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Management of Industrial Dye Wastes Through Adsorption By Functionalized Graft Copolymers

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ABSTRACT

The sorption of Methyl Green (basic dye) by different grafted polymers with individual acrylonitrile (AN) and its binary comonomer mixture with N-vinylpyrrolidone (NVP) has been investigated. It was found that at approximately equal levels of graft yield of AN, poly(tetrafluoroethylene-hexafluoropropylene) (FEP) showed the highest dye sorption of the basic dye while the grafted low density polyethylene (LDPE) displayed the lowest dye sorption.. On the other hand, the different grafted polymers with AN/NVP binary monomers which having an approximately equal total graft yield (TGY) showed a dye sorption for the same basic dye according to the order: HDPE > FEP > LDPE > PP. Nevertheless, it was found that the dye sorption values by the grafted polymers with AN/NVP mixtures are much higher than those by the grafted polymers with individual AN monomer. The dyeability of HDPE grafted with individual AN and the comonomer mixture AN/NVP towards basic and disperse dyes was utilized to investigate the synergism during radiation grafting of the comonomer mixture. Results showed that such graft materials are promising in practical use for the treatment of industrial dye wastes from textile factories.

Introduction

The industrial expansion of the textile and dying industry in the world causes great problems of environmental pollution. These pollutions can not be consumed easily by ordinary processes because they are highly variable in composition. The common methods employed for treating textile wastewater include various combinations of biological, physical and chemical processes. The dye molecules are oftenenly possess big structure, hence they are very difficult to break down biologically and cannot be treated efficiently by any combination of biological, chemical and physical methods. Moreover, the cost of textile waste treatment is increasing rapidly and this has prompted further research efforts to identify other more efficient treatment methods in an attempt to lower the treatment cost.[1-3]

The radiation-induced degradation of dye waste has been extensively reported.[4-6] Even though, the ionizing radiation may promising in this field, the radiochemical yield products of the degraded dye wastes are not granted. The elimination and purification of such dye waste by sorption using grafted polymers with active groups may be considered the most practical method from the view point of environmental pollution. The latter application is the objective of the present work.

Experimental

Materials

The different grafted films used throughout this work were obtained by the direct radiation grafting of acrylonitrile (AN) and its binary comonomer mixtures with N-vinyl pyrrolidone (NVP) onto low and high density polyethylene (LDPE)& (HDPE), polypropylene (PP), and poly(tetrafluoroethylene-hexafluoropropylene) (FEP) films. The details of radiation grafting procedure was described elsewhere[7] . However, the graft yield (in the case of individual grafting of AN) and the total graft yield (in the case of grafting of comonomer mixtures of AN and NVP) were determined by the percentage increase in weight of the grafted films based on the weights before grafting. Three dyestuffs belonging to different classes were used and kindly supplied by Hoechst AG (Germany) .These dyestuffs are: Remarcry blue 3G (basic dye), Methyl Green (basic dye), and Samaras Red 2BSL9 (disperse dye).

Dye Sorption Studies

The dye sorption of the basic dye Methyl Green by the different grafted polymers under investigation with either AN or AN/NVP comonomer mixture was tested. In this procedure, the dye was first dissolved in boiled water and added to the bath without any additives. The dye sorption was carried out at different temperatures for various lengths of times. A general procedure was used to determine the dye uptake on the grafted polymers based on measuring the light absorption of the coloured solution after dye sorption. In this method, a standard calibration curve was first made representing a relation between known different concentrations of the basis dye and the corresponding light absorption. The light absorption measurements were performed using an UV/VIS spectrophotometer (Unicam UV_2 Series).

Dyeing with basic dye

The dye bath was first prepared by pasting the required concentration of the basic dye (based on film weight) with minimum amount of acetic acid and then dissolved in boiled water. The dissolved dye was added to the bath such that the samples to liquor ratio was 1: 50 The samples to be dyed were then introduced into the bath at 30 °C and the temperature was raised to the boil within 30 minutes. The dyeing was continued for 60 minutes during which Glouber salt (Sodium sulphate) was added for complete exhaustion. The dye bath was let to cool down slowly and then the samples were rinsed in cold water. The dyed samples were soaped with a solution containing 5g / L Na_2CO_3 and 1g/L detergent, washed with hot and cold water and left for air drying.

Dyeing with Disperse Dye.

The dye of this group must brought into a state of fine suspension in the dye bath. Therefore, the required concentration is continuously stirred with 20 times of its weight of water at 60 °C for at least 10 minutes. The samples to be dyed were then introduced into the cold bath and then the temperature is raised slowly up to 80 °C . The dyeing is continued at that temperature for one hour till the shade of colour is leveled. Finally, the samples were washed and soaped as mentioned in the case of dyeing with basic dye. It is to be noted that a dispersing agent Setamol WS was added to the dye bath at 2% concentration (based on liquor volume) to ensure complete suspension of the dyestuff.

