

Dielectric and microhardness studies of methylene blue doped PMMA matrix

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Pure and methylene blue (MB) doped poly(methyl methacrylate) (PMMA) samples were prepared by free radical vinyl polymerization. The effect of methylene blue, which itself is polar in nature, on the glass transition temperature, electric permittivity, and microhardness of the PMMA matrix was studied. It was found that incorporation of the dye increases the electric permittivity and decreases the glass transition temperature of the system. The maximum value of the loss tangent below the glass transition temperature suggests the rotation of the ester side group (β relaxation). MB can also act as a retarder of free radical polymerization causing reduction in the hardness value.

Key words: PMMA; methylene blue; electric permittivity; microhardness

1. Introduction

Organic dye-polymer composites have received considerable attention as a family of potentially new electrooptic materials, because of their interesting dielectric properties such as the ability of an electric field to polarize the material to create electric dipoles. These are basically insulators having the property of storing and dissipating electrical energy when subjected to an electromagnetic field. Organic dyes possess conjugated molecular structures with terminating electron donors and acceptors and large dipole moments, and hence can be oriented in a high static field. The dyes can change the electric permittivity and the electrooptic coefficients of the polymer system [1, 2]. The dye polymers are used in dye lasers, storage materials, capacitors, etc. Many of dye polymer systems have a number of advantages as nonlinear optical materials with high optical quality and processibility. Therefore it is important to understand the effect of the organic dye molecules on the physical, dielectric and mechanical properties of such systems.

The structure of the polymer determines its polarity and hence many of the dielectric properties of the polymer. In polar plastics, dipoles are created by an imbalance in

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the distribution of electrons, and in the presence of an electric field the dipoles will tend to align with the field direction. Examples of polar plastics are PMMA, polyvinyl chloride (PVC), polyamide (PA, Nylon), polycarbonate (PC) etc. to name a few. These materials tend to be only moderately good as insulators. The addition of the polar dye such as methylene blue, enables the system to be more polarizable, hence contributing more to the electric permittivity [3]. In addition, such polar dyes can modify the glass transition temperature and microhardness of the polymer. In view of these facts, we report the effect of methylene blue on the glass transition temperature, electric permittivity, and the hardness of a pure PMMA matrix.

2. Experimental

Five samples A, B, C, D and E with varying concentrations of methylene blue were prepared (Table 1) by bulk polymerization.

Table 1. Compositions and physical parameters of the samples

Parameter	Sample				
	A	B	C	D	E
PMMA V [cm^3]	2	2	2	2	2
Methylene blue c [M]	0	0.5×10^{-3}	1×10^{-3}	1.5×10^{-3}	2×10^{-3}
Thickness [mm]	1.15	0.77	0.90	0.80	1.10
Area [mm^2]	50	67	55	0.65	55

For the preparation of samples, the monomer MMA is mixed with a respective dye dissolved in ethyl alcohol in the ratio 4:1. 1 g of benzoyl peroxide per 100 cm^3 of the solution is used as an polymerization inhibitor. Accurately weighed MB is dissolved in ethanol since it has limited solubility in the monomer MMA. The monomer–alcohol mixture containing the dye and the inhibitor, in a glass test tube were kept in a bath maintained at 50°C for polymerization. After polymerization the samples were cut into pieces of millimetre thickness using a crystal cutter and then thoroughly polished for further studies. The thickness of the sample was measured with a digital screw gauge. The dielectric measurements were done using an impedance analyzer (Hioki impedance analyzer model 3531). The microhardness measurements of the samples were done using a Vicker's microhardness tester (Lietz). The glass transition temperature of the samples was measured by differential scanning calorimetry (Shimadzu DSC-60) under nitrogen atmosphere.

3. Results and discussion

PMMA is a transparent polymer, used as a shatterproof replacement of glass in a variety of applications. The material is one of the hardest polymers, rigid with

a glossy finish and good weather resistance. PMMA is a synthetic resin belonging to the family of polymeric organic compounds, and is made by free radical vinyl polymerization from the monomer methyl methacrylate (Fig. 1), having the chemical formula $(C_5H_8O_2)_n$. The structure of a PMMA macromolecule is linear with respect to the main carbon chain.

Methylene blue, belonging to a thiazene class of dyes, is also known as methylthionine chloride or 3,7 bis (dimethyl amino) phenothiazin-5-ium chloride or swiss blue. It has the molecular formula $C_{16}H_{18}ClN_3S$ and the molecular mass of 319.85 g/mol and the melting point of about 190 °C. It is stable under ordinary conditions. The structure of PMMA and methylene blue are shown in Fig. 2.

