



Preparation and characterization of Merocyanine dye coated cellulose Tri acetate film using low temperature Plasma

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Abstract : Abstract :In this present work, the surfaces of Merocyanine dye film were modified by Low pressure glow discharge plasma as a function of time. The optical properties were investigated by UV-Visible absorbance method, due to the treatment of plasma the optical properties of the film also changed. Characterization by FTIR spectroscopy showed a small difference between the untreated and plasma treated film. ¹³C NMR spectroscopic study was employed to elucidate the structure of the Merocyanine dye film. The qualitative and quantitative analysis of the elements in Merocyanine dye film had been carried out using Energy Dispersive X-ray analysis (EDAX) and Carbon, Hydrogen, Nitrogen and Sulfur (CHNS) analyzer. SEM analysis revealed the change in surface morphology when treated with plasma. The crystalline structure of the film was investigated by X-ray diffraction. From the result, it was established that the peak is more intense for the treated one. DTA/TGA measurements demonstrated the thermal stability of the plasma treated film. SHG test showed the efficiency of the plasma treated film.

Keywords: Merocyanine dye film, Glow discharge plasma, NMR, Cellulose Tri Acetate CTA.

1. Introduction

In the recent years, the plasma based approaches have gained considerable popularity for increasing the surface energy of materials. The majority of studies focuses on the applicability of plasma treated surfaces or polymers as bonding layers for immobilization of molecules [1]. Interestingly, the plasma can be classified in to plasma treatment, plasma etching and plasma polymerization based on the outcome of interactions with materials. Further, depending on various factors such as deposition, process conditions, substrates and etching can dominate in modifications on the material surfaces [2]. The limitations of plasma technologies are the diversity of functional groups produced by the chemical reactions that occur in plasma. Plasma causes various bond fissions, ionization and secondary collisions. Subsequent reactions and ionization processes result in a spread of functionalities on the plasma treated surfaces. [3]. Here, we have focused on surfaces of cellulose tri acetate film coated merocyanine dye which are chemically reactive groups. Apart from this, the merocyanine dye coated cellulose tri acetate film that creates surface chemistries suitable for interfacial reactions [4-6]. The materials, methods and process vapours that create surfaces with these chemical groups are first discussed, followed by studies that have investigated these surface chemistries for the applications in solar cell, photographic emulsions etc. Characterization and understanding of plasma produced surfaces is the successful implementation of cellulose tri acetate film coated merocyanine dye for industrial applications.

In this work, various tools have been used to characterize the merocyanine dye cellulose tri acetate film surfaces, such as Fourier Transform Infrared spectroscopy (FTIR), Powder X-ray diffraction analysis and gravimetric technique which has been used to determine identification of functional groups, crystalline of the surface [7] and the thermal stability of the film. Further, the optical property of the film surface was analyzed using UV-Visible spectroscopy and ^{13}C NMR spectroscopic study was employed to elucidate the structure of the film. This plasma treatments are in industrial use film surface can be variable and thereby can found conclusions when comparing different time treatment surfaces with untreated one. The main aspect of this research was to analyze the effects of plasma treated fabric by various characteristic studies and also to find the physical and absorption properties.

2. Materials and Methods

2.1 Materials

Merocyanine dye of CY 334 ($\text{C}_{12}\text{H}_{17}\text{N}_3\text{OS}$) was used without further purification. Methylenechloride and methanol was used as solvent for the Cellulose Triacetate (CTA) film preparation.

2.2 Preparation of Cellulose Triacetate Film (CTA)

100 gms of cellulose triacetate is weighed in a one litre wide mouth glass stopper bottle added to an 500 ml of solvent mixture (Methylene chloride and methanol by 9:1 ratio). The mouth of the bottle is closed with a stopper. When the mass becomes fairly thick, mount the bottle onto a tumbling type shaker till the solution is complete. Obtained viscous solution was then casted on Au-coated glass plate and dried at room temperature and transparent Cellulose Triacetate (CTA) films were prepared. Cellulose Triacetate (CTA) films were dip coated from Merocyanine dye solution. The obtained films are hereafter referred to as the merocyanine dye film.