Colour Difference Measurements

A computerized microcolour unit manufactured by Dr. Lange (Germany) was used for colour measurements. The L* ; a* ; and b* interceptions used in this system is based on the CIE-Colour Triangle(Commission International De Eclaire units X,Y,Z). In this system, the L* value represents the dark-white axis, a* represents the green-red axis and b* represents the blue-yellow axis. The L*, a* and b* values of the ungrafted films were measured and taken as a reference and the colour difference ΔE of the grafted films after dyeing was determined as follows:

$$\Delta\,(CD) = \sqrt{(\Delta\, L^*)^2 + (\Delta a^*)^2 + (\Delta\, b^*)^2}$$

RESULTS AND DISCUSSION

In the present work, the colour difference Δ(CD) values were correlated with the corresponding quantity of dye uptake on the different substrates. This is because the measurement of colour difference is an easy method rather than measuring the light absorption for every single test. First, the light absorption of different molar solutions of the used basic dye was measured as shown in Fig.1. From this standard curve, it can be seen that the ratio between the light absorption and the dye concentration, in moles, is equal to 12.27×10^3. The dye sorption by HDPE film grafted with AN was carried out for different lengths of time in solution containing constant concentration of the used basic dye. The colour difference of the HDPE films was measured and at the same time the dye uptake content was calculated using the standard curve in Fig.1. From these experiments, it was found that the colour difference Δ(CD) and the dye uptake content were always related to the following equation:

$$\text{Colour difference } \Delta(CD) = \text{Dye contents (Moles)} \times 68.64 \times 10^3 .$$

Dye sorption by LDPE and HDPE Graft Copolymers

Figures 2 and 3 show the basic dye sorption rate curves for grafted LDPE with PAN and PAN/PNVP copolymer at different temperatures. It can be seen that the rate of dye sorption in terms of colour difference increases gradually with time up to 60 min. thereafter, an equilibrium state is reached. This behaviour is observed for both the grafted LDPE with PAN and PAN/PNVP copolymer at low temperature range up to 60 °C. At higher temperature, the rate of dye sorption is found to increase remarkably with time. Meanwhile, the value of the initial rate of dye sorption for LDPE grafted with PAN/PNVP copolymer is twice that for LDPE grafted with PAN.

The temperature is considered to be one of the important factors influencing the dye sorption by polymeric materials. This is due to its responsibility for the diffusion of dye into the super structure of the polymer. Moreover, it accelerates the reaction between the cationic group of the dye and the accessible grafted groups on the polymer film. Therefore, it can be concluded that the dye sorption is a temperature dependent reaction. In this case, the initial rate constant of dye sorption is related to the activation energy E* and the absolute temperature T in the Arrhenius equation as follows :

$$log\ k = constant - E^*/R^{(1/T)}$$

Also, the change in colour difference is directly proportional to the quantity of the sorped dye by the substrate and hence is approximately equal to the rate of dye sorption reaction. The dependency of the initial rate of dye sorption on temperature for grafted LDPE with PAN and PAN/PNVP are shown in Arrehenius plots (Fig.3). The calculated activation energies of dye sorption reaction by LDPE-g-PAN and LDPE-g-PAN/PNVP are found to be 6.01 and 5.59 kcal/mole, respectively. It can be concluded that the dye sorption is enhanced at higher temperature and that the dye sorption by LDPE-g-PAN/PNVP is higher than that of LDPE-g-PAN graft copolymer since it possesses the lowest activation energy.

The enhancement in dye sorption can be explained on the basis of two factors: (1) Principally due to the introduction of suitable functional groups in the polymer structure via grafting and thus becoming the centers for dye sorption and reaction with the appropriate class of dye molecule,.(2)The opening up of the polymer structure during graft copolymerization, will create an additional resting places and more accessibility for the dye molecule. It follows that, during graft coplymerization, these factors are working simultaneously to enhance the dye sorption. However, it seems that grafted LDPE with either the individual PAN or with the PAN/PNVP mixture possesses a significant dye sorption and strong affinity towards the used cationic dye. Nevertheless, can not certainly determine which component in the graft copolymer mixture is responsible for the increased dye sorption. This is because the composition of the graft copolymer mixture is complicated especially the used LDPE graft copolymer with PAN and that with PAN/PNVP mixture have nearly the same graft yield.

The dye sorption rate curves of HDPE-g-PAN and PAN/PNVP copolymer at different temperatures are shown in Figs.5 and 6. It is clear that the dye sorption of the basic dye significantly increases with increasing time and temperature, however, the dye sorption at 80 °C is much higher than that at low temperatures. Moreover, the dye sorption by HDPE-g-(PAN/PNVP) copolymer is almost two and half times that by grafted HDPE with individual PAN polymer. The dependence of the initial rate of dye sorption reaction with grafted HDPE on temperature is shown in Fig. 7. The calculated activation energies of the dye sorption reaction were found to be 9.13 and 11.9 kcal/mol for HDPE -g-PAN and HDPE-g-(PAN/PNVP) respectively. Thus, the dye sorption by the second graft copolymer is higher than that of the first since it exerts the lowest activation energy.