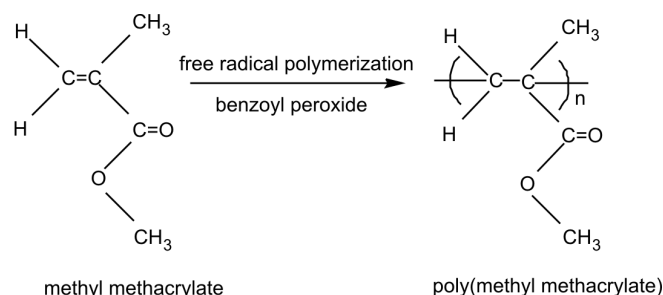


Fig. 1. Polymerization of MMA

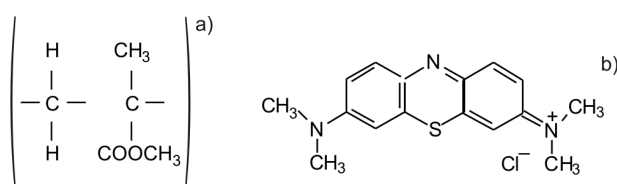


Fig. 2. The structure of PMMA (a) and methylene blue (b)

MB molecule is a polar molecule exhibiting good dielectric properties [4]. Methylene blue can also be used as a photosensitizer in free radical polymerization. The dye can be used as a polymerization inhibitor of several vinyl monomers [5].

Electric permittivity is a measure of the ability of a material to be polarized by an electric field. The dielectric properties of PMMA are determined by the strong electric dipole in the ester side group associated with the orientation of the ester group in the electric field [6, 7]. The electric permittivity decreases with frequency for pure PMMA (Fig. 3). The MB doped samples also show the same behaviour. For polar plastics, the alternating current frequency is an important factor because of the time taken to align the polar dipoles. At very low frequencies the dipoles have sufficient time to align with the field before it changes direction and hence the electric permittivity is high. At high frequencies, the dipoles do not have sufficient time to align before the field changes its direction and hence the electric permittivity is lower [8]. At intermediate

frequencies, the dipoles move but do not complete their movement before the field changes direction and they must realign with the changed field.

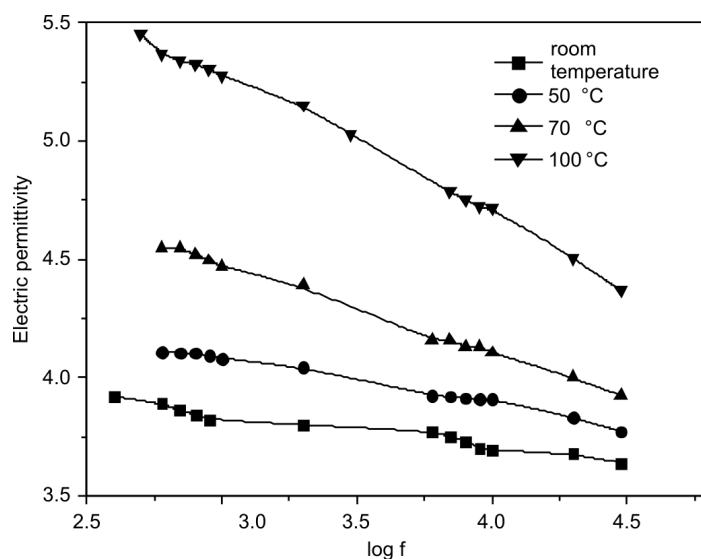


Fig. 3. Dependence of electric permittivity on the frequency of sample A at various temperatures

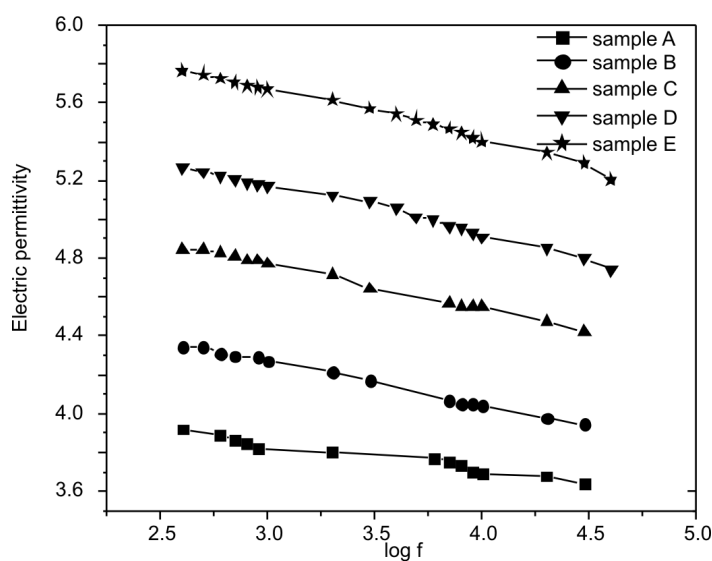


Fig. 4. Dependence of electric permittivity on the frequency of doped and undoped samples at room temperature