2.3 Plasma Treatment

The surface of merocyanine dye film was modified using DC glow discharge plasma reactor. It consists of a cylindrical stainless chamber of length 50 cm and internal diameter 30cm. Two aluminium plates were used as anode and cathode inside the chamber. Inside the chamber vacuum was created .A pressure of 0.03m bar measured by pirani gauge was maintained inside the chamber. At this low air pressure ,a dc voltage of 450V was applied between the electrodes to ignite the glow discharge. The samples were treated for two different exposure time at 10W power level. DTA/TGA measurements demonstrate thermal stability of the treated film compared to the untreated films.

3. Results and Discussion

3.1 UV Visible Spectral Analysis

Absorption of electromagnetic radiation is with promotion of valence electron from lower energy level to a higher energy level in the visible region (400-750 nm).Absorption or emission of light by a molecule depends on electron transition between molecular orbital energy levels same as absorption or emission of electromagnetic radiation by an atom. Absorption of Electromagnetic radiation of merocyanine dye coated cellulose tri acetate film surface for untreated and plasma treated film can be determined by using the relationship

Table .1 Absorption Spectra and Peak Intensity for Untreated and Plasma Treated Dye Thin Film.

Absorption peak position in			Intensity		
Untreated film(nm)	Treated film 300s (nm)	Treated film 600s (nm)	Untreated film(nm)	Treated film 300s (nm)	Treated film 600s (nm)
452	462	459.5	1.48	2.49	1.52

$$\Delta E = hc/\lambda$$

Where, h-Planck's constant, c-Velocity of light,

λ -Maximum wavelength

The free electron models proposed by Kuhn treat this system theoretically [8]. He assumed that pi electrons, which are freely in motion, can determine the spectral characteristic in the visible region. Figure.1, shows the UV-Visible spectra of merocyanine dye coated cellulose tri acetate film for untreated and plasma treated films in the 400-600 nm. It is observed that the bands were shifted gypsochromely which corresponds to the first electron transition. It is observed that the substrate does not influence the film absorption peak position but the absorption intensity is higher for plasma treated film [9]. The absorption spectra for untreated and plasma treated dye thin film shows the absorption takes place at the range of 450-465 nm corresponding to π - π^* electron transition from ground state (s_0) to the first singlet excited state (s_1). The table.1 shows the values of absorption spectra and peak intensity for untreated and plasma treated dye thin film.

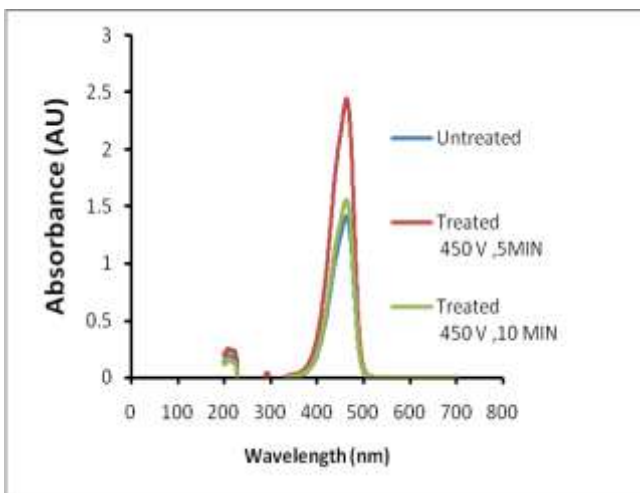
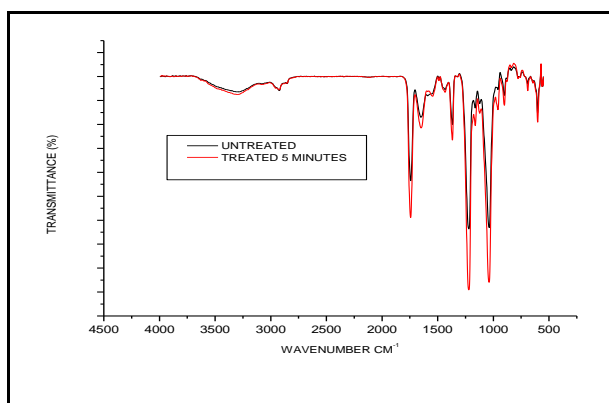


Figure.1 Absorption Spectra of untreated and plasma treated Cyanine dye film for 450V 5min and 10 min

