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The Dyeing Properties of Grafted Polyamide Fibres

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ABSTRACT

Dyeing of grafted polyamide-6 fibres with anionic and cationic dyes was performed in order to investigate the possibility of changing the fibre dyeability. It was observed that grafting of polyamide fibres decreased its anionic dyeability and increased the cationic dyeability.

Increasing the graft yield on the polyamide fibres resulted in a decrease in the relative specific dyeing rate constant and a decrease in the apparent activation energy of diffusion of anionic dyes. The contrary was true for cationic dyeing.

Calculations of the affinity and heat of dyeing revealed negative values for both anionic and cationic moieties on the grafted polyamide fibres.

It was also found that dyes having a low ratio of organicity to inorganicity, irrespective of their being cationic or anionic, tend to form ionic bonds with the functional groups in the modified substrate.

1 INTRODUCTION

The dyeing properties of polyamide fibres are greatly affected by grafting reactions.[1–5] The uptake of cationic dyes by the grafted fibres increases in the case of grafting with acrylic acid and acrylamide.[6] Improvements in the wet fastness properties, as well as the hygroscopic nature of grafted polyamide fibres when using vinyl monomers bearing acid groups, result from treating the dyed fibres with a fixing agent and a monovalent positive ion.[7] Mukherjee & Goel[8] studied the dyeing behaviour of polyamide fibres grafted with various vinyl monomers using disperse dyes. The dye uptake was found to approach a maximum for methyl methacrylate grafted fibres followed by ethyl and then n-butyl methacrylate grafted samples at a comparable graft level. It was found that the disperse dye uptake was not dependent on the nature of the functional groups of the grafted polyamide fibres, but was more dependent on the structural characteristics induced by grafting.[9–11] The dyeing differences of grafted polyamide fibres have been ascribed to the influence of the grafting on the physical character of the polyamide fibre structure as well as to the nature of the dyes.[12,13]

Hirata & Fujii[14] studied the grafting of polyamide fibres by interfacial polymerization with methacrylic acid, methyl methacrylate and 2-(dimethylamino)ethyl methacrylate. They concluded that changes in the physicochemical properties of the modified fibre surfaces greatly affect the dyeability of the modified fibres.[14]

We have previously reported[15] kinetic studies on the grafting reaction of acrylic acid onto polyamide-6 fibres. This present paper describes vinyl graft copolymerization onto polyamide-6 fibres thus inducing changes in the dyeing characteristics of the modified fibres with both anionic and cationic dyes. Kinetic studies of the dyeing process are also reported.

2 EXPERIMENTAL

2.1 Materials

Polyamide fibres (210 denier/35 filament yarn), density $1{\cdot}14\,g\,cm^{-2}$, was soaped, rinsed thoroughly and air-dried.

Various chemical classes of anionic and cationic dyes were used, namely:

Anionic dyes
C.I. Acid Blue 23 (anthraquinone); Acid Orange 7 (monoazo); Acid Red 85 (diazo); and Acid Blue 3 (TPM).

Cationic dyes
C.I. Basic Brown 1 (azo); Basic Red 2 (azine); Basic Red 1 (Xanthene); and Basic Blue 1 (TPM).

2.2 Grafting technique

Samples (1 g) were subjected to grafting reactions using acrylic acid monomer and $K_2S_2O_8$ as initiator, by introducing the fibres into 50 ml of the reaction solution at a prescribed temperature. The reaction solution consisted of water, monomer and copper sulphate. After an elapsed time, the reaction mixture was filtered. The residues were washed with water, dried at 105°C for 2 h and cooled to room temperature in a desiccator until attaining constant weight. The dried samples were then extracted with boiling water, dried, and weighed. The percentage graft yield was calculated as follows:

$$\text{Graft yield} = \frac{P - P_0}{P_0} \times 100\%$$

where P is the weight of grafted sample and P_0 is the weight of the original sample. Samples having a graft yield of *c.* 5–20% were used for the evaluation of the dyeing characteristics.

2.3 Dyeing technique

The substrate (1 g) was dyed in 100 ml of dye solution at constant temperature and adjusted to pH 4 with a sodium acetate/acetic acid buffer system. Dyeing was performed in a thermostatic water bath with agitation of the liquor. The dyeing time, temperature, dye concentration and dye nature were changed according to the prescribed experimental conditions.

