Pure and methylene blue (MB) doped Poly methyl methacrylate (PMMA) samples were prepared using free radical vinyl polymerization. The effect of methylene blue, which itself is polar in nature, on the glass transition temperature, dielectric constant, and microhardness of the PMMA matrix was studied. It is observed that the incorporation of dye can increase the dielectric constant and decrease the glass transition temperature of the system. MB can also act as a retarder of free radical polymerization causing reduction in the hardness value. Colourimetric studies were undertaken to obtain the colour coordinates of the three dye polymeric systems BTB/PMMA in the blue region, Rh6G/PMMA in the green region and MB/PMMA in the red region. Further these coordinates were superimposed with the CIE 1931 chromaticity diagram to determine the purity values.
4.1. Dielectric and Hardness Studies

4.1.1 Introduction

Organic dye–polymer composites have received considerable attention as a family of new potential electro-optic materials because of its interesting dielectric properties. Dielectric materials have interesting electric properties because of 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 electromagnetic field. Organic dyes possess conjugated molecular structures with terminating electron donors and acceptors and large dipole moments. These can be oriented in a high static field. These dyes can change the dielectric constant and the electro-optic coefficients of the polymer system [1, 2]. The dye-polymeres are used in the field of dye lasers, storage materials, capacitors etc. Many of the 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.

Most plastics are dielectrics or insulators (poor conductors of electricity) and resist the flow of current. This is one of the most useful properties of plastics and makes much of our modern society possible through the use of plastics as wire coatings, switches and other electrical and electronic products. In polar plastics, dipoles are created by an imbalance in the distribution of electrons and in the presence of
an electric field the dipoles will attempt to move to align with the field. This will create ‘dipole polarization’ of the material and because of the movement of the dipoles is involved there is a time element to the movement. 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 non-polar plastics are truly covalent and generally have symmetrical molecules. In these materials there are no polar dipoles present and the application of an electric field does not try to align any dipoles. The electric field does, however, move the electrons slightly in the direction of the electric field to create ‘electron polarization’. In this case the only movement is that of electrons and this is effectively instantaneous. Examples of non-polar plastics are polytetrafluoroethylene (PTFE and many other fluoropolymers), polyethylene (PE), polypropene (PP) and polystyrene (PS) and these materials tend to have high resistivities and low dielectric constants.

For polar plastics the alternating current frequency is an important factor because of the time taken to align the polar dipoles. For non-polar plastics the dielectric constant is independent of the alternating current frequency non-polar plastics always have dielectric constants of less than 3.

The structure of the polymer determines whether it is polar or non-polar in nature and this determines many of the dielectric properties of the polymer. The addition of the polar dye like methylene blue enables the system to be more polarizable contributing more to the
dielectric constant [3]. In addition to this, 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, dielectric constant and the hardness of the pure PMMA matrix.

4.1.2 Experimental

Five samples A, B, C, D and E with varying concentration of methylene blue were prepared as tabulated in Table 4.1 by bulk polymerization. For the preparation of the samples, the monomer MMA is mixed with the respective dye dissolved in ethyl alcohol in the ratio 4:1. 1gm of benzoyl peroxide per 100ml of the solution is used as an initiator for polymerization. Accurately weighed MB is dissolved in ethanol since it has limited solubility in the monomer MMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>2ml</td>
<td>2ml</td>
<td>2ml</td>
<td>2ml</td>
<td>2ml</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>0 M</td>
<td>0.5x10^{-3}M</td>
<td>1x10^{-3}M</td>
<td>1.5x10^{-3}M</td>
<td>2x10^{-3}M</td>
</tr>
<tr>
<td>Thickness</td>
<td>1.15mm</td>
<td>0.77mm</td>
<td>0.90mm</td>
<td>0.80mm</td>
<td>1.10mm</td>
</tr>
<tr>
<td>Area</td>
<td>50mm$^2$</td>
<td>67mm$^2$</td>
<td>55mm$^2$</td>
<td>0.65mm$^2$</td>
<td>55mm$^2$</td>
</tr>
</tbody>
</table>

The monomer-alcohol mixture containing the dye and the initiator, taken in a glass test tube is kept in a constant temperature bath maintained at 50°C for polymerization. After polymerization the
samples were cut into millimeter thickness pieces using a crystal cutter and then polished well for further studies. The thickness of the samples were measured using digital screw gauge. The dielectric measurements were done using an impedance analyzer (Hioki Impedance analyzer model 3531). The microhardness measurements of the samples were measured using Vickers microhardness tester (Leitz). The glass transition temperature was obtained using differential scanning calorimetry (DSC) for the samples under nitrogen atmosphere. The scanning electron micrograph of the cross-section of the samples is taken using Jeol JSM 6390 Scanning Electron Microscope.

