

Role of Interfaces in Enhancing Electromechanical Properties of Nanocomposites

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Abstract- Aim of this study is to analyze formation of interfaces and their role in enhancing properties of a composite. The study also covers discussion on classical approach and how this approach fails to describe nanocomposite system. In a nanocomposite, Van Der Waal interactions are short ranged strong forces, which help in strong adhesion between polymer and filler giving good mechanical properties. Enhancement of interfacial properties of the composite depends on many factors like shape, size, concentration, type of filler material etc. Mathematical analysis has been done taking these factors in consideration. It has been found that when filler particle size is reduced below 5nm, increment rate of interfacial volume fraction increases five times and when particle size is further reduced to 2nm or below, this rate of increment further goes up by five times.

Keywords: double layer, interface, interfacial volume fraction, nanocomposites, and short range forces.

I. INTRODUCTION

Nanotechnology covers a wide range of technologies which can measure, manipulate, or incorporate materials with at least one dimension between approx. 1 and 100 nanometres (nm) as defined by the American Society of Testing materials. Even within the nanometric range, when nanofillers of same material but different sizes are added into the matrix, the resulting composite material exhibits different mechanical, thermal, optical and electrical properties. For example, quantum dots emit different colours according to their sizes. Thus, particle size plays a very important role in determining properties of the composite. Polymer based nano composites (PNCs) find application in many fields as they show enhanced mechanical properties due to strong interaction between filler particles and polymer matrix particles. They also exhibit good chemical properties due to large surface to volume ratio on adding nanofillers. Various materials are used as nanofillers depending on the application. For example, carbon nanotubes, due to their good electrical conductivity, are used for low cost solar cells, electronics and anti-static composite materials. As TiO_2 fillers have large band gap, they find application for ultraviolet protection, photo catalyst, photovoltaic and sensing. Nanoclay combined with nylon is used to increase hardness of plastic polymer. Silver nanoparticles are good as antibacterial agent; Gold nanoparticles with diameter under 5nm are used as catalyst for several chemical reactions; cerium oxide reduces the exhaust of harmful emissions from diesel fuel [1]. In this paper role of

interface in determining the properties of the nanocomposite has been thoroughly studied.

II. FORMATION OF INTERFACE AROUND NANOFILLERS

When nano fillers are added into the matrix, their uniform dispersion is very important to achieve desired properties. Process of annealing is usually preferred for getting nanofillers uniformly dispersed into the composite. After dispersion, interfaces are formed around each filler particle giving double layer formation (Fig.1). The interface formed is a set of charged layers that determine the dielectric characteristics of the interface.

III. ROLE OF INTERFACE IN ENHANCING THE ELECTRICAL AND MECHANICAL PROPERTIES OF THE COMPOSITE

The interfaces formed by adding filler particles into the matrix play an important role and affect the bulk properties of the material, especially when filler concentration is sufficient to allow percolation [2]. For micro filler particles, very high concentration of filler is required for such situation. Interfaces formed have both active and passive control over the properties of the material and have both electrostrictive and piezoelectric characteristics. When nanofillers are added to a matrix, voltage endurance and breakdown strength of the composite so formed is enhanced up to a certain concentration of filler loading only and on further loading, these properties show reversal of behaviour. For example, in epoxy- SiO_2 composite, these properties get reversed after 0.4wt% of filler loading. [3]. Surrounding temperature also affects the properties of a nanocomposite. Change in these properties is generally dominant at room temperature and below. For example, electrolyte with 10 wt.% SiO_2 filler has maximum ionic conductivity of 2.3×10^{-5} S/cm at 25°C [4].

