Summary and Conclusions

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The work carried out on this thesis presented in five main chapters.

The first chapter, is the general introduction, which contains literature survey about the investigated samples and the aim of work.

The second chapter, describes the theoretical and the different calculation methods used for analyzing the results (DC-, AC-conductivity, dielectric constant (ε`), dielectric loss (ε``), optical parameter (E_g and E_u), photochemical quantum yield (Q_c), fluorescent quantum yield (Q_f) and photoelectrochemical solar cell parameters.

The third chapter, shows the experimental methods including the preparation of pure PMMA; PMMA-dye samples by casting method; preparation of TiO_2 using in preparation of photoelectrochemical solar cell and preparation of photoelectrochemical solar cell based on dye sensitized TiO_2. This chapter includes also the techniques used in the investigation of the samples (TG, DTA and IR) and in measuring the electrical, optical properties and solar cell parameters.

The fourth chapter, deals with the thermal stability and the characterization of the investigated samples where the results were reported and discussed.

The fifth chapter, is divided into four parts: The first part deals with the study of DC- and AC-conductivity of pure PMMA and PMMA-dye samples at a temperature range from room temperature to 373 and frequency of (30 – 1000 kHz).

The second part of this chapter is concerned with the electrical studies of the relative permittivity (ε`) and the dielectric loss (ε``) of the samples under investigation. The measurements were carried out at a temperature rang from room temperature to 373 K and frequency of (30 – 1000 kHz).

The third part deals with the study of photostability of pure PMMA and PMMA-dye samples under indoor and outdoor testing, June, July and August (summer 2001), in a wavelength range from 200 – 700 nm. The optical parameters (E_g and E_u), photochemical quantum yield (Q_c) and fluorescent quantum yield (Q_f) were also calculated and discussed.

The fourth part deals with the study of the effect of chemical structure of different dyes on solar energy efficiencies illuminated under sunlight in 22nd of August in Benha city afternoon. Solar cell parameters including, the open circuit voltage (V_{oc}), short circuit current (I_{sc}), the fill factor (FF) and overall energy conversion (η_y) were also calculated.

The main conclusions are the following:

(1) DTA-thermograms show that the thermal stability of most PMMA-dye samples is nearly the same as pure polymer. This indicates that these samples are stable when expose to the sunlight and can be used as solar collector.

(2) IR-spectra indicate the shift occurring in aliphatic carbonyl group C=O of PMMA to lower wave number for P_2, P_3, P_4,P_8, P_{10}, P_{11},P_9 and P_{12} samples indicating the participate of carbonyl group in inter association hydrogen bond with hydroxyl and amino group of these dyes due to amphoteric nature of this group.

(3) IR-spectra of PMMA-dye samples after exposure to the unfiltered and sunlight show that the intensity and the position of bands of IR spectrum for the samples after irradiation changed slightly due to some degradation of the polymer and the dye molecules. This indicate that the investigated dyes in this work are stable to large extent in sunlight and can be used in the working of solar cells and collectors.

(4) The DC-conductivity obtained at 353 K was found to increase in the order:

For (P_8, P_9, P_{10})

$$P < P_{10} < P_9 < P_8$$

For (P_4, P_5, P_6)

$$P < P_4 < P_5 < P_6$$

For (P_1, P_2, P_3, P_7)

$$P < P_7 < P_3 < P_2 < P_1$$

While for (P_{11}) and (P_{12})

$$P < P_{12} < P_{11}$$

All the above mentioned orders goes in parallel way with the increase in the electron density of the introducing groups to the main chemical structure of the investigated samples.

(5) The conductivity of polymer-dye samples is higher than pure polymer. This indicates that the introducing of the dye acts as an electron donor material, which enhances the conductivity.

(6) The activation energy, E_a, for the conduction process in PMMA-dye samples is less than that observed for pure PMMA. This refers to the facilitating the conduction process through the presence of dye molecules.

