Chapter 1

Polymeric Dielectric Materials

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Background and brief history

The definition for dielectric constant relates to the permittivity of the material (symbol use here ε). The permittivity expresses the ability of a material to polarise in response to an applied field. It is the ratio of the permittivity of the dielectric to the permittivity of a vacuum. Physically it means the greater the polarisation developed by a material in an applied field of given strength, the greater the dielectric constant will be. Traditionally dielectric materials are made from inorganic substances eg. mica and silicon dioxide. However polymers are gaining wider use as dielectric materials. This is due to the easier processing, flexibility, able to tailor made for specific uses and better resistance to chemical attack. As early as mid-60's polymers eg polyvinyl fluoride [1] and aromatic-containing polymers [2] are used as dielectric materials in capacitors. Further improvement in organic film fabrication was established as revealed in US Patent 4153925. Polymers can be fabricated fairly easily into thin film by solution casting and spin coating, immersion in organic substrate, electron or UV radiation and glow discharge methods. This is mainly due to lower thermal properties such as glass transition and melting temperature which contribute to a lower temperature processing windows. Their solubility is controllable without offsetting their intrinsic properties. In the case of inorganic material and ceramic, they have much higher thermal properties hence temperature requirement leads to an extreme end of processing temperatures. On the other hand polymers cannot stand too high a temperature. Their coefficient of thermal expansion is relatively larger than ceramic materials and susceptible to atmospheric and hydrolytic degradation. Table 1 shows the values of dielectric properties of several polymers with comparisons with several inorganic materials.

Inorganic/ceramics materials have higher dielectric constant than polymers. Water has a relatively high dielectric constant. This is quite cumbersome as any traces of moisture trapped or absorb will dramatically alter the desired dielectric properties. Inorganic

materials generally have higher dielectric constant compared to polymeric materials. Intrinsically they contains ions and polar groups which contribute to their high dielectric constant. Air having a dielectric constant of 1.02 is taken as reference dielectric.

Materials	Dielectric constant, ε	Materials	Dielectric constant, ε
TiO_2	100	Fluorinated polyimide	2.5 – 2.9
H_2O	78	Methylsilsesquioxane	2.6 – 2.8
neoprene	9.8	Polyarelene ether	2.8 – 2.9
PVDF	6.0	Polyethylene	2.3 – 2.7
SiO2	3.9 – 4.5	Polystyrene	2.5 – 2.9
Fluorosilicate glass	3.2 – 4.0	Teflon AF	2.1
Polyimide	2.8 – 3.2	Air	1.02

Table 1. Dielectric constant of several polymers and inorganic materials. (Adapted from Ref 3)

1.2. Application of polymeric dielectric materials.

Both dielectrics with low and high dielectric constant are essential in electronic industries. Low dielectric constant is required basically as insulators. They are known as passivation materials. Their applications ranged in isolating signal-carrying conductors from each other, fast signal propagation, interlayer dielectric to reduce the resistance-capacitance (RC) time delays, crosstalk and power dissipation in the high density and high speed integration [4]. They are of necessity in very dense multi-layered IC's, wherein coupling between very close metal lines need to be suppressed to prevent degradation in device performance. This role involve packaging and encapsulation. In electronic packaging, they separate interlayers and provide isolated pathways for electronic devices connection in multilayer printed circuit boards. As the trends are towards miniaturization in microprocessor fabrication, any decrease in relative permittivity will reduces the deleterious effect of stray and coupling capacitances. Dielectric naterials are also employed to encapsulate the balls which bridged the die and substrate. This encapsulation is specifically called underfill which helps to protect any circuitary failures as well as reducing thermal mismatch between the bridging layers.(Figure 1) In LED encapsulation low dielectric materials is used for insulation at the lead frame housing.

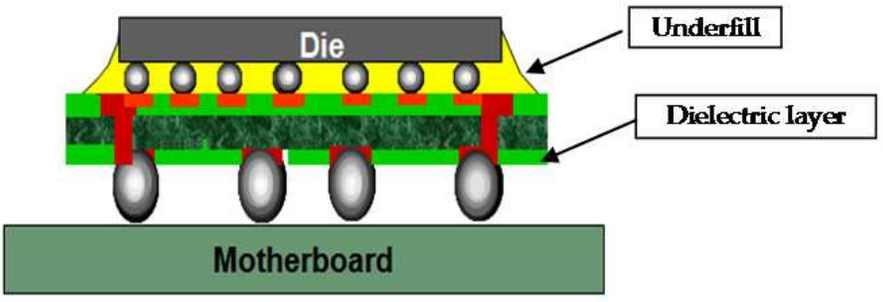


Figure 1. Application of dielectric polymers in IC packaging

As an active components, designing is geared towards high ε value and are used as polarizable media for capacitors, in apparatus used for the propagation or reflection of electromagnetic waves, and for a variety of artifacts, such as rectifiers and semiconductor devices, piezoelectric transducers, dielectric amplifiers, and memory elements. Despite being insulators, hence non-polar, these materials can be made polar by introducing small amount of impurities. In this state, the material is able to store large amount of charges at small applied electrical field. This is the case with polyvinylidene fluoride when introduced with impurities chlorotrifluoroethylene.[5] Indeed several works have been performed on polymers like polyimide with added Al_2O_3, $BaTiO_3$ and ZrO_3 'impurities' [6,7,8] which showed an improved dielectric constant. Once there is large charge storage, it can be readily released on demand. In a rectifier, a capacitor is used to smooth off the pulsating direct current.

2. Theory of dielectric properties in polymer

2.1. Mechanism of interaction with electric field

Quantitative treatment of a dielectric in an electric field can be summarized using Clausius–Mossotti equation (1).

$$\mathrm{P} = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \cdot \frac{M}{\rho} = \frac{N_A \alpha}{3\varepsilon_0} \tag{1}$$

P is the molar polarisability, ε_r is the relative permittivity, ε_o is the permittivity in vacuum, M is molecular weight of a repeat unit, ϱ is density, α is polarisability, N_a is the Avogadro constant. This equation shows that dielectric constant is dependent on polarisability and free volume of the constituents element present in the materials. Polarisability refer to the proportionality constant for the formation of dipole under the influence of electric field. Thus its value is typical for each different type of atom or molecule.[9] The relation between polarizability with the permittivity of the dielectric material can be shown as in Equation (2):

$$\varepsilon_r = 1 + \frac{N\alpha}{\varepsilon_0} \tag{2}$$

It shows that relative permittivity ε_r is the ratio of total permittivity of one mole of material with that in vacuum. The dependency of free volume of relative permittivity thus originate from the volume involved in one mole of the material. Again the molar volume is characteristic of each different type of atom or molecule. Molar polarization therefore is obtained if the molar volume is introduced into these derivations leading to Clausius–Mossotti equation.

Physically, polarisability is induced when there is electric field applied onto the materials. In the absence of electric field, the electrons are distributed evenly around the nuclei.

When the electric field is applied the electron cloud is displaced from the nuclei in the direction opposite to the applied field. This result in separation of positive and negative charges and the molecules behave like an electric dipole. There are three mode of polarizations [10]:

i. Electronic polarization – slight displacement of electrons with respect to the nucleus.
ii. Atomic polarization – distortion of atomic position in a molecule or lattice
iii. Orientational polarization – For polar molecules, there is a tendency for permanent dipole to align by the electric field to give a net polarization in that direction

When a static electric field is applied on to these materials the dipoles become permanently polarized giving a dielectric constant as ε_{static}. However if the field changes as when alternating electric current is applied, polarization will also oscillate with the changing electric field. All three modes of polarization contributing to the overall dielectric constant will be dependent on the frequency of the oscillating electric field. Obviously the electronic polarization is instantaneous as it is able to follow in phase with the changing electric field compared to atomic polarization which in turn better able to follow the oscillating electric field compared to the orientational polarization. Certain structures and elements display a higher polarisibility than the others. Aromatic rings, sulphur, iodine and bromine are considered as highly polarisable. The present of these groups induced an increase in dielectric constant. The π bond in the aromatic rings is loosely attached compared to the sigma bond. Therefore it is easily polarized. For large size atoms like bromine and iodine, the electron cloud is so large and further apart from the influence of electrostatic attraction of the positive nucleus. It is expected to display a high polarisibility. This is as oppose to fluorine which has small atomic radius and concentrated negative charge. It is able to hold the electron cloud much tightly resulted in a low polarisability. This will induce a lower dielectric constant.

