

Interfacial Effects in Filled and Reinforced Polymeric Composites

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Abstract

Interfacial effect in polymeric composites have been studied extensively. This report deals mainly with the effects of interfacial space charge and interface structure. A model for the dynamic process of interfacial space charge accumulation is proposed. The new model might interpret some interface phenomena which is difficult to be explained in terms of traditional Maxwell-Wagner theory. An interface structure is also presented, by which the importance of surface treatment of glass Fiber for improving the properties of FRP could be well understood.

1. Introduction

Polymeric composites with fillers or reinforcements have been widely used for HV electrical insulation systems. In such composites, contact areas between polymer and inorganic Filters or glass fibers must necessarily exist, which we call "interfaces". Under electric stress, two interfacial phenomena may occur: according to interfacial polarization, in the contact area of two different dielectrics both permittivity and loss tangent of the composite may be increased, resulting in increase in dielectric losses; the electrical strength in interfaces may be lower than that of each component, resulting in a reduction of the breakdown strength and freeing stability. Interfaces often predominate over the entire electrical properties of the composites, therefore the investigation of interfacial effects is not only very interesting theoretically but also very important practically [1,2,3].

Interfacial phenomena in two layer dielectric systems have traditionally been interpreted in terms of a Maxwell-Wagner-Sillars(MWS) model, which assumes that only the conductivity and the permittivity of each dielectric dominate interfacial

effects, and the conductivity is constant. However, this assumption does not always hold. For example, some composites such as silica-epoxy resin and polyethylene (PE)-ethylenevinylacetate(EVA) demonstrate remarkable polarity dependence of conductivity, which can not be explained in terms of MWS model. Also, the thermally stimulated current (TSC) spectra of silica-epoxy resin and PE-EVA often show peaks which do not appear in the component single layers, indicating that carrier traps exist in the interfaces [4,5,6,7]. It is recognized that space charge accumulation in interfaces (i. e. interfacial space charge) is important for interfacial phenomena[8,9]. However, so far the accumulation process and the effects of the interfacial space charge have not been fully understood. The interfacial effects occurring in fiberglass reinforced polymer(FRP) are quite similar to those observed in filled polymer, excepting that in the presence of water, permittivity and loss tangent are distinctly increased. However, the main problem of FRP are the freeing and breakdown strength [1,3,10,11,12,13,14]. When applying electric stress, treeing and breakdown paths follow exclusively the reinforcing fibers in interface area.

Investigations show that surface coating of glass fibers, the so called "finish", is of main influence on the properties of FRP. Therefore, it can be assumed that the composition and the structure of interface layer have significant effects on the properties of composites, which have been reported in a few papers. This paper deals with some interfacial effects in filled and reinforced polymeric composites, especially concentrating on the interfacial space charge effects and the interface structure effects.

