanical and electrical performance.

3. The Physics and Chemistry of the Interface

So far the interface has been defined as a region of uniform thickness δ different from filler (A) and matrix (B). In general the boundaries of δ are ill defined since the interface is a region through which the atomic forces defining filler A become increasingly modified to become those defining matrix B. The interface is thus a path of communication between A and B. A wide range of properties, both physical and chemical, may change in going from A to B and an appropriate δ may be defined for each⁽⁴⁾. The interface and therefore δ may refer to a molecular or

Fig. 4. Non-uniform patch landscape around particles encouraging easy pathways, a and difficult ones, b through composite via matrix or particle networks

ion species or to an electron concentration. In a dielectric context it might refer to the electric field, the dielectric permittivity or to an optical parameter. Sometimes an integral interface property will be of interest, for example the interface capacitance, its mechanical tension, colour or reflectivity.

It should be emphasised that the interface is not solely defined by its nanometric thickness δ but is much more extensive in its lateral dimensions surrounding the filler particle as Figs. 2 and 3 for interface volume and area indicate. The chosen property for which δ is defined is unlikely to be uniform over this lateral dimension however, so that the interface becomes a landscape of patches, each perhaps only of nanometric area. This can set up preferred pathways through the matrix between the particles (Fig. 4). Patches can be nanometric in area and result in highly localised physical and chemical activity and there can be further interfacial boundaries between them which may change over time.

The situation of preferred localized pathways becomes recognizable in another familiar form for a composite with an oblate particle with an aspect ratio in which c tends to zero. The result is a plane surface of infinite extent but patchy properties in contact with a polymer matrix. The microphysics of contacts between macroscopic electrodes and polymers has been reviewed⁽⁶⁾ and many of the mechanisms invoked there will operate in nano-particle-polymer composites.

The intensity and distribution of any chosen interfacial property depends on the local collective action of atomic and molecular forces and how they change in passing from particle to matrix (A to B) over the distance δ . The forces are firstly the short-range hard core ones arising from overlap of the electron clouds and associated with covalent bonding and secondly the electrical ones giving rise to unipolar and dipole interactions. The dipole-related polarization forces are known collectively as van der Waals forces and will give rise to attraction between the elements of the composite system.

Unipolar charge and its distribution are important in determining the behaviour of composites. The charge can arise in the nanometric particle phase A in several ways, as ionised donor or acceptor states or as adsorbed ions in the case of insulators or as surface charge in the case of metals. Such charge may appear particularly during the composite formation stage, for example by

Fig. 5. The Stern-Gouy-Chapman counter charge layer in the interface outside a particle A shown charged positively; The potential $\psi(r)$, field $E(r)$ and counter charge concentration $\rho(r)$ decrease with distance r from the particle surface

frictional charging during a blending stage when strong shearing forces are frequently used or electrolytically when a solvent route is used. Specific cases of frictional charging depending on the triboelectric effect have been suggested by Tanaka et al.⁽⁵⁾ who give an appropriate triboelectric series for materials of interest. In many situations it would not be sensible to use a simple central ion model for the particle A but to consider that the charge resides in its surface. The interface with B then accommodates the counter-charges which represent the solvating electrical response of the polymer matrix and is usually described in terms of the Stern / Gouy-Chapman double layer model as illustrated in Fig. 5. It is composed of a part immediately adjacent to the surface of A, the compact Stern layer and a more distant diffuse part, the Gouy-Chapman layer. Many authors have described the situation in detail. A brief statement is given in Ref. (4). The field is high in the Stern layer and processes occurring there are regulated by specific short-range interactions. The Gouy-Chapman layer consists of space charge distributed according to a combination of the Poisson equation and the Boltzmann law.

The importance of the diffuse space charge layer surrounding each particle is that it provides a repulsive force between them, which will counter the van der Waals attraction during the preparation stage and encourage dispersion of the particles in the composite. The repulsion is not due to electrostatic interaction however but to the generation of a repulsive osmotic pressure to maintain the configurational entropy of the overlapping diffuse layers. The result of the combination of forces is that the system can be stabilised at some inter-particle spacing which is the basis of the well-known DLVO theory of colloid stability.

