Studies in Dielectric Properties of Various Polymers and its Correlation with Surface Free Energy

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Abstract:

Polarizabilty is the basis for dielectric properties of materials. Polymers are important class of materials as they are flexible and can be moulded to any complicated shape depending upon its application in electronic industry as an insulating material. Similarly surfaces properties particularly surface free energy of polymers play an important role in interfacial phenomenon. Polymers are widely used in packaging industry. Surface free energy of polymers has profound effect on various properties such as adhesion, wettability, printability etc, important from packaging applications. Surface free energy of polar polymers is higher as compared to non polar surfaces. Therefore, in the present investigation we try to understand the relation between dielectric properties and surface free energy in general and polar components of surface free energy in particular of variety of polymers. There is no relation between polar components of plasma processed polymers and dielectric constant.

Key words: Dielectric properties, contact angle, surface free energy.

Introduction:

Polymers with well defined surface and bulk properties are of interest for development of technologies. Polymeric materials find large number of applications because of their unique properties such as, low cost, light weight, abundantly available, easy processability, can be moulded and recycled, excellent chemical resistance, non corrosive in nature etc [1, 2]. Adhesion, wettability, printability etc. strongly depends upon surface morphology and chemical composition, the presence of polar / non polar groups on the surface [2]. Most of the polymers used as a dielectric material in many types of capacitors because of their very low dielectric loss and good dielectric strength. The electrical behaviour of material depends upon polarity and molecular dipole distribution. The dielectric properties of material are always responsible for the electrical behaviour of the same material. Dielectric spectroscopy is a useful technique for the investigation of polarizability of the material [3]. Dielectric properties refer to the bulk property of

the material where as surface free energy (SFE) arises due to the chemical composition of top layer of few hundreds of Angstroms. However, for both the dielectric as well as surface free energy the presence of polar groups are important. The measurement of contact angle with various probe liquids can be used to determine SFE.

In the present investigation, we have selected variety of unmodified / untreated polymers because we believe that the surface composition of such polymers is same as that of the bulk and hence the surface property (contact angle and surface free energy) and bulk property (dielectric constant) can be correlated. However, if such polymers are subjected to some surface modification techniques such as plasma, glow discharge, Dielectric Barrier (DB) discharge, corona, flame, enzyme treatment etc, which modifies only surfaces where as bulk remains unchanged, no correlation between surface energy and dielectric properties could be found. All these techniques modify surfaces to ≈ 100 Å top layers. Even if we consider thin polymer film e.g. 50 micron film, the modification is less than 0.02 % top layer. Therefore, surface modified polymers will not show any change in dielectric properties. Thus, contact angle and SFE of unmodified / untreated polymers is correlated with the dielectric properties of the polymers.

Experimental

Materials and Methods

The polymers in the form of films were used to investigate dielectric and surface energy properties are given in the Table 1. Polytetrafluoroethylene (PTFE), Polypropylene (PP), Polyethylene (PE) and Polyethyleneterapthlate (PET) films were purchased from local market. Polystyrene (PS), Poly (methyl methacrylate) (PMMA), Poly(methyl methacrylate –co- butylacrylate) (PMMABA) and Polyvinylidene fluoride (PVDF) materials were received in granular form. The granules were dissolved in suitable solvent (Chloroform) and the required films were prepared by solution casting method. These films were cleaned with Acetone in an ultrasonic bath for 3 min and then dried in air. The thickness of films used in the present investigation is given in Table 1.

Table 1. : - List of polymers with their thicknesses

No.	Polymers	Thickness (μm)
1	Polytetrafluroethylene (PTFE) (Teflon)	312
2	Polypropylene (PP),	150
3	Polyethylene (PE)	40
4	Polystyrene (PS)	50
5	Poly(methyl acrylate –co- butylacrylate) (PMMABA)	60

6	Poly(methyl methacrylate) (PMMA)	50
7	Polyethyleneterapthlate (PET)	160
8	Polyvinylidene fluoride (PVDF)	50

Plasma Processing:

A typical bell jar type plasma reactor having a height of 30 cm and a diameter of 30 cm was used. The two electrodes were capacitively coupled to the RF source capable of giving power output up to 100 W. For gas and monomer, inlet ports were fitted onto the base plate. Magnetron is fitted on base plate of plasma chamber to confine the plasma glow discharge up to volume of 275 cm^3. Polymer films used in present work were cut in to the size of 10 mm x 50 mm. Working pressure was adjusted to 0.2 mbar and gas flow rate to 15 SCCM. The more details of the plasma processing chamber have been reported elsewhere [4].

Contact angle measurements and estimation of surface free energy:

The surface free energy (SFE) of various polymeric films was calculated by measuring the contact angle (CA) using a sessile drop method. Water (W), glycerol (G), formamide (F), and ethylene glycol (EG) of known surface tension (γ_L), polar (γ_L^p) and disperse (γ_L^d) components were used as the probe liquids to measure the angle of contact. At least 10 readings were taken at different places on the sample and the mean is reported here. The error in the measurement was ± 2 degree. The SFE was calculated from CA measurement using Fowke's approximation, Neumann's approach, Zisman and Good's method. For calculation of SFE using Neumann's approach, simplified equations proposed by Deshmukh and Shetty were used [5].