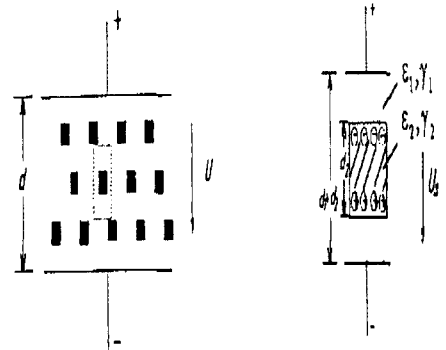
2. Effects of Interfacial Space Charge

Dynamic process of interfacial space charge accumulation

In polymeric composites with inorganic filler, polymer matrix is a continuous phase, while filler is a dispersed phase. The inorganic fillers may be crystalline or non-crystalline, whose particles take the shape of spheres, discs, or needles. But the filler particles often cluster and result in non-uniform or irregular shapes when dispersed in polymer matrix, especially at high filling concentration. Let it be supposed that in an idealized filled system filler particles take shape of cube and distribute in matrix uniformly (Figure 1 (a)), and a unit model involving one cube of particle is adopted for discussion of the process of interfacial charge formation (Figure 1(b)) [15,16]. In this paper the subscripts "1" represent for continuous phase—polymer, the subscripts "2" represent for dispersed phase—filler. Under electric stress the total effect of fillers is the summation of the responses of many such units. In general, $\epsilon_1 < \epsilon_2$ and $\gamma_1 \gg \gamma_2$, where ϵ_1 and ϵ_2 are the permittivities of polymer and filler, γ_1 and γ_2 are the conductivities of polymer and filler, respectively. When a dc voltage U is applied on the composite system, the voltage on the unit model is U_s , and

$$U_s = \frac{d_2}{V_{D2}d} U$$

where V_{D2} is the volume concentration of filler, d_2 is the thickness of filler particle, d is the total thickness of the composite in Figure 1 (a).



(a) Idealized filled system (b) Unit Model under electric stress

Figure 1. Model for discussion on interfacial space charge accumulation

According to Maxwell's two-layer model, the conduction current on two sides of interface are different, resulting in residual free charges at interface. However, interfacial effect is not always so simple. In fact, the interface involve a certain of volume. Experimental results show that carrier traps existing in the interface play the most important role in interfacial space charge formation. Also investigations indicate that the conductivity γ_2 is not a constant, but varies with the space charge density formed in interface. In filled polymeric composites such as EPR filled with silica, the impurity ions are considered as the main carriers in filler particles. Assuming that the positive ions accumulating in the interface near the negative electrode uniformly distribute with a density of σ (c / m^2), γ_2 can be expressed by

$$\gamma_2 = \left(N_2 - \frac{\sigma}{d_2} \right) \mu_2 \quad (1)$$

where N_2 is the volume density of ions in dielectric 2 (filler) at the voltage application time $t=0$, μ_2 is the mobility of ions.

Then space charges accumulate in interface at rate

$$\frac{d\sigma}{dt} = \gamma_2 E_2 - \gamma_1 E_1 \quad (2)$$

where E_1, E_2 are electric stresses in the matrix and filler, respectively, which can be found from boundary conditions. substituting the E_1, E_2 and equation (1) into equation (2), we have

$$\frac{d\sigma}{dt} = \frac{A\sigma^2 - B\sigma + C}{\varepsilon_1 d_2 + \varepsilon_2 d_1} \quad (3)$$

$$A = \mu_2 d_1 / d_2$$

$$B = \mu_2 \varepsilon_1 U_s / d_2 + N_2 \mu_2 d_1 + \gamma_1 d_2$$

where $C = U_s (N_2 \mu_2 \varepsilon_1 - \gamma_1 \varepsilon_2)$

The solution of equation (3) is

$$\sigma(t) = \frac{\sigma_1 \sigma_2 (1 - e^{-Rt})}{\sigma_1 - \sigma_2 e^{-Rt}} \quad (4)$$

where $R = (B^2 - 4AC)^{1/2}, \sigma_1 = \frac{B + (B^2 - 4AC)^{1/2}}{2A}$

and $\sigma_2 = \frac{B - (B^2 - 4AC)^{1/2}}{2A}$

σ increases with time over voltage application and finally reaches a saturated value, which is expressed as

$$\sigma_{\infty} = \sigma_2 \quad (5)$$

C, B are relevant with voltage U_s , which is proportional to U , then σ_{∞} can be expressed as a function of U , as shown in Figure 2.

