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Studies on Polystyrene/Polymethyl methacrylate Thin-Films: Structural and optical Properties

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ABSTRACT

The thin film blends such as Polystyrene (PS) and Polymethyle Mythcrylate (PMMA) were prepared by dip coating technique. Pure and blended forms of thin films are to be characterized in the context of FTIR and XRD methods for micro structural analysis. AC conduction properties of polymers in the frequency range 10 kHz to 10 MHz at various temperatures (303–343 K) are reported and studies suggest that electron hopping is responsible for conduction. The activation energies associated with these thin films and optical properties are also studied.

Keywords: Polystyrene, Polymethyl Methacrylate, Polymer blends, AC conduction, Optical properties

I. INTRODUCTION

Since a few decades thin film technology has made rapid growth and development with advent of different kinds of chemical, analytical techniques such as vapour deposition, anodization, film deposition methods and others[1-4]. This has led to the progress of microelectronics, optoelectronics and other fields which further require understanding in physical aspects of thin films and their mechanisms [5]. There is hence need to understand variety of thin films such as PS and PMMA, especially in blended form[6]. Also it is known that, thin films have large surface to volume ratios and consequently the surface of thin film plays a vital role in determining thin film properties [7].

The nature and properties are of keen interest for researchers in the area of electrical conduction and dielectric properties [8]. Interestingly it is of great interest to understand and evaluate optical characteristics of thin films. However it is of interest to understand optical behaviour of thin films in view of their wide applications in electronic and electrical industry [9]. Because of extensive usage of thin films, we have chosen polystyrene (PS) and Poly methyl methacrylate (PMMA) for the study and the objective of this study was to obtain a better understanding of

the structural and optical properties in the pure and blend thin films of PS and PMMA.

II. EXPERIMENTAL

SELECTION AND CLEANING OF SUBSTRATES

The glass slides were kept in a glass container containing chromic acid solution for 30 minutes to dissolve fatty materials by specification. They were then cleaned with detergent solution followed by distilled water washing. The substrates were then placed in an electric bath for about 30 minutes. The shock waves created in the solvent rendered the removal of possible residue from the substrates. The substrates were then dried and subjected to vapour degreasing with isopropyl alcohol to increase the rate of surface contaminant removal. Finally, the substrates were kept in an oven for about 1 hour for drying.

SOLUTION GROWTH TECHNIQUE

The solution growth technique has an important feature [10-12]. Polystyrene (PS) and Polymethyle methacrylate (PMMA) films were formed from a solution of 2g of low molecular weight PMMA and PS dissolved in 100ml of benzene separately. These solutions of particular concentration were prepared in a glass beakers and it was continuously stirred for three hours by means of a Teflon coated pellet using a magnetic stirrer cum heater. Pre cleaned glass substrates were immersed vertically into the solution for a period of about 10 to 60 minutes so as to get 0.7μm film thickness. The substrates were withdrawn from the solution and then dried in an oven at 333K for one hour in order to eliminate the traces of solvent. Two substrates were immersed into the solution at a time and hence a set of films of same thickness was obtained. The procedure was repeated many times to prepare the required number of PMMA and PS film samples. Using the same procedure the PS and PMMA blend films of the ratio of 25:75 are prepared. The details of the samples taken are discussed in the Table 1.

Table 1: The details of the samples used

Sl. No.	Code	Film % of Blend	Starting chemicals in 100ml Benzene
1.	PS – Pure	PS – Pure	PS - 2 gm
2.	PMMA - Pure	PMMA - Pure	PMMA - 2 gm
3.	PMMA - 250 PS - 750	PMMA : PS (25:75)	PMMA - 0.5 gm PS - 2 gm

X-ray Diffractometer (XRD)

In the present investigation, the structure of the polymer films is analyzed using Shimadzu X-ray diffractometer (XRD - 6000) with the Nickel filtered CuK_α radiation (λ = 0.15418nm) at 40kV and 20mA in the 2θ range 10^0 to 80^0.

