Direct correlation between free volume and dielectric constant in a fluorine-containing polyimide blend

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Abstract. The dielectric constant of fluorinated polyimides and their blends is known to decrease with increase in free volume due to decrease in the number of polarizable groups per unit volume. Interestingly, we report here a polyimide which when blended with a fluoro-polymer showed a positive deviation of dielectric constant with free volume. In our experiment, we have used a blend of poly(ether imide) and poly(vinylidene fluorine-*co*-hexafluoropropylene) and the interaction between them was studied using FTIR, XRD, TGA and SEM. The blend was investigated by PALS, DB and DEA. Surprisingly, with the increase in the free volume content in this blend, the dielectric constant also increases. This change is attributed to additional space available for the polarizable groups to orient themselves to the applied electric field.

1. Introduction

The dielectric constant of a polymer is mainly influenced by two parameters. First is the molecular polarizability that can be changed by modifying the type and number of polarizable groups. Second is the free volume associated with the polymer. Since the dielectric constant (ε) of air is close to one, introducing free volume (porosity) to a polymer reduces its dielectric constant [1]. Apart from molecular polarizability and free volume of the polymer, the moisture content in a polymer can also influence the dielectric constant. Addition of hydrophobic atoms like fluorine into a polymer can diminish the moisture content and decrease the dielectric constant [1].

Polymers having fluorine atoms in their structure are classified as fluoropolymers. Amongst fluoropolymers, poly(vinylidene fluoride) (PVDF) and its copolymers are technologically important since they possess high dielectric constant and hence used in charge storage applications. Particularly, when PVDF is copolymerized with hexafluoro propylene (HFP), the pendant trifluoro methyl group ($-CF_3$) in it do not allow efficient chain packing and thus contributes to free volume [2].

Polyimides are rigid and thermally stable polymers obtained by the polycondensation reaction of diamines with dianhydrides. Apart from thermal stability, polyimides are also endowed with high glass transition temperature (T_g), good mechanical properties, low dielectric constant, high breakdown voltage. They find extensive use in aerospace and electronic applications. Poly(ether imide) (PEI) is a high performance aromatic amorphous thermoplastic polyimide aiming at replacing metals as well as targeting other specialty applications such as electronics, automotives and membranes [3].

Various strategies have been adopted in the past to decrease the dielectric constant of polymides like incorporating suitable diamine and dianhydride moieties (that minimizes polarizability and

introduces high degree of free volume) as well as adding fluorine atoms in to the polyimide molecular structure which results to increase in free volume. An important contribution in understanding the molecular process that lead to dielectric properties in fluorine-containing polyimides was made at NASA-Langley [4]. The authors have studied the effect of change in free volume on the dielectric constant in them and found a correlation of high free volume content and low dielectric constant [4]. Later, other groups have also found that ε of a polyimide decreases with increasing wt% of fluorine content in different polyimides [5,6]. To the best of our knowledge, the effect of fluorine atoms on the dielectric constant and free volume properties of a polyimide has not been studied by blending it with a fluorine-containing polymer. Here we have studied the effect of fluorine on poly(ether imide) (PEI) by blending it with the fluoropolymer poly(vinylidine fluoride-*co*-hexafluoropropylene).

2. Experimental

2.1. Blend preparation
The copolymer of vinylidene fluoride and hexa fluoropropylene P(VDF-*co*-HFP) having M_w = 400,000 g/mol was obtained from Sigma-Aldrich in pellet form. Henceforth, this copolymer will be termed as PVH. The PEI of grade Ultem-1000 with M_w = 55,000 g/mol was obtained in powder form from SABIC innovative plastics, Europe. Blends with various weight percentage of PVH/PEI were prepared by conventional melt-mixing and the samples are designated as $PHPI_{00}$, $PHPI_{20}$, $PHPI_{40}$, $PHPI_{50}$, $PHPI_{60}$, $PHPI_{80}$, $PHPI_{85}$, $PHPI_{90}$, $PHPI_{95}$ and $PHPI_{100}$, where the subscripts denote the PEI content (wt %) in the blend.