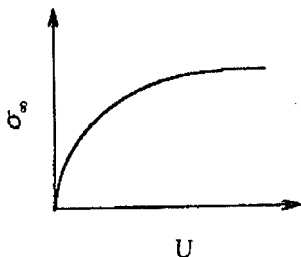


Figure 2. Variation of σ_{∞} with applied voltage

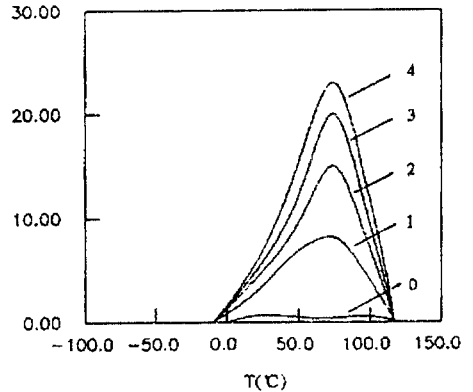


Figure 3. TSC of silica(10 phr) Filled EPDM (60 °C, 15mins. 0: unfilled, 500V; 1: filled, 500V; 2: filled 500V; 3: filled, 1.5KV; 4: filled, 2KV)

From the above analysis, it can be seen that space charges accumulate in interfaces gradually, and reaches a steady value which depends on the applied voltage.

TSC tests were conducted on cross linked EPDM samples filled with silica, as shown in Figure 3 to illustrate the existence of interfacial charges. A large current peak appeared at about 74 °C for filled sample. The peak is caused by the release of charges accumulated in interfaces under poling voltage and temperature. TSC magnitudes increased with increasing voltage. Calculation also indicates that the augments of released charges slowed down with increasing voltage, which is just similar to that shown in Figure 2. Therefore, the TSC results indicates that the theoretical analysis of the dynamic process of interfacial charge accumulation is reasonable.

Effects of interfacial space charge on dielectric properties

It can be seen from above that ionic charges accumulate in both interfaces of each cubic Filler particles in polymer matrix with equal quantity and opposite polarity. Then the particles can be regarded as polarons (μ_i).

Thus the polarization caused by interfacial charges is given by

$$P_0 = M\mu_i \quad (6)$$

where M is total amount of particles.

It can be derived that P_0 is relevant with σ_∞ as follows

$$P_0 = \sigma_\infty V_{D2} \quad (7)$$

Interfacial charging and discharging under alternative electric stress may produce a relaxation process with distributive relaxation time. At room temperature and low electric stress, the peak of loss tangent of interfacial relaxation will appear at ultralow frequency if tile relaxation has a long relaxation time. However, large loss tangent will be observed at power frequency when interfacial relaxation time is small. Analysis indicates that remarkable interfacial relaxation loss will be produced when γ_2 come to 10^{-9} s / m. Therefore, water absorption will aggravate this kind of harmful interfacial effect. Figure 4 shows how does loss tangent of EPDM samples filled with different type of Si-Os vary with filler concentration, and Figure 5 is the relation of volume conductivity with filler concentration.

From Figure 4 it can be seen that loss tangent of filled composites increased remarkably, while the correspondent cause for the increase can not be seen in Figure 5. In addition, loss tangent caused by conductance is given by

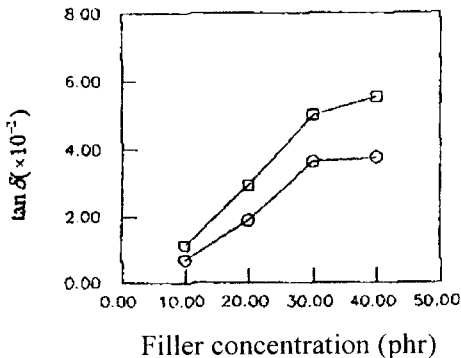


Figure 4. Relation of loss tangent with filler concentration

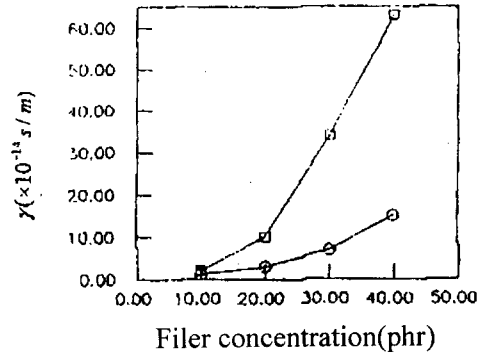


Figure 5. Relation of de volume conductivity with filler concentration

(□: filled with aerosol SiO₂, O: filled with precipitated SiO₂)