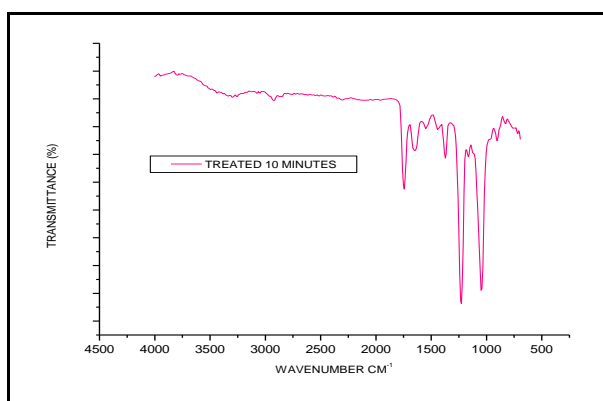
The above spectral behaviors can be interpreted by kasha's ID exciton-coupling model [10]. According to this model, the N-fold degenerate singlet excited states of the N nearest dye molecules are split into N non-degenerated one-excitons states which are due to the interaction among the oscillating transition dipoles of the N dye molecules. The optical transition from the ground state to lower one-exciton states give rise to a stronger absorption band in the shorter wavelength region for plasma treated film and weaker absorption band for untreated film. The transition is allowed only between the ground state and the lowest one-exciton states, resulting in a sharp, intense absorption band for treating film compared to the untreated. So, it is concluded that the increase in the amplitude of the peak in the absorbance spectrum film and a shift in the cutoff wavelength formed by plasma treatment which the requirement for optical applications is observed.

3.2 Fourier Transform Infrared (FTIR) Analysis:

The FTIR spectra in the functional regions ($2000-400\text{ cm}^{-1}$) of untreated, treated films with plasma are illuminated in Figure 2(a) and (b). It is clear that there are no noticeable changes among the characteristic peaks of film. The bands are consistent with the functional groups present in the film. The explanation is that only partial degradation of the deposited dye happens, the substrate does not influence the quality of the deposited dye material. The factors which determine the dye's chemical degradation by the deposition process are the plasma treatment and the chemical structure of dyes. The characteristic IR absorption bands observed are consistent with the functional groups present in the film and the values are recorded in Table.2 [11,12].



(a)



(b)

Figure 2. (a) FTIR spectra of untreated and plasma treated (5 Minutes) Cyanine dye film (b) FTIR spectra of plasma treated (10 Minutes) Cyanine dye film

Table. 2. FTIR data of Untreated and plasma treated Cyanine dye film

Band Position cm^{-1}			Mode Assignment
Untreated	Treated (450V 5 Min)	Treated (450V 10Min)	
3320.10	3346.33	3302.13	O-H Stretching, N-H Stretching
2868.00	2970.22	2924.09	C-H Stretching
1733.91	1747.4	1743.65	C=O Stretching Aldehydic

1627.84	1668.34	1651.07	C=C Ring Stretching
1523.68	1593.12	1550.77	C=N Stretching
1388.67	1452.32	1442.75	C-C Symmetric Bending
1363.60	1371.32	1373.32	C-N Symmetric Stretching
1213.16	1228.59	1226.73	C-C (or) C-N Symmetric Bending
1132.15	1170.73	1165.00	C-N Stretching
1029.93	1045.36	1049.28	N-C-H Symmetric Bending
927.71	906.49	902.69	N-C-H Symmetric Bending
891.06	788.84	825.53	C-N-H Symmetric Bending
703.98	698.19	740.67	C=S Stretching

3.3 Nuclear Magnetic Resonance (NMR) spectral analysis

The ^{13}C NMR spectrums are depicted in Figures 3(a) and 3(b). The appearance of 10 distinct peaks in the spectrum establishes the molecular structure of the complex species with a greater degree of certainty [13-15]. The chemical shifts for the untreated and plasma treated samples are listed in Table (3). It is observed that there is a slight change in the chemical shift values due to the plasma treatment.