Free volume is also an important factor in determining the dielectric constant. Free volume is defined as the volume which is not occupied by the polymeric material. The free volume associated with one mole of repeat units of the polymer may be estimated by subtracting the occupied molar volume of a repeat unit, V_o, from the total molar volume, M/ϱ, where M is the molar mass of the repeat unit. [10] The fractional free volume V_n is given by Equation (3):

$$V_n = \frac{M/\rho - V_0}{M/\rho} \tag{3}$$

The addition of pendant groups, flexible bridging units, and bulky groups which limit chain packing density have been utilised to enhance free volume. [21] The presence of free volume in the form of pores will similarly result in a decrease in dielectric constant as it being occupied by air whose relative permittivity is about one. A higher fractional free volume means that the density of the material will be lower resulting in a lower polarisible group

per unit volume. Replacement of hydrogen with fluorine result in lowering of dielectric constant since fluorine occupies higher volume. Thus beside being low polarisability, introduction of fluorine induce a significant decrease of dielectric constant through an increase in free volume.

2.2. Effect of chain polarity

Polymers can be polar or non-polar. This feature affect significantly the dielectric properties. Examples of polar polymers include PMMA, PVC, PA (Nylon), PC while non-polar polymers include PTFE (and many other fluoropolymers), PE, PP and PS. Under alternating electric field, polar polymers require sometime to aligned the dipoles. At very low frequencies the dipoles have sufficient time to align with the field before it changes direction. At very high frequencies the dipoles do not have time to align before the field changes direction. At intermediate frequencies the dipoles move but have not completed their movement before the field changes direction and they must realign with the changed field. The electronic polarization and to some extent atomic polarization, is instantaneous weather at high or low frequency for both polar and non polar polymers. Therefore, polar polymers at low frequencies (eg 60 Hz) generally have dielectric constants of between 3 and 9 and at high frequencies (eg 100 Hz) generally have dielectric constants of between 3 and 5. For non-polar polymer the dielectric constant is independent of the alternating current frequency because the electron polarization is effectively instantaneous hence they always have dielectric constants of less than 3. The chain geometry determines whether a polymer is polar or non-polar. If the polymer is held in a fix confirmation, the resulting dipole will depend whether their dipole moments reinforce or cancell each other. In the case of extended configuration of PTFE, the high dipole moment of $–CF_2-$ units at each alternating carbon backbone cancelled each other since their vector are in opposite directions. Its dielectric constant therefore is low (2.1). On the other hand, PVC has its dipole moment directing parallel to each other resulting in reinforcement of dipole. Its dielectric constant is 4.5. This is illustrated as in Figure 2.

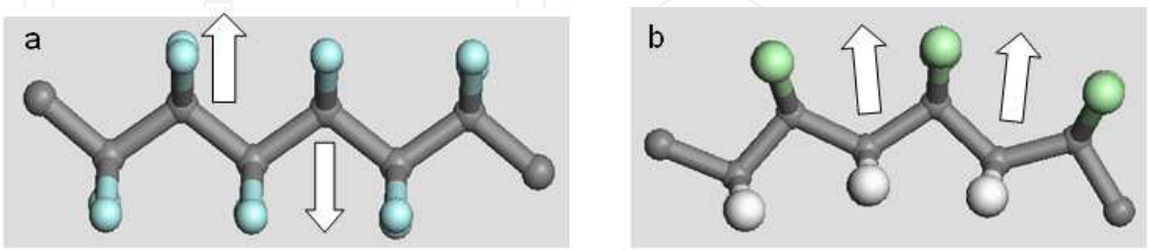


Figure 2. PTFE (a) and PVC (b) with arrow showing the net dipole moment.

The designing of dielectric material so as to achived the desired dielectric properties should take careful consideration of net polarity of the structure. This has been exemplified by the opposite effect in indiscriminately subsitituting fluorine atom into a polyimide chain resulting in an increase in otherwise low dielectric constant material.[11] There is no dipole polarization contribution for non-polar polymers as found in polar polymers. This different

mode of mechanism lead to the resonance spectra in the case of electronic polarization which occur at frequency beyond 10^{12} Hz. At below this frequency, the relaxation spectra prevail relating to the behavior of dipole polarization. This observation can best be summarized as in the following Figure 3:

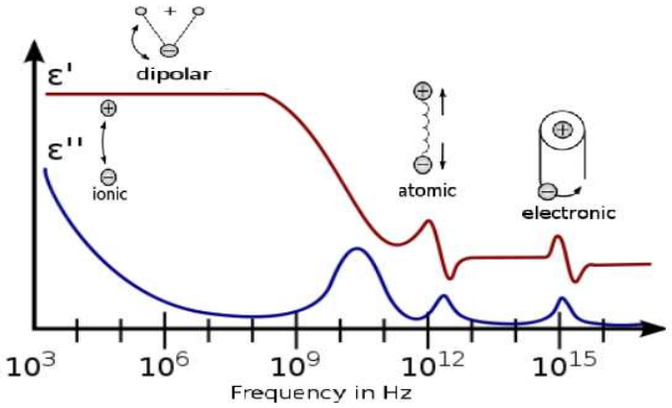


Figure 3. Dielectric constant and loss dispersion of dielectric materials against frequency (adapted from Wikipedia)

2.3. Relaxation and dielectric loss

Relative permittivity can be express in complex form as in Equation (4) below:

$$\varepsilon^{*} = \varepsilon' - j\varepsilon'' \tag{4}$$

It consist of the real part which is dielectric constant and the imaginary part which is the dielectric loss. The ratio between the dielectric loss with the dielectric constant is quantified as tan δ ie:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Dielectric loss result from the inability of polarization process in a molecules to follow the rate of change of the oscillating applied electric field. This arise from the relaxation time (τ) in a polymer which is the time taken for the dipoles to return to its original random orientation. It does not occur instatntaneously but the polarization diminished exponentially. If the relaxation time is smaller or comparable to the rate of oscillating electric field, then there would be no or minimum loss. However when the rate of electric field oscillate well faster than the relaxation time, the polarization cannot follow the oscillating frequency resulting in the energy absorption and dissipated as heat. Dipole polarisability is frequency dependent and can be shown as in Equation (5)

$$\alpha_{\mathrm{d}} = \frac{\alpha_o}{1 + j\omega t} \tag{5}$$

where α_d is the dipole polarisability and α_o is the low frequency (static) polarisability. It normally occur in the microwave region. Figure 3 above shows the variation in real dielectric constant with the imaginary dielectric loss. There is a sudden drop in dipole polarization region (< 10^{12} Hz) for dielectric constant ε accompanied with the maximum dielectric loss ε″. This maximum represent the complete failure for the dipole to follow the oscillating electric field beyond which the dipole remain freeze with no effective contribution to the dielectric constant. The mechanism for electronic and atomic polarization occur at higher frequency (shorter wavelength eg. infra-red region). This region involved excitation of electrons which is characterized by the quantized energy level hence is known as resonance behaviour. The dielectric constant display a maximum before a symmetrical drop about a certain frequency. These maximum and minimum represent the optimum polarization in phase with the oscillating frequency. The frequency at which the turning point occur is term the natural frequency ω_o. At this point the frequency of applied electric field is at resonant with the natural frequency hence there is a maximum absorption. Consequently this lead to maximum dielectric loss ε′.