In many practical nano-composite situations, nano-particle equality is not always achieved especially when surface-active

agents are employed. Neither the structure of the nanoparticle nor uniformity over its surface can be assured. A recent review⁽⁷⁾ has considered the interaction between dissimilar particles with correspondingly different Stern and Gouy-Chapman layers in which so-called regulation (adjustment of charge or potential) occurs as the distance of separation is reduced. This has emphasised the role of the Stern layers and thus the particle charge in regulation and has shown that a transition from long-range repulsion to short-range attraction can occur without involving van der Waals forces.

Surface heterogeneity in terms of a three-dimensional surface topology or non-uniform charge distribution in the Stern layer has been discussed by Zembala⁽⁸⁾ with reference to electrokinetic phenomena (electrophoresis, electro-osmosis and streaming current) generated when relative movement between a solid particle and a surrounding liquid matrix distorts the interface; a situation likely to arise during any mixing process in nano-composite preparation.

Whether prepared from a melt or a solution phase, it may be expected that the charge distribution established about the particles will tend to be retained in the solid composite albeit in a less mobile form and will then be important in determining the properties of the composite. When the matrix phase is polymeric, further features are present which will affect the interface properties.

The first feature is that the particle will influence the free movement of the adjacent polymer chains. In the bulk matrix, free movement and thus the sphere of influence of the chain will be characterised by a persistence length or radius of gyration R_g which is likely to be of the order of 50 nm. Even if the polymer segments make only weak bonds with the surface of the filler particles, a reduction in entropy will result from the distortion and restriction of polymer chain conformations there. The interaction is likely to be enhanced when the nanoparticle surface contour scales appropriately with the polymer segment conformation⁽⁹⁾. Local crystallinity, cross-link density and flexibility will be changed⁽¹⁰⁾. This alone will lead to interface properties being different from those of the bulk polymer matrix. Any tethering of the chains to the particles by organophilic or compatibility agents will enhance these effects. Since R_g and therefore the range of the interface δ can be large, interface zones can begin to overlap at relatively low filler concentrations to produce changes in overall mechanical, thermal and electrical properties⁽¹⁰⁾.

The second feature is that the polymer will respond to the presence of the double layer space charge. The charges making up this layer will either be those of foreign ions which were present adventitiously during preparation or electrons and holes. Both sets will become trapped and localized by a polarization response from the polymer (the polaron state) at the interface⁽¹¹⁾. The Stern and Gouy-Chapman layers are overwhelmingly of one sign of charge (counter to that of the particle) and therefore self-repulsive but locked into the polymer network by the polaron response at the trap sites of the polymer. The polymer takes on some of the features of a polyelectrolyte of which the electrostatic contribution to the persistence length (and therefore R_g) has been considered by Le Bret⁽¹²⁾ and others. The overall effect is to influence polymer properties such as conformational entropy, local elasticity and free volume and to make the chains stiffer. The importance of these interfacial polymer-bound charge states in influencing conduction and breakdown will be considered in Section 5.2.

In a mobile phase during formation of the composite the approach of two particles is likely to require distortion of the intervening polymer chains and their counter charge atmospheres and some reduction of entropy while still beyond the range of DLVO forces. This will encourage particle repulsion, which will be enhanced if there is specific binding between polymer and particle. On the other hand weak binding and strong interaction between the polymer chains, possibly via cross-linking processes, will encourage encapsulation of particle clusters in the polymer matrix possibly to the detriment of the composite.

There have been a number of recent reports, which develop these ideas. Evmenenko et al⁽¹³⁾ describe conformational rearrangements in the interfacial region between polydimethylsiloxane and hydroxylated silica surfaces and enumerate the various 'entropic' forces related to polymer configurational confinement at surfaces. Immobilized layers of reduced density are formed because the drive to increase configurational entropy causes the polymer to partially leave the surface, a process of 'entropic repulsion' which may take long times to become established.

There is considerable, but inconsistent, literature concerning micro- and nano-composites of layered silicates (clays) with polyethylene. Phase-separated, intercalated and exfoliated morphologies are possible depending on the interaction between the polymer and the silicate stacks. The importance of miscibility in determining the morphology has been demonstrated recently by Chrissopoulou et al⁽¹⁴⁾ employing polymeric surfactants and compatibilizers to influence the interaction between the polymer and the surface of the silicate particle. Exfoliated silicate platelets, 1 nm thick and 100 nm in diameter are oblate particles with very low aspect ratios and thus large surface areas and interface volumes, Figs 2 and 3. It is shown that the morphologies of these nano-composites can be controlled by employing appropriate surface-active additives and the viscoelasticity changed from liquid to solid-like as the structure changes from phase-separated to intercalated and exfoliated inter-connected or percolated forms.