(7) The AC-conductivity obtained at 353 K and 100 kHz was found to increase in the following order:

For (P_8, P_9, P_{10})

$$P < P_{10} < P_9 < P_8$$

For (P_1, P_2, P_3, P_7)

$$P < P_7 < P_3 < P_2 < P_1$$

This order is the same as that observed for DC-results and going in parallel way with the decreasing in the wave number of carbonyl group as due to its interaction with the group present in the dye.

While For (P_4, P_5, P_6) the reverse order was obtained

$$P < P_5 < P_6 < P_4$$

For (P_{11}) and (P_{12})

$$P < P_{12} \simeq P_{11}$$

The more enhancements in σ_{AC} for P_4 and P_{12} may be attributed to more contribution of polarization conductivity in these samples.

(8) The AC-conductivity values obtained for PMMA is comparatively low. This because of the dipole in long chain polymer is not quite free to rotate.

(9) For all polymer-dye samples σ_{AC} was found to be higher than that of σ_{DC} referring to the presence of polarization effect.

(10) The σ_{AC} values for polymer-dye samples are higher than those obtained for pure PMMA which can be attributed to the large dipole of dye content.

(11) The drop in σ_{AC} value at $T = 343$ K for P_1, P_5 and at $T = 353$ K for P_{10}, P_4 indicating that at these temperatures, thermal energy disturb the dipole arrangement occurred in the samples or a phase transition has occurred to a phase of lower conductivity value.

(12) The increase in σ with increasing ω ($\omega = 2\pi F$, where F is the frequency) indicates that the hopping mechanism dominates in the investigated samples.

(13) The activation energy, E_a, values obtained from AC- measurements are lower than those obtained from DC-measurements.

(14) The E_a-values for all polymer-dye samples were found to be decreased by increasing applied frequency. This can be explained on the basis of the high frequency acts as a pumping force helps the charge carriers to jump between the different localized states.

(15) For pure PMMA the values of (ε`) is deceased with increasing frequency. The decrease in ($\varepsilon$`) with frequency can be attributed to the lag of dipole oscillations behind those of the field at high frequencies.

(16) For all polymer-dye samples except (P_4) the values of (ε`) is higher than those of pure PMMA . This is because the large size of dye molecules compared to that of the side group of the polymer.

(17) The disapperance of $\varepsilon`_{max}$ which is observed in pure polymer could be attributed to increasing the average of molecular weight of the samples.

(18) For P_4 dye-doped sample: ε` has comparatively lower values compared with those of pure polymer. This reflects the weak polar nature of this dye

(19) The appearance of only a single peak in ε``-T curves in our results for PMMA could be assigned to $\alpha\beta$ process where the side groups cooperate with the backbone motions in micro-Brownian.

(20) The addition of dyes to PMMA causes an increase in the intensity of the loss peak accompanied by a shift in its position to lower temperature values 333 K and 353 K for each of P_5 and P_1 respectively, compared with that of the pure PMMA. This can be attributed to an increase in the dipole concentration by addition of dye molecules, which causes such effect not only via its own polarity but also by changing the nature of the relaxation process. The existence of hydrogen-bonding interaction between the ester side group and the acidic hydrogen atoms of hydroxylic group in the case of P_2, P_3, P_8, P_9, P_{10}, P_{12} and amino group in P_4, P_{11} hinders the β relaxation (the internal rotation of the side group) and causes the disapperance of this maxima in these samples.

(21) The results showed that the plot of $(\alpha E)^2$ versus the photon energy (E) give a linear behaviour that can be considered as an evidence for the direct transition (n = 1/2).

(22) The E_g value for pure PMMA is decreased by doping with dye. This is attributed to the increase in the degree of disorder because the dye molecules are laged between the polymer chains.

(23) For all polymer-dye samples there is no significant variation in the band gap near the absorption edge upon exposure to unfiltered light at different times. For pure PMMA there is no variation in value of E_g after 195 min. which indicate that PMMA is a good matrix for dyes under investigation and could act as an inert medium.