2.4 Dye extraction

The dyed materials were extracted with a hot DMF/water (1:1) mixture[16] and the amount of extracted dye was determined spectrophotometrically.

2.5 Physicochemical evaluations: time of half-dyeing

Dyeing of polyamide fibres was performed on a 5 g sample using 2% dye (o.w.f.). Each set included dyeings for 5, 10, 30, 60 min and also for 8 h. Samples from the dyebath were removed immediately after the prescribed dyeing time and the amount of dye remaining in the liquor was determined by spectrophotometric techniques.[17] For each dyeing temperature, the percentage exhaustion was plotted versus dyeing time. Time of half-dyeing ($t_{1/2}$, min) was determined from these plots.

2.6 Specific dye rate constant (K')

The specific dyeing rate constant (K') can be further estimated[18] using the equation:

$$K' = 0{\cdot}5C_\infty(d \, . \, t_{1/2})^{1/2}$$

where d is the fibre diameter (cm) and C_∞ is the percentage of dye absorbed at equilibrium conditions.

The values of the times of half-dyeing of the polyamide fibres determined as above were used in calculating the specific dyeing rate constant.

2.7 Apparent diffusion coefficient

Polyamide fibre samples (1 g) were dyed in dye solutions (800 ml) for 8 h. The dye taken up by the fibre was extracted with DMF/water (1:1) and the concentration of the dye in the fibre (C_∞) was determined spectrophotometrically. A further dyeing was performed for a short period (10 min) and C_t was similarly determined. The values of C_t/C_∞ were calculated and the apparent diffusion coefficient (D) could then be calculated using Hill's equation.[17]

$$D = \frac{C_t}{C_\infty} \cdot \frac{d^2}{T} \times 100\,\text{cm}^2\,\text{s}^{-1}$$

2.8 Affinity, heat of dyeing and entropy

A 5% dyeing was carried out on two 0·5 g polyamide samples at 80°C for 2 h using a liquor ratio of 80:1. At the end of the dyeing, the samples were removed and rinsed several times with cold distilled water.[17] One of the samples was treated with 80 ml of distilled water in a stoppered flask for 2 h at 80°C and the other was similarly treated for 4 h at 60°C. The samples were then removed, rinsed several times with distilled water and air-dried. The amounts of dye in the desorption solution, as well as that remaining on the treated samples, were determined spectrophotometrically. The partition coefficient (k) of the dye was estimated from:

$$k = \frac{\text{Concentration of dye in fibres (mg kg}^{-1}\text{ fibres)}}{\text{Concentration of dye in solution (mg litre}^{-1}\text{)}}$$

The affinity ($\Delta\mu^0$) was determined according to: $-\Delta\mu^0 = 2{\cdot}3\,RT\log k$ (cal mol^{-1}) where μ^0 is the standard chemical potential, R is the gas constant and T is the absolute temperature.

The heat of dyeing (ΔH^0) was further determined from:

$$\Delta H^0 = \left[\frac{\Delta\mu_1^0}{T_1} - \frac{\Delta\mu_2^0}{T_2}\right] \Big/ \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

The entropy change (ΔS^0) was calculated[19] from the equation:

$$\Delta\mu^0 = \Delta H^0 - T\Delta S^0$$

These data allow a comparison to be made between the behaviour of the anionic and cationic dyes on the grafted polyamide.

3 RESULTS AND DISCUSSION

3.1 Effect of grafting on the dyeability of polyamide fibres

Grafting of polyamide fibres was carried as described above. Stock grafted samples of 5–20% graft yield were prepared. Dyeing investigations were carried out on control and grafted samples using the anionic and cationic dyestuffs. The rates of dyeing of the samples were measured using absorptiometric techniques. Samples of the dye liquor were withdrawn at various times after the start of dyeing. Measurements of the dye concentrations against the original liquor were performed and the dye taken up by the fibres was thus calculated.

Figures 1 and 2 show the dependence of dye uptake of the polyamide fibres (expressed as g dye/100 g fibre) on the dyeing time for both the modified and the control fibres. Increasing the graft yield percentage results in a gradual decrease in the uptake of acid dyestuff compared with the control sample. The reverse tendency is observed using cationic dyes (Fig. 2), where the control sample has the least dye uptake. The cationic dyeability of the grafted samples increased gradually with increase in graft yield. This can be ascribed to the introduction of carboxyl groups into the polymer backbone as a result of the grafting with acrylic acid. This hinders the uptake of acid dyes and favours that of cationic dyes.

