Effect of Carbon Black and Water Absorption on Dielectric behavior of EP-modified SiO_2 composites

E.A.Al-Ajaj

Baghdad University , College of Science , Physics Department
akramajaj@yahoo.com

Abstract

Epoxy (EP) – Silica (SiO_2) composites are well known composites used in microelectronic industry . So it is important to study their dielectric behavior under different conditions such as the presence carbon black (UV absorber) and immersion in the water for 30 days .

Dielectric properties were calculated over the frequency range $10^2 – 10^6$ Hz for epoxy composites with different weight % of micrometer 1.5µm SiO_2 particles (60%, 65% and 70wt%) modified with 0.5wt% silane coupling agent to improve adhesion between EP and SiO_2 phases .

Similar dielectric constant (ε') behavior was observed for all composites , where ε' values decrease slightly with increasing frequency .

Dielectric loss behavior shows relaxation peak around 10^4Hz for composites with and without carbon black .

0.35% weight gain was observed for immersed composites in water and highest relaxation peaks intensity were observed at higher frequency (around 10^5 Hz) .

Recovery study was performed on immersed composites and no chemical changes have taken place .

Keywords
Dielectric behavior
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تأثير أسود الكاربون وامتصاصية الماء على سلوك العزل للايبوكسي المدعم بمتراكبات SiO_2

إكرام عطا العجاج
جامعة بغداد –كلية العلوم – قسم الفيزياء

الخلاصة:

متراكبات الايبوكسي – سيليكا متراكبات معروفة في مجال صناعة المايكرو الكترونكس . لهذا من المهم تدقيق تصرف العازل تحت مختلف الظروف مثل وجود المضافات والتعرض الطويل المدى الى الرطوبة في المدى المطلوب للترددات . . لهذا تم تدقيق خواص العزل باضافة اسود الكاربون المعروف بامتصاصية للاشعة فوق البنفسجية (UV) وغمره في الماء لفترة ٣٠ يوما.

خواص العزل تم حسابها في مدى الترددات $10^2 - 10^7$ هرتز لمتراكبات الايبوكسي مع نسب وزنية مختلفة من حبيبات $(1.5\mu m)SiO_2$ (60% ، 65% ، 70%) تم تحويرها باضافة رابط هو السايلين (0.5wt% Silane) الذي يعمل على تحسين الالتصاق بين اطوار EP و SiO2 .

لوحظ تشابه في تصرف ε' لكل المتراكبات حيث ان قيم ε' تقل بشكل قليل جدا مع زيادة الترددات . ان تصرف ε'' يظهر ذروة استرخاء بحدود 10^4 هرتز لكل المتراكبات بدون او مع وجود اسود الكاربون ولكن مع زيادة في شدة ذروة الاسترخاء للمتراكبات التي تحوي اسود الكاربون والتي تفسر بانها تعود الى الاسترخاء في الايبوكسي .

لوحظ ان هناك 0.35% زيادة في الوزن للمتراكبات المغمورة في الماء . ان اعلى ذروة استرخاء لوحظت بحدود ١٠° هرتز للمتراكبات المغمورة في الماء (تأثير استقطاب واكييز – سيلرز)

تم اعادة المعالجة عكسيا للمتراكبات المغمورة بالماء (تجفيف) ووجد انه لايوجد تغييرات كيميائية للمتراكبات المحورة المغمورة في الماء .

Introduction

The main types of polymer matrix composites can be classified according to the embedded phases which could be fibers , particles (SiO_2 or carbon black)or wool . The choice of the particulate fillers affect the composites properties especially dielectrical and electrical properties . [1,2,3]

Polymer – ceramic composites are used in forming capacitors , high voltage insulators , printed boards and majority of integrated circuits are packaged by epoxy (EP) – silica (SiO_2) composites , as they are cheap , easy to process, having excellent mechanical and dielectrical properties [4,5] . Many works have been appeared studying dielectric properties for EP-SiO_2 composites under different effects , such as thermal stress during course of curing , role of interface in explaining Maxwell – sillars relaxation , the influence of curing conditions on structural , mechanical and dielectrical properties , moisture , water absorption and additives [5,6,7] .

The mechanical and dielectrical properties of EP-SiO_2 composites are highly dependent on interactions between surfaces of the filler particles and EP resin [5] . Therefore the surfaces SiO_2 particles were modified by mixing with silane coupling agent . Silane coupling agents are monomeric silicon chemicals used in a wide range of applications due to their ability to chemically bond organic polymers to inorganic materials such as glass , mineral filler , metals and their oxides [8] .