Effective elastic properties of the electro elastic material mixed with filler particles, having macroscopically inhomogeneous systems made of different homogeneous substances, can be established only when the micro geometry of the composite is known precisely. Classically, at the macroscopic levels, position dependent local elastic stiffness tensor $C(\vec{r})$ (of a complex matrix in a viscoelastic material) of a two component composite, made of homogeneous materials

of stiffness tensors C_1 and C_2 can be written with the help

$$C(\vec{r}) = C_2 + \phi(\vec{r})(C_1 - C_2) = C_2 + \phi\delta C. \quad (1)$$

where, $\phi(\vec{r}) = \begin{cases} 1, \vec{r} \text{ inside } C_1 \text{ material} \\ 0, \vec{r} \text{ outside } C_1 \text{ material} \end{cases}$

At macroscopic scale (Fig.2) permittivity of transition layer $\epsilon(z)$ (interface between two dielectrics of permittivity ϵ_1, ϵ_2) is given by:

$$\epsilon(z) = \epsilon_1 + (\epsilon_2 - \epsilon_1)S(z). \quad (2)$$

of a step function ϕ as

where, the grading function $S(z)$, for a layer of thickness z_t is given by [5],

$$S(z) = \begin{cases} 0, \text{ for } z < -z_t \\ (z + z_t) / z_t, \text{ for } -z_t < z < 0 \\ 1, \text{ for } z > 0 \end{cases}$$

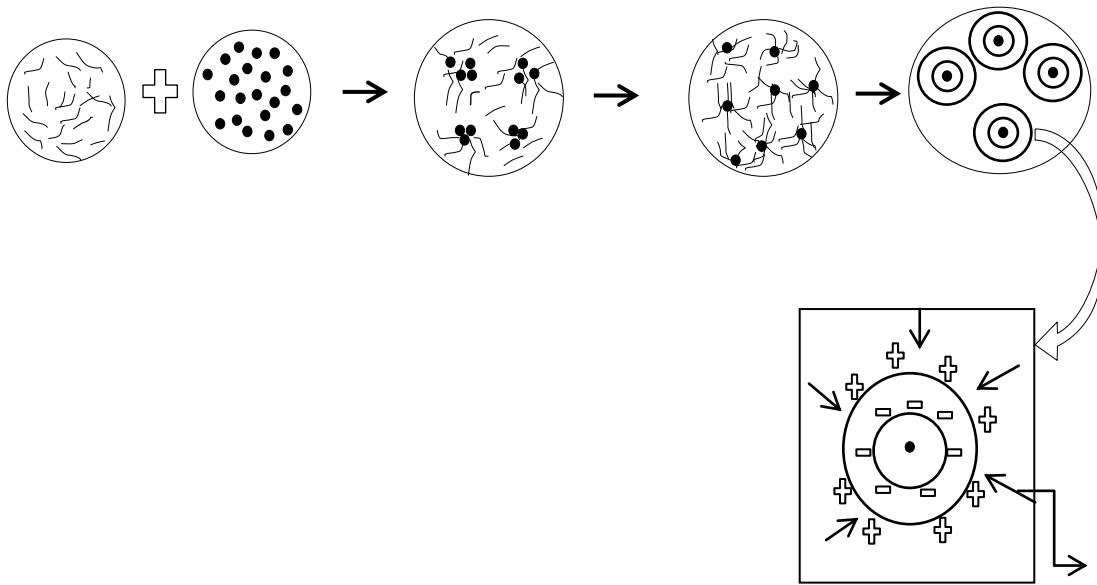


Fig.1. Schematic diagram showing dispersion of nanofillers in the matrix and double layer formation around it

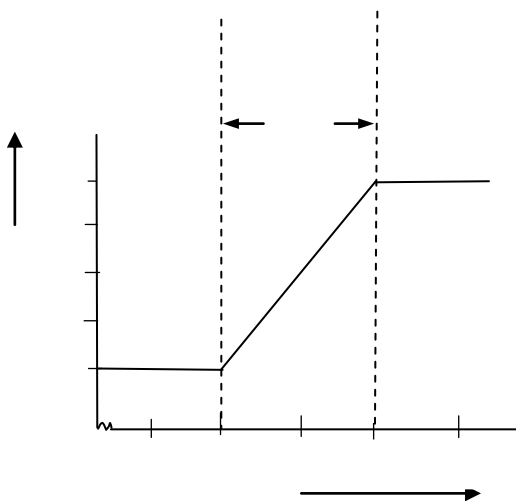


Fig.2. Spatial variation of the dielectric constant in the transition layer between two dielectrics.