Figure 3 shows how the electric permittivity changes with temperature. The increase is due to an increase of polarization arising from the freer molecular motion of

polymer chains which allows orientation of dipolar units in the applied field. The increase is steeper at lower frequencies. At lower temperatures, the dipoles are rigidly fixed and hence the field cannot change the the dipoles. All the five samples exhibit the same behaviour at various frequencies. From Figure 4 it is evident that the electric permittivity increases when the dye is added to the matrix. Since MB is a polar molecule, the addition of the dye causes the number of dipoles to increase, which in turn increases the electric permittivity of the system [3]. The addition of a polar dye enables the system to be more polarizable and enhances the electric permittivity.

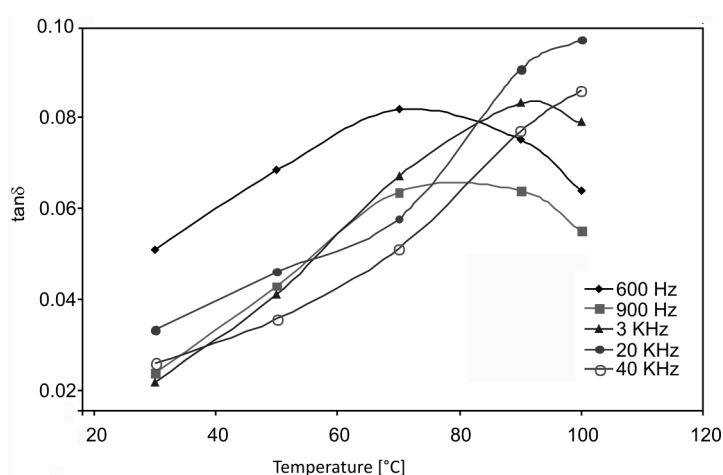


Fig. 5. Temperature dependence of loss tangent on temperature at various frequencies for sample A

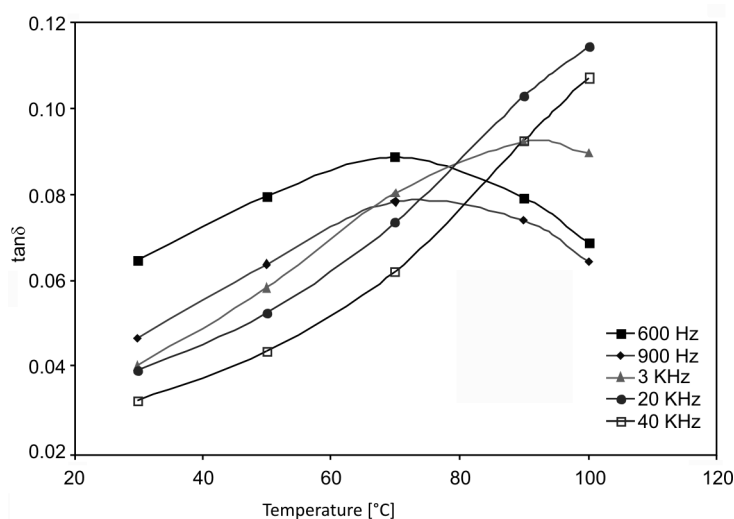


Fig. 6. Temperature dependence of loss tangent on temperature at various frequencies for sample C

The variations of loss tangent with temperature at various frequencies for samples A and C are shown in Figs. 5 and 6. Each $\tan\delta$ curve has a maximum depending on the frequency of the applied field. In these figures, a loss peak appears at a temperature below the glass transition temperature (108 °C) for lower frequencies. This loss peak is usually associated with β relaxation which occurs at temperatures lower than the glass transition temperature. Here the β relaxation is assigned to the orientation of the ester side group [6]. The maximum values of $\tan\delta$ shift to a higher temperature with increasing applied frequencies. These shifts of the peak towards higher temperature with increasing frequencies are clearly an indication of the dipolar type of relaxation, which arises due to the relaxation process involving the movements of the dipoles.