Fourier Transform Infrared Spectroscopy (FTIR)

In the present work Bruker IFS – 66V, FT – IR Instrument was used to study the structure of pure and blended PS and PMMA. The sample chosen for the studies are 1) PS-pure, 2) PMMA-pure and 3) PS/PMMA blended. For blended thin film samples a ratio of 75:25 is used.

The sample preparation is carefully carried out for the chosen types of thin films. In this method the sample is mixed with a suitable dry alkali halide, ground in a mortar or ball mill. This produces a clear transparent disc. It is essential that the crystal size be reduced to about 2.5 μm. The most commonly used alkali halide is Potassium Bromide (KBr), which is completely transparent in the commonly scanned region.

Studies of A.C. Conductivity Characteristics

The thin films of PS and PMMA in pure and blended forms have been studied for the characteristics of thin films of conductivity (σ) verses frequency (f) at different temperatures. The AC conductivity for pure

PS and PMMA, blend films were calculated at different temperatures using the equation,

$$\sigma = \omega C p \tan\delta \, (d/A)$$

where, σ = Conductivity

ω = Angular frequency

The temperature considered is 300K, 323K, and 343K. The characteristics of thin films are studied from 10 KHz to 10MHz using precision LCR meter. This has facility to measure resistance / conductivity over a wide range of frequency. A three terminal electrode system with attached fixture to instrument would help to obtain a uniform electric field gradient across the specimen. The measurements, thus obtained with this experimental arrangement will be precise and accurate enough to plus or minus 1%. The Figure 2.6 will show the arrangement of electrode system with LCR meter. A circular disc of sample with area of 50 cm^{-2} can be readily fixed into this electrode system. Once the sample is fixed into the apparatus, signal is driven through the sample. Software programmed which is inbuilt in the apparatus would record resistance at different frequencies. A spectrum of sample with frequency and resistance can be readily obtained in this experimental arrangement.

Optical properties

The optical behaviour of thin film concerns mostly measuring the optical quantities like transmittance (T), reflectance (R), absorbance (A) and then applying these measurements to find out the various optical constants such as the extinction coefficient (K_f), absorption coefficient (α) and refractive index (n_f) of the films. The optical absorption studies have been used to gain information's regarding the electronic structure of solids.

III. RESULTS AND DISCUSSION

Structural Analysis; XRD Analysis

Fig. 1 shows the X – ray diffractograms of pure and blend PS and PMMA films of thickness, about 0.7μm. The absence of any characteristic peak indicates the amorphous structure of these films. However the presence of a very broad hump in the diffractogram reveals the mixed state of polycrystalline and amorphous structure of these films. Such a state could not be ruled out, because, polymer in general have homogeneous mixture of polycrystalline and amorphous regions [6].