The effect of percolation on the viscoelasticity of nano-composites is also emphasised by work on multi-walled carbon nanotubes in polyethylene terephthalate⁽¹⁵⁾. Unlike the highly oblate silicate platelet the carbon nanotube is prolate in form with a high aspect ratio of $\sim 10^3$, yet, like the silicate system has a large surface and interface volume in the composite form. With increased nanotube loading transition from liquid-like to solid-like viscoelasticity occurs with a low percolation threshold of 0.6 wt %. Such a low threshold, indicative of inter-connectivity, suggests a large interface volume of modified, less viscous polymer in keeping with the discussion above. The authors suggest that local crystallization of the polymer and restricted chain relaxation occurs in the interfaces. They also find a 0.9 wt % threshold for a transition from an electrically insulating to a conductive composite.

4. Mechanical Macroscopic Properties of Composites

The existence of a significant interface volume in the nano-composite, especially at extreme filler aspect ratios, with properties different from the matrix polymer it replaces will influence important macroscopic properties of the composite. Whereas in the bulk matrix the polymer chains are free to minimise conformational energy and maximise entropy,

interaction with the filler surfaces restricts this freedom and induces a pseudo-crystallinity. As a result the thermal conductivity of the composite increases⁽¹⁰⁾. This is in agreement with the fact that the thermal conductivity of crystalline polymers is greater than that of amorphous ones and increases as the temperature is lowered through the glass transition temperature T_g . The raising of T_g for nano-composites is to be expected from an increase in an effective local crystallinity.

In a similar manner, when interface characteristics become dominant the composite can exhibit changed viscoelastic moduli or, as in the case of highly cross-linked polyimide, an increase in durability and strength to failure⁽¹⁰⁾. As will be discussed below, the changes induced in the mechanical properties could have a direct influence on electrical strength.

5. Electrical Macroscopic Properties of Composites

From the discussion so far it will be clear that the electrical properties of nano-composites are likely to be complex and subtle. Moreover the electrical properties of the interfaces will have a prominent if not dominant role to play. Roy et al⁽¹⁶⁾ have given a valuable discussion of these factors in relation to silica-polyethylene composites. Two aspects may be distinguished and will be discussed separately below. They are the dielectric response generally measured at low fields and over a range of frequencies, which is determined by local properties of the particle/matrix pair and the insulating/conductive property at high fields and involving long-range charge transport through the particle-matrix system. The extensive nature of the latter requiring particle-matrix interaction invites comparison with the mechanical properties mentioned above.

5.1 Dielectric Permittivity The study of the effective frequency-dependent macroscopic dielectric permittivity $\bar{\epsilon}_c(\omega)$ of composite materials has an extensive bibliography⁽¹⁷⁾. It has been based on the premise that dielectric materials, especially those in common use, are unlikely to be pure single phases but will contain two, or sometimes more, discrete constituents or phases with different permittivities. The starting point has been the Maxwell-Wagner model for spherical non-interacting particles with a complex frequency, dependent permittivity $\bar{\epsilon}_A(\omega)$ imbedded in a matrix of permittivity $\bar{\epsilon}_B(\omega)$. The model has been developed with increasing complexity by recognizing that $\bar{\epsilon}_c(\omega)$ will be additionally dependent on the shape of the particles and their orientation. Refs. (18) to (20) are examples of this extended treatment.

Traditionally the composite particles have been considered as microscopic but not nanoscopic elements. The implications of a shift to the latter have not always been appreciated. As has been demonstrated in Section 2 above, it will mean the presence and sometimes the dominance in terms of volume and surface area of the interface between particle and matrix. Consequently its dielectric properties will have to be considered and an apparent two-phase particle-matrix dielectric becomes a three-phase one. The effect of the presence of the interface as a dielectric of finite extent rather than a dimensionless, although polarizable, boundary is two-fold. Firstly the dielectric relaxation properties of the interface $\bar{\epsilon}_{AB}(\omega)$ may become unexpectedly prominent in the frequency characteristic of the permittivity $\bar{\epsilon}_c(\omega)$ of the composite. Secondly a three-part, rather than a two-part, model for $\bar{\epsilon}_c(\omega)$ with increased complexity will be required to represent it.