(24) A large variation in E_u is observed by doping PMMA with different dyes. This is attributed to the effect of internal potential fluctuation with structure disorder. For pure PMMA, the obtained data show also an equal value for the localized band tail width before and after exposure to unfiltered light after 195 min. While for P_4, P_7, P_8, P_9, P_{10} and P_{11} the band tail width goes to higher value, whereas a small value difference of the localized band tail were obtained for P_1, P_2, P_3, P_5, P_6 and P_{12}. This indicates that there is a variation in E_u for dye contains anion salt P_{11} and that containing imidazolidine ring P_7. Moreover, for the P_5 and P_6 which are derivatives from group contains pyrazolone ring there is a small difference of the localized band tail than P_4. From the obtained results one can consider that adding dyes to polymer matrix with a large band gap compared to the absorption edges of dyes introduced energy levels in the concentrator band gap that produced electron-hole pairs followed by the annihilation process through a set of equidistant energy levels that accordingly produced sets of very specific wavelength.

(25) For all polymer-dye samples the optical density of dyes upon exposure to unfiltered light is decreased by increasing time of exposure. And the percent of dyes remains after 90 min. increases in the following order:

For (P_4, P_5, P_6) which contain pyrazolone ring

$$P_4 > P_5 > P_6$$

For (P_8, P_9, P_{10}) containing coumarin ring

$$P_{10} > P_9 > P_8$$

For salts (P_{11}, P_{12})

$$P_{11} > P_{12}$$

This order of degradation rate coincides well with the stability of the samples towards light irradiation. Generally, the compounds containing pyrazolone ring showed more stability towards light irradiation. This gives an evidence for using derivatives from this homologous series to prepare some solar collectors. On the other hand the dye containing anion salt P_{11} is more sensitive to light. The results also showed that the rate of degradation of samples upon exposure to unfiltered light is higher than that of filtered one due to presence of UV component.

(28) The photodegradation of P_7, P_8, P_9 and P_{10} are very high and faded after 2 hrs. while P_{11} faded after 12 hrs. The decrease observed in absorbance value can be attributed to photochemical decomposition of these dyes as a result of absorption of the solar radiation. On the other hand the photostability for the samples P_5, P_6 and P_{12} was found to be high, this indicates that these dyes are the most stable ones.

(29) The photochemical quantum yield for all investigated samples was found to follow the following order:

For (P_1, P_2, P_3, P_7)

$$P_7 > P_1 > P_3 > P_2$$

For (P_4, P_5, P_6) which contain pyrazolone ring

$$P_4 > P_5 > P_6$$

For (P_8, P_9, P_{10}) containing coumarin ring

$$P_{10} > P_9 > P_8$$

For salts (P_{11}, P_{12})

$$P_{11} > P_{12}$$

This order is go in parallel way with the rate of degradation of these samples. And from all these groups we found that P_2, P_6, P_8 and P_{12} have lower Q_c value compared with other dyes and can be selected as solar collectors.

(30) It is observed that the fluorescence intensity follows the following order:

$$P_9 > P_{10} > P_8 > P_3 > P_{11}$$

This indicates that P_9 has the highest fluorescence intensity, therefor it is selected here to use as fluorescent solar collector. P_8 shows the emission at longer wavelength than P_9 and P_{10}; this goes in parallel way with the substitution by $-OCH_3$ than $-OH$ and $-CH_3$.

(31) The Stokes shift decreases in the following order:

$$P_9 > P_{10} > P_8 > P_3 > P_{11}$$

This refers to a large self absorption of the emitted radiation by P_{11} molecules.

(32) P_9 has the highest Q_f, therefore this sample has been selected for field performance of fluorescent solar collectors in this work.

(33) The fluorescent intensity is decreased after exposure to sun radiation due to bleach of these dyes and P_3, P_8, P_9 show the emission band at longer wavelength (red shift) while P_{10} shows the emission at shorter