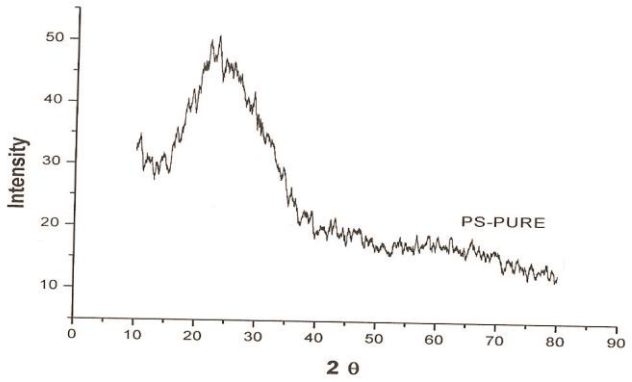


Fig. 1: (a) X – ray diffractograms of pure PS

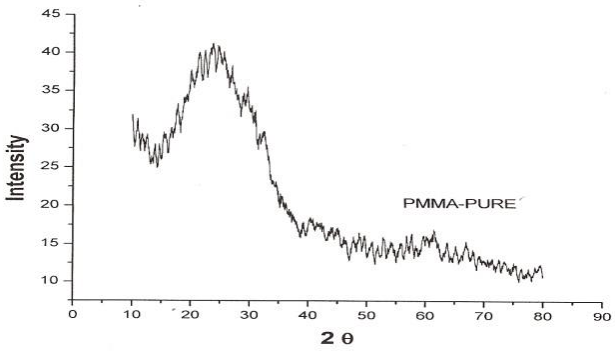


Fig. 1: (b) X – ray diffractograms of pure PMMA

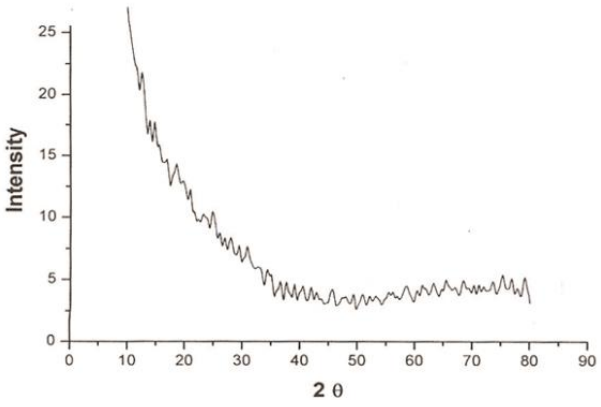


Fig. 1: (c) X – ray diffractograms of blend film

FT – IR ANALYSIS

In the present work, the Fourier transform Infrared (FT–IR) spectra were taken for pure and blend, PS and PMMA films[7]. The peaks obtained in the present study are shown in Fig. 2(a,b,c). The vibrational bands observed at 752 and 842 cm^{-1} in the blend are ascribed to C-H bending mode of PS and PMMA respectively. The vibrational bands observed at 1036 cm^{-1} in the blend polymer is ascribed to ring stretching of polystyrene. The vibrational bands observed at 1238, 1377 and 1728 cm^{-1} in the blend polymer matrix are ascribed to C-O-C asymmetric stretching, CH_3 symmetric bending and C=O stretching vibrations of PMMA respectively. The vibration bands observed at 1442, 2940 cm^{-1} in the blend complex are ascribed to CH_2 bending and CH stretching vibrations of polystyrene respectively. In the blend polymer complexes the shifting of vibrational bands and appearance of intense peaks ascribed to the corresponding polymers have been observed.