Dye Sorption by PP and FEP Graft Copolymers

Figures 8-11 show the dye sorption by PP and FEP grafted with PAN polymer and PAN/PNVP copolymer as a function of time at different temperatures. It is obvious that the dye sorption increases as the time and temperature have been increased. Such trend is observed irrespective of the substrate and the grafting system. However, PP -g-AN possesses higher dye sorption than PP-g-(AN /NVP)one. On the other hand, the grafted FEP with PAN or (AN/NVP) possesses an approximately equal dye sorption of the basic dye. Arrhenius plots of the temperature dependence of the initial rate of dye sorption by grafted PP and FEP on temperature are shown in Figs.12 and 13. The calculated activation energies from these plots for the dye sorption by PP-g-PAN, PP-g-P(AN/NVP), FEP-g-PAN and FEP-g-P(AN/NVP) were found to be 10.34, 4.11, 3.1 and 6.9 kcal/mol, respectively.

On the basis of the above results, several point may be concluded:

(1) The grafted polymers with either individual PAN chains or PAN/PNVP copolymer displayed a dye sorption affinity for the used basic dye at different extents depends on the type of the polymer.

(2) The dye sorption by the different grafted polymers with individual PAN at higher elevated temperature and longer lengths of sorption time can be arranged in terms of colour difference Δ(CD) as follows:

FEP-g-AN > PP-g-AN > HDPE-g-AN > LDPE-g-AN

(3) The results of the rate of dye sorption indicate that the grafted FEP with individual AN monomer displayed the highest value with respect to the other grafted polymers while LDPE possesses the lowest dye sorption. These findings are in good agreement with the calculated activation energies in which the dye sorption reaction by grafted FEP goes with the lowest value, whereas, the dye sorption reaction by grafted HDPE displays a relatively higher activation energy.

(4)The relatively higher dye sorption showed by the grafted polymer with PAN/PNVP copolymer cannot be explained until the composition of the relative grafted fractions from each monomer are known. This is because both moites as seen before have a dye affinity for the used basic dye, however, certainly one possess higher dye affinity than the other. The determination of the different grafted fractions may give a better understanding for this phenomenon.

Investigation of the Synergism During grafting Binary Comonomer Mixtures by a Dyeing Method

The proposed dyeing method is based on different aspects

(1). All polymers under investigation are hydrophobic in nature and have no direct affinity for any class of dyestuffs. This is due to the absence of reactive groups capable to react with the appropriate class of dyestuffs. In accordance, the dyeability can be imparted to different polymers by introducing suitable functional groups along the macrostructure accessible to react with the different dyestuffs. This property can be achieved via graft copolymerization in which new groups can be introduced.

(2) The radiation grafting of different binary monomers mixtures of AN and NVP onto the different polymeric substrates will produce graft copolymers having different compositions of PAN and PNVP grafts. Such composition of these graft copolymers will depend in the first place on the synergism, i.e., the mutual effect and the respective reactivity of the two monomers during graft copolymerization. Therefore, the estimation of such composition in the graft copolymer will help to explain the synergism during graft copolymerization.

(3) The change in the dye affinity for the different grafted copolymers with PAN/PNVP for basic and disperse dyes were used to determine quantitatively the graft yield fractions of PAN and PNVP corresponding to the different grafted comonomer mixtures.

The applied dyeability method can be explained in the following steps taking HDPE-g-P(AN/NVP) copolymer as an example for dyeing with the Remacryl Blue basic dye. In this method, HDPE that grafted with individual AN or NVP to different graft yields were dyed with the basic dye. The colour difference Δ(CD) of the different grafted HDPE substrates was measured and plotted against the graft yields as shown in Fig. 14. It can be seen that the colour difference Δ(CD) increases gradually with increasing the graft yields of PAN. On the other hand, the colour difference Δ(CD) is also increased with increasing graft yields of PNVP on HDPE but to higher extent. These trends indicate that both PAN and PNVP grafted chains have a dye affinity for the used basic dye.This reference curve was utilized to determine separately the contribution of each PAN and PNVP graft fraction in the final graft copolymer obtained by grafting of AN/NVP binary monomers mixture onto HDPE under certain conditions. For example, HDPE was grafted by different AN/NVP compositions and the total graft yield (TGY.s) were determined by the percentage increase in weight. The grafted HDPE was dyed with the same basic dye and the colour difference was measured and recorded as shown in Table 1.

Table 1. Colour Difference and Graft Yields Fractions of HDPE Grafted With AN/NVP binary mixtures at Different Comonomer compositions of AN and NVP (Dyed with Remacryl Blue the Basic dye)

Comonomer Composition AN	Comonomer Composition NVP	Total Graft Yield (%)	Colour Difference (ΔE)	Graft Yield Fraction of (PAN)	Graft Yield Fraction of (NVP)
40%	60%	110	23.2	75.22	34.78
50%	50%	123	18.4	86.75	36.25
80%	20%	128	13.2	82.59	45.41

Grafting conditions: $[FeCl_3]$ = 0.1 (wt%), [MEK] =40%, [AN:NVP] =[40:60] = 60(wt%).