So mixing surface modified micrometer SiO_2 particles with EP resin was used to form stronger bonds between EP and SiO_2 . There are two methods to modify the silica surfaces , which are either by annealing at high temperature (up to 1000^oC) or by application of a silane coupling agent . Samples of modified micrometer silica particles prepared by different methods depend on the interactions between surfaces of the filler particles and EP resin [5] .

Dielectric properties are known to change due to many factors . The effect of two factors was chosen in this study : the effect of adding carbon black , also known as UV absorber and immersion the composites in water for 30 days .

The energy of UV radiation has approximately the same magnitude of the common chemical bonds in polymers (C-H , C-C and C-O) which have bond strengths of 4.28 , 3.44 and 3.45 eV respectively . However , chemical bond scission occurs when |UV energy is larger than that of polymer bonds and affects the properties [9] .

The possibility that absorbed water could change dielectrical properties of composites by weakening the bonds between the fillers and polymer resins lead to simulate the effects of long term exposure to moisture by immersion the composites in water for different periods of time at room temperature and higher temperature , to study the mechanical , electrical and dielectrical properties of the immersed composites [10,11,12] .

Appearance of nanofillers such as Al_2O_3 , MgO , ZnO and SiO_2 particles for polymer composites a provided new research area in recent years and offered new opportunities for designing new fields of dielectrics with high dielectric constants . Such nanoparticles tend to affect the dielectric properties of nanocomposites differently from micro particles [13,14,15] . However, Nelson et.al (2004) reported higher values of relative dielectric constant for EP – TiO_2 composites with 10 % TiO_2 micro particles , while decreasing values were observed for EP composites with 10wt% TiO_2 nanoparticles [16] . Dielectric properties for EP-nano and microparticles Al_2O_3 , ZnO_2 and TiO_2 are reported and observed higher dielectric values at high temperature for composites with above micro filler particles which indicate that the interaction zone

surrounding the nanoparticles has profound effect on dielectric behavior .
Tanaka et.al. , (2004) reported higher electrical conductivity for polymer composites with nanosilica particles than those with microsilica particles [17]. Roye et.al (2005) reported a decrease in dielectric permittivity of nanocomposites of Polyethylene with nano SiO_2 particles [18] and Zou et.al (2006) reported mechanical and dielectric weakness in the EP- SiO_2 nanocomposites at different relative humidities and temperatures [19] .

Experimental Part

1- Sample preparation

The weight percentage of SiO2 particles as filler for Ep-SiO2 composites (W_f) is calculated from the following equation $W_f=w_f/w_c$, were w_f and w_c are the filler and composites weight percentage respectively shown in figure (1) .

Hand lay up method was used to prepare sheets of EP – SiO_2 composites with different weight percentage of micrometer size (1.5 μm) SiO_2 particles (AFM). To prepare composites sheets , a glass mold was prepared with wax to prevent adhesion of composites with glass plates .

The surfaces of silica particles were modified by treating them with 0.5wt% of silane coupling agent as the surfaces silica particles contain layers of adsorbed water molecules [5] . Silane coupling agent was hydrolyzed for one hour in an aqueous alcoholic solution (ethyl alcohol and water , 4:1 by volume) , Silica particles were then treated with above solution and thoroughly mixed in air then heated for 3 hours at 150^oC . To ensure a good mixing and minimizing the voids , stirring continues for 30 minutes ,

The prepared sheets for EP – modified micrometer SiO_2 composites were kept at room temperature for 3 hours , then post cured at 120^oC for 12 hours .

Nine EP-SiO_2 samples were prepared , the first three composites are modified EP-SiO_2 composites with 0.5wt% silane coupling agent with different weight percentages of SiO_2 .

The second set are EP-modified SiO_2 composites containing carbon black (fixing epoxy / carbon black weight percentage) with the required wt% of modified SiO_2 particles .

The possibility that absorbed water may affect dielectrical properties by weakining the bonds between EP and modified SiO_2 particles , an attempt was made to simulate long term of humidity exposure by immersing the composites in water for 30 days .

Table (1) presents EP- modified SiO_2 composites with different SiO_2 wt% , carbon blank and immersed in water for 30 days at room temperature .