The emphasis of the review by Brosseau and Talbot⁽²¹⁾

concerning the behaviour of $\bar{\epsilon}_c(\omega)$ at GHz frequencies for nano-sized powder compacts of Ni, γFeO_2 , Co and ZnO in an epoxy resin binder is in this direction. They suggest that the effective continuous medium theory of Bruggeman frequently employed for such dielectric systems is not satisfactory because the likely interactions between the particles when close together are not taken into account. Microscopic local fields in the neighbourhood of particle interfaces are likely to differ considerably from bulk values. The close packing of particles explored by Brousseau and Talbot would encourage an extensive and relatively continuous interface network with dielectric properties different from those of the particles.

The calculations by Xue⁽²²⁾ of the effective dielectric constant of a range of ellipsoidal particles with interfacial shells of different permittivity and thickness are instructive. They highlight the very diverse array of values that are possible, especially when the particles are of low aspect ratio (thin discs) and the interface volume large as in Fig. 2.

A series of papers by Todd and co-workers is concerned with the properties of filler particle-polymer matrix composites used for encapsulation in high-frequency applications. The systems considered employ various chemical coupling agents to achieve particle-polymer matrix compatibility so that the polymer molecules become bonded or otherwise oriented at the particle-polymer matrix interface. The importance of the interface in determining the overall permittivity of the system is stressed in several ways. They emphasise for example that, for a given volume of filler, a smaller particle size creates a larger fraction of interface volume and greater polarization at the interface boundaries. As the filler volume fraction increases, so does that of the interface but non-linearly and a percolation threshold can be reached at which interfaces overlap⁽²³⁾. The presence of the interface creates a three-phase system with distinct permittivities for each phase. Depending on the dielectric constants of filler and matrix and the dielectric constant and extent of the interface, the effective dielectric constant exhibits an extreme behaviour as a fraction of filler concentration. The latest paper⁽²⁴⁾ reports the development of a model for the effective complex permittivity $\bar{\epsilon}_c(\omega)$ of the composite, taking account of a finite interface region which can have characteristics different from those of filler or matrix. The effect of the interface region can shift the permittivity significantly away from predictions based on standard two-phase mixture models and outside the previously established theoretical bounds (the Hashin-Shtrikman bounds) for these mixtures.

These papers are not specifically concerned with nanometric fillers, but since the interface will become more prominent as the filler particle shrinks to nanometric size so it can be expected that the role of the interface in determining the effective permittivities of nano-composites will become important. Indeed this appears to have been demonstrated for organophilic silicate-propylene nano-composites where a low frequency (0.1–30 kHz) relaxation process is found to increase in strength and move to higher frequencies with increased silicate content⁽²⁵⁾.

The dielectric properties of more complex composites consisting of metal-coated filler particles has been analysed by Bowler⁽²⁶⁾. The coating is assumed to be lossy and the particles to be spheroidal. It is shown how particle shape, orientation in the field and coating thickness can have a significant effect on the dielectric relaxation of the composite. The dielectric loss is sensitive to coating thickness and uniformity and to orientation of

Fig. 6. The dielectric situation for a filler particle/matrix as used by Youngs et al⁽²⁷⁾⁽²⁸⁾ showing additional permittivities; $\bar{\epsilon}_{\text{glass/Ti}}$, $\bar{\epsilon}_{\text{Ti/Alumina}}$ and $\bar{\epsilon}_{\text{Alumina/wax}}$ resulting from interface layers

the particles in the field.

Examples of these complex composites with filler particles consisting of micro-size glass bubbles coated with nanometric layers of tungsten and embedded in a paraffin wax matrix have been described by Youngs et al⁽²⁷⁾⁽²⁸⁾. Composites consisting of solid metal particles in an insulating matrix have been widely studied for application as screening materials at microwave frequencies. They show that employing a nanometric metal layer has a dramatic effect on the dielectric relaxation frequency of the composite, shifting it down by six decades when compared with that expected theoretically for a composite of solid tungsten particles of equivalent radius which would be 10^{16} Hz. It is suggested that the relaxation relates to interfacial polarization produced by conduction electrons in the metal shell and that this conductivity is reduced considerably because of a reduced mean free path in the thin tungsten layer which may also become discontinuous.

The particle is dielectrically complex as can be seen from Fig. 6, especially when a protective insulating coating of alumina is included. It becomes even more so when account is taken of double layers which, in equilibrium, will become established at the several interfaces, glass/tungsten, tungsten/alumina and alumina/wax. Each of these is likely to exhibit the characteristic charge separations and distributions of the Stern Gouy-Chapman model extending over nanometric distances (Section 3).