2.2. Characterization
The FTIR spectrophotometer of Perkin Elmer (model Spectrum 100) was used to identify the possible interacting groups between the polymers. The XRD measurements were performed with PAN Analytical X-ray systems (model X'pert PRO) (Cu K_α radiation, λ = 1.54 Å) in the 2θ range 5° to 80°. Thermo gravimetric analysis was performed using a TGA instrument (Mettler–Toledo TGA/SDTA 851^e) in the temperature range 30 to 1000 ^{o}C. The surface morphology of the blends was examined using a Carl Zeiss EVO 50 SEM, with 10 kV operating voltage. Prior to SEM measurements, the blends were treated with acetone at room temperature for 24 h, in order to remove PVH phase from them. The DSC Q200 (TA instruments) was employed for carrying out the DSC measurements. The PALS measurements were performed at room temperature using a conventional fast-fast coincidence system having a time resolution of about 200 ps. The lifetime spectra were resolved in to three lifetime components using PATFIT program and were also analyzed using the MELT program to obtain a continuous distribution of the annihilation lifetime. The DB measurement system consists of ORTEC high-purity germanium (HpGe) detector having 1.3 keV energy resolution at 662 keV gamma line of ^{137}Cs source. The rheological measurements were performed using a Rosand capillary rheometer of Malvern make (model RH7) at 380 ^{o}C in air medium. The Dielectric measurements were conducted at a frequency of 1kHz using DS 6000 Dielectric Analyzer of M/s. Lacerta Technology, UK using circular electrodes (dia = 33 mm) and the samples used were ca. 0.4 mm thick.

3. Results and Discussion

3.1. Interaction between PVH and PEI
The FTIR results infer a possible dipole-dipole interaction exists between electron deficient imide group of PEI and electro-negative $>CF_2$ groups of PVH. The X-ray scattering profile of PVH reveals two sharp close diffraction peaks at 2θ = 18.2^o and 20.7^o, a well separated peak at 26.6^o and a broad peak close to 40° which are the characteristic crystalline peaks of PVDF. These sharp peaks lose their identity at higher PEI content ($\geq$ 80%) indicating that the dipolar interaction is significant when the PEI content is high. The introduction of fluorine is known to improve the thermo-oxidative stability of polyimides. TGA measurements on PEI exhibited two step decomposition in air medium and the

second step corresponds to its thermo-oxidation. With a mere 20% addition of PVH, the thermo-oxidative stability of PEI enhances by ca. 53 ^{o}C which is a clear indication that the fluorine groups of PVH has interacted with PEI. The SEM photomicrograph of the blend at higher PEI content (PEI $\geq$ 80%) exhibits maximum interfaces which again support good interaction between the two polymers (Fig. 1). From the DSC measurements, the glass transition temperature of PVH is found to be ca. -30 ^{o}C and that of PEI is ca. 218 ^{o}C.
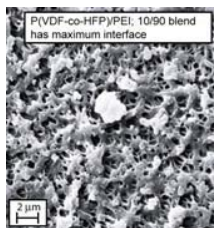

Fig.1. SEM picture showing maximum interfaces for the blend when the PEI content is $\geq$80%.

3.2. Free volume and Dielectric constant

The positron annihilation lifetime results for this blend series reveal three lifetime components and the variation of the long-lived lifetime component that corresponds to o-Ps pick-off lifetime (τ_3) was used to obtain the free volume hole size using the Tao-Eldrup relation. The average free volume size was calculated using the formula $V_{f3} = (4/3)\pi R^3$. The relative free volume fraction (F_{vr}) is then found as $F_{vr} = V_{f3} * I_3$, where I_3 being the o-Ps intensity.
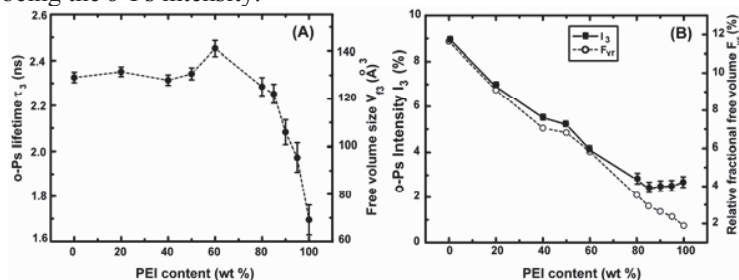

Fig.2. Variation of (A) o-Ps lifetime (τ_3) and free volume size (V_{f3}) and (B) o-Ps intensity (I_3) and the relative fractional free volume (F_{vr}) as a function of PEI content. The lines through the data point are for visual aid.