As a matter of fact, the recorded colour differences in Table 1. represent the contribution of colour difference from both PAN and PNVP graft fractions present in the final graft copolymer. For the HDPE sample grafted through the bath containing 40% AN and 60% NVP, the total colour differences(TCD) is found to be 23.2. From Fig. 14, this value of TCD corresponds to 80% graft yield of PNVP or 173% graft yield of PAN. Since, the colour difference is an added quantity, thus, a graft copolymers of HDPE composed of these fractions having TGY of 253% should results a TCD of 46.4. Also, a graft copolymer of HDPE having half or double of this value should give half or double of the value of TCD too. Therefore, it may be concluded that the mole fractions of the grafted PAN and PNVP is constant at any condition. It follows that the mole fraction of PNVP in the graft copolymer in this case will equal to 0.3162 while the mole fraction of PAN will equal to 0.6838. Accordingly, the true graft yield fractions of PNVP and PAN in the used comonomer mixture will equal to 34.78% and 75.22%, respectively. Figure 14 can again be used to determine the corresponding graft yield fraction of PAN and PNVP for the grafting different comonomer mixtures shown in

Table 1.By applying the same procedure, the calculated graft yield fractions of PAN and PNVP in the graft copolymer could be obtained as shown in Table 1.

It can be seen that by increasing the content of AN monomer in the binary comonomer mixtures from 40% to 50%, the corresponding graft yield fraction of PAN is increases and then tends to decrease by increasing its content from 50% to 80% in the reaction medium. Moreover, it can be occluded that the presence of NVP in the grafting solution initiates the build up of PAN grafting onto HDPE.

In order to see the reproducibility and validity of the proposed calculation method depending on the colour difference, the grafted HDPE films with different (AN/NVP) composition were dyed with another class of dyestuffs (disperse dye, Samaron Red 2BSL)and presented in Table 2. Figure 15 shows, also, the colour difference on HDPE grafted films with individual AN and NVP to different graft yields and dyed with the disperse dye Samaron Red 2BSL. It is evident that, HDPE-g-PNVP substrate shows higher dyeability with the used disperse dye than HDPE-g-PAN substrate. Moreover, the dye affinity for both grafted HDPE films is much higher than their dye affinity for the used basic dye . This was obvious from the higher values of colour difference in the latter case. These trends can be attributed to the higher affinity of disperse dyes for synthetic groups and the hydrophobic nature of this class of dyestuffs.

Table.2. Colour Difference of HDPE grafted with Different ComonomerMixtures of AN and NVP, Dyed with the Disperse Dye Samaron Red

Comonomer Composition (AN	NVP)	Total Graft Yield (%)	Colour Difference Δ(CD)	Grafted Yield PAN (%)	Grafted Yield PNVP (%)
40%	60%	110	75.5	61.82	38.18
50%	50%	123	73.2	84.73	38.27
80%	20%	128	71.2	80.56	47.44

Comparing the results obtained on tables 1 and 2. by applying the proposed dyeability procedure, it can be concluded that this method is valid for the different dyestuffs used. Moreover, the dyeability method confirm the positive synergistic effect of AN and NVP over each other during radiation graft copolymerization.

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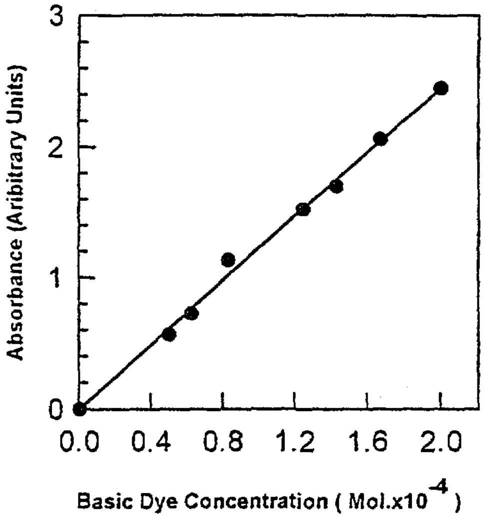

Fig. 1. Visible light absorbance of different concentrations of the basic dye Methyl Green.

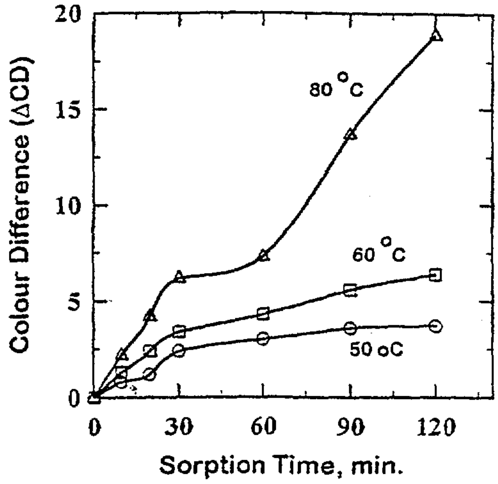

Fig.2. Effect of sorption time on the colour difference of LDPE-g-PAN 72% at different temperatures by using the basic dye (Methyl Green).