2.4. Effect of temperature

Temperature affect dielectric properties. As the temperature is increased the intermolecular forces between polymer chains is broken which enhances thermal agitation. The polar group will be more free to orient allowing it to keep up with the changing electric field. At lower temperature, the segmental motion of the chain is practically freezed and this will reduce the dielectric constant. At sufficiently higher temperature, the dielectric constant is again reduced due to strong thermal motion which disturb the orientation of the dipoles. At this latter stage the polarization effectively contribute minimal dielectric constant. Beside the kinetic energy acquired, free space in the polymer matrix is of necessity so as to induce segmental movement. Throughout the measured frequency and temperature, electronic and atomic polarization are spontaneous. The dipole polarization, on the other hand, would significantly be affected during heat treatment by effectively reducing the relaxation time (τ) since the polymer chain τ would reduced as the temperature is increased hence the polymer segment would be better able to follow in phase with the oscillating electric field. Significant chain and segmental motions occur in polymers and they are identified as follows [39]:

i. α relaxation: Micro-Brownian motion of the whole chain. Formally this motion is designated as glass transition.
ii. β relaxation: Rotation of polar groups about C-C bond eg. CH_2Cl and $–COOC_2H_5$, conformational flip of cyclic unit.
iii. γ relaxation: libration of phenyl ring and limited C-H segmental chain movement.

The dielectric loss will show maxima at respective relaxation mechanisms as the temperature is increased. The loss in dielectric can be schematically represented as in the following Figure 4

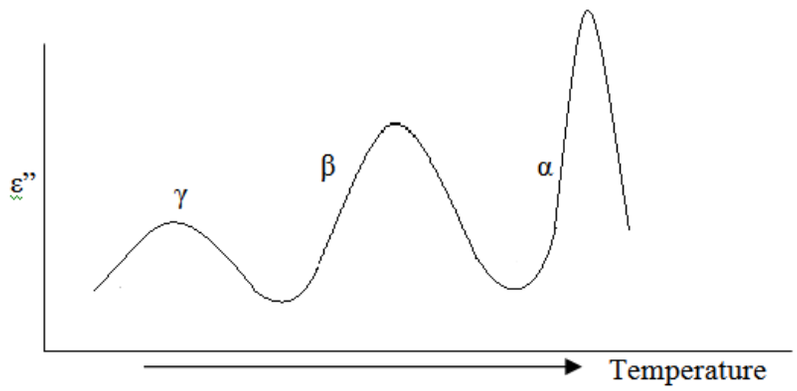


Figure 4. Schematic dielectric loss curve for polymer as temperature is increased.

The γ relaxation occur at lower temperature as it involved small entities of phenyl rings and C-H units whose motion are readily perturbed at low thermal energy. This is followed by β relaxation and finally α relaxation corresponding to the longer scale segmental motion. The broadness for each peaks signify dispersion in relaxation time as the result of different local environment of polarisable groups.

3. Structure-properties relationship.

3.1. Dielectric relaxation.

The earliest model of relaxation behavior is originally derived from Debye relaxation model [12] In this model, real and imaginary part of dielectric constant can be represented as in Figure 5

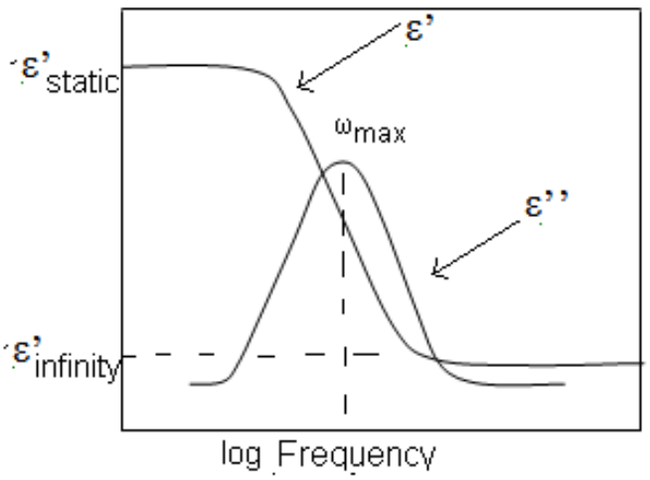


Figure 5. Debye dielectric dispersion curve.

where

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_{o-\varepsilon_\infty}}{1+\omega^2\tau^2}$$

$$\varepsilon'' = \frac{\varepsilon_{o-\varepsilon_\infty}}{1+\omega^2\tau^2}\omega\tau$$

This model relates the dielectric properties with the relaxation time. The relationship between ε′and ε′′ can be formulated by eliminating the parameter ωτ to give Equation (6):

$$\left(\varepsilon' - \frac{\varepsilon_s+\varepsilon_\infty}{2}\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_s-\varepsilon_\infty}{2}\right)^2 \tag{6}$$

This is a form of a semispherical plot which is popularly known as Cole-Cole plot. See Figure 6.

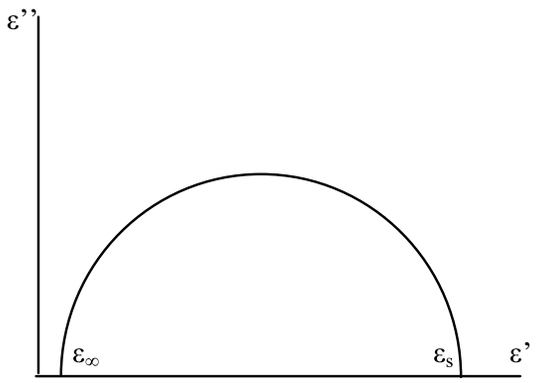


Figure 6. Cole-Cole Plot showing the relationship between dielectric constant and dielectric loss.

The plot shows that at dielectric constant of infinite frequency, ε∞ and static dielectric constant, εs there will be no loss. Maximum loss occur at the midpoint between the two dielectric values. The larger the different between the static and infinite dielectric constant, the higher will be the loss. This model fit very well with polar small molecular liquids. However, polymeric materials are bigger in size, higher viscosity with entanglement between chains. This contribute to visco-elastic properties which requires some modifications to the original model. It can be noted that the above relationship involved only one specific relaxation time. This is contrary in polymeric system whose relaxation time is dependent on mobility of dipoles which behave differently in varying local environments. This result in distribution in relaxtion time. Modification include Cole and Cole semiemperical equation [13] Davidson and Cole [14] Williams and Watt [15] and Navriliak and Nagami [16]. The last modification lead to the new equation (7):

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_{o-\varepsilon_\infty}}{(1+\left(\omega^2\tau^2\right)^\alpha).^\beta} \tag{7}$$

where α and β is in the range 0 and 1. No physical meaning as yet is assignable to these parameters.[17] This modification result in a broader peak and smaller loss value with asymmetrical in features. The behaviour of dielectric constant and loss at variable frequencies and temperatures is exemplified in the following Figure 7 for polyvinylchloride.

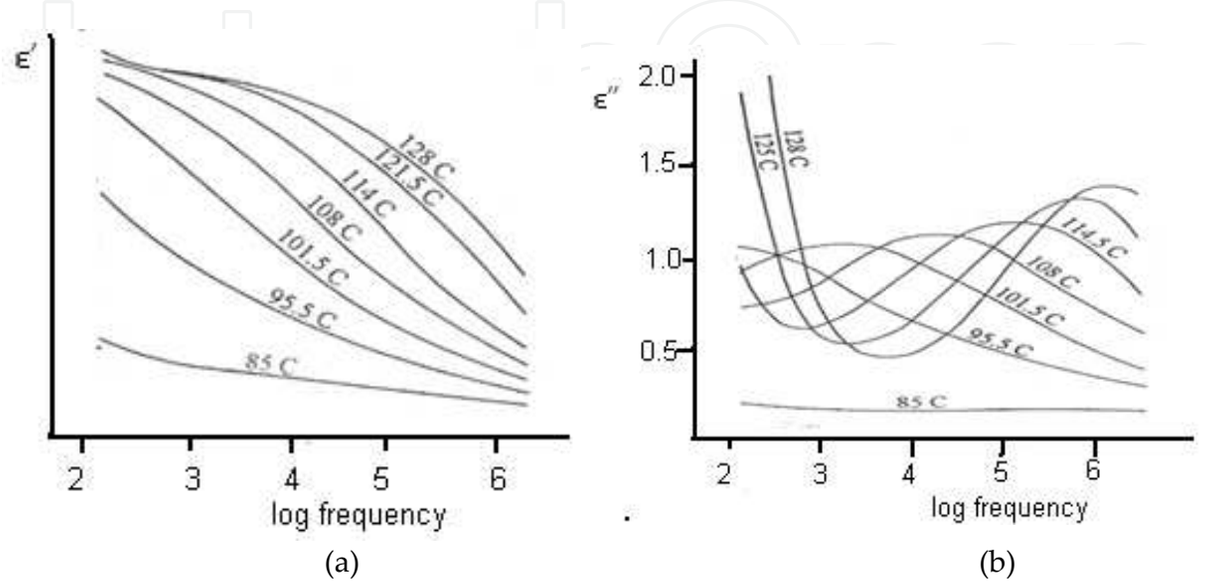


Figure 7. Plot of dielectric constant (a) and dielectric loss with the change in frequency and temperature for polyvinylchloride. (From Ref 18)