It is interesting to compare this situation with that analysed by Chew and Sen⁽²⁹⁾ for the conductive atmosphere surrounding a particle in an electrolyte which involves the presence of a double layer (Fig. 5). At low frequency charge carriers can be transferred efficiently around the interface leading to induced polarization and a large dipole moment. The effective permittivity of the suspension can now exceed that of the particles. Chew and Sen

emphasise the importance of the excess counter ion component of the diffuse double layer about the particle. In an applied field the counter ion current piles up charge at the polar ends of the particle which discharges into the surrounding matrix (electrolyte) by a process of diffusion as well as conduction. At low frequency the counter ion current can be strong and the diffusion cloud large. This leads to an out-of-phase dipole moment. This process weakens as the frequency increases. The consequence is a frequency-dependent dielectric response, which turns out to be much broader than a Debye response.

Acknowledging that the micro-bubbles in the experiments of Youngs et al are likely to become charged during composite preparation, the presence of double layers is not improbable and the Chew and Sen⁽²⁹⁾ model for dielectric relaxation then offers an alternative explanation for the relaxation frequency characteristics obtained.

The work by Arroyo et al⁽³⁰⁾ on the dielectric dispersion of colloidal suspensions is also relevant. Particular attention is paid to the dielectric contribution of the lateral conduction in the Stern layer region of the double layer around particles. The conclusion is that surface conductance in this layer increases the magnitude of the low frequency dielectric constant but has most influence when the diffuse layer thickness is least, namely when particles are small.

5.2 Insulating Properties The other major interest in nanometric polymer composites is their potential as insulating materials of improved performance, especially under high voltage conditions. There is evidence that they will exhibit lower conductivity, higher breakdown strengths and improved endurance especially when compared with micrometric composites. The rationale of this work is still somewhat obscure however and the development has not yet reached maturity. It is useful therefore to use the model developed in Section 2 above to consider some of the factors which will influence conduction and breakdown under high fields.

5.2.1 Conduction Unlike dielectric permittivity which focuses on the environment of a single nanometric filler particle, conduction is an extensive property involving charge transport through the particle-matrix system. Two situations arise in which the filler particle is either more or less conductive than the matrix. Gold or silica particles in an epoxy resin would be representative. Within the filler particle itself, charge transport will normally be limited to polarizing the particle and causing only a transient current. Any steady current will involve pathways through the polymer matrix and the nature and extent of these becomes a controlling feature of conduction in the composite. Four factors are involved as follows.

- (i) Whether the particles are conductors or insulators.
- (ii) The development of the double-layer distribution of localised charge in the interface spaces δ around the particles.
- (iii) The local change in the structural properties of the polymer consequent on the restriction in conformation induced by contact with the particle.
- (iv) The nature of the relatively uncharged 'bulk' polymer outside the interface regions, which provides connectivity through the composite.

These factors suggest a multi-layered model for the situation; a proposal discussed in some detail by Tanaka et al⁽⁵⁾ with particular reference to the partial discharge resistance of layered silicates in a polyamide matrix. They describe a three-layer model with a first

Fig. 7. The electron acceptor and negative ion energy states, E_A and donor and positive ion states, E_D of the polymer in the interface and matrix regions with respect to the isolated single molecule gas values A_g and I_g and the polarization energies P_i and P_m ($P_i < P_m$)

Fig. 8. Paths for itinerant charge; A: Path via interface double-layer with easy transfer at 1 and difficult transfer at 2; B: Path entirely in bulk matrix, C: Bulk matrix path impeded at X by adjoining interfaces

bonded layer, a second bound layer and a loose outer layer with a electrical double layer overlapping all three. Although three regions outside the particle can be identified in this way it might be misleading to consider that they have precise limits. On moving out from the particle the factors (ii) and (iii) above are highly inter-active and are merged smoothly into (iv).

In the case of insulating particles, the itinerant field-induced charge providing conduction between the electrodes will normally pass through the region of uncharged polymer (iv). Transport in this region, whether ionic (positive or negative) or electronic (electrons or holes), is likely to be by thermally activated resonance tunnelling between trapping states whose energy is largely influenced by local polarization of the polymer. These states and the hopping transport between them have been described on several occasions earlier^{(6)(11),(31)} and will not be considered in detail here.