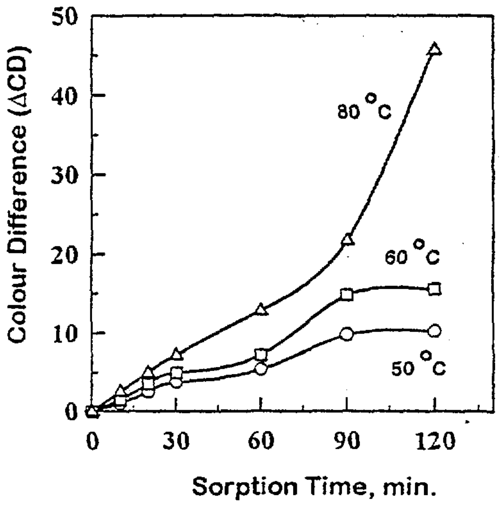

Fig.3: Effect of sorption time on the colour difference of LDPE-g-P(AN/NVP) 77% at different temperatures by using the basic dye (Methyl Green).

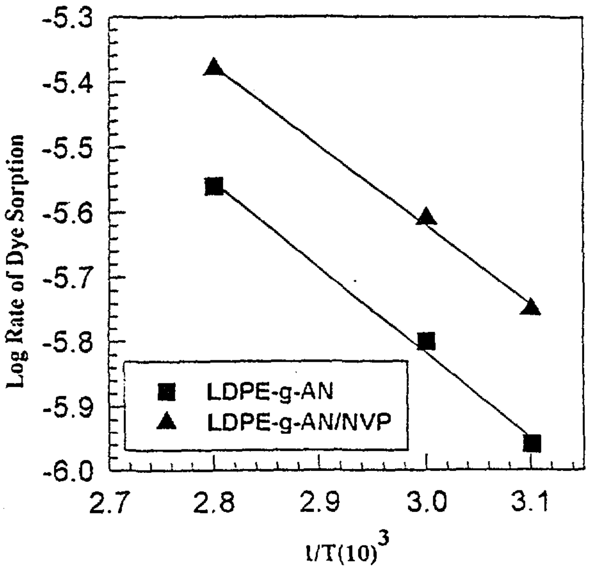

Fig 4.Arrhenius plots of the dye sorption by grafted LDPE Films

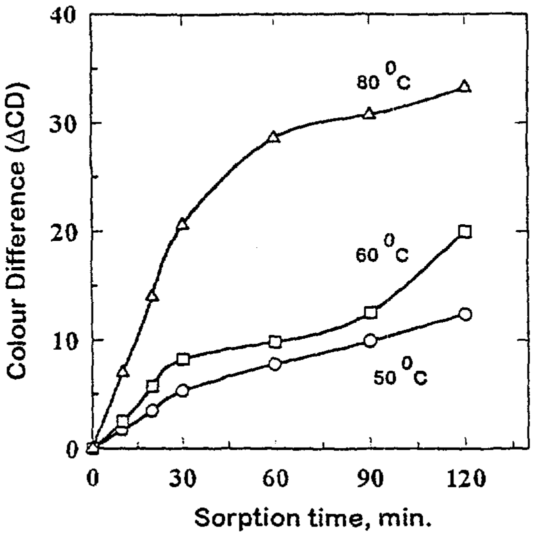

Fig.5. Effect of sorption time on the colour difference of HDPE-g-PAN 109% at different temperatures by using the basic dye (Methyl Green).

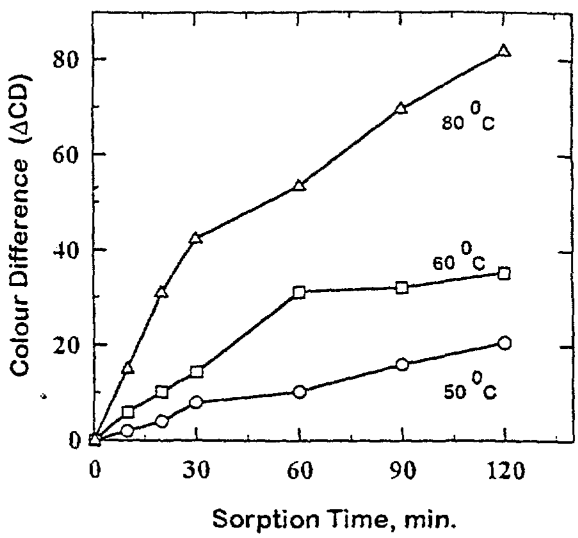

Fig.6. Effect of sorption time on the colour difference of HDPE-g-P(AN/NVP) 88% at different temperatures by usingthe basic dye (Methyl Green).