Table .3. ^{13}C NMR data of untreated and plasma treated Cyanine dye film

Functional group assignments	Chemical Shifts (δ –ppm)	
	Untreated	Treated
N-CH ₃	20.478	20.459
C-CH ₂	20.563	20.547
N-CH ₃	20.788	20.770
C=S	120.125	120.108
C=CH	120.175	120.157
CH-CH	125.613	125.597
C-CH ₂	129.869	129.853
C=O	169.298	169.282
C=CH	169.744	169.725
Pentane ring	170.224	170.209

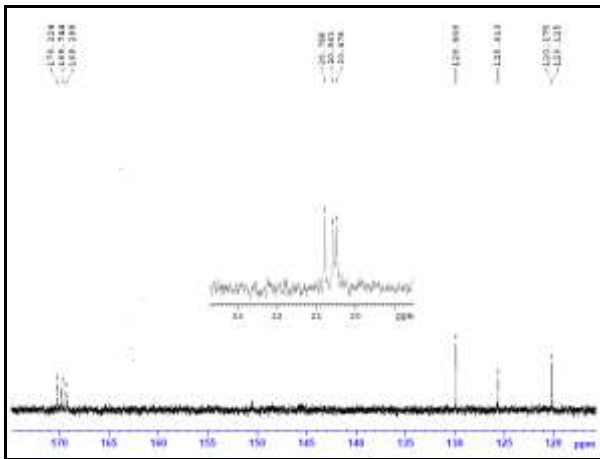


Figure 3. (a) ^{13}C NMR spectrum of plasma untreated film

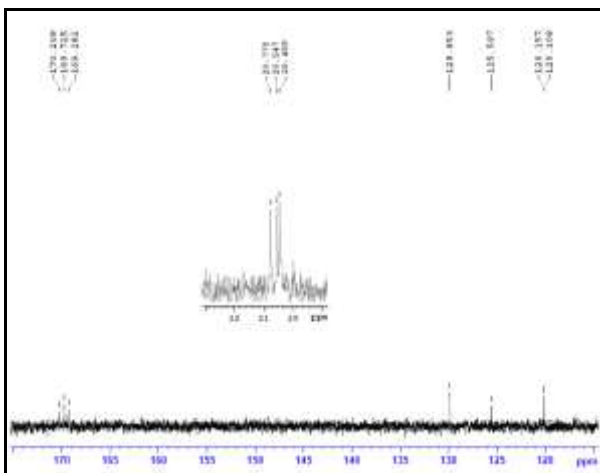


Figure 3. (b) ^{13}C NMR spectrum of plasma treated film

3.4 Carbon Hydrogen Nitrogen Sulphur (CHNS) analysis

The elemental analysis of untreated and plasma treated Cyanine dye film was carried using a Vario EL III Carbon Hydrogen Nitrogen Sulphur (CHNS) analyzer to determine the percentage composition of elements present in it. There was no change in the elemental composition of the plasma treated sample as listed in the Table (4). Both experimental and calculated, determined percentage components are in good agreement. The molecular formula for the given dye film has been confirmed as $\text{C}_{12}\text{H}_{18}\text{N}_3\text{OS}$.

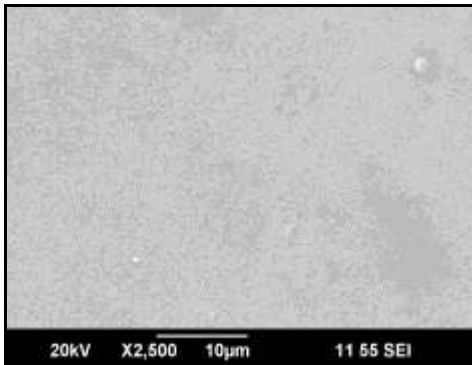
Table. 4 Elemental composition of untreated and plasma treated Cyanine dye film

Element	Percentage Composition	
	Experimental	Calculated
Carbon	56.79	57.11
Hydrogen	6.99	7.19
Nitrogen	16.05	16.65

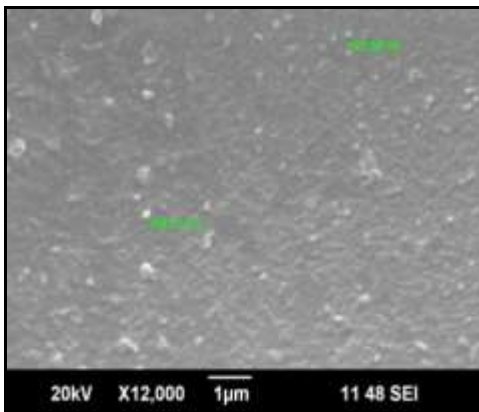
3.5 Scanning Electron Microscope (SEM) Analysis

The morphologies of the untreated and films treated were observed by SEM ,as shown in Figures 4(a),4(b) and 4(c). It is obvious that there is great difference among the films. For the untreated film the surface is comparatively smooth while treated with plasma for 300s the surface was less roughish the film is not seen to