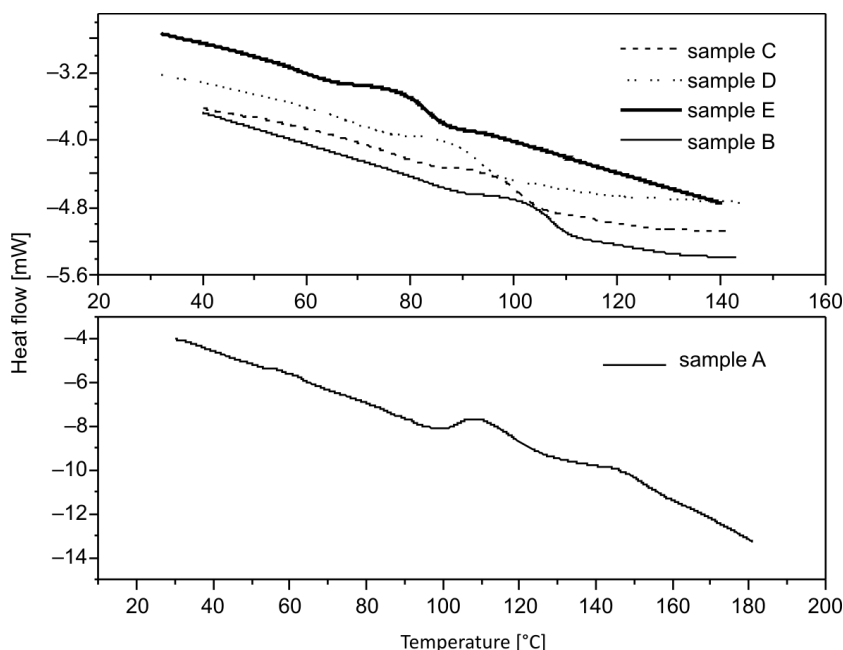


Fig. 7. DSC thermograms of doped and undoped samples

Elastic and plastic properties of polymers depend on the chain length, the degree of cross linking and the crystallinity of the material. Short chains are associated with low modulus and hardness [9]. The DSC curves for doped and undoped samples are shown in Fig. 7. For PMMA, the transition region is 95–120 °C, and the transition temperature is found to be 108 °C. The transition temperature T_g depends on the molecular weight, side branches, steric hindrance, type of bonding within the molecular structure (covalent or non-covalent), presence of plasticizers, copolymers and other physical conditions like pressure [10]. In the case of PMMA doped with MB (5×10^{-4} M), the transition region is 90–110 °C, and the transition temperature is around 103 °C. But for the MB (2×10^{-3} M) doped PMMA sample, the transition region is around 70–83 °C. The transition temperature is 77 °C. The difference in the glass transition

temperature (T_g) between pure and MB doped PMMA is due to the plasticizing effect of methylene blue on the PMMA matrix. Plasticizers are usually low molecular weight non-volatile substances, which, when added to a polymer, improve its flexibility, processibility and hence utility. Here it is an external plastification by the methylene blue in the PMMA matrix, i.e. T_g is lowered by the physical addition of the plasticizer methylene blue. As the polymer becomes softer, the transition temperature also decreases and it will lead to the decrease in the hardness value.

Vicker's hardness H_v is given by

$$H_v = \frac{1.854P}{d^2}$$

where P is the test load [kg] and d is the indentation diagonal length [mm] is measured based on the test load and on the indentation diagonal length. It is an important mechanical property that may be defined as a measure of the resistance of a material to the application of a contact load.