4.1.3 Results and Discussion

4.1.3.1 Poly Methyl Methacrylate (PMMA)

PMMA is one of the earliest polymers. It is a clear transparent polymer, used as a shatter proof replacement of glass in a variety of applications. The material is one of the hardest polymers, rigid with glossy finish and good weather resistance. It 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, having the chemical formula \((\text{C}_2\text{O}_5\text{H}_8)_n\).
The structure of PMMA macromolecule is linear with respect to the main carbon chain.

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{CH}_3 \\
\text{COOCH}_3
\end{array}
\]

### 4.1.3.2 Methylene Blue (MB)

Methylene Blue a thiazene class of dye, is also known as methylthionine chloride or 3, 7 bis (dimethyl amino) phenazathonium chloride or swiss blue. It has a molecular formula C\textsubscript{16}H\textsubscript{18}CIN\textsubscript{3}S. It has a molecular mass of 319.85g/mol and a melting point of about 190°C. It is stable under ordinary conditions. Methylene blue has the following structure (Figure 4.1).

![Molecular structure of methylene blue](image)

Figure 4.1 Molecular structure of methylene blue.

MB molecule is polar in nature. It shows good dielectric properties to the applied electric field [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]. The dielectric constant measures how well a material separates the plates in a capacitor. It is defined as the ratio of the capacitance of a set of electrodes with the dielectric material between them to the capacitance of the same electrodes with a vacuum between them. The dielectric
properties of PMMA are determined by the strong electric dipole in the ester side group and the dipole moment is associated with the orientation of the ester group in the electric field [6, 7]. Figure 4.2 shows the variation of dielectric constant with frequency at different temperatures for pure PMMA.

The dielectric constant shows decreasing nature with frequency. The MB doped samples also show the same nature (Figures 4.3 - 4.6).
Figure 4.3 Variation of dielectric constant with frequency for sample B at different temperatures.

Figure 4.4 Dielectric constant with frequency for sample C
Figure 4.5 Variation of dielectric constant with frequency for sample D

Figure 4.6 Variation of dielectric constant with frequency for sample E
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 the dielectric constant is high. At high frequencies the dipoles do not have sufficient time to align before the field changes direction and hence the dielectric constant is lower [8]. 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.

From the figures it is observed that the dielectric constant increases with temperature. The increase is due to an increase of polarization arising from the facilitation of the molecular motion of polymer chains which allows orientation of dipolar units in the applied field. The increase is steeper at lower frequency. At lower temperature the dipoles are rigidly fixed and hence the field cannot change the condition of the dipoles. All the five samples show the same nature at all frequencies. From Figures 4.7 & 4.8, it is clear that the dielectric constant value increases when the dye is added to the matrix. Since MB is polar in nature and the addition of the dye causes the number of dipoles to increase which in turn increases the dielectric constant of the system [3]. The addition of a polar dye enables the system to be more polarizable and contributes to the dielectric constant. The values of dielectric constant for the samples at different temperatures are tabulated in Table 4.2.
Dielectric, Colourimetric,...PMMA Matrices

Figure 4.7 Variation of dielectric constant for different samples at room temperature.