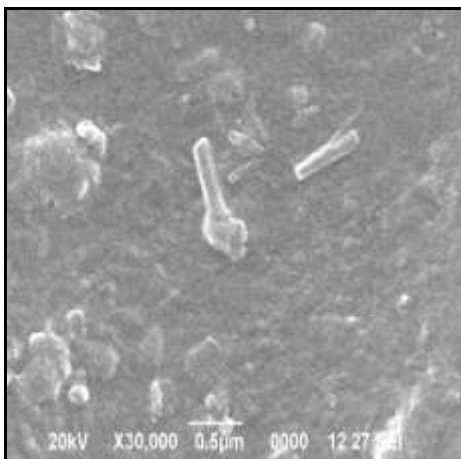
be continuous but consists of particulates with size ranging between 143.37-167.50 nm [16-17]. Figure 4(b) indicates that the shorter treatment time changes only the chemistry of the uppermost cyanine dye film surface layers. As shown in Figure 4(c) the film treated with 600s creates a boundary a boundary layer and a crystalloid was formed which improves the bonding strength.



4 (a)



4(b)



4(c)

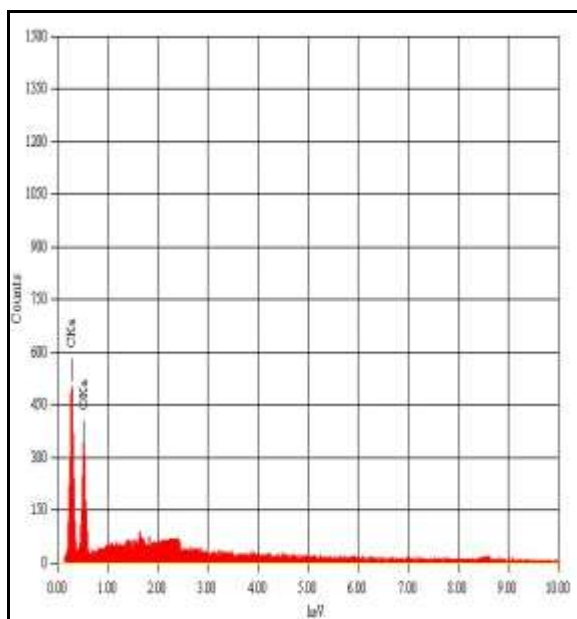
Figure 4 (a) SEM representation of untreated cyanine dye film surface (b) and 4(c) SEM representation of plasma treated (5Minutes and 10 Minutes) cyanine dye film surface

The SEM results clearly show that the plasma is a significant factor influencing the roughness of dye film. The main reasons behind is for a cyanine dye the factors like volatility, polarity, viscosity and so on would change the film's morphological structure during the treatment with plasma. Parameters such as dye

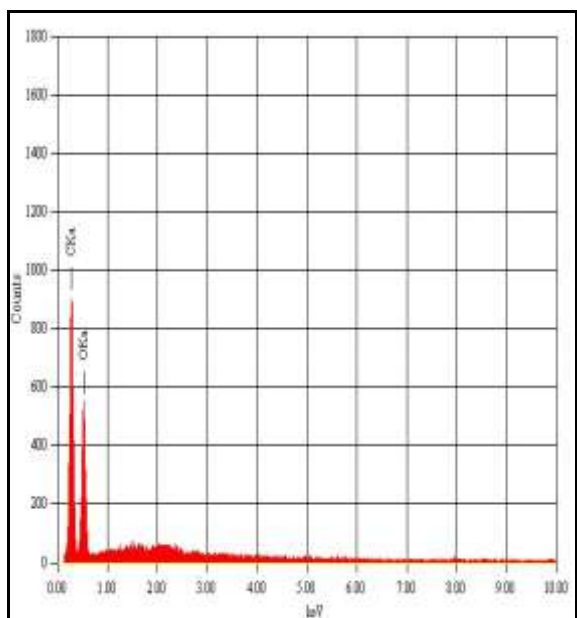
concentration, plasma treatment time, time deposition of film in dye solution etc. Therefore it is difficult to maintain a uniform crystallite size. Unsymmetrical variation of the grain size is not unrealistic.