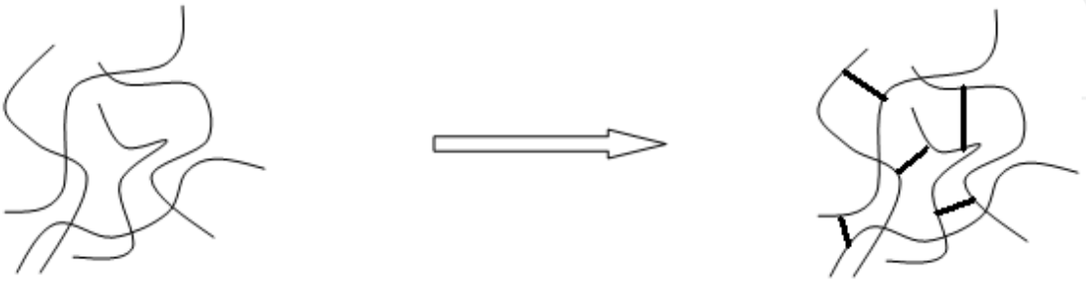
Figure 7a shows the variation of ε′ and ε″ at the region of glass transition (85 ^{0}C) of polyvinylchloride. At the onset of glass transition the PVC showed a relatively low dielectric constant of 4.1 to 3.2 within the measured frequency range. With the increased in temperature, chain mobility begin to increase thus reducing the relaxation time. The dipole polarization of the polymer chain is better able to align in phase with the changing frequency and this account for the increase in dielectric constant as the temperature is increased. However this alignment with the applied oscillating field gradually failed as the frequency is increased. The optimum rate of decreased of dielectric constant occur at higher frequency as the temperature is increased. This correspond to the maximum dielectric loss in Fig 7b. Based on Cole-Cole plot, when there is a big difference in static and infinite dielectric constant, as under high thermal treatment, then the dielectric loss will be correspondingly large. It can be noted that at temperature 128 ^{o}C, there is a large dielectric loss occurring at higher frequency compared to those of lower temperature. Glass transition of polymer is a vital consideration that need to take into account during use of polymers as this affect the dielectric properties substantially. Substitution of fluorine into polyimide, for example, only affect the electronic polarization since PI is mostly used at temperature lower then its Tg (<260 ^{o}C). At this temperature, no effective polar orientation occurr which reduce any possibility of intrusion effect from this mechanism into the dielectric properties. The following Table 2 present the dielectric constant and loss of commercially used polymers.

Material	Dielectric constant (ε′)	Loss tangent (tan δ)	Frequency (Hz)
ABS (plastic)	2.0 – 3.5	0.005 – 0.0190	
Butyl rubber	2.35 2.35	0.001 0.0009	1 MHz 3 GHz
Gutta percha	2.6		
HDPE	1.0 – 5.0	0.00004 – 0.001	
Kapton (Type 100) (Type 200)	3.9 2.9		
Neoprene rubber	6.26 4.0	0.038 0.34	1 MHz 3 GHz
Nylon	3.2 - 5		
Polyamide	2.5 – 2.6		
Polycarbonate	2.8 – 3.4	0.00066 – 0.01	
Polypropylene	2.2		
Polystyrene	2.5 – 2.6	0.0001 0.00033	100 MHz 3 GHz
PVC	3		
Silicone (RTV)	3.6		
Teflon (PTFE)	2.0 – 2.1	0.0005 0.00028	100 Hz 3 GHz

Table 2. Dielectric parameters for some polymers at various frequencies.

3.2. Effect of cross-link between chains

Polymers are often cross-linked to improve their properties. The cross linking or curing process can be conveniently monitored based on relaxation time changes with the progress of reaction. This is exemplified during curing of diglycidylether bisphenol A (DGEBA) with diethyltetraamine (DETA)[19]. During the cross-linking process, the chains are covalently bonded to each other which induce chain rigidity.



Scheme 1. Affect of crosslink network on rigidity of polymer chains

This rigidity is proportional to cross-link density henceforth affecting the change in relaxation time. This can be illustrated in the following Figure 8:

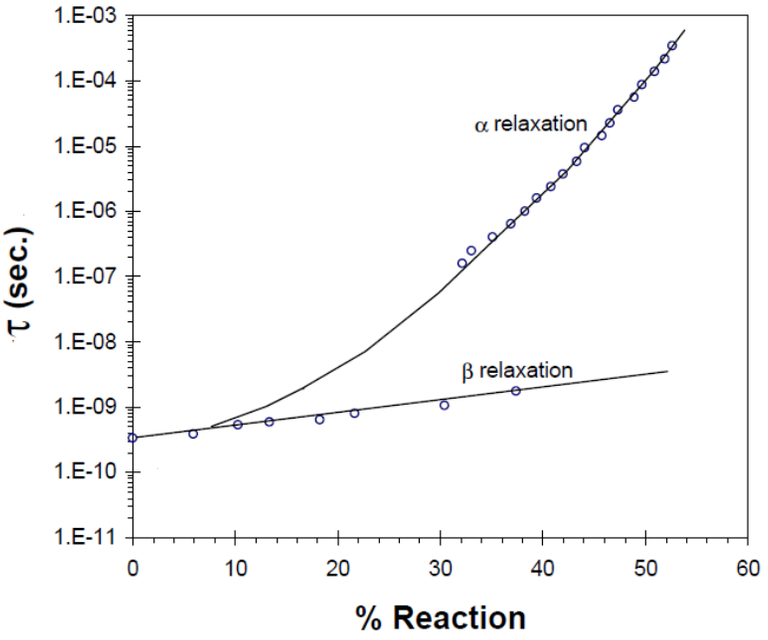


Figure 8. Effect of degree of reaction on the α and β relaxation time of DGEBA-DETA system

Figure 8 shows that both the α and β relaxation time increase with the increase in amount of cross-linking reaction. With the increase in cross-link density, the polymer chains are mostly bounded to each other much tighter hence inducing a longer time to return to their original equilibrium configuration. The rate of increase in α relaxation is higher as it approaches glassy state compared to β relaxation as the former relates to the segmental chain motion of larger in scale compared to the latter. The dielectric constant ε and loss is illustrated in the following Figure 9. In Figure 9a there is a significant drop in dielectric constant which correspond to the maximum frequency for dielectric loss in Figure 9b . This transition represent the frequency at which the dipole polarization is completely out of phase with the applied oscillating electric field. The maximum frequency ω_{max} of dielectric loss was extracted and applied into the equation $\tau = 1/\omega_{max}$ to yield the α relaxation time. It can be observed that as the level of curing is increased the maximum dielectric loss shift towards lower frequency while the change in dielectric constant at α_{static} with $\alpha_{infinity}$ become diminished. This behaviour represent the gradual transition from the rubbery state to glassy state of the polymer with the increase of cross-link density.