(phr: parts per hundred parts of rubber in weight)

$$\tan \delta_c = \frac{\gamma}{\omega \epsilon_0 \epsilon_r} = 1.8 \times 10^{10} \frac{\gamma}{f \epsilon_r}$$

ϵ_r is relative permittivity. Thus even γ reaches 10^{-12} s / m,

$$\tan \delta_c = 1.8 \times 10^{10} \frac{10^{-12}}{50 \times \epsilon_r} (10^{-4})$$

it is much smaller than the measured $\tan \delta$ (magnitude of order 10^{-2} therefore the large loss tangent in Figure 4 were not caused by conductance. It is probably From interfacial relaxation due to interfacial charges.

3. Effects of Interface Structure

In this section, we mainly deal with the effects of interface structure of FRP on dielectric and electrical properties.

The interface structure of FRP without treatment

FRP composites consist of two components, i. e. polymer matrix (for instance, epoxy resin) and reinforced material glass fiber). Glass fiber is an inorganic dielectric with many polar groups (for example, -OH, -NH₂), and possesses higher

surface energy (about five times higher than that of epoxy). Therefore, during process the glass fiber will absorb low molecule polar substances such as the moisture in epoxy, unsolidified epoxy resin, residual hardener and impurity ions. The moisture absorbed on glass fiber surface reacts with hardener (acid anhydride) producing free acid, which has polar groups such as $-COOH$ and is easily absorbed on the surface of glass fiber. At the same time, a certain number of alkaline metallic ions separated from the bulk exist on the surface of glass fiber. In addition, a certain number of cavities also were formed at the contact area between epoxy resin and glass fiber due to the poor binding. All of the substances on glass fiber surfaces constitute a low-density region, in which the molecular structures change gradually from glass fiber to epoxy resin. After curing of epoxy, this low density volume will form a fixed interface with a certain of volume, as shown in Figure 6(a). This interface has relatively large permittivity, loss tangent and conductivity due to the existence of moisture, impurity ions, low molecular substances and defects in it and the interfaces are often the path of freeing and breakdown. Therefore, interfaces will lead to a remarkable reduction of entire properties of FRP composites.

Improvement of interface structure by treatment

The interface between glass fiber and matrix resin (epoxy) may be regarded as an adhesive area. Prior to curing, the liquefied epoxy resin soaks into the glass fiber surface. The polar groups in the molecules of two components (i. e. fiber and epoxy) attract each other, resulting in an adhesive strength. Liquefied epoxy should be easy to soak into the surface of glass fiber because the surface tension of glass is larger than that of epoxy resin. So a fine adhesion between glass fiber and epoxy might be expected. However, the surface of glass fibers is covered by lubricant for manufacturing reason, which reduces the surface tension. In addition, the moisture and the pollutants with larger surface activity in

surroundings, which are absorbed on glass fiber surface, also reduce the surface tension. Therefore, in fact, it is not easy for liquefied epoxy to soak into the glass fiber surfaces. That means a fine adhesion may not be realized. In order to solve this problem a suitable surface treatment for glass fiber is necessary prior to the epoxy resin impregnation of glass fiber. Since the firm adhesion may be regarded as a valence bonding, it is expected that if glass fibers are treated by coupling agent which may react with both glass fiber and epoxy resin to form chemical bonding, then the bonding strength between glass fiber and epoxy resin will be enhanced. Two kinds of end groups exist in the molecules of coupling agent. One kind of end groups close to glass fiber may react with the surface of glass fiber to form hydrogen bond, while another kind of end groups close to epoxy resin may react with epoxy resin to form special network structure and epoxy-coupling agent copolymer. Thus, two components of FRP are firmly bonded by coupling agent treatment, which is also called "finish". The interface structure of FRP treated by coupling agent is shown in Figure 6(b).