3.5.1 Energy Dispersive X-ray (EDAX) Analysis

Figures 3(a) and (b) shows the EDAX pattern of the untreated and plasma treated dye film surfaces and they contain C and O peaks .In the elemental composition, the C and O content increases when compared to untreated one. The result indicates that the carbon and oxygen component was incorporated into the dye film surface when treated by plasma.



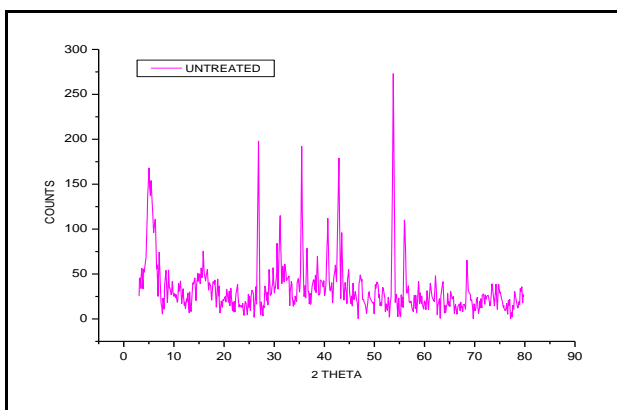
5(a)



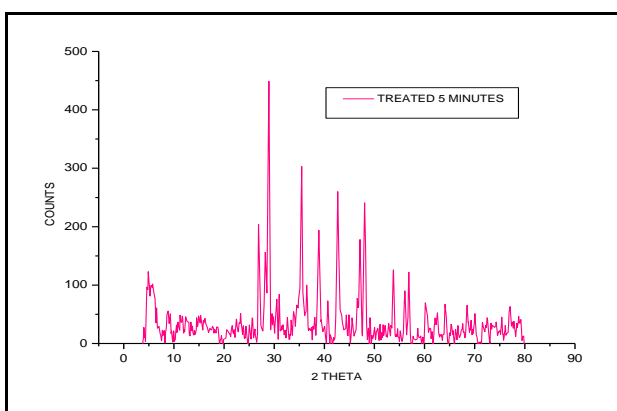
5(b)

Figures 5 (a) and 5 (b) EDAX pattern of untreated plasma treated (5 Minutes) cyanine dye film.

3.6 X-ray Diffraction Analysis (XRD) analysis

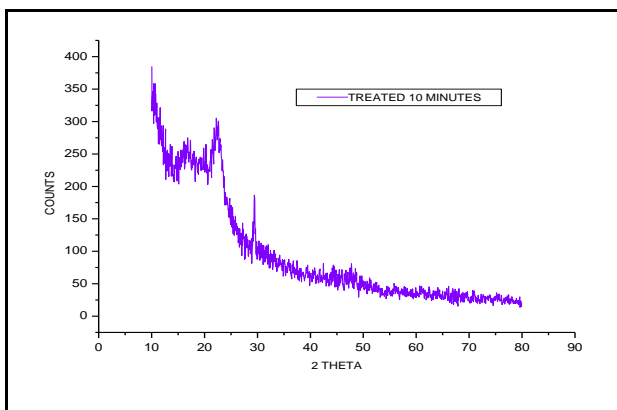


6(a)



6(b)

Figures 6(a) and (b) X-ray diffraction patterns of untreated and plasma treated (5 Minutes) cyanine dye film.



6(c)

Figure 6(c) X-ray diffraction patterns of plasma treated (10 Minutes) cyanine dye film.

Table (5) X-ray diffraction data of untreated and plasma treated cyanine dye film

UNTREATED				TREATED 5 MINUTES				TREATED 10 MINUTES			
2 θ	θ	FWHM	CRYSTAL LITE SIZE	2 θ	θ	FWHM	CRYSTAL LITE SIZE	2 θ	θ	FWHM	CRYSTAL LITE SIZE
26.871	13.4355	0.202	70.572	28.936	14.468	0.223	64.212	17	8.5	1	7.9669
53.757	26.8785	0.323	48.1261	35.491	17.7455	0.237	61.422	22	11	2	4.00438
35.498	17.749	0.214	68.0297	42.661	21.3305	0.422	35.269	29.40	14.7	0.22	36.9369
42.902	21.451	0.214	69.6136	48.041	24.0205	0.342	44.38	-	-	-	-
-	-	-	-	26.885	13.4425	0.186	76.642	-	-	-	-
-	-	-	-	53.780	26.89	0.340	45.722	-	-	-	-
-	-	-	-	47.108	23.554	0.308	49.109	-	-	-	-