It can be expected that polarization will be more facile in this region than in the bordering interface region because the latter is already populated with the entropically stable space charge of the surface double-layer and has additionally been made less flexible and thus less polarizable. Consequently polaron trapping states for itinerant charge in the two regions will be as shown in Fig. 7. Electron acceptor states and negative ion states will be at lower energy in the matrix bulk than in the interface regions and similarly donor (hole) and positive ion states will be at higher energies. Charge transfer from the matrix bulk into the interface will be much less probable than transfer the other way. The effect

of this on the current paths is illustrated in Fig. 8. Whilst charge might pass more readily around a particle via the double layer and be able to leave it to enter the bulk matrix, it will need to be replenished by charge entering from the bulk on the other side. According to the energy disposition of the polaron states shown in Fig. 7 this will be a more difficult step. Consequently the current will tend to be confined to the bulk polymer matrix. However another factor has to be considered. The bulk polymer path is constricted in the region of the nearest approach between particles which is $d-2\delta$. At the same time this constriction means that the interfaces are closer together there. Where d becomes less than 2δ the interfaces are brought into contact and a path entirely through the adjoining interfaces become possible. Fig. 1 indicates that an increase in the wt% or a reduction in particle size will reduce $d-2\delta$ and encourage this situation.

In practice $d-2\delta$ will have a distribution of values so that some paths will be effectively sealed to current flow via the bulk polymer but open to current via the interfaces. Some pathways of either sort may also become difficult because of their orientation in the field direction. It is easy to appreciate that quite complex percolation limits may exist for the two processes. Change of particle size or filler concentration will alter the two percolations in opposite sense.

There are many reports which confirm the dependence of conductivity on particle size and concentration. Which process is operative in each case may be difficult to determine. Fothergill et al⁽³²⁾, working on nanocomposites of TiO_2 , Al_2O_3 and ZnO well distributed in epoxy resin, concluded that conduction through overlapping interfacial zones was dominant. It would be interesting, using an appropriate plot similar to Fig. 1 to estimate the likely d and interface δ for these particular nanocomposites.

If the filler were not distributed uniformly it would be possible to have zones in the composite, perhaps of macroscopic size, exhibiting each form of conductivity. The local conductivity in a zone might act to reduce internal space charge without seriously affecting bulk conductivity, a point of view advanced by Nelson et al⁽³³⁾. The situation becomes much more complex if spheroidal particles are involved. Cao et al⁽³⁴⁾ have shown how layered silicate composites would have strongly anisotropic electrical and thermal properties. This would be true whatever the mode of conductivity.

If the filler particles are more conductive than the matrix polymer then a different set of conditions determine the overall conductivity of the composite. The natural paths will be through the particles and across the interfacial and bulk matrix polymer between them. The current in the particles will be electronic (electrons or holes) and continuity will require their injection and ejection at the polarized boundaries of the particles with the interfaces and transport through the intervening interface and bulk polymer over the shortest distance d (Fig. 9). Transport in this gap where the field will be high is likely to be by field-assisted resonance hopping since in most cases d is likely to be several nanometres and too great for direct tunnelling. An increase in particle concentration F and/or a decrease in particle size will decrease d and increase the conductivity, (ultimately below a percolation limit). These effects have been well illustrated by Hong et al⁽³⁵⁾ for a composite of the semiconductor ZnO in LDPE.

The generation of limited zones of conduction by the introduction of filler particles, whether more or less conductive than the matrix, will under alternating field conditions give rise to

Fig. 9. Current path in composite with conducting particles

Fig. 10. (a) Limited discrete breakdown paths in a composite with insulating particles; Path elements such as XX are not in the field direction; Cracks such as CC could develop and subsequent partial discharges in them lead to macroscopic inter-connection: (b) Breakdown path in a composite with conductive particles; The path is through the particles and across the matrix at points where the inter-particle spacing d is a minimum

a conductive loss process. The $\tan \delta$ of this would be an important indicator of the nature of the composite and the role of the filler particles.

5.2.2 Space charge There are a number of reports⁽⁹⁾⁽³⁶⁾⁽³⁷⁾ that space charge as determined by PEA methods is much less in insulating nano-composites. Space charge is usually detected in single-phase polymeric matrices in the neighbourhood of electrodes, either as injected and trapped homocharge or as heterocharge transported to and collecting outside a blocking electrode. The confinement of current to channels defined by the presence of particles, as suggested above, and the consequent localisation of the injection or ejection processes at the terminations of these at the electrodes could lead to localised space charge patches of nanometric size. The average space charge density over a macroscopic electrode cross-section might then be small and much less than that generated at electrodes in a single-phase polymer.