Measurement of Dielectric Properties:

Dielectric properties were measured at room temperature with Wayne Kerr 6500B Precision Impedance Analyzer (20Hz-20MHz, DC Bias 0-40V). The dielectric constant reported here was measured at a fixed frequency 1 KHz for all the samples under investigation. The diameter of both the electrode was 10 mm. Aluminum sheet having 10 mm diameter hole at the centre was put on the sample while applying silver paste so that the area of contact is same for all the sample films. The films were silver- coated from both sides to achieve better electrode contact. The relative dielectric constant was calculated from the measurement of the parallel capacitance with the following formula: [3, 6]

$$\varepsilon_r = \frac{C_p}{C_0} = \frac{C_p \times D}{A \times \varepsilon_0} \tag{1}$$

Where C_p is the parallel capacitance of the polymeric film (acts as dielectric) that was placed between two electrodes and C_0 is the parallel plate capacitance of two electrodes without dielectric material. If the dielectric completely fills the space between the plates, the capacitance increases by the dimensionless factor ε_r. Where (ε_r) is relative dielectric constant / relative permittivity, (C_p) parallel capacitance, (D) thickness of polymeric film, (A) area of electrode and (ε_0) free space permittivity and its value is 8.854×10^{-12} F/m.

Results and Discussion:

Contact angle and surface free energy measurements:

Angle of contact of various liquids mentioned above with different polymeric substrates was measured using sessile drop method. The average of 10 readings is given in Table 2.

Table 2 Contact angle on various polymer substrates

Polymer Sample	CA for Probe Liquid			
	W	G	F	EG
PTFE	106.96	88.40	83.68	72.00
PP	97.15	85.39	81.73	59.57
PE	89.10	74.25	69.08	55.45
PS	84.80	76.75	70.15	61.78
PMMABA	79.19	70.51	62.95	57.01
PMMA	77.53	75.22	57.45	53.62
PET	75.63	67.58	62.87	50.93
PVDF	77.65	65.35	69.07	57.77

The contact angle is the angle, conventionally measured through the liquid, by the tangent drawn at a point where liquid interface meets solid surface as shown in fig 1 below.
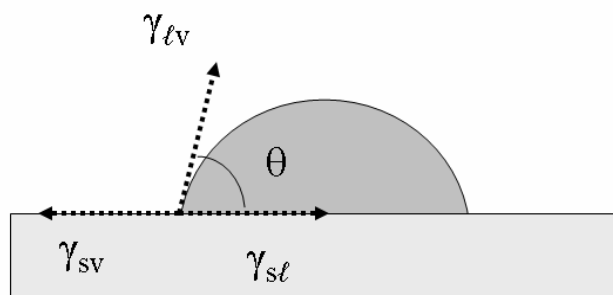

Fig. 1 Angle of contact and various forces

The origin of solid surface tension arises from existence of unbalanced intermolecular forces among molecules at the interfaces. In order to minimize this force, liquids takes shape of a drop whereas due to absence of mobility, solid surfaces are very different and unique from liquids, hence, one cannot measure the solid surface tension (solid surface free energy or simply surface energy) of a solid phase directly as is the case for liquid phase. The possibility of estimating solid surface tension from contact angle relies on a relation, which was recognized by Young in 1805.

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$$

(2)

Where γ_{lv} is the liquid–vapour surface tension or simply surface tension of a liquid, γ_{sv} is the solid surface tension or solid SFE, γ_{sl} is solid–liquid interfacial tension, and θ is angle of contact. In the above equation only two terms the contact angle and liquid surface tension, can be determined easily. It means Young's equation contains only two measurable quantities, γ_{lv} and θ. To determine γ_{sv} and γ_{sl}, an additional expression / relation relating these quantities must be sought. This has inspired many scientists to attempt to find solid surface free energy and they have proposed various theories. The basis, usefulness, and limitations of various theories are described in detail elsewhere [5]. Fowkes approximation and Zisman method requires contact angle data of at least three liquids. Zisman did pioneering work in this field [7, 8]. He was the first to calculate critical surface tension of solids. Zisman's relation is empirical. He plotted cos θ versus liquid surface tension (γ_{lv}) and a quasi-linear relationship between cosine of contact angle and liquid surface tension was observed. The graph was extended to get intercept on the line drawn (parallel to X axis) at cos $\theta = 1$, the corresponding value on X axis gives the critical surface tension. This critical surface tension is usually less than that of the actual surface tension of a solid. However, in many cases, Zisman's model for estimating surface free energies provides workable solution.