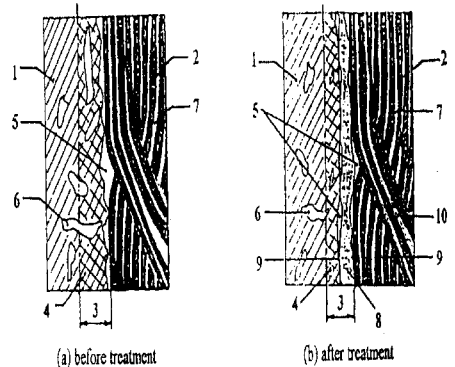


Figure 6. Interface structure model of FRP before and after treatment

(1-epoxy resin, 2-glass fiber, 3-interface structure, 4-abnormal resin layer, 5-gas cavities at interface, 6-gas cavities in epoxy resin, 7-gas cavities in glass fibers, 8-coupling agent, 9-regions interface eliminated, 10-coupling agent filling in cavities in glass fibers)

Compared with the untreated FRP, it can be seen that the submicroscopic structure of interface office treated FRP is improved. The interface of the untreated FRP is glass-epoxy physical bonding, and interface volume is relatively large; while for the coupling agent treated FRP, two chemical bondings are formed in the contact area between two components, i. e. glass fiber-coupling agent bonding and coupling agent-epoxy bonding, and the interface volume is relatively small due to the firmly chemical bonding, whose dimension is in the magnitude order of molecular size.

Effects of surface treatment of glass fibers or fillers on the dielectric and electric properties

The leakage currents of untreated and treated FRP arc shown in Table I. The glass fiber in FRP samples used for leakage current measurement is arranged in the direction parallel to electric stress. From Table 1, it can be seen that surface treatment of glass fiber by using coupling agent (silane) reduces the leakage current remarkably, especially under wet condition.

Table 1. Leakage current of FRP with and without treatment.

T	condition	Leakage current(A) (without treatment)	Leakage current(A) (with treatment)
20 °C	dry	1.3×10^{-11}	7.0×10^{-12}
	wet	7.4×10^{-11}	3.7×10^{-11}
30 °C	dry	2.0×10^{-11}	1.3×10^{-11}
	wet	1.2×10^{-11}	6.8×10^{-11}
50 °C	dry	7.8×10^{-11}	6.8×10^{-11}
	wet	3.0×10^{-10}	1.4×10^{-10}
80 °C	dry	1.1×10^{-9}	8.5×10^{-10}
	wet	1.5×10^{-9}	5.0×10^{-10}

Measurements show that the resistivities of glass arid epoxy resin are $10^{11-13} \Omega$ and $10^{13-15} \Omega$ 0m respectively. According to the dimension parameters, the calculated volume leakage currents of glass fiber and epoxy resill are $8 \times (10^{-13} - 10^{-15})A$ and $1.6 \times (10^{-13} - 10^{-15})A$, respectively, which is much less than the measured leakage current of FRP listed in Table 1. It means that the conduction processes in FRP mainly result

from interfacial conduction. As mentioned above, surface treatments result in the change of interface structure, which reduces the probability for impurity ions and moisture to ,enter the interface, thus reducing the interfacial conduction and the effect of moisture.

The above discussion on surface treatment of glass fiber is also suitable for the polymeric composites with fillers. The TSC results and the corresponding loss tangent of EPDM filled with precipitated silica are shown in Figure 7 and Figure 8, respectively. Figure 7 indicates that surface treatment of fillers may reduce the space charges accumulated in interfaces. Figure 8 shows that surface treatment of filler may also reduce the loss tangent of composites.