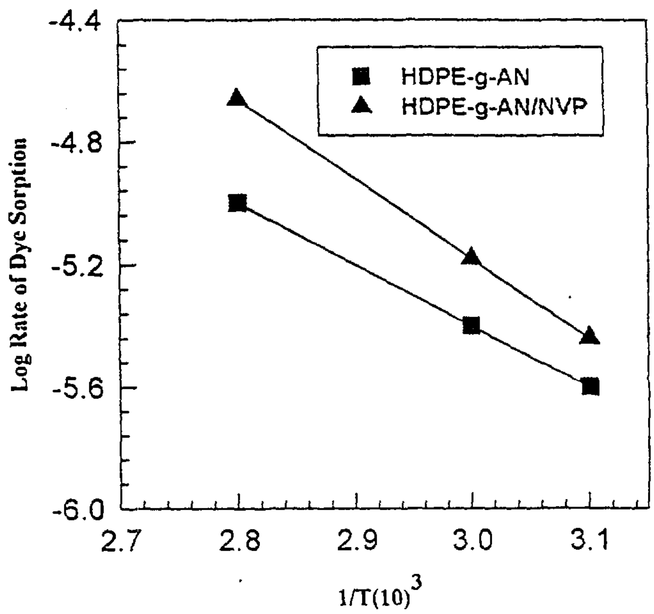

Fig 7. Arrhenius plots of the dye sorption grafted by HDPE Films

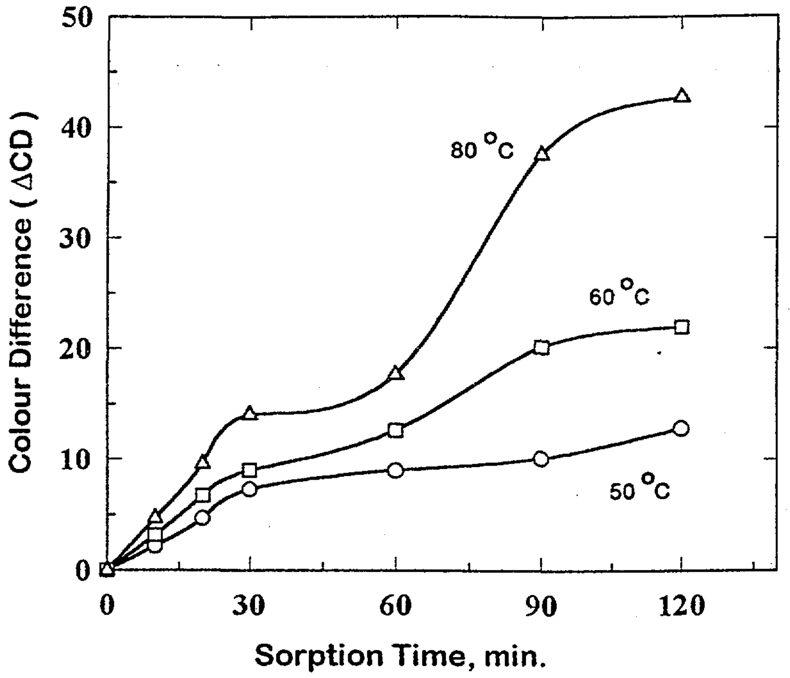

Fig.8 Effect of sorption time on the colour difference of PP-g-PAN 95% at different temperatures by using the basic dye (Methyl Green).

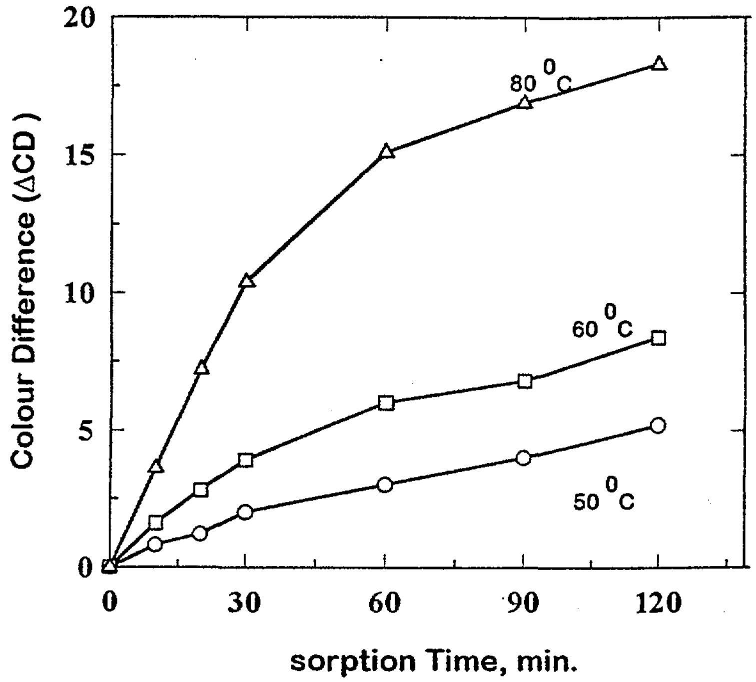

Fig.9. Effect of sorption time on the colour difference of PP-g-P(AN/NVP) 49% at different temperatures by using the basic dye (Methyl Green).