3.2 Time of half-dyeing

Polyamide fibres grafted to graft levels 5–20% with polyacrylic acid were dyed with anionic and cationic dyes at 70°C and 90°C. Figures 3 and 4 show

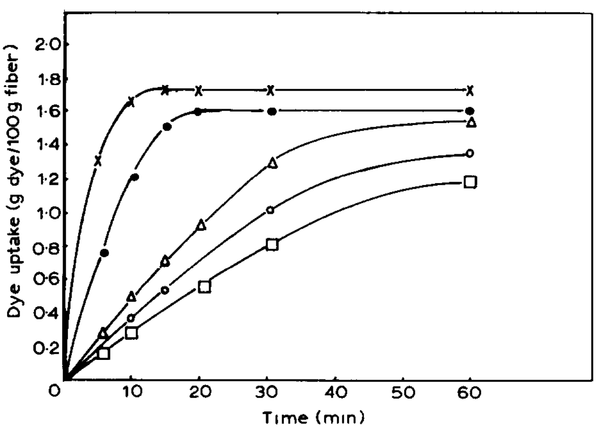

Fig. 1. Rate of dyeing of polyamide fibres with acidic dyestuff. Dyeing: C.I. Acid Red 85, 2% o.w.f., pH 4, 90°C, liquor ratio 1:100. ×, Control. Graft yield: ●, 5%; △, 10%; ○, 15%; □, 20%.

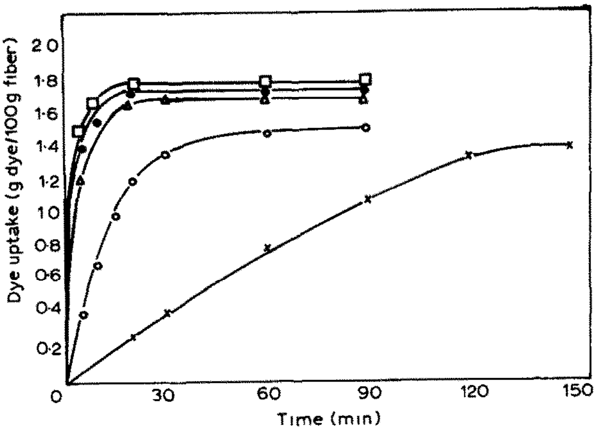

Fig. 2. Rate of dyeing of polyamide fibres with cationic dyestuff. Dyeing: C.I. Basic Blue 1, 2% o.w.f., pH 4, 90°C, liquor ratio 1:100. ×, Control. Graft yield: ○, 5%; △, 10%; ●, 15%; □, 20%.

the relation between the relative half-dyeing time (ratio of $t_{1/2}$ of pretreated to $t_{1/2}$ of untreated substrate) and the percentage grafting. It can be observed that grafting levels have a significant influence in reducing the anionic dyeability of the fibres (Fig. 3), and in imparting a significant increase in the case of the cationic dyeability (Fig. 4). Time of half-dyeing estimations provided an indirect measure of the rate of diffusion of the dye molecules into the substrate.

3.3 Specific dyeing rate constant (K')

Figures 5 and 6 show the corresponding relative specific dyeing rate constant (ratio of K' for grafted fibres to K' for untreated fibres) in relation to the graft yield percentages. It can be seen that on increasing the graft yield on the polyamide fibres, a decrease in the relative specific dyeing rate constant in the case of anionic dyeing (Fig. 5) and an increase in the case of cationic dyeing (Fig. 6) occurs. The modification in the fibre structure involves a change in the dye uptake character which was clearly reflected in the diffusion characteristics. Application of C.I. Acid Red 2 and C.I. Basic Orange 7 to the polyamide fibre gave the lowest relative $t_{1/2}$ values. This would reflect the influence of inter-relating dye molecule characteristics such as size, shape, configuration, mobilization within the polymer phase and the ratio of organic to inorganic character of the dye molecules.[20]

3.4 Dye diffusion

The apparent diffusion coefficients (D) of C.I. Basic Red 1 and C.I. Acid Red 85 in modified polyamide fibres were determined by carrying out the dyeing