Table (1) EP – SiO_2 composites

EP-modified SiO_2 Composites by silane Coupling agent	EP-m60wt% SiO_2 EP-m65wt% SiO_2 EP-m70wt% SiO_2
Composites with carbon black (c.b.)	Ep/c.b.-m60wt% SiO_2 EP/c.b.-m65wt%SiO_2 EP/c.b.-m70wt% SiO_2
Composites immersed in water	imm EP-m60wt% SiO_2 imm EP-m65wt%SiO_2 imm EP-m70wt% SiO_2

2-Dielectric measurements

All EP – SiO_2 composites sheets were cut in the form of discs with 20mm diameter and 2mm thickness for dielectric measurements . Every sample was grinded perfectly to obtain smooth surfaces and perfect electrodes adhesion with the samples .

The three electrodes method (LCR meter) using dielectric analyzer model HP4274A and HP4275A was used . Aluminum electrodes were deposited on both sides of the composite disc by using thermal evaporation technique under 10^{-5} mbar pressure using Edward coating unit E306A. Two dielectric parameters are measured directly ; capacitance (c) and the dissipation facto (tan δ) over the frequency range 10^2-10^6 Hz .

From these measurements , the dielectric constant (ε') and the dielectric loss (ε'') values over the required range of frequency were calculated using the following equations :

$$\varepsilon' = \frac{cd}{\varepsilon_o A} ---------(1)$$

$$\varepsilon'' = \varepsilon' \tan\delta ----------(2)$$

Where d is the disc thickness , A is the effective surface area of the disc and ε_o is the dielectric constant in vacuum [20] .

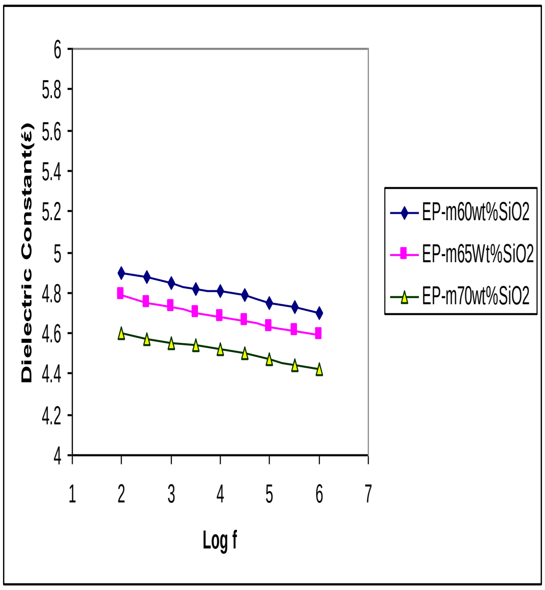
Results and Discussion

Results of ε' and ε'' over the frequency range 10^2-10^6 Hz , without and with carbon black and for samples immersed in water for 30 days are reported and discussed .

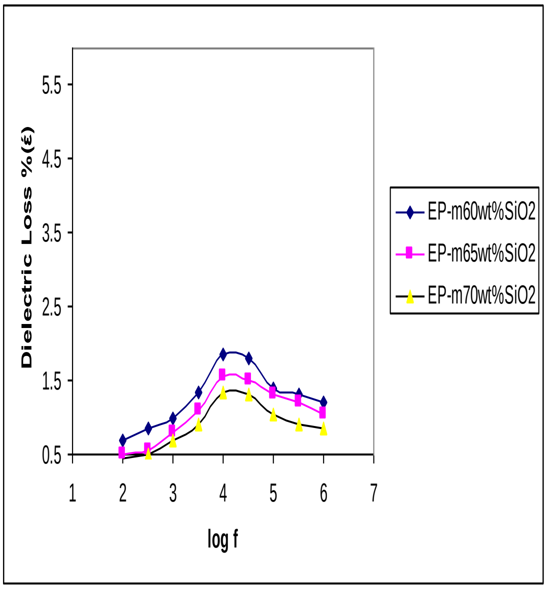
1- EP – modified micrometer SiO_2 composites

Dielectric constant values for the first three composites with different wt% micrometer modified SiO_2 particles decrease slightly with increasing frequency over the frequency range 10^2-10^6 Hz as shown in Fig.(1) . Such behavior is expected and explained as composites consist of two or more materials with different dielectric constants may have microscopic kinds of interface problems which appear as weak structure through the composites . However , EP composites with 60wt %SiO_2 shows higher value of ε' than other two composites . This is due to heterogenoity of the filled epoxy (SiO_2) which causes virtual electric charges trapped and concentrated at the EP-SiO_2 interface [6] .