A. INTERMOLECULAR FORCES IN THE INTERACTION ZONE (INTERFACIAL REGION)

There are a number of short range, long range, known and unknown interaction forces acting at the interface between the filler particles and the matrix particles. Quantum mechanical forces between the filler particle and the matrix particle are due to considerable overlapping of two wave functions associated with the two interacting particles, leading to indistinguishable electrons which are not associated with the individual atoms. For the electrically neutral interacting particles, steric forces are absent and the short range attractive Vander Waals force is generally represented by Lennard - Jones potential (Fig.3) and is given by:

$$\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^6} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

$$\sigma = \left(\frac{A}{B} \right)^{\frac{1}{6}}, \epsilon = \frac{B^2}{4A} \text{ or where, } A = 4\epsilon\sigma^{12} \text{ and } B = 4\epsilon\sigma^6$$

(3)

Where,

ϵ is the characteristic energy of interaction between the interacting particles,

r is the distance between the particles,

σ is the collision diameter i.e. at $r < \sigma$, $\phi = 0$ [6].

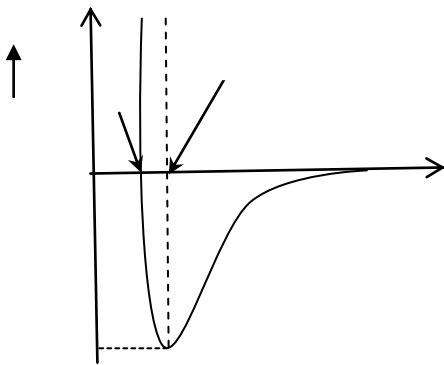


Fig.3. Lennard-Jones Potential curve

Distance dependent Van Der Waals interactions are very strong and short ranged (effective up to few nanometer ranges) for nanofiller particles interacting with the matrix particle. Whereas, macroscopic Van Der Waals interactions are of long range with high retardation effect for distances more than 100 Angstrom. At macroscopic level, the energy of adhesion between two surfaces, with surface energies γ_1 and γ_2 , is the energy per unit area and required to separate two bodies in contact and is given in terms of interfacial energy γ_{12} as

$$W = 2\gamma_{12}; \gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2}.$$

As short range forces exist at the nanometric interface, the effective thickness may always be in nanometric dimension or even less than 10 nm and the physical properties vary asymptotically at the interface. The modified forces at the interface are responsible for exerting interfacial tension due to strong bonding of nanofillers with the matrix and the strong bondings are possible only when the interparticle separation is few nanometers as predicted by Lennard Jones potential model. That is why the nanofillers enhance the mechanical strength up to a large extent. On introduction of large amount of filler particles (more than the critical value), the interfaces would be overlapped even after uniform distribution of filler particles and it will lead to distortion creating adverse effects. As the size of filler

particle decreases from millimetric to nanometric range, the interfaces increasingly dominate the bulk properties.

B. LOSSES IN COMPOSITES

Variation of tan delta at different particle concentrations has been plotted using the data [7]. Frequency considered for the study is 10^5 Hz.

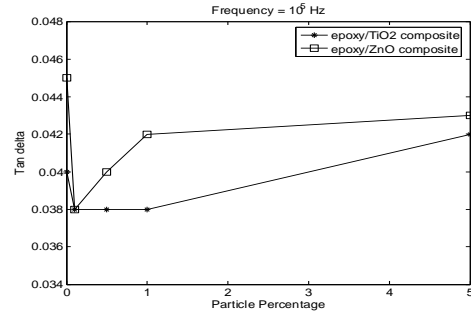


Fig.4. Graph showing variation of tan delta values of epoxy-TiO₂ and epoxy-ZnO composites for different filler particle percentage at 10⁵ Hz.