Figure 4.8 Dielectric constant for all the samples at 100°C.
Table 4.2 Dielectric constants of the samples.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Room Temperature</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>600</td>
<td>3.87</td>
<td>4.32</td>
</tr>
<tr>
<td>10KHz</td>
<td>3.69</td>
<td>3.82</td>
</tr>
<tr>
<td>20KHz</td>
<td>3.67</td>
<td>3.72</td>
</tr>
<tr>
<td>40KHz</td>
<td>3.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The 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 all the samples are shown in Figure 4.9.
For PMMA the transition region (95°C-120°C) and the transition temperature is found to be 108°C. The $T_g$ depends on the molecular weight, side branches, steric hindrance, covalent and non-covalent bonding within the molecular structure, presence of plasticizer, copolymers and other physical conditions such as pressure [10]. In the case of PMMA doped with MB (5$x10^{-4}$M) the transition region is 90-110°C, and the transition temperature is around 103°C. But for the MB (2$x10^{-3}$M) doped PMMA sample the transition region is around 70-83°C and the transition temperature is at 77°C. Here there is a difference of around 30°C in the transition temperature ($T_g$) as compared to that of pure PMMA sample. This 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 plasticization by the methylene blue on the PMMA matrix, i.e. the $T_g$ 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. In order to ascertain the effect on the hardness value we here also conducted the microhardness studies of the samples. The Vicker’s hardness ($H_v$) is measured based on the test load and 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.
The 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). Figure 4.10 shows the variation of hardness value with the load of indentation. At around 30gm of the load the hardness value is saturated and all the samples show the same pattern. The hardness values \((H_v)\) and the transition temperature \((T_g)\) for the various samples are summarised in Table 4.3. From the table it is clear that the hardness analysis yields a highest \(H_v\) value of 17 for sample A, while a lowest value of 7 for sample E. Since the dye is a plasticizer, the addition of the dye makes the polymer softer and consequently as expected the \(T_g\) of the dye polymer system is decreased. Such a softening behaviour in the presence of organic molecules like DR1 in PMMA [1], lead
phthalocyanine in polycarbonate [11], dibutyl phthalate, tricresyl phosphate in PVC [12] and MNA in PMMA [13] have already been reported.

Table 4.3 Transition temperature and Vicker’s hardness.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Transition temperature (°C)</th>
<th>Hardness (Kg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>108</td>
<td>17</td>
</tr>
<tr>
<td>B</td>
<td>103</td>
<td>13</td>
</tr>
<tr>
<td>C</td>
<td>95</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>86</td>
<td>8.5</td>
</tr>
<tr>
<td>E</td>
<td>77</td>
<td>7</td>
</tr>
</tbody>
</table>

The plasticizers substantially reduce the brittleness of many amorphous polymers. Here this effect is due to the reduction in cohesive forces of attraction between polymer chains. The dye molecules penetrate into the polymer matrix and establish polar attractive forces between these molecules 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 [5]. 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 when MB is added to it.
4.1.3.3 SEM Analysis

A direct evidence of the plasticizing effect of the dyes on PMMA was obtained from the scanning electron micrographs. A representative SEM of the sample cross-section fractured in liquid nitrogen (cryo cutting) for the pure and doped samples (PMMA and MB/PMMA) are shown in Figure 4.11. Both photographs were taken with 5kV electrons at a magnification of 8500.

![Figure 4.11 SEM micrographs of the crosssection of (a) pure PMMA and (b) MB/PMMA](image)

The doped sample shows relatively uniform and smooth surface compared to that of pure PMMA. This is a clear indication of the plasticizing effect of the dye molecules on PMMA.

4.2 Colourimetry

4.2.1 Colourimetry and Colour Coordinates

Any colour sensation can be reproduced by the judicious combination of three monochromatic components. In terms of colour, we have additive processes (emittance) and subtractive processes
Dielectric, Colourimetric,…PMMA Matrices

(reflectance). For the emittance the primaries RED, GREEN and BLUE are setup for the colour matching system. This is the way by which colour is produced in the colour display. YELLOW, CYAN and MAGENTA is termed as the colour primaries for the subtractive colour mixtures, because these are the minimal number of pigments required to produce all other colours.

In the study of the perception of colour, one of the first mathematically defined colour spaces was the CIE 1931 XYZ colour space (also known as CIE 1931 colour space), created by the Commission Internationale Eclairage (International Commission on Illumination), CIE in 1931.

The CIE has defined a set of three colour-matching functions, called $x(\lambda)$, $y(\lambda)$ and $z(\lambda)$ which is the amount of primaries required to reproduce all of the monochromatic light. They are merely the auxiliary functions, which give how these primaries should be mixed together to generate the metamer (matching visual appearances of two colour stimuli, two light sources, made up of different mixtures of various wavelengths, may appear to be the same colour; this effect is called metamerism.) of the monochromatic colours. These are the spectral sensitivity curves of three linear light detectors that yield the CIEXYZ ‘tristimulus values’ $X$, $Y$, and $Z$. The tabulated numerical values of these functions are known collectively as the CIE standard observer. The tristimulus values of a colour are the amounts of the three primary colours in a three-component additive colour model needed to match that test colour. The tristimulus values are most often given in
Chapter 4

the CIE 1931 colour space. Two light sources have the same apparent colour to an observer when they have the same tristimulus values, no matter what spectral distributions of light were used to produce them.