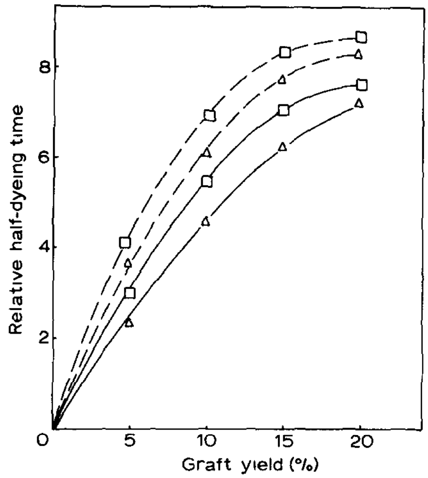

Fig. 3. Dependence of the relative half-dyeing times, for grafted polyamide fibres dyed with anionic dyes, on the percentages of graft yield. Dyeing: 2% o.w.f., pH 4, liquor ratio 1:100. ——, 70°C; - - -, 90°C; △, C.I. Acid Red 85; □, C.I. Acid Blue 23.

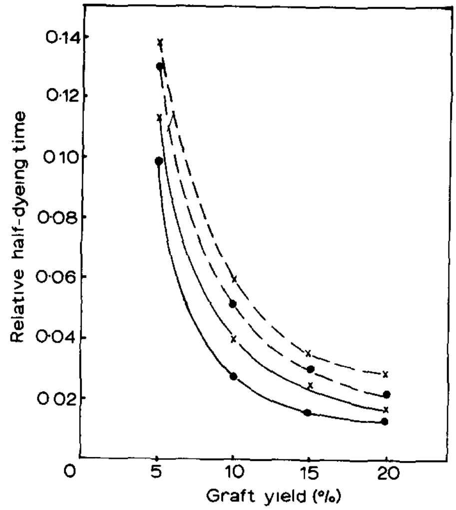

Fig. 4. Dependence of the relative half-dyeing times for grafted polyamide fibres dyed with cationic dyes, on the percentage of graft yield. Dyeing: 2% o.w.f., pH 4, liquor ratio 1:100. ——, 70°C; - - - -, 90°C; ×, C.I. Basic Blue 1; ●, C.I. Basic Brown 1.

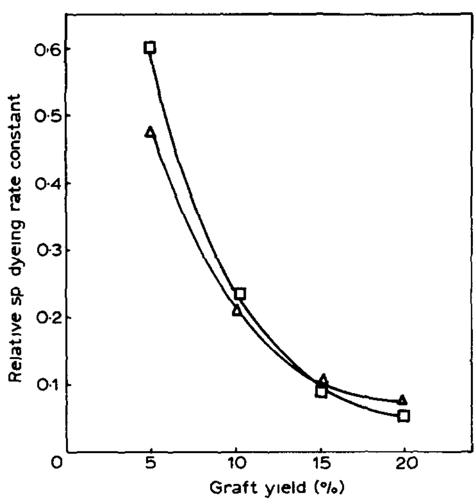

Fig. 5. Relative specific dyeing rate constant for the dyed polyamide fibres modified by grafting versus the percentage of graft yield. Dyeing: 2% o.w.f., pH 4, 90°C, liquor ratio 1:100. □, C.I. Acid Blue 3; △, C.I. Acid Orange 7.

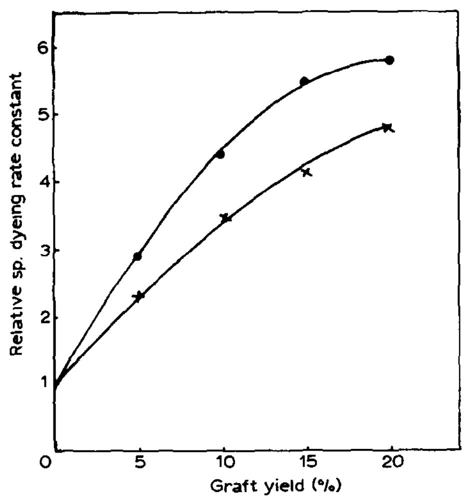

Fig. 6. Relative specific dyeing rate constant for the dyed polyamide fibres modified by grafting versus the percentage of graft yield. Dyeing: 2% o.w.f., pH 4, 90°C, liquor ratio 1:100. ●, C.I. Basic Red 1; ×, C.I. Basic Red 2.