3.2.1. Polarizability and free volume

Polarizability and free volume are two important factors that influence the dielectric properties as formulated in the Clausius–Mossotti equation. These effects can be exemplified by introducing fluorine into a polymer chains.[20] Fluorination of polyimide film was performed through gaseous phase in a vacuum chamber. The impregnated fluorine content was determined using XPS analysis and the dielectric constant is shown as in following Table 3:

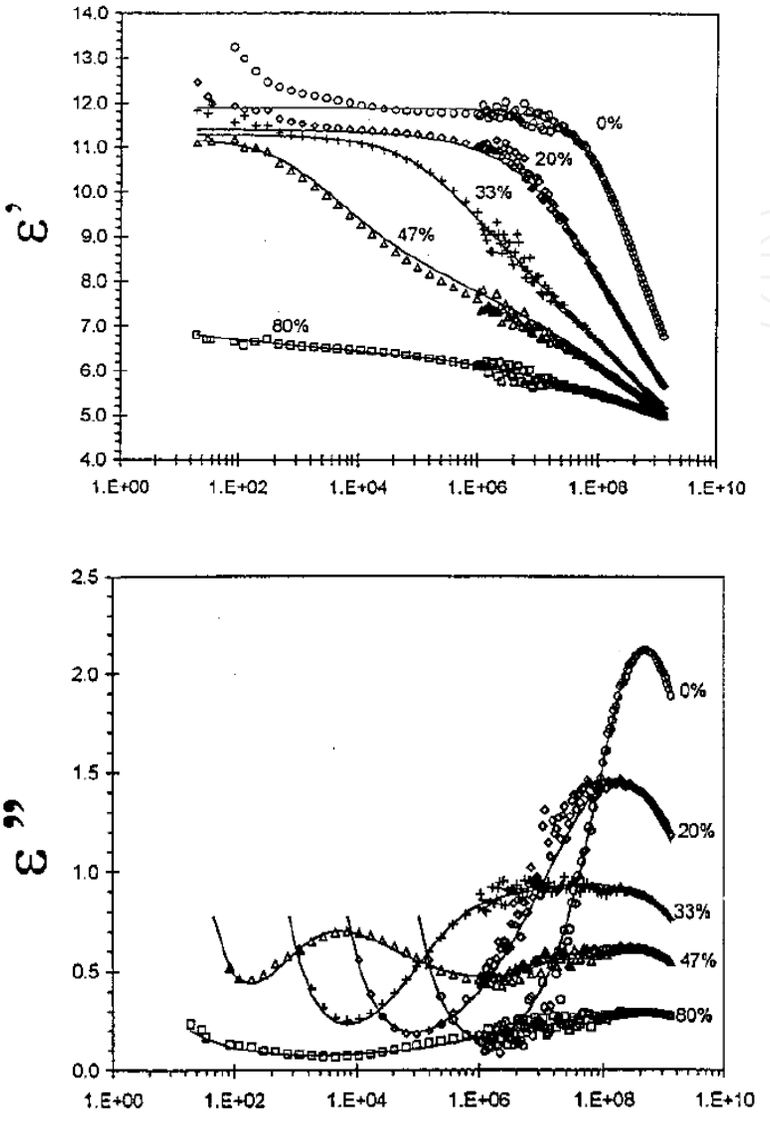
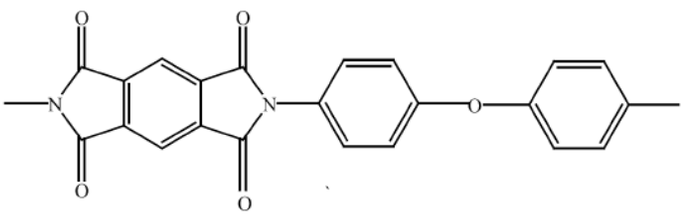


Figure 9. Effect of cross-link density on dielectric constant (ε′ above) and dielectric loss (ε″ below) for DGEBA-DETA system



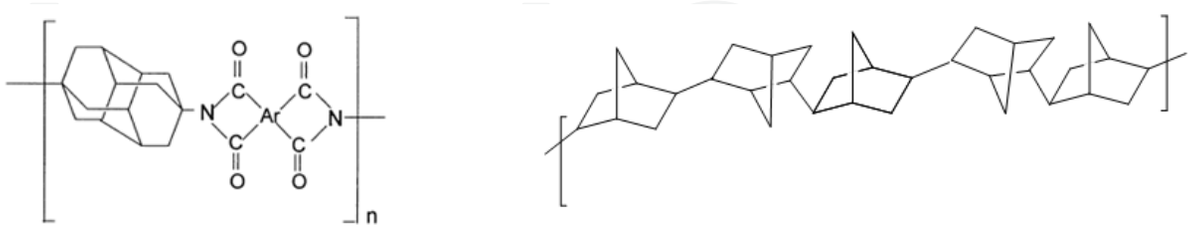
Scheme 2. Repeat unit of the polyimde (from Ref 20)

Sample	F_{1s}/C_{1s}(%)	Dielectric constant,ε	
		10^2(Hz)	10^6 (Hz)
F0	0	2.93	2.90
F2	57.8	2.64	2.60
F3	67.7	2.42	2.41
F4	78.6	2.28	2.27
F5	87.4	2.37	2.26

Table 3. The effect of Fluorine content on the dielectric constant of a polyimide

Similar result was obtained in a series of polyimides synthesised from starting monomers bearing varying percentage of fluorine content. [21] The decreased in dielectric constant as the fluorine content is increased can be explained as due to the low polarizability of fluorine. The electrons of fluorine being very tightly held and close to the nucleus. The polarizability of the fluorinated polyimides is decreased as the number of fluorine atoms is increased, due to the lower electronic polarizability of a C–F bond relative to that of a C–H bond that has been displaced. [22,23] The free volume concomitantly increases due to the relatively large volume of fluorine compared with hydrogen, which reduces the number of polarizable groups per unit volume.

The effect of free volume can be seen when introducing adamantane into a polyimide chain. [24] Adamantane is a bulky group which induce an increase in the free volume. The dielectric constant achieved was 2.7 at 1 KHz. This value is well below the commercial Kapton H film (25.4 μm) with a dielectric constant of approximately 3.5 at 1 kHz and 3.3 at 10 MHz. Besides, hydrophobicity was reduced thus preventing absorption of moisture. Low dielectric loss is important for a good capacitors and insulation. The strategy of introducing bulky substituents is further exemplified in a commercial Avatrel™ dielectric polymer made up of polynorbonene for passivation applications. It has a dielectric constant of 2.55, a loss tangent less than 0.002. These electrical properties held constant up to above 1 GHz. The bulky structures in these polymers are illustrated in the following Figure 10:



(a) (b)

Figure 10. Adamantane structure incorporated into polyimide chain (a, from Ref 12) and the generic structure for polynorbonene (b).

3.3. Dielectric breakdown

Electrical breakdown occurs when the dielectric strength which is the maximum electric field applicable on dielectric material is exceeded. It underwent catastrophic failure leading

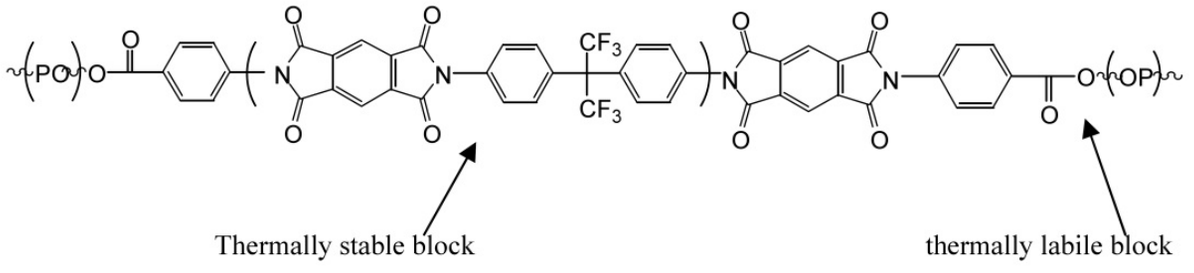
to short circuit or blown fuse. This occurs when at a given applied voltage the heat generated due to the losses is greater than the heat dissipated and if the voltage is applied long enough period then the dielectric is unable to reach a state of internal thermal equilibrium. The favourable condition for the occurrence of breakdown is large thickness of the dielectric, high temperature of both the dielectric and the surrounding, continous application of high voltage and large dielectric loss (high tan δ). The last factor is the most important to occur at high frequency. The high humidity in air can similarly affect dielectric breakdown through electrolytic process.

4. Designing of polymer dielectric materials

Based on the preceding discussions, designing of polymer dielectric materials can be made using several approaches. The following examples review two approaches undertaken of late namely free volume and copolymerization.