Figures 6 (a), 6(b) and 6(c) shows the XRD patterns of merocyanine dye coated cellulose tri acetate thin films. The diffraction scan was carried out using *cuka* radiation ($\lambda=1.54 \text{ \AA}$) [18]. The characteristic peaks were identified and these were at $2\theta=26.8785, 35.491, 42.661, 48.041$. It is clearly seen that there is no significant change in position of the diffraction peaks except that the peak is more intense for the treated one. It is observed from the XRD patterns that there are no secondary phases indicating that the merocyanine dye has been incorporated in to the lattice as a substitutional atom. The crystallite size (ϵ) for untreated and plasma treated merocyanine dye coated cellulose tri acetate film can be expressed as $\epsilon=k\lambda/\beta\cos\theta$ where k is a constant whose value is very close to unity, β is the full width at half maxima expressed in radians θ is the brass angle. The value of ϵ is represented in Table (5). From table it is seen that the change in ϵ is not symmetric. This is because the value of ϵ depends on the crystallographic axes as well as plasma treatment time. The value of ϵ is related to large number of physical parameters such as dye concentration, plasma treatment time, time deposition of film in dye solution etc. Therefore it is difficult to maintain a uniform crystallite size. Unsymmetric variation of the grain size is not unrealistic.

3.7 Differential Thermal and Thermo gravimetric (DT-TG) Analysis

DTA and TGA analyses are of immense importance as far as the fabrication technology is concerned as they provide thermal stability of the thin film material for fabrication where a considerable amount of heat is generated during the cutting process. Thermo gravimetric analysis of untreated and plasma treated cyanine dye films were measured and the plots are shown in Figures (7a), (7b) and (7c). Degradation proceeds through a single stage process which occurs at 300°C for the untreated film and for the plasma treated film degradation occurs about 350°C for 300s and 330°C for 600s.

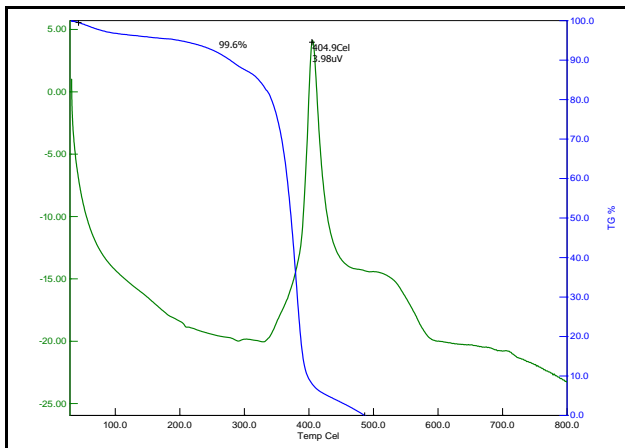
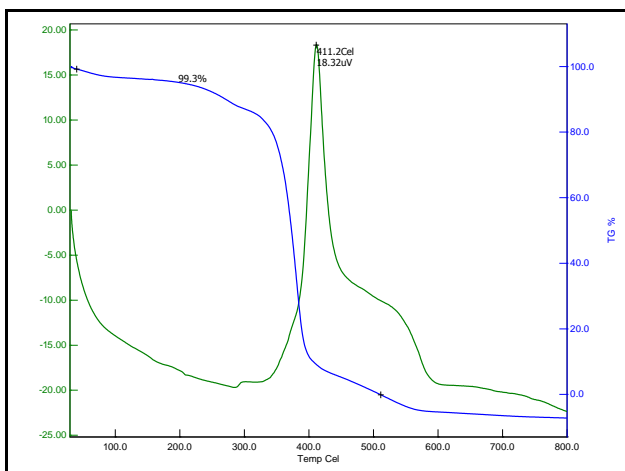
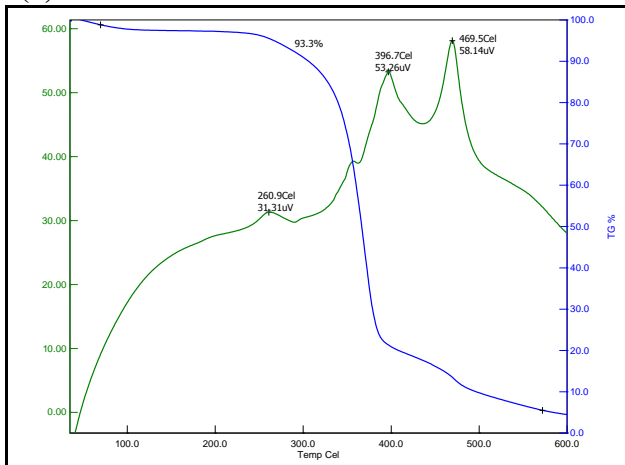