The o-Ps lifetime shows an initial constancy and attains a maximum when the PEI content is 60% and starts to decrease significantly at later stages (PEI $\geq$ 80%). The increase in lifetime with PEI content is due to increase in free volume which is an indication of non-compatibility between the two polymers (Fig. 2A). But, when the PEI content is $\geq$ 80%, the free volume decreases significantly that goes in agreement with the dipolar interaction between the two polymers at higher PEI content as given by FTIR, XRD and TGA measurements. Also, the SEM showed increased interfaces in this range of PEI content. The free volume distribution pattern of the blends lie within the distribution limits of their pure polymers at higher PEI contents (PEI $\geq$ 80%), revealing good interaction between the two polymers. The I_3 continuously decreases with increasing PEI content (I_3 increases with increase in PVH content) till the PEI content is $\geq$80% and thereafter remains almost constant. The increase of I_3 with increase in PVH (fluorine) content indicates anti-inhibition effect. The constancy of I_3 at higher PEI content indicates that the o-Ps formation is not that significant at the interfaces. The DB results reveal that the 'S' parameter decreases with increase in o-Ps intensity, inferring that the high kinetic energy of the p-electrons of fluorine participates in the annihilation process and thus reveals the information regarding 'chemical environment' inside these free volume 'holes'. To verify the free volume results, shear viscosity measurements were done which showed high viscosity for PEI compared to PVH which is in agreement with the free volume results.
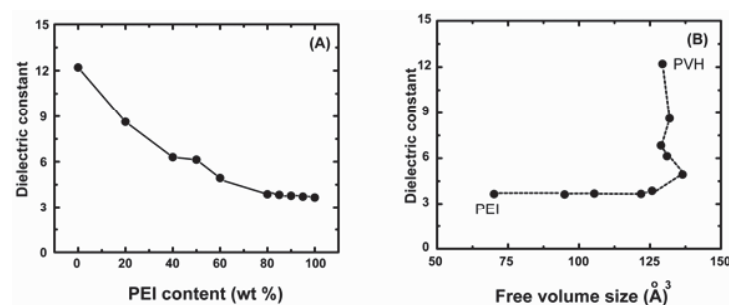
Fig.3. Variation of (A) dielectric constant as a function of PEI content in the blend and (B) dielectric constant as a function of free volume size. The lines through the data point are for visual aid.

The dielectric constant (ε) decreases with increase in the PEI content but at higher PEI content, the change in ε becomes insignificant (Fig. 3A). In case of heterogeneous systems like polymer blends, dielectric constant arises mainly due electronic polarization, interfacial polarization and / or dipole orientation polarization [1,2,5]. The interfacial polarization arises due to accumulation of mobile charges at the interfaces constituted by unlike phases. The almost constant value of ε even when the interfaces are maximum (as revealed by SEM when PEI content is $\geq 80\%$), indicates that interfacial polarization is not contributing significantly to the observed change in dielectric constant. The dipole orientation polarization arises due to redistribution of charges when a group of atoms with a net permanent dipole moment reorient itself in space fast enough to keep in pace with the oscillations of an applied alternating electric field. The dielectric constant remains almost constant with increase in free volume size till the size reaches ca. 125 Å^3 and thereafter it steeply increases (see Fig. 3B). The process of dipole orientation polarization accompanies the movement of polymer chain segments and the movement requires considerable free volume in the matrix. If the two polymers are compatible, it is difficult for the dipoles to orient and relax in the applied field [5] and for this reason we observe almost constant value of ε when the PEI content is $\geq 80\%$ (see Fig 3B). The process of dipole orientation polarization becomes significant when the PEI content in the blend is $< 80\%$ and at this composition, we know that the interaction of PEI and PVH is insignificant. This incompatibility results to more free volume in the blend which in turn increases the chain mobility and the associated dipole orientation polarization.

4. Conclusions

The origin of dielectric constant in this blend is identified to be mainly from dipole orientation polarization owing to the availability of more free volume. The positive variation of dielectric constant with free volume content is distinct from the generally observed behaviour in polyimides and their blends studied so far. The present results would be of help in more effective design of polymeric electrical charge storage devices.

References
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