4.1. Free volume

Based on Maxwell-Garnet theory, the presence of second phase of lower dielectric constant in a composite will affect a significant decrease in dielectric constant.[25] This concept was applied in generating foam structure with the introduction of air-filled pores. At least two methods were utilised. One is to synthesised block copolymer of different thermal lability [26] and the other is performing solution etching of soluble component in a composite matrix. [27] The former method involved the use of block copolymer composed of high temperature and high Tg polymer and a second component of lower thermal property which can preferentially undergoes thermal decomposition. One of such a triblock polymer is shown below:



Scheme 3. Triblock polyimide structure illustrating the thermally labile and stable segments.

This triblock composed of thermally stable polyimide and thermally labile phosphate ester block. This copolymer is subjected to thermal treatment such that the temperature is sufficient to degrade the thermally labile block and leaving the thermally stable block intact. A small size scale of microphase saparation is then generated with spherical pore morphology, monodispersed in size and discontinuous. These nanopores are filled with air (ε = 1.0) which is responsible for the reduction in dielectric constant. Thermally labile oligomers include polymethylstyrene, polypropylene oxide and polymethylmethacrylate.

Nanofoam with dielectric constant of 2.3 was achievable with system made-up from PMDA/4BDAF/PPO triblock of void volume 16%. Figure 11 illustrate the relationship between the void content with the dielectric constant for PMDA/3FDA/PPO triblock system.[28]

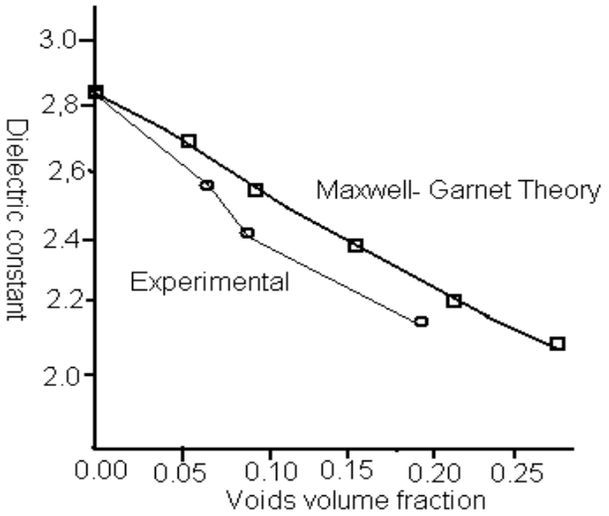
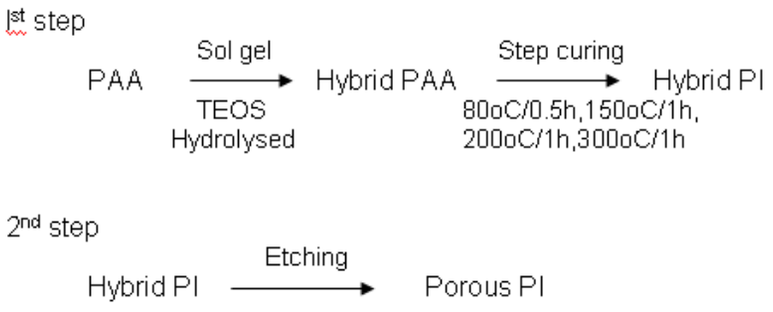


Figure 11. Relation between the dielectric constant with the void fractional volume in PMDA/3FDA/PPO triblock system.

In solution etching method, porosity were achieved by solution etching of soluble component in a nanocomposites leaving the chemically stable matrix intact. This was attempted using polyamic acid, a polyimide prepolymer, as the matrix while inorganic TEOS was incorporated through sol-gel method. Once the inorganic phase was homogeneously distributed in the polymer matrix, the composite was thermally cured followed by hydrofluoride etching. This will dissolved away the acid labile inorganic phase with the generation of nanosize closed cell pore of uniform density. The steps involved during its fabrication is illustrated as in the following Scheme (4):



Scheme 4. Preparation of porous Polyimide using sol-gel method

The level of porosity is dependent on the TEOS content incorporated into the polymer matrix. Table 4 shows the dependence in dielectric constant on fluorine content and level of porosity based on TEOS content added during the materials fabrication

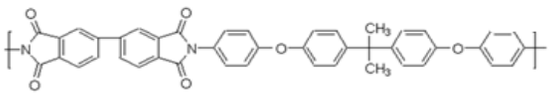
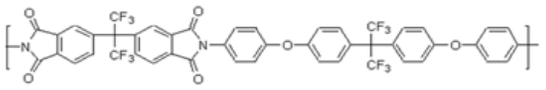
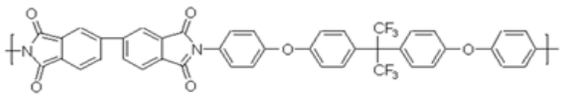
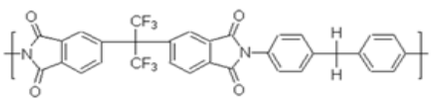
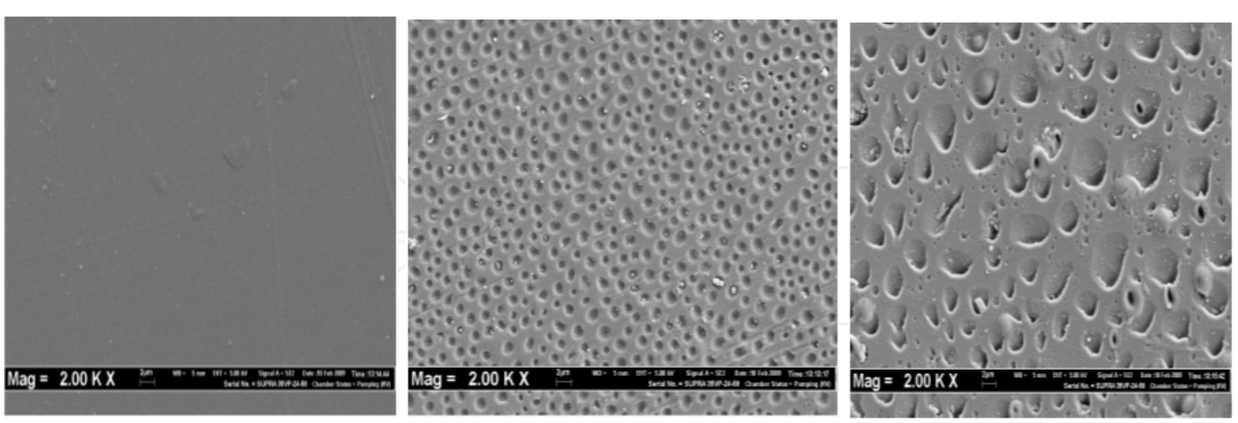
	F (Wt %)	0% TEO	10% TEOS	% TEOS
 BAPP-BPDA	0	2.71	2.84	3.41
 6FDA-BDAF	15	2.45	2.71	3.25
 BDAF- BPDA	17	2.61	2.69	3.18
 6FDA-MDA	33	2.50	2.62	2.98

Table 4. Dielectric constant of a series of polyimides at varying TEOS content

The results above display a general trend of decreasing dielectric constant as the TEOS concentration used during sol gel technique were increased. This was ascribed to an increased in void structures which reduced the dielectric property as the result of the presence of air. There was a linear decreased in dielectric constant as the weight percent of fluorine content in the structures were increased. Further the rate of decrease is almost constant between different TEOS content. Of the four synthesized polyimides, BAPP-BPDA showed the highest dielectric constant since this sample contains no fluorine. The SEM picture for the fracture surface morphology is shown in the following Figure 12.