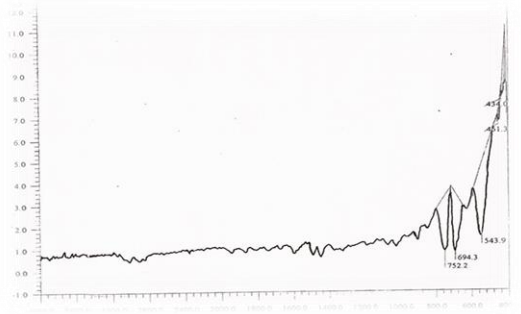


Fig. 2: (a) FT-IR Spectra of Pure PS

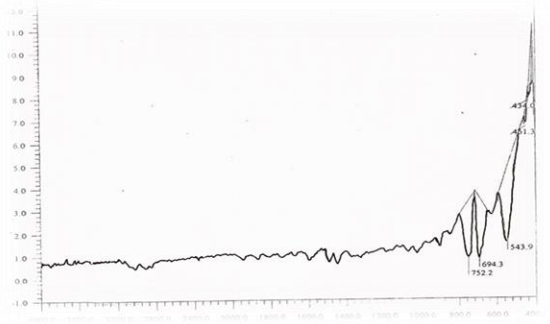


Fig. 2: (b) FT-IR Spectra of Pure PMMA

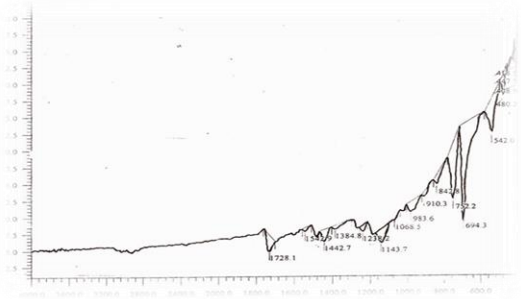


Fig. 2: (c) FT-IR Spectra of PS and PMMA Blend film

A.C. CONDUCTION

The AC conductivity for pure PS and PMMA, blend films were studied and the plots of AC conductivity versus frequency (10 KHz -10 MHz) for pure PS, PMMA and blend films are shown in Fig. 3(a,b,c). The conductivity of the pure and blend samples vary with frequency for the temperature range (303 K–343 K). The AC conductivity observed to be proportional to ω, where n is seen to vary depending on the frequency and temperature range studied. In case of pure and blend PS and PMMA film the conductivity increases almost linearly with frequency at 303 K and 343 K.

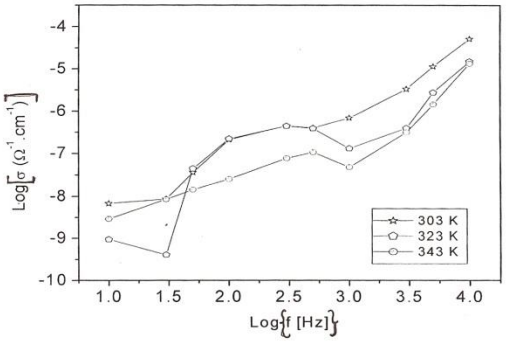


Fig.3 (a): Variation of Log σ with frequency at different temperature for PS pure film

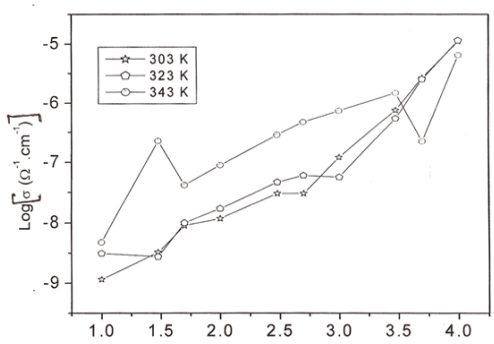


Fig.3 (b):Variation of Log σ with frequency at different temperature for PMMA pure film

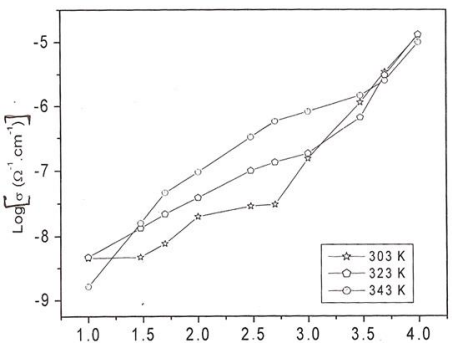


Fig.3 (c):Variation of Log σ with frequency at different temperature for PMMA 25-PS75 film

Also it is seen that the conductivity shows two regions i.e. below 100 KHz and above 100 KHz. The value of n for pure PS film is 0.5(<100 KHz) and 0.92(>100 KHz) at 303K similarly at 343K, the value of n is 0.47 (<100 KHz) and 0.86 (>100 KHz). This indicates that the conduction is taking place due to hopping of charge carriers between randomly distributed trapping centers [13]. In the case of pure PMMA films n value is .84 (<100 KHz) and 1.48 (>100 KHz) at 303K. Similarly at 343K, the value of n is .81 (<100 KHz) and 1.39 (>100 KHz). For PMMA/PS 25:75 blended film, the n value at 303K is 0.72 to 1.38 and 0.369 to 1.27 for 343K.

In presence of two/three dispersive regions in the conductivity versus frequency plot suggests that there are two / three dissipation mechanisms operating in the frequency range studied. This behaviour suggests that the mechanism responsible for a.c. conduction is of the hopping type. It is consistent with the results reported on various hopping systems [14].