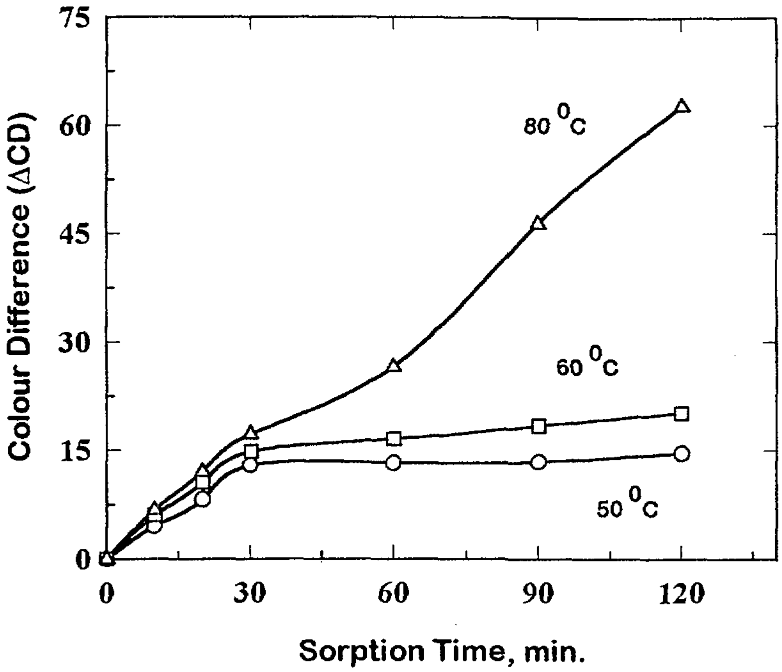

Fig.10. Effect of sorption time on the colour difference of FEP-g-PAN 95% at different temperature by using the basic dye.(Methyl Green).

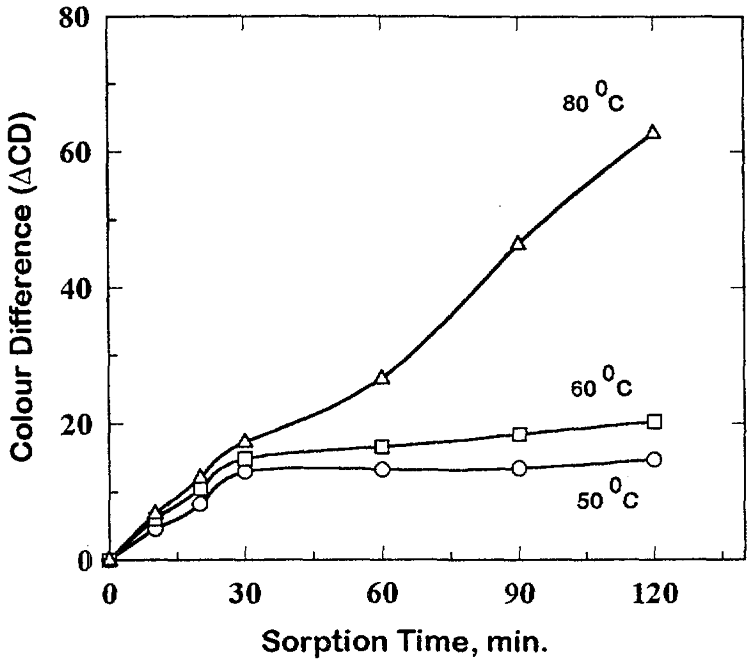

Fig.11. Effect of sorption time on the colour difference of FEP-g-P(AN/NVP) 93% at different temperatures by usingthe basic dye (Methyl Green).