5.2.3 Breakdown Electrical breakdown in composites will require the development of a path of field-induced structural failure across the sample and will be fundamentally different for composites with insulating or conducting particles. With insulating particles, the path may be expected to avoid the particles and as a result will be as shown for spherical particles in Fig.10(a). The elements of the path such as XX in avoiding the particles will not

always be along the field line. In nanometric composites the path elements will themselves be of nanometric dimension, at least for the usual particle concentrations employed. When the particles are conductive, breakdown will be as in Fig.10(b) with the path elements in the matrix between particles.

In both cases breakdown across a macroscopic sample will require a progression of limited breakdowns through the path elements but the progression is unlikely to be continuous, as it might be for a single-phase insulator in which a tree forms, but stepped irregularly in space and probably in time.

The nature of the breakdown mechanism in discrete path elements is open to speculation but it seems unlikely that processes involving charge multiplication by collision ionization will be efficient in such small volumes of limited extension. It is suggested instead that the mechanism outlined by Jones et al⁽³¹⁾ might be generally applicable to polymeric composites, perhaps weakened structurally by the presence of particles. The mechanism involves the mechanical forces generated in a direction transverse to the electric field overcoming the local structural forces of the insulation and so causing a sub-microscopic void or crack to develop in the field direction, perhaps preceded by a craze development. Crack development would be limited by the confines of the element in the composite and would depend on its orientation with respect to the field. Cracks would be naturally discretised (Fig. 10) and their connection over greater distances, perhaps in a zigzag manner might be expected but would take time to develop. The outcome would be a bush-like development with much more branching than for a conventional tree in a single-phase insulator. It is useful to note that in a review in 1996 by Varlow and Auckland⁽³⁸⁾ concluded that mechanical effects dominate the conventional treeing process and that localised mechanical failure on a molecular scale is associated with it.

If field-generated mechanical stresses are present the local structural response in the path element becomes important. The stresses will be tensions transverse to the field direction⁽³¹⁾ causing mechanical strains in these same transverse directions. Thus if a path element lies in the field direction, the strains will tend to produce expansion in the cross-section opening sub-microscopic cracks along the field line.

Each path element will consist of a central core of matrix bounded by interface regions which can be expected to be less flexible and elastic than the core, especially when organophilic agents have been employed. Under the tension produced by the field the induced crack is likely therefore to be located in the central matrix. At the same time however the double-layer in the interface, subjected to a lateral field, will polarise around the particle. If the concentration of particles is sufficient or the particle radius small enough so that $d-\delta$ approaches zero, the path in the matrix is effectively shorted by the lateral interface path and a matrix crack in that element is avoided. The likelihood of crack development through bulk matrix declines and the more conductive lateral interface path takes over. Nelson et al⁽³⁹⁾ report experiments relevant to this argument, finding that the electric strength of 38 nm TiO_2 particles in epoxy resin decreased as the concentration F increased from 10 to 40%. As can be judged from Fig.1 for the ideal case, the inter-particle spacing for 40 nm particles will come down from 120 to 35 nm as F increases from 10 to 40%. This would mean the gradual exclusion of matrix material from the path at minimum cross-section and the onset of

lateral conduction via interfaces if the total interface thickness 2δ was about 35 nm, which is reasonable.

The delaying action provided by the discrete structure of the composite is reflected in the work of Ding and Varlow⁽⁴⁰⁾ who have reported that the addition of nanometric ZnO particles to epoxy resin improves the resistance to tree channel advance from a point electrode and increases the time to breakdown. They suggest that the creation of sub-microscopic, i.e. nanometric voids around the particles, ahead of the advancing tree channel, blunts the tip and slows the advance. They do not take account particularly of the likely morphology of the composite created by the particles, nor that the sub-microvoids might be created, or at least enhanced, by the fields at the head of the trees.

A closely related model has been suggested by Imai et al⁽⁴¹⁾ for treeing in a composite of silicate particles in epoxy resin. The trees have multiple, simultaneously developing, branches, which can deviate considerably from the field line. They find that trees develop at 5.2 V/mm for the base resin but do not occur until a field of 7.8 kV/mm in the composite and then develop more slowly.