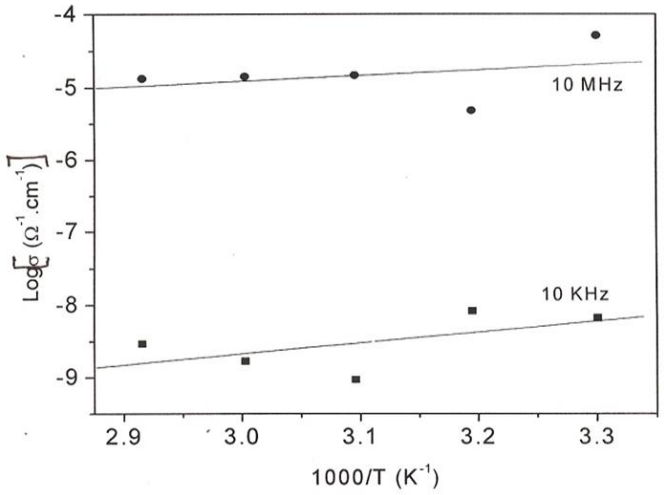


Fig.4 (a) : Log σ versus 1000/T (K^{-1}) for PS pure filmFig.4 (b) : Log σ versus 1000/T (K^{-1}) for PMMA pure film

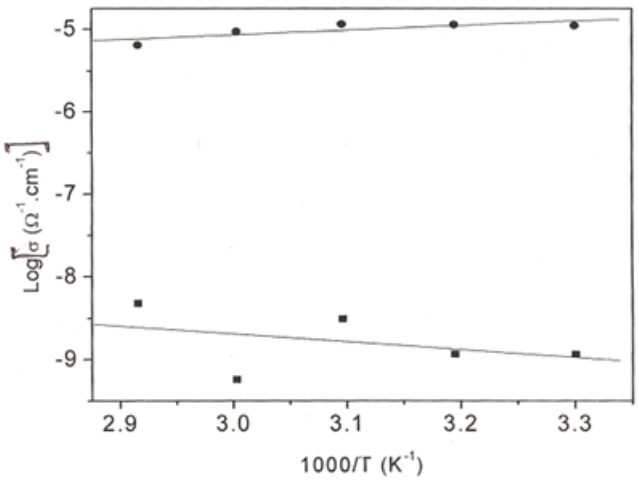
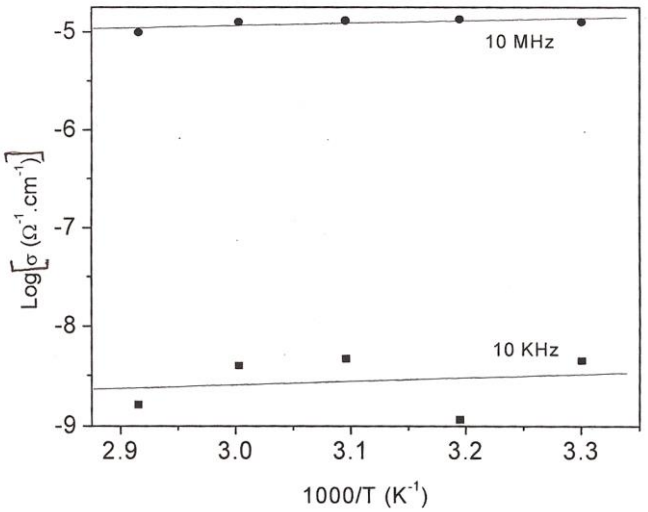


Fig.4 (c):Log σ versus 1000/T (K^{-1}) for PMMA 25- PS 75 film



The Fig. 4(a,b,c) depicts the variation of conductivity (σ) with temperature of pure PS, PMMA and blend films at 10 KHz and 10 MHz the activation energies have also been calculated from the slope of the log σ versus (1/T) plots and shown in Table 2.

Table – 2: The activation energies of pure and blend thin film.

Polymer	Frequency (KHz)	Activation Energy (eV)
Pure PS	10 KHz 10 MHz	0.52 0.77
Pure PMMA	10 KHz 10 MHz	0.96 0.55
PMMA:PS 25:75	10 KHz 10 MHz	0.42 0.75

OPTICAL PROPERTIES

The measured normal transmittance spectra of polymer films i.e., pure PS, PMMA and blend films are shown in Fig. 5. It is revealed from the figure that the transmittance increases as wavelength increases up to 17% for pure PS film. In case of pure PMMA film, the transmittance is 25%, the transmittance is nearly 70% for blend film. The transmittance of the films increases with increase in wavelength [15], which indicates that these films are slightly transparent in the IR region.