Good and Girifalco [9] formulated a theory of interfacial tension between two phases (1 and 2) using geometric mean (statistical mechanics) to the surface tension of each phase. Single liquid contact angle data is sufficient to calculate SFE using Good's method. Therefore, we have calculated SFE using Good's equation for the given polymer surface for all the liquids and the average value of SFE is reported here. According to Fowkes, surface energy can assumed as the result of several components such as dispersion, dipole-dipole, induced dipole-dipole, hydrogen bonding, pi bonding, acceptor-donor interactions, electrostatic, etc. It makes use of graphical representation to generate / evaluate the polar (γ_s^p) and disperse (γ_s^d) components of solid surface energy (γ_s). The total SFE can be given as [10, 11],

$$\gamma_s = \gamma_s^p + \gamma_s^d$$

(3)

Even though the surface energy of two polymers is same, there can be large difference in their surface properties such as wettability, adhesion, printability etc. because of different values of polar component present in the surface energy. Wettability, adhesion, printability etc are very important from packaging point of view [2, 12]. Obviously, the one in which polar component is more than other, will show better properties. Therefore, estimation of polar and disperse components of SFE is vital for the intended use of the polymer. The method of estimation of SFE of solids using Fowkes approximation is described elsewhere [13].

Neumann has discussed the surface tension of solids from purely thermodynamic point of view. Neumann has derived the equation for the determination of solid SFE from single liquid contact angle measurement. The beauty of this equation is that the variation in the value of SFE obtained due to use of different probe liquid is minimum. Therefore, in the present investigation, we have reported average value of SFE calculated from different probe liquids. The intension of calculating SFE using various approaches is that each method has its merit and to know the variations among all the methods.

It is well known that when a water drop is put on the hydrophobic polymer surface, it balls up. It is due to very low solid SFE of the polymer. Hence higher is the angle of contact; lower is the solid SFE or simply surface energy. It is clear from Table 2 that PTFE is the most hydrophobic one and PVDF is the most hydrophilic amongst the studied polymers.

The SFE calculated from various methods and relative dielectric constant (ε_r) of the polymers is given in Table 3.

Table 3. SFE and relative dielectric constant of different polymers.

Polymer sample	Method of calculation of SFE mJ/m^2						Dielectric constant (ε_r)	
	Z	G	N	F			M	L
				γ_s^p	γ_s^d	γ_{sv}		
PTFE	19.00	19.19	22.79	0.85	19.46	20.31	2.18	2.0 - 2.1 [14]
PP	22.30	21.53	26.20	3.37	19.53	23.90	2.21	2.2 – 2.3 [14]
PE	30.14	24.47	31.19	3.37	27.29	30.66	2.22	2.3 – 2.35 [15]
PS	22.00	24.39	30.64	7.90	17.73	25.63	2.33	2.49 – 2.6 [14]
PMMABA	27.00	28.27	33.91	9.76	19.71	29.47	2.6	Not Available
PMMA	28.68	29.14	34.58	10.53	19.59	30.12	3.19	3.3 – 3.9 [16]
PET	30.00	30.29	35.56	11.27	21.52	32.79	3.21	3.0 – 3.3 [17]
PVDF	25.30	26.97	33.98	14.75	12.87	27.62	9.12	8 – 10.4 [18]

Abbreviations used in Table 3: Z = Zisman, G = Good, N = Neumann, F = Fowkes, M = Measured and L = reported in Literature.

It was observed that the values of SFE of various polymers calculated from different techniques are in good agreement with each other. In general, the trend showed by various techniques is similar, though there is some difference in the absolute values of SFE. This may be due to the different approaches such as thermodynamic, geometrical mean, empirical etc. Measured values of relative dielectric constant of various polymers are in concurrence with the values reported in literature. However, it is difficult to correlate total SFE with relative dielectric constant (ε_r). Further, it was observed that there is relation between polar component of SFE and the relative dielectric constant of polymers. It clearly indicates that the polymers having higher dielectric constant have more polar groups in turn more polar components. However, this does not hold good for plasma surface modified polymers. In order to corroborate this, a few polymers were subjected to 10 min air plasma processed. The data obtained for these polymers is presented in Table 4.

Table 4. Polar components and dielectric constant of treated & untreated polymers.

Polymer Sample	Polar component of SFE (mJ/m^2)		Dielectric constant (ε_r)	
	Untreated	Treated	Untreated	Treated
PP	3.37	14.44	2.21	2.22
PE	3.37	32.50	2.22	2.20
PET	11.27	35.84	3.21	3.21

Though there is considerable difference in the polar components of SFE of untreated and plasma treated polymer, the values of relative dielectric constant (ε_r) remain unchanged. This is because, plasma surface modification is carried out for ≈100 Å top layer only, where as bulk polymer (99.9 % volume) remain unchanged. Also the extent of surface modification and incorporation of polar groups onto the polymer surfaces depends upon the chemical structure, degree of crystallinity of the polymer [19, 20].

Conclusion

Dielectric constant and polar component of SFE showed similar trend in the unmodified / untreated polymers. Properties such as adhesion, wettablity, printability etc are very important from packaging point of view and are strongly dependent on polar components of surface energy. Therefore just by measuring the dielectric property of the polymers, one can predict whether the polymer is suitable for packaging application or not and the need of a surface modification technique. Secondly, we also conclude that the plasma surface modification carried out on the topmost layers does not affect dielectric properties of the polymers. Thus, confirming the limitations of the correlations of SFE in general and polar components in particular, with relative dielectric constant.

Acknowledgements

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