Figure 2 shows ε'' behavior , with relaxation peaks observed around 10^4 Hz for the three composites , but with higher intensity for EP-composites with 60wt % SiO_2 . Grave et.al observed similar relaxation peak around the same frequency range in pure epoxy and concluded that such relaxation is intrinsic to the epoxy network (unreacted hardener epoxy group [21] .



Fig(1) : Frequency dependence of dielectric constant (ε') for EP-modified SiO_2 composites .



Fig(2) : Frequency dependence of dielectric loss% (ε'') for EP-modified SiO_2 composites.

1- EP modified -SiO_2 composites with carbon black

The energy of UV radiation is comparable to the dissociation energies of polymer covalent bonds , thus the absorption of UV by carbon black in polymeric composite could result in chain cross linking or molecular chain scission [22] . However, it seems that the strength between the bonds of the polymer composite is higher than the energy of UV radiation as similar behavior for ε' and ε'' are observed for EP- composites with and without carbon black as shown in figures 3 and 4 . Higher values of ε' and ε'' for composites with carbon black are observed .

The increase in dielectric values could be due to the interfacial polarization which takes places in multiphase materials as the field is distorted due to the motion of some charge carriers that accumulated at the interface .

Also , higher relaxation peaks intensities are observed around the same range of frequency . Such relaxation peaks were reported by other authors who related these peaks to the epoxy matrix net work and not to carbon black these results agree well with the data reported by Gonon et.al for unmodified EP-SiO2 composites [6] .

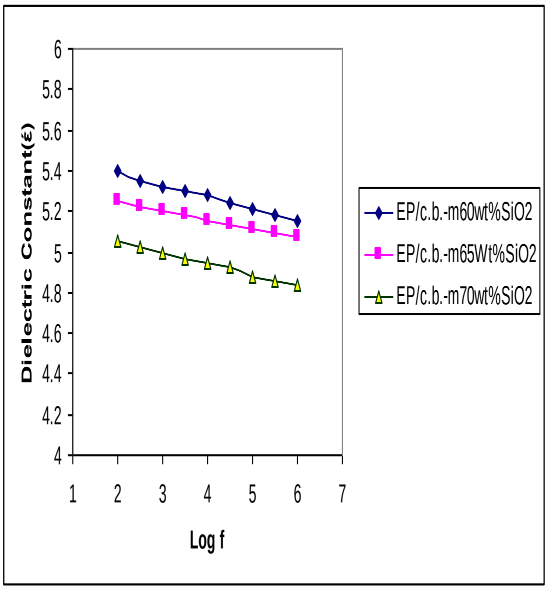


Fig.(3) : Frequency dependence of dielectric constant (ε') for EP-modified SiO_2 composites with Carbon black (c.b.)

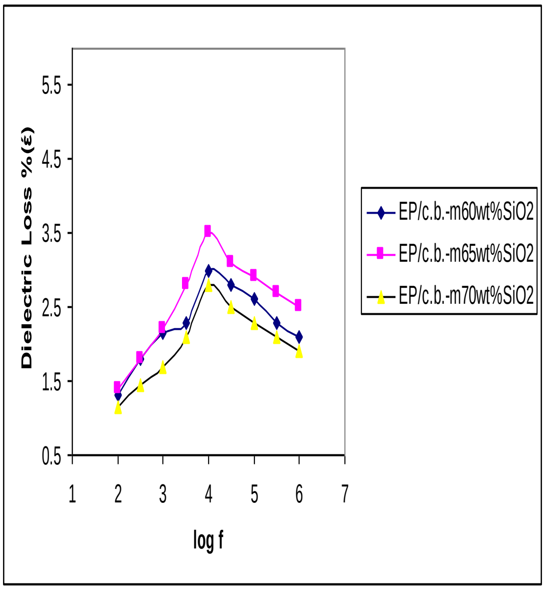


Fig.(4) : Frequency dependence of dielectric loss (ε'') for EP-modified SiO_2 composites with Carbon black (c.b.)

2- EP – SiO_2 composites immersed in water

Within 30 days of composites immersion in distilled water at room temperature , 0.35% weight gain was observed . This behavior of gaining 0.35% weight after immersion in water for long time is expected as many polymeric composites are capable of absorbing relatively small amount of water from the surrounding environment , due to their surfaces ability to absorb or desorb water[9] .