In case of epoxy-TiO₂ nanocomposite (Fig.4), tan delta value decreases sharply up to 0.1vol.% of filler and thereafter remains constant till 1% concentration. After 1vol.% filler concentration, there is a rise in tan delta value and it is observed that losses are higher as compared to pure material at 5vol.% filler concentration. Similarly, for epoxy-ZnO nanocomposite (Fig.4), sharp reduction in tan delta values is observed up to 0.1vol. % concentration but thereafter sharp increase is noted up to 1vol.% concentration. After 1vol.% concentration, rise in very minimal as compared to steep rise in case of TiO₂. Further, in ZnO nanocomposite, tan delta values are always less than pure material values for all filler concentrations up to 5vol. %. Thus, it can be said that on adding ZnO nanofillers to the epoxy material losses are reduced.

V. SUBSTANTIAL ENHANCEMENT OF INTERFACE MATRIX VOLUME RATIO

When nanoparticles are added to a matrix, substantial increase in interfacial volume fraction ratio is observed, which leads to enhanced properties of the nanocomposites. Filler particles can either be of regular or irregular shape. Two regular shapes (sphere and disc) have been considered and calculations have been done for increase in interfacial volume fraction ratio in respect of two concentrations (vol. %) of filler. Interface thickness has been kept constant in all calculations.

In both the graphs (Fig. 5 and Fig. 6), variation of interfacial volume fraction with particle size has been plotted at two concentrations (6 vol. % & 8 vol. %) of filler particles. The rate of increase in interfacial volume fraction is five times when particle size is reduced below 5nm and this rate further goes up by five times when particle size is reduced below 2nm. Further, it is observed that interfacial volume fraction is 6.67 times in case of

disc shaped particle as compared to sphere shaped particle for same size and concentration of filler particles.

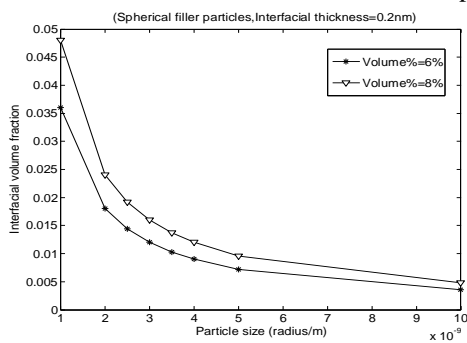


Fig.5. Plot between interfacial volume fraction and size of sphere shaped particles for two filler concentrations at 0.2nm interfacial thickness.

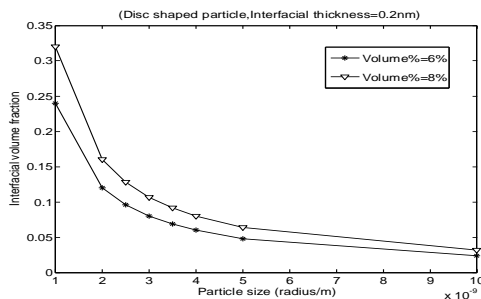


Fig.6. Plot between interfacial volume fraction and size of disc shaped filler particles for two filler concentrations at 0.2nm interfacial thickness.

VI. DISCUSSION AND CONCLUSION

Interfaces formed around nanoparticles in a composite are mainly responsible for enhancement of its properties. Even for low concentration of nanofillers, desired properties can be achieved, whereas for micro fillers comparatively large concentration is required to achieve the same results. Nanocomposites show good electrical, mechanical, optical, chemical, physical properties as the Van Der Waals interactions are very strong being short ranged. On the other hand, for macroscopic system these forces are long ranged with high retardation effect. Further, interfacial properties depend on many factors like shape, size, concentration, material etc. of filler particles. Nanocomposite with ZnO nanofillers shows less loss as compared to TiO₂ nanocomposite. We found that interfacial volume fraction increases substantially when particle size reduces below 5nm and this rate of increment goes further up when particle size is reduced below 2nm for spherical and disc shaped filler particles. It is also concluded that for disc shaped filler particle, interfacial volume fraction is 6.67 times as compared to sphere shaped particle for same size and concentration of filler.

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