In practical cases, such as that described in Ref. (41), the particles are not always spherical nor as uniformly distributed as intended. These factors will have a marked influence on the path elements and their distribution. In the case of the silicate-polymer composites for example, the particles are quasi-oblate spheroids intercalated with the polymer and their orientation with respect to the field becomes crucial. Extreme cases can be distinguished. For an orientation in which the axis of rotation is in the field direction, the matrix and interface paths are largely parallel and in the field direction. The interface path then tends to short out the matrix. On the other hand, when the axis of rotation is at right angles to the field, the matrix and interface paths are normal to the field and conduction along the interface is not important. The matrix path is highly convoluted and the continuing path in the field direction is devious. This orientation should result in low conductivity and high strength.

5.2.4 Partial discharges If breakdown in a composite consists of a series of discrete, independent and largely nanometric failures, each failed path element could ultimately develop to become the site of an independent partial discharge. Partial discharge phenomena in composites have been frequently reported. Nelson⁽⁴²⁾ and Tanaka⁽⁵⁾ have discussed the situation and concluded that polymer nano-composites are generally more resistant to partial discharge than either the base resin or the micro-composite. It would seem that partial discharge phenomena in insulating nanoparticle composites is a natural outcome of the discrete path element model.

If the particles are conductive the preferred breakdown path will seek to go through the particles and cross between them in directions normal to their surfaces as in Fig. 10b. The inter-particle space is now involved differently and the preferred path is likely to be in a normal direction through the interfaces and across the intervening matrix at the minimum spacing d . These paths will be of nanometric length and subjected to high fields and are likely to fail by an electro-mechanical process of crack generation⁽³¹⁾ possibly preceded by high field conduction and ending in a partial discharge. For a fixed particle size, increasing the concentration F will lower the strength of each path since d and $d-\delta$ will be reduced. Likewise reducing the particle size r for a fixed concentration F will also cause a decrease in d but at the

same time cause an increase in the concentration of inter-particle paths.

Many of the conduction and breakdown mechanisms discussed above will have relevance for the conduction and breakdown of nanocomposite surfaces but this complex topic, of which there is a growing literature, will not be considered here

6. Prospects

The increased attention being paid to nano-composites and the expectation that it will lead to greatly improved materials marks a considerable change in the dielectric and insulation scene. Until the recent past there has been a general understanding that improvement in electrical qualities will come about by improvement in purity and the close control of likely impurities. Polymer nanocomposites disprove that assumption and thereby open up new vistas.

The simple, essentially geometric, analysis given in Section 2 provides a useful background for understanding the features introduced by nanometric particles but it highlights many practical questions. Particles are more likely to be approximately spheroidal than spherical, are likely to be poorly oriented and not uniformly distributed on the nanometric scale. All these factors have a profound influence on the local nanometric geometry and the associated electrical properties. Improvement in the control of these factors will be important for consistent performance.

Methods to obtain ordered nano-structures employing template structures have been reviewed by Hultheen and Martin⁽⁴³⁾. An example of their use is the dispersion of platinum nano-particles in nanoporous carbon⁽⁴⁴⁾. So far these methods are not on a scale that would be required for application in nano-electrical engineering. Electric field-assisted assembly and such processes as dielectrophoresis could be valuable in ordering structures during composite assembly and could be applied macroscopically. Extrusion is likely to be helpful in the ordering of prolate spheroidal particles while extension of the Langmuir-Blodgett and related self-ordering techniques could be used to produce layered nano-structures. Cao et al⁽³⁴⁾, outlining the future of nano-dielectrics in the electrical power industry, go forward to this nano-structure phase where systems will be specifically designed to have appropriate dielectric properties.

It is clear that the nanometric properties of the particle-polymer interface are vital in determining electrical, mechanical, optical and chemical properties of the composites on the macro scale. These need to be understood more deeply than they are at present. The stability of the interface will be essential for maintaining the properties of the composite in the long term. Under thermal and electrical cycling (ageing) especially when impurities may be present or are able to diffuse into the composite, the interface properties may change considerably. In particular water and oxygen may be expected to be present in many practical situations and both are known to have significant interface-altering properties. The study of single nanometric particle-polymer interfaces in detail by modern surface scanning techniques would be valuable and should be emphasised.

It should be noted that Tanaka et al⁽⁵⁾ in 2004 provided an extensive summary of published work on polymer nano-composites in a variety of dielectric and insulating environments and concluded that much needed to be done to reconcile the diverse and sometimes contradictory results that had been obtained. They suggested that, until the interface or

interaction zone between particle and polymer is better understood, many of the results would remain inexplicable.

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