The CIE standard colour primaries model the response of the three photoreceptors in the human eye and is referred to as ‘standard CIE observer’. The standard observer is characterized by three colour matching functions. The colour matching functions are the numerical description of the chromatic response of the observer. The finalized response curves for the standard observer is known as the ‘Tristimulus Response Curves’ and is shown in Figure 4.12. These are defined in terms of the colour matching functions $x, y$ and $z$ or the tristimulus

Figure 4.12 Tristimulus response of human eye response functions. From the figure it is clear that $x$, the red tristimulus value has a certain amount of blue in it in order to duplicate the response of the red preceptor in the retina of the eye. The energy of
any spectral curve is defined as a summation of intensities times wavelengths. By multiplying the spectral curve energy by the overlap of each tristimulus response curve we get the ‘tristimulus values’. The tristimulus values for a colour with a spectral power distribution \( I(\lambda) \) can be calculated using the colour matching function \( \bar{x}(\lambda), \bar{y}(\lambda) \) and \( \bar{z}(\lambda) \).

\[
X = \int_{0}^{\infty} I(\lambda)\bar{x}(\lambda) d\lambda \tag{4.1}
\]

\[
Y = \int_{0}^{\infty} I(\lambda)\bar{y}(\lambda) d\lambda \tag{4.2}
\]

\[
Z = \int_{0}^{\infty} I(\lambda)\bar{z}(\lambda) d\lambda \tag{4.3}
\]

where \( \lambda \) is the wavelength of the equivalent monochromatic light in nm. A colour is said to be achromatic if \( X=Y=Z \).

These tristimulus values \( XYZ \) are useful for defining a colour, but for the visualization the CIE 1931(x, y) - Chromaticity diagram is used where \( x, y \) are chromaticity coordinates calculated from tristimulus values. \( x = \frac{X}{X+Y+Z}, y = \frac{Y}{X+Y+Z}, z = \frac{Z}{X+Y+Z} \) where \( x + y + z = 1 \). Since monochromatic radiation is a boundary of colour mixing, the chromaticity coordinate diagram can be constructed with \( x \) and \( y \), the advantage of which is that we have a set of normalized values which can be used to compare colours having different intensity
values. We can find any colour or hue, in terms of its x and y coordinates. These diagrams are based on the 1931 2-degree CIE xyz colour matching functions that remain international standards in both colourimetry and photometry. CIE defined a standard set of real primaries of wavelengths red = 700, green = 546 and blue = 435nm. They have defined the chromaticity coordinates for this in the CIE space as R (0.73467, 0.26533, 0.00), G (0.27376, 0.71741, 0.00883) and B (0.16658, 0.00886, 0.82456) respectively [14].

The chromaticity coordinates can be calculated from the luminescence spectrum according to the chromaticity definition and using CIE data. It is nearly impossible to use each and every wavelength present. For these vertical lines that are spaced according to the peak height of each function is drawn. Thus we have a set of lines whose spacing varies inversely to peak height, i.e. the higher intensity, the closer the spacing, \(x = 550-650\) nm, \(y = 510-600\) nm and \(z = 420-480\) nm. This could be achieved by using tristimulus values times the height of the experimental curve, times the energy distribution of the standard source. By multiplying the line heights of a spectrum by these values and then summing up we obtain the values of X, Y and Z.

**4.2.2 Red, Green and Blue Emission from Dye/PMMA Matrices**

In order to get red, green and blue emissions, samples of PMMA doped with methylene blue (MB), rhodamine 6G (Rh 6G) and bromothymol blue (BTB) respectively were prepared.
Rhodamine 6G, (Ethyl O-(6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl)benzoate monohydrochloride), belongs to xanthene group of dyes. Its molecular weight is 479.02 gms. Its chemical formula is C_{28}H_{31}N_{2}O_{3}Cl. This dye has used for different lasing applications which give excellent lasing results [15]. The structure of rhodamine 6G is given in Figure 4.13.