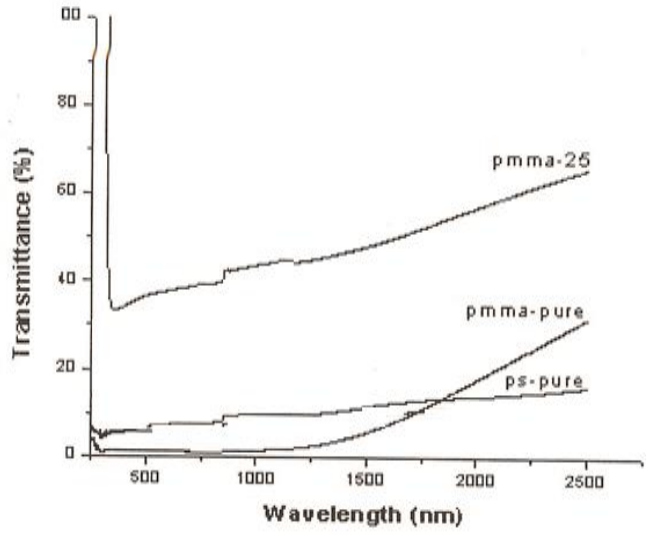


Fig. 5: Transmission spectra of pure PS and PMMA and blend (25:75) films.

The values of n, k_f and α are determined and the spectral distribution of refractive index 'n' for pure PS, PMMA and blend (25:75) films respectively are shown in Fig. 6 and Fig. 7.

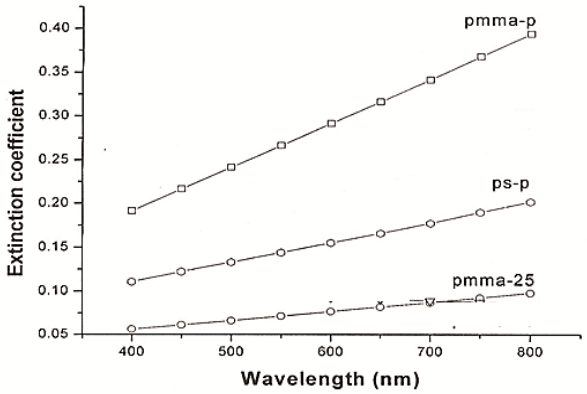


Fig. 6: Extinction coefficient of pure PS and PMMA and blend films

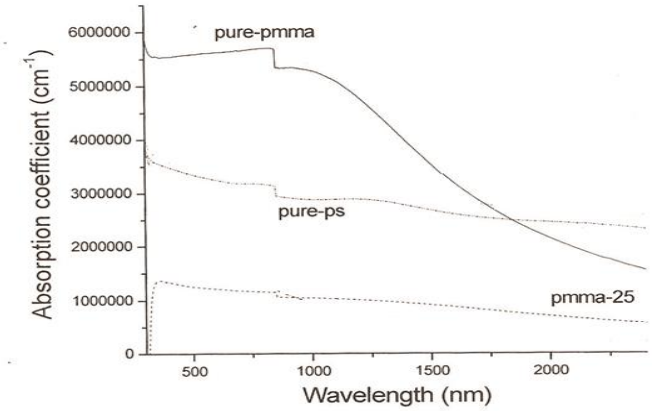


Fig. 7: Absorption coefficient of pure PS and PMMA and blend films

The refractive indices are wavelength dependent [16]. For pure PS film, the refractive index increases from 1.62 to 1.76 steadily and then decreases down to 1.59. In case of pure PMMA film, the refractive index slightly increases from 1.58 to 1.67 and decreases slowly to 1.57 as wavelength increases. When PMMA is blended with PS i.e., in PMMA:PS (25:75) sample the refractive index increases from 1.59 to 1.65 and decreases gradually to 1.61, to reach stability. The comparative graph for refractive index of all the samples is shown in Fig. 8(a,b,c).