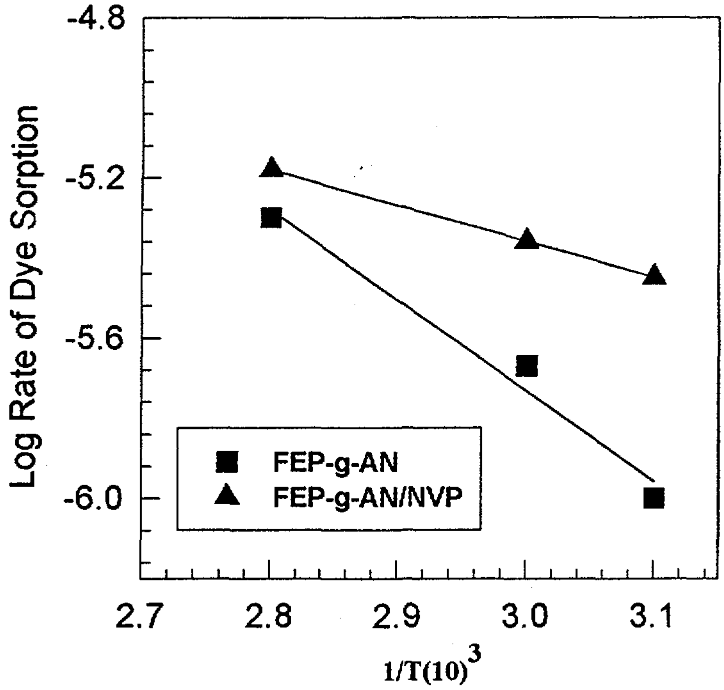

Fig 12. Arrhenius plots of the dye sorption by grafted PP Films

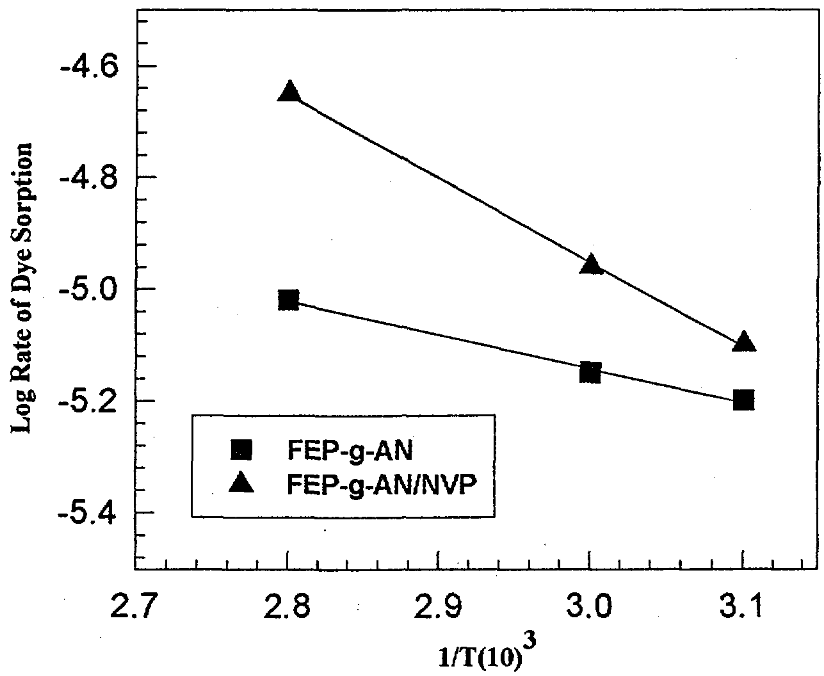

Fig 13. Arrhenius plots of the dye sorption by grafted LDPE Films

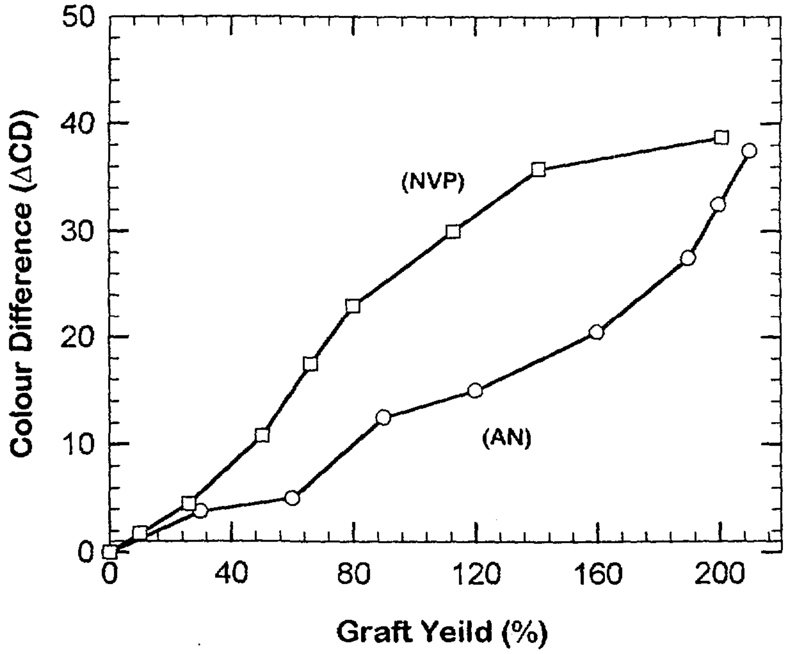

Fig.14.Colour difference (ΔCD) due to the basic dye (Remacryl Blue) in the grafted HDPE with AN and NVP as a functionof grafting yield.

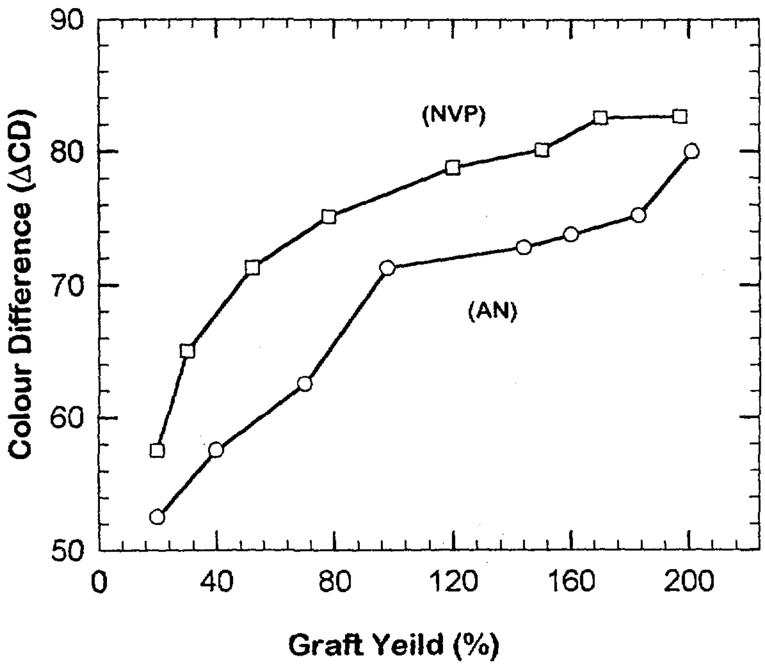

Fig.15. Colour difference (ΔCD) due to the disperse dye (Samaron Red) in the gafted HDPE with AN and NVP as a function of grafting yield.