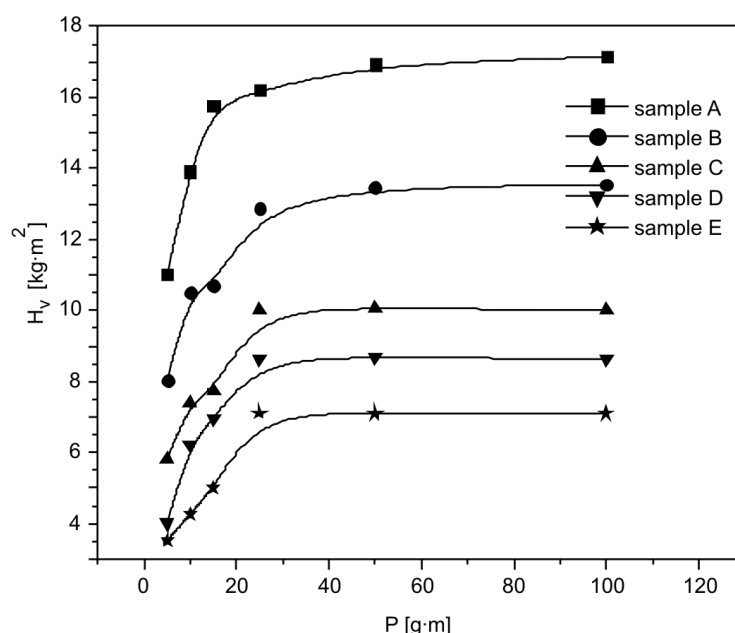


Fig. 8. Vicker's hardness in function of load for all the samples

The dependence of hardness on the load of indentation is shown in Fig. 8. The values of hardness reach saturation around a load of 30 g. The H_v and T_g values for various samples are summarized in Table 2. It is obvious that the hardness is the highest ($H_v = 17$) for sample A, and the lowest (7) for sample E. Since the dye is a plasticizer, the addition of the dye makes the polymer softer and consequently, as expected, T_g of the dye polymer system is decreased. Such a softening behaviour in the presence

of organic molecules such as DR1 in PMMA [1], lead phthalocyanine in polycarbonate [11], dibutyl phthalate, tricresyl phosphate in PVC [12] and MNA in PMMA [13] is already known. The plasticizers substantially reduce the brittleness of many amorphous polymers by reducing the cohesive forces of attraction between polymer chains. The dye molecules penetrate into the polymer matrix and establish polar attractive forces between it and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thereby reducing the T_g value [12]. Moreover MB is a strong retarder of the polymerization of the vinyl monomer MMA [4]. This may affect the length of the polymeric chain to some extent. This may also be one of the reasons for the softening of the polymer PMMA.

Table 2. Vicker's hardness and transition temperature for various samples

Sample	Hardness [kg/m ²]	Transition temperature [°C]
A	17	108
B	13	103
C	10	95
D	8.5	86
E	7	77

4. Conclusion

The electric permittivity of PMMA samples is found to increase with temperature and after addition of the dye. It decreases in function of increasing frequency. The dipolar nature of the dielectric relaxation is confirmed by the temperature dependences of the loss tangent at various frequencies. The dye has a plasticizing effect on the polymer which reduces the glass transition temperature of the system. The reduction in the hardness value, in turn, can result in a lowering of the glass transition temperature. These two facts have been substantiated by the DSC and microhardness measurements. MB can also act as a retarder of free radical polymerization, which affects the length of the polymeric chain. This can also be another cause for the reduction in the hardness value.

References

- [1] LEI DU, RUNT J., SAFARI A., NEWNHAM R.E., *Macromolecules*, 20 (1987), 1797.
- [2] SINGER K.D., SOHN J.E., LALAMA S.J., *Appl. Phys. Lett.*, 49 (1986), 248.
- [3] JAMES HUNT P., FITZGERALD JOHN J., *Dielectric Spectroscopy of Polymeric Materials. Fundamentals and Applications*, Am. Chem. Soc., Washington DC, 1997.
- [4] MURTHY V.R.K., PRASADA T.A., SOBHANADRI J., *J. Phys.D: Appl. Phys.*, 10 (1977), 2405.

- [5] NIRANJAN K. DAS., BROJA M.MANDAL., *Polymer.*, 23 (1982), 1653.
- [6] MAZUR K., *J. Phys. D Appl. Phys.*, 30 (1997), 1383.
- [7] NARULA G.K., THIRIPATHI A., PILLAI P.K.C., *J. Mater. Sci.*, 26 (1991), 4130.
- [8] AKRAM M., JAVED A., RIZVI Z.T., *Turk. J. Phys.*, 29 (2005), 355.
- [9] TABOR D., *Rev. Phys. Techn.*, 1 (1970), 145.
- [10] MADEKA H., KOKINI J.L., *Cereal Chem.*, 73 (1996), 433.
- [11] RANADE A., WANG H., HILTNER A., BAER E., SHIRK S.J., LEPKOWICZ R.S., *Polymer.*, 48 (2007), 624.
- [12] GOWARIKER V.R., VISWANATHAN N.V., SREEDHAR JAYADEV., *Polymer Science*, Wiley, 1992.
- [13] SUGIARA T., FUJII K., HAGA H., YAMAMOTO S., *Appl. Phys. Lett.*, 69 (1996), 2971.

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