The dye bromothymol blue [Benzoxathiol-3-ylidene) bis [2 bromo-3-methyl-6-(1-methylethyl) phenol] S,S-dioxide], with chemical formula C_{27}H_{28}Br_{2}O_{5}S, molecular weight 624.39 and melting point 202 °C. The structure of bromothymol blue is given in Figure 4.14.
The photographs of the transparent samples are given in Figure 4.15. The excitation and emission spectra of MB/PMMA, Rh6G/PMMA and BTB/PMMA are shown in Figures 4.16, 4.17 and 4.18 respectively.

Figure 4.15 Photographs of (a) MB/PMMA, (b) Rh 6G/PMMA and (c) BTB/PMMA

Figure 4.16 Excitation and emission spectra of MB/PMMA matrix
Figure 4.17 Excitation and emission spectra of Rh6G doped PMMA matrix

Figure 4.18 Excitation and emission spectra of bromothymol blue in PMMA matrix
The MB/PMMA shows a broad spectrum in the red region from 600nm-700nm (for ex-590nm), with fluorescence maxima at 645 nm. For Rh6G/PMMA the excitation maximum is at 535 nm and emission is at 550nm. Similarly BTB gives an emission in the blue region from 410nm-600nm with a peak maximum at 470nm.

The optical micrograph showing the fluorescence image taken by using an optical microscope, OLYMPUS-BX51, is shown Figure 4.19 for the dye doped samples.

![Image of optical micrographs showing fluorescence for MB/PMMA, Rh6G/PMMA, and BTB/PMMA.](image)

Figure 4.19 Optical micrographs showing fluorescence for (a) MB/PMMA, (b) Rh6G/PMMA and (c) BTB/PMMA.

The chromaticity coordinates x, y, z, for these three emissions, can be calculated using the above mentioned equations. The computed coordinates for these three dyes in PMMA matrices are superimposed in the CIE chromaticity diagram (Figure 4.20). The coordinates are well fitted in the corresponding red, green and blue regions respectively. The purity of the colours can also be calculated from the CIE chromaticity diagram. Purity is defined as the ratio of the distance from the reference illuminant to the colour coordinate and to the above mentioned intersection in the colour diagram. The colour purity is the
measure of the saturation of a colour, defined as the ratio of the distance from the white point (1/3, 1/3) to a given coordinate (x, y) and the distance from white point to shaped locus intersection [16]. The values are tabulated in Table 4.4.

We have incorporated all the three dyes in a single matrix and the colourimetric features of such system were not much encouraging. This may be due to the energy transfer, cross relaxation spectral shifts molecular aggregation etc. One has to optimise the concentration values of the dyes in such matrices for getting favourable colourimetric characteristics.

**Table 4.4 CIE parameters of the samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>CIE 1931 chromaticity (x, y)</th>
<th>Colour Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB/PMMA</td>
<td>(0.72, 0.275)</td>
<td>100%</td>
</tr>
<tr>
<td>Rh6G/PMMA</td>
<td>(0.315, 0.67)</td>
<td>94%</td>
</tr>
<tr>
<td>BTB/PMMA</td>
<td>(0.164, 0.239)</td>
<td>64%</td>
</tr>
</tbody>
</table>
The value of the dielectric constant is found to increase with temperature and by the addition of the dye. The dielectric constant has a decreasing nature with increasing frequency. Dye has a plasticizing effect on the polymer, which reduced the glass transition temperature of the system. The lowering of the glass transition can impart a reduction in the hardness value. These two facts have been substantiated by the DSC and microhardness measurements. MB can

![CIE chromaticity diagram with three colour coordinates](image)
also act as a retarder of free radical polymerization, which affects the length of the polymeric chain this can be another cause of the reduction in the hardness value. The colour purity and the colour coordinates are estimated using the fluorescence spectrum for MB/PMMA, Rh6G/PMMA and BTB/PMMA samples. The red emission from MB shows 100% purity whiles the green emission from Rh6G shows 94% purity. The blue emission from BTB shows only 64% purity. These systems can be used for red, green and blue emissions for electronic display applications. It is concluded that a single matrix display device demands optimizing the dye concentrations in PMMA matrices.
References