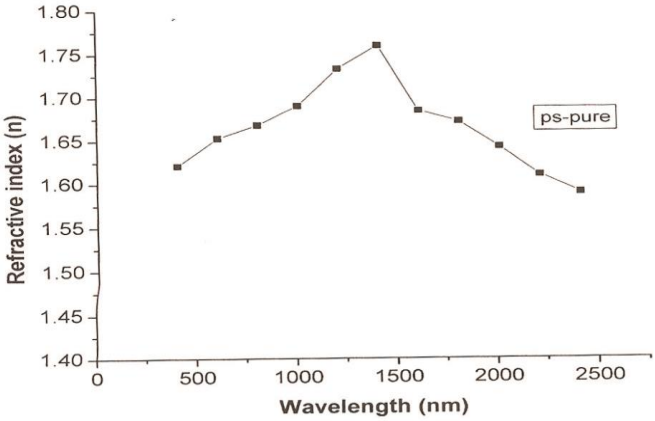


Fig.8 (a): Refractive index Vs Wavelength for PS Pure film

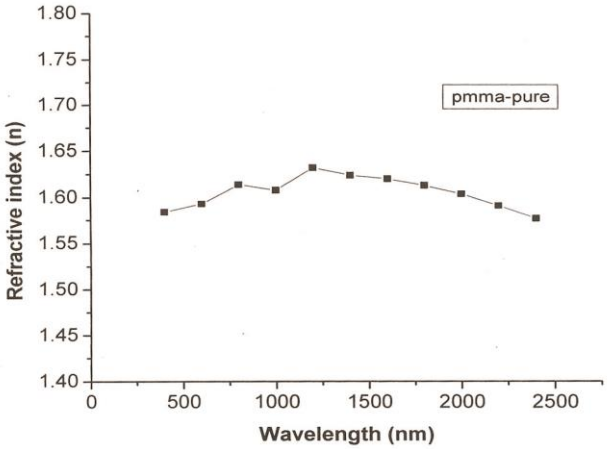


Fig.8 (b): Refractive index Vs Wavelength for PS Pure film

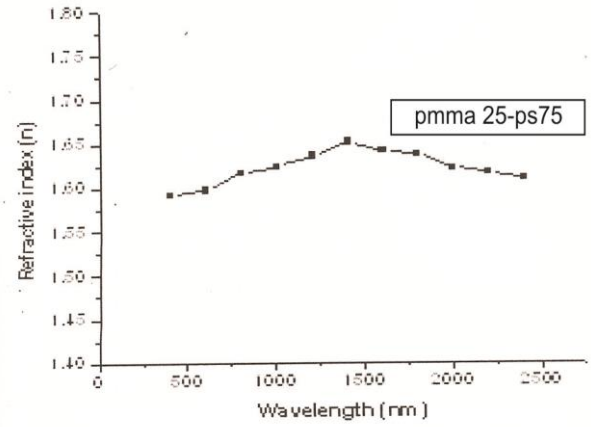


Fig.8 (c): Refractive index Vs Wavelength for blend PMMA:PS (25:75) film

IV. CONCLUSION

PS/PMMA blends were prepared by solution dip method. These blends were characterized by FTIR and X-ray diffractometer. The FTIR results of polymer blend indicate that there are no shifts of the peaks of any group in PS/PMMA spectrum; this confirms the formation of physical blend. XRD indicated that the diffractogram for PS and PMMA have broad peak in intensity with 2θ spectra, While blend thin film there is no such broad peak in diffractogram. This confirms the fact that structure is both crystalline and amorphous state. AC conduction properties of polymers in the frequency range 10 kHz to 10 MHz at various temperatures (303–343 K) are reported and studies suggest that electron hopping is responsible for conduction. The transmittance of PS and PMMA films increases with wavelength and it will indicate that these films are transparent in IR region of Electromagnetic spectrum. The RI of thin films PS and PMMA and blend exhibited dependence on the wavelength of incident light. The blend thin film shows stable in value in low wavelength region.

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