Figure 7(a) DTA and TGA trace of untreated merocyanine dye film



7(b)



7(c)

Figure 7(b) 5(Minutes) & Figure 7(c) 10 (Minutes) DTA and TGA trace of treated merocyanine dye film

This suggests that cyanine dye film treated with plasma are thermally labile than untreated because the degradation temperature increases for plasma treated film. Decomposition temperature of cyanine dye films were also measured by TGA, and these were at 500 °C for untreated, 800 °C for 300s treated film and 600 °C for 600s treated film. The DTA response curve shows a sharp exothermic peak at 404.9 °C which can be attributed to the melting point of the material of the dye for the untreated film. Further the film has no phase transition till the material reaches the melting point. For the treated film 300s the material is stable upto 350 °C, which is the melting point of the substance. The above this point the material begins to attain an exothermic transition and begins to decompose. The sharpness of this peak show the good degree of crystallinity of the sample [19-20].

For the treated film 600s the decomposition of the sample is taking place in three different stages. There is a sharp exothermic peak at 260.9 °C. It coincides with the first stage of weight loss in TGA trace. There is one sharper exothermic peak at 396.7 °C. This corresponds to the second stage of weight loss in the TGA trace and the third stage of weight loss in TGA trace coincides with the sharp exothermic peak at 469.5 °C in DTA trace. The maximum temperature for NLO applications of cyanine dye film is limited to 260.9.

3.8 Non-Linear Optical Studies

Since the process of Second harmonic generation (SHG) is relevant to new laser technology and the electro-optic effect, SHG efficiency of the film was determined by Kurtz powder technique [21]. Q-switched ND-YAG laser beam of $\lambda=1064$ nm with a pulse energy of 0.68 J and a 10 ns pulse width was used. To eliminate the fundamental and to collect the output with the intensity of 532 nm component from the sample a monochromator was used. The second harmonic generation was focused by a lens detected by photo multiplier tube and then confirmed by the emission of the green light (532 nm) [22- 23]. A sample of the KDP (Potassium Di-hydrogen Phosphate) was used as the reference material in SHG measurement and the behavior of SHG in Merocyanine dye was confirmed from the output of green light emission against 8.8 mJ for KDP crystal. The measured pulse energy for untreated Cyanine dye film was 0.8 mJ as against 8.8 mJ for KDP crystal. The SHG Conversion efficiency of the untreated Cyanine dye film was found to be 0.09 times that of standard KDP crystal as reference material. For the treated Cyanine dye film, the measured pulse energy was 3.1 mJ for 300s and 9.1mJ for 600s as against 8.8 mJ for KDP crystal. The SHG conversion efficiency was found to be 0.35(300s) and 0.2159(600s) times that of standard KDP Crystal. Thus Cyanine dye film treated with plasma has more efficiency when compared to untreated Cyanine dye film.

4. Conclusion

The Merocyanine dye was deposited on CTA film substrate using dip coating method. The obtained Merocyanine dye films were treated by glow discharge plasma. Results of UV and FTIR show increase in absorbance spectrum and shifts in the wave numbers. The morphological characterization of the film was analyzed by SEM and EDAX analysis. The result of SEM shows roughness of the dye film surface and Energy Dispersive X-ray Analysis shows increase in the content of carbon and oxygen. XRD characterization studies showed crystallinity of the cyanine dye film surface. DTA/TGA analysis shows thermal stability for the plasma treated film compared to untreated one. NLO study shows cyanine dye film treated with plasma has more efficiency compared to untreated film. The molecular formula for the given dye film has been confirmed by CHNS and ¹³C NMR test. The above morphological and chemical change improves the bonding strength of the modified Merocyanine dye film surface. The plasma modified cyanine dye film surface has more efficient for wide applications in industry.

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