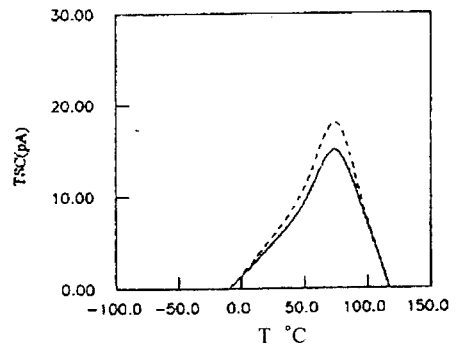


Figure 7. TSC of silica(precipitated, 10phr) filled EPDM samples with and without treatment

As is well known, electric treeing and breakdown often develop along the interfaces of composites. Surface treatments of glass fibers lead to a firm bonding between polymer matrix and glass fiber or fillers, thus undoubtedly enhancing the treeing stability and breakdown strength, especially under wet condition. Investigators reported that the reduction of breakdown strength of FRP due to the effects of moisture can be controlled by surface treatment of glass fiber. Similar results were obtained in our experiments.

Under wet conditions, the average ac breakdown strength of 10 samples with thickness of 2mm in which fiber direction is parallel to electric stress, are 10.5KV/mm and 7.5K.V/mm for treated and

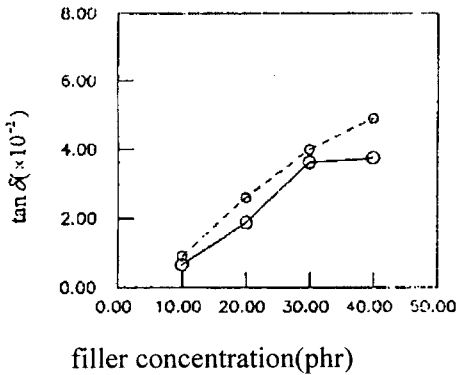


Figure 8. Relation of Loss tangent of silica (precipitated, 10phr) filled EPDM samples with and without treatment with filler concentration (solid line: with treatment, dashed line: without treatment)

untreated FRP, respectively. The effects of interfaces on treeing characteristics have been reported in our previous paper[14]. When glass fiber is arranged in direction parallel to electric stress, trees always develop in the interfaces between fibers and epoxy resin, and Follow along a zigzag line. If glass fiber is not in direction parallel to electric stress, i. e. an angle(θ) exists between fiber and electric field direction, then the treeing voltage as a function of the angle(θ), as shown in Figure 9. From Figure 9,

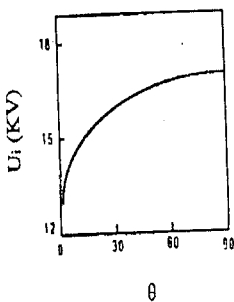


Figure 9. Dependence of treeing initiation voltage of FRP on the angle θ

it can be seen that treeing initiation voltages decrease with angle θ decreasing. When θ is

smaller than 45° , surface treatment of glass fiber is effective. the treeing imitation voltages of coupling agent treated FRP is 5 to 25 percent higher than that of the untreated samples, depending on the Na' and K' content in glass fiber.

4. Summary

Investigation of interfacial phenomena is a very important topic for electrical engineering. Although the interface effects in polymeric composites have been investigated extensively, the mechanisms concerning interfacial phenomena have not yet been fully understood. Some interfacial phenomena in double layer dielectric systems such as epoxy-mica composite may be interpreted in terms of traditional Maxwell-Wagner model. However, experimental results indicate that Maxwell model does not always hold. It is recognized that space charge play an important role in interfacial phenomena. Therefore, based oil experimental results, the authors proposed a model describing the dynamic process of interface space charge accumulation in composites. A certain effects of interface on dielectric properties may be well understood based on the new model.

Recently coupling agents are extensively adopted to improve the properties of polymeric composites. In this report interface structure patterns of FRP without and with coupling agent treatment are presented. According to the patterns, some questions on interface, for example the chemical nature and dimension of interface, influence of moisture, breakdown strength and treeing stability of composites, might be understood. Interfacial problems are very complicated, thus it is necessary to further investigate the interface effects and the approaches to improve the properties of composites.

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