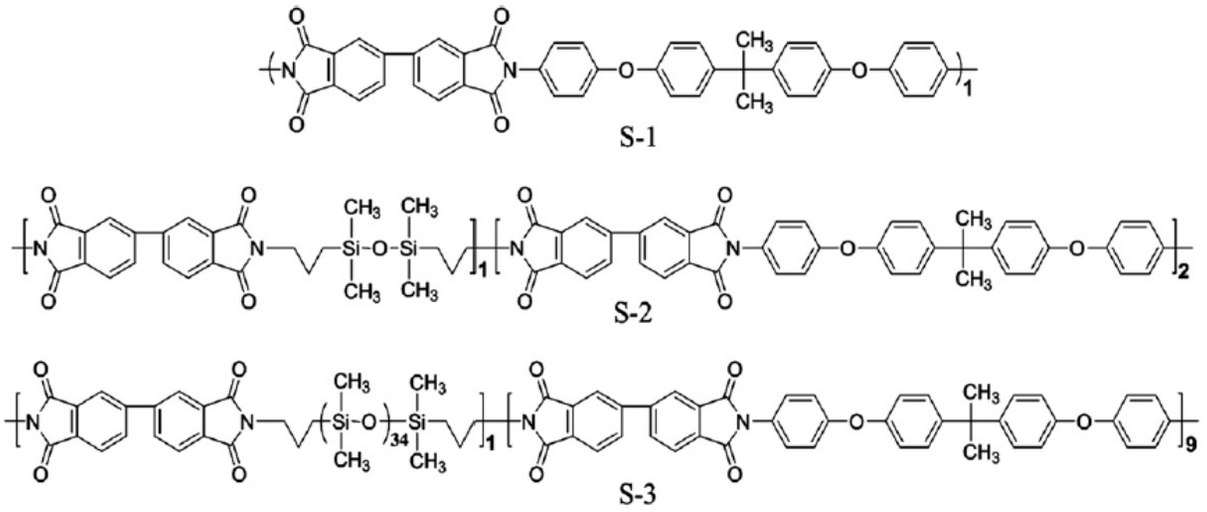
(a) (b) (c)

Figure 12. SEM scan of fracture surface of pure (a) PI/SiO_2 10% (b) and PI/SiO_2 20 % porosity (c)

Simpsons *et al* [21] concluded that the presence of fluorine increases the free volume, lower electronic polarization and can either increase or decrease the dielectric constant depending on whether the substitution of the atoms are symmetric or asymmetric.

4.2. Copolymerisation

Copolymerisation of two or more polymers together is a strategy to produce a new materials of tailored dielectric properties. In copolymersation, two or more different monomer units were covalently bound thus producing a synergesic effect of respective constituents. Copolymerisation of polyimide with polysiloxane is popularly performed due to the complementary chemical and mechanical properties between the two. The polyimide has superior thermal and mechanical properties but too intractable to normal processing methods. For example the modulus of polyimides are in the range of 10^9 to 10^{12} Pa but their Tg are above 260 ^oC. On the other hand the polysiloxane is flexible and easily processable beside having a stable thermal degradation (> 400 ^oC). Copolymers of these materials produce an optimized dielectric material of practical application for several electronic packagings. Attempt was made with the following structures. [29]



Scheme 5. Series of PI-polysiloxane copolymers

Their dielectric constant are shown in the following Table 5:

Sample	Dielectric constant at 1 kHz 293 ^oC	n (Si-O repeat unit)
S1	2.90	0
S2	2.57	1
S3	2.43	34

Table 5. Effect of silicone content in silicon-polyimide copolymers on dielectric constant.

The table above shows there is a decreasing trend in dielectric constant with the increase in siloxane units. Silicon is comparatively larger than a carbon atom and the Si - O bond is more flexible than the C - C bond. Thus, the bulky silicone units would be less mobile. Its presence affects the bulk movement of the whole polyimide network which reduces the efficiency of the dipole in reacting to polarity change during treatment with an alternating frequency. Furthermore, the molar polarization significantly decreases as the result of an increase in free

volume. Several recent studies have demonstrated a similar trend of a decreasing dielectric constant, with an increasing siloxane content into polyimide structures [30,31]

5. Composites

The traditionally used inorganic material as a dielectric possesses several superior qualities such as excellent thermal, dielectric and magnetic properties. However they are brittle and consume high energy for processing. [32] On the other hand polymers are more flexible, strong resistivity and offer a tractable prosessibility. The disadvantages of polymeric materials are that they possesses lower thermal and dielectric properties. Combining the two materials in the form of nanocomposites offer an alternative in fabricating material of synergesic properties which displayed a tremendous improvement in dielectric properties with high flexibility and ease of processing. Their combination could readily geared towards miniaturization of electronic devices fabrication.

5.1. Polyimide-ceramic composites

Of late several attempts were made towards this strategy. Incorporation of alumina (Al_2O_3), barium titanate ($BaTiO_3$), titania (TiO_2) and zirconia (ZrO_2) into PI matrix were attempted.. [33,34] Several methods were employed in preparing these nanocomposites. It has been established that method of preparation affect the dielectric properties of these materials. A nanocomposite of PI/Al_2O_3 was prepared by mechanical stirring of prepolymer polyamic acid with the inorganic filler followed by thermal curing. [35] The nanocomposite showed an improved dielectric constant compared to a neat polymer material from about 3.0 to 3.4 at 1 MHz. This values increases correspondingly with the amount of filler loading. A further increase in dielectric constant was achieved when mixing was performed using ultrasonication. It has been shown from SEM result that this improvement was due to a better mixing during the latter treatment. Under these processes, the crystal structure of the inorganic fillers remains intact as shown by XRD data. The effect of good miscibility in improving the dielectric constant was proven when using a 3-Aminopropyltrimethoxysilane-treated (APS) ultrasonication. The APS served as an interface layer between the two immiscible organic PI with inorganic filler which reduced any agglomeration between the different phases. This is brought about possibly through the formation of hydrogen bond between the amine moeity of APS with the polar group of polyimide while the inorganic part of the methoxysilane of APS form secondary interaction with the inorganic fillers. Figure 13 reveals the SEM images of PI/ Al_2O_3 composites doped by the treated Al_2O_3 powder.

PA0 demonstrated a neat and clean morphology. The Al_2O_3 particles were homogeneously dispersed into PI matrix in all PA10, PA20 and PA30. The inset images revealed the average size of Al_2O_3 was around 2μm - 4μm. There was no obvious aggregation observed suggesting the improved compatibility between PI matrix and Al_2O_3 attributed to the APS coupling agent. The bahaviour of PI-nanocomposites for $BaTiO_3$, TiO_2 and ZrO_2 displayed similar trend with that of PI-Al_2O_3 nanocomposites. They can be summarized as in the following Figures 14:

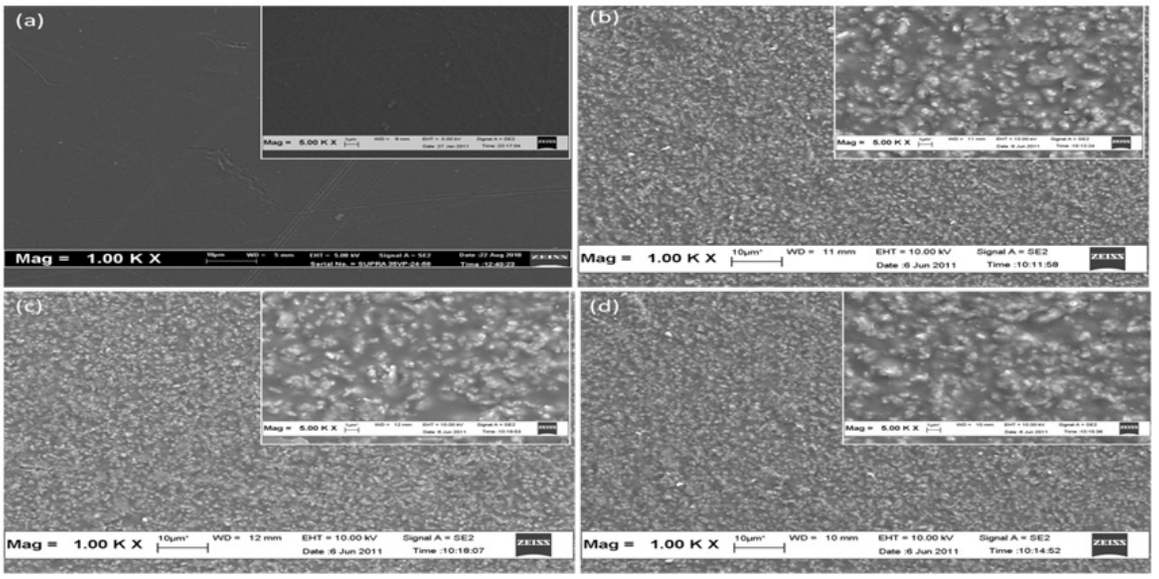


Figure 13. The morphology of PA0, PA10, PA20 and PA30 (a, b, c and d), respectively.