Dielectric properties behavior for the immersed composites show similar behavior as that of the other previous six composites but with slightly higher values of ε' , where ε' for immersed EP – 60wt % SiO_2 at 10^2 Hz is equal to 5.51 as shown in fig.5 . This increase in ε' values is attributed to the increase of total segmental dipole moment related to water absorption Slight increase in dielectric values is expected due to the presence of water molecules which have a high ε' (ε' =80) compared to the value of 4 or 5 for EP resin . Surface modification of micrometer size SiO_2 particles for all composites is important as dielectrical properties are highly dependent on the surfaces of silica particles which contain layers of absorbed water molecules . Without such surfaces modification , the adsorbed water at the surfaces permeat additional water molecules into composites and result in deterioration of its properties[5] .

Slight increase in the relaxation peaks at higher frequency (around 10^5 Hz) are observed as shown in fig.6 . Such behavior is due to the preferential water absorption (Maxwell – Wagner Sillar polarization) [12] . The increase in intensity could be due to pairing of water with dipoles responsible for the observed relaxation . However , others reported a decrease in loss values under the influence of humidity at low water concentration (<0.1wt%) for unmodified composites .
Recovery study was performed on these immersed composites by airing them for 30 days then curing them at the same temperature and time in an open atmosphere . Similar dielectric results and behavior were observed for above composites with and without at recovery study which indicate that no chemical change has taken place after immersion in water , a result which agrees well with the results reported by Singh et.al [12] .

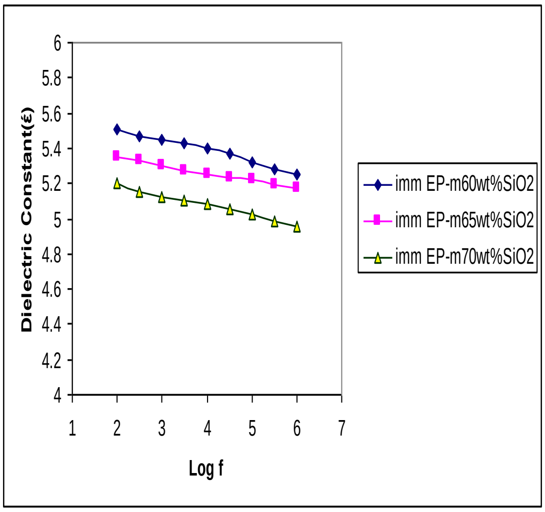


Fig.(5) : Frequency dependence of dielectric constant (ε') for EP-modified SiO_2 composites after immersion in water for 30 days

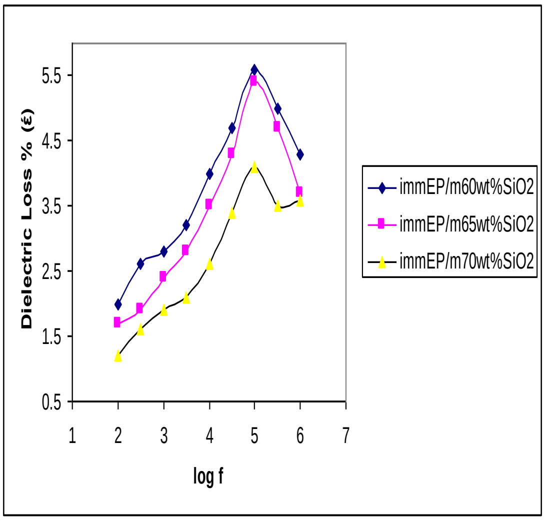


Fig.(6) : Frequency dependence of dielectric loss (ε'') for EP-modified SiO_2 composites after immersion in water for 30 days

Conclusion

Modification of SiO_2 particles with 0.5wt% silane coupling agent was performer to get better electrical insulation, however , slight decrease in ε'

values over the frequency rang 10^2-10^6 Hz was observed .

Mixing the composites with carbon black enhance the values of ε' and ε'' which could be due to chain cross linking .

Highest values of the relaxation peaks at higher frequency (10^5 Hz) was observed for composites immersed in water for 30 days , this could be due to a preferential water absorption at silica – epoxy interfaces with weight gain equal to 0.35%, despite the modification mode for the surfaces of SiO_2 particles to minimize the deterioration of the dielectrical properties.

Finally recovery study indicates that no chemical changes have taken place for composites immersed in water for 30 days.

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