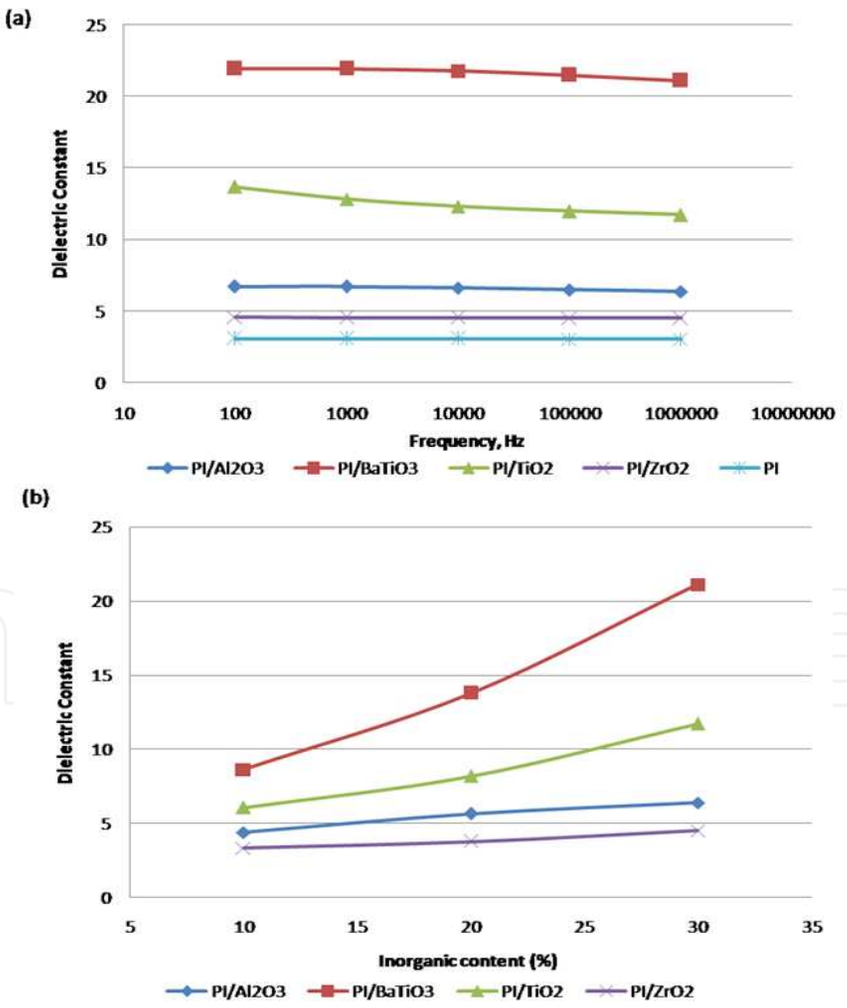


Figure 14. Dielectric constant of PI/inorganic (a) with 30 wt% inorganic content at varying frequency and (b) at 1MHz for several type of inorganic fillers.

All composite systems displayed a decreased in dielectric constant with the increase in frequencies. The dielectric constants increased as the inorganic filler content were increased. This can be attributed to the increase in polarizability group with the incorporation of the inorganic fillers which replace significant part of the PI in the matrix. As the result the polarizable units per unit volume and the space charge polarizability which occurred at the interfaces between PI matrix and inorganic particles were increased. Fig 13(a) shows the dielectric constant of PI/$BaTiO_3$ composite films demonstrating the highest value of dielectric constant followed by PI/TiO_2, PI/Al_2O_3, PI/ZrO_2 and neat PI films. Apparently this property is dependent on the dielectric constant of the respective fillers. $BaTiO_3$ was known to display highest value of dielectric constant [36] followed by TiO_2, ZrO_2 and Al_2O_3 in their neat form. $BaTiO_3$ possesed perovskite structure which is capable to polarize in the absence of electric field. This feature remains in the composite as the crystal structure remains intact as established in XRD data. The low dielectric constant for PI/ZrO_2 was attributed to the poor compatibility between phases resulted in the presence of voids and even led to cracks. The presence of voids naturally induce a low dielectric constant.

5.2. Composite models

Several models were proposed in predicting the dielectric constant of the composites which include Maxwell-Wagner model, Logarithmic Mixing Law and Bruggeman Model. [37] These models allow designing of composite materials based on respective dielectric constant of the polymer, inorganic filler, composition ratio as well as the filler sizes. The slight discrepancy of these models which do not fit to most composite systems are mainly due to inconsistency in treatment for the interphase interaction hence further modification is required. An interphase interaction factor, K, was introduced during fitting into this models.[38] A typical plot of composite dielectric constant with respect to the volume fraction of the fillers is illustrated in the following Figure 15:

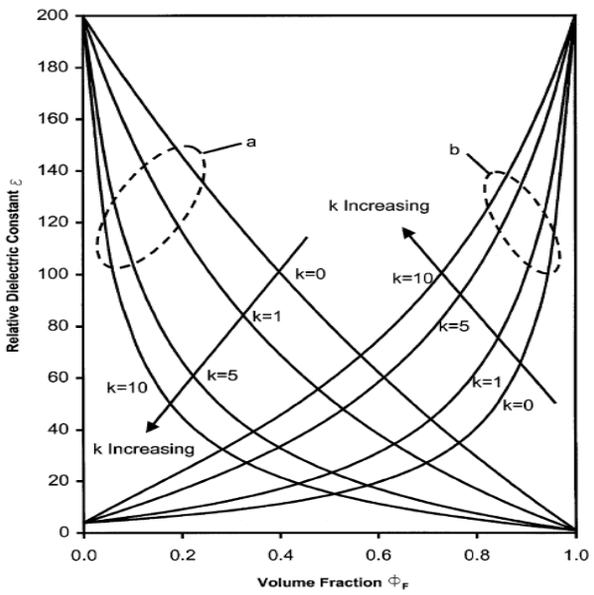


Figure 15. The prediction of the effective dielectric constant as a function of filler volume fraction for different K values. (a) The case of $\varepsilon_{polymer} > \varepsilon_{filler}$. (b) The case of $\varepsilon_{polymer} > \varepsilon_{filler}$ (Adapted from Ref 38)

At K = 0, there is no interaction between phases while a high K values showed a strong interaction. This interaction also dependent on the filler sizes. For a given volume fraction filler, a smaller particle size has a larger fraction of interphase volume in the region between the filler and the matrix granting more polarization to operate. Thus they lead to a relative increase in dielectric constant.

A major concern with polymer/ceramic composites is the heterogeneity in phase which lead to formation of cracks and voids. This effect is known as Maxwell-Wagner effect which reduce the dielectric constant. A more serious type of heterogeneity is that the composite comprised of conductive inorganic fillers which could lead to a mistaken interpretation of dipole polarization occurring at very low frequency region.

6. Conclusion

Polymers offer an alternative to the traditionally inorganic and ceramic material as dielectric amterials. This is due to their highly flexible, tractable processing, good chemical stability and readily tunable properties. The main drawback is they have lower thermal stability which limit their wider applications. Generally their dielectric constant is lower than non-polymeric materials. The mechanism which contribute to the dielectric properties are the interaction of electric field with electronic, atomic and dipole poalarization. These are dependent on polarizabity of constituents structure and the free volume as formulated in Clausius-Mossotti equation. The electronic and to some extent the atomic polarization are instantaneous throughout the measureable range of frequencies. However in dipole polarization there is relaxation time allowing an exponential decay of motion to return to equilibrium state. This different behavior contribute significantly to the values of dielectric constant and dielectric loss. These properties can be utilized to detect for any local or segmental motion during change in frequency and temperature treatment. Dielectric properties can be design by introducing polarizable groups into polymer chains, increasing free volume by inducing porosity as well as copolymerization. Increasing dielectric constant can be effectively made by producing nanocomposites with inorganic fillers possessing high dielectric constant.

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