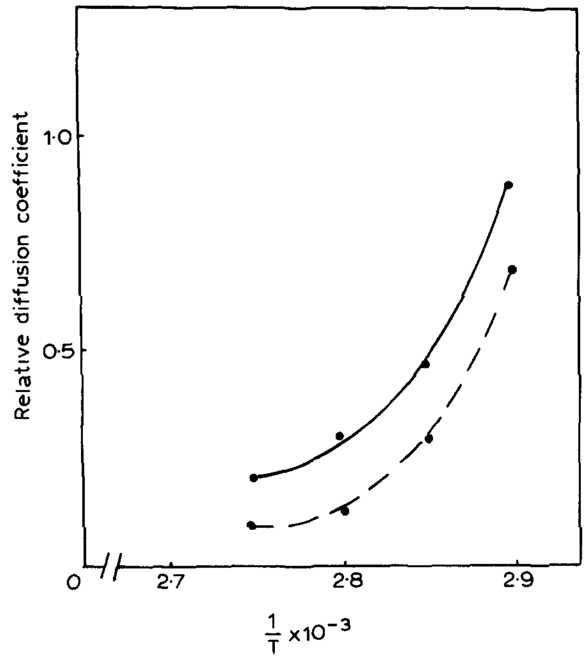

Fig. 7. Dependence of the relative apparent diffusion of anionic dye in grafted polyamide fibres on the absolute temperature of dyeing (T). Dyeing: 5% o.w.f., pH 4, liquor ratio 1:800. ●, C.I. Acid Red 85; ——, 5% graft yield; – – –, 15% graft yield.

process from an infinite bath. On the assumption that the fibres have approximately circular cross-sections, the diffusion coefficients were calculated according to Hill's equation.[21] The relative apparent diffusion coefficients of an anionic dye into the modified polyamide fibres (D for grafted/D for untreated fibres) versus the dyeing temperatures are depicted in Fig. 7. It is observed that the relative D values decreased rapidly as the temperature increased from 70 to 80°C, the rate of decrease then slowing down with further rise of the temperature to 90°C. This may be attributed to two factors, namely resistance to mobility offered by the substrate macromolecular matrix and the immobilization of a large fraction of the dye by virtue of the strong forces of adsorption between the dye molecules and substrate. Increasing the grafting level of the substrate gave a weaker possibility for anionic dye diffusion. This may also be attributed to the decrease of the chemical sites which usually interact with anionic dyes. However, the grafting of polyacrylic acid to the polyamide fibre backbone induced an increasing facility for the attachment of cationic dyes and this was progressively dependent on the graft yield content in the fibres (Fig. 8).

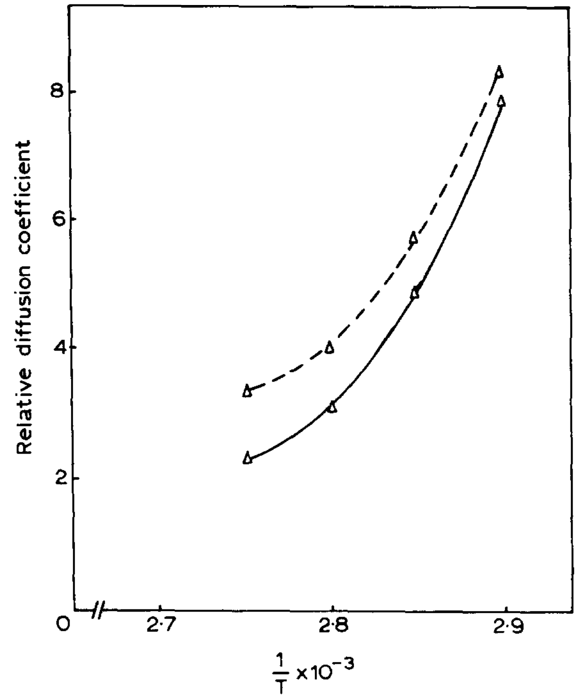

Fig. 8. Dependence of the relative apparent diffusion coefficient of cationic dye in grafted polyamide fibres on the absolute temperature of dyeing (T). Dyeing: 5% o.w.f., pH 4, liquor ratio 1:800. △, C.I. Basic Red 1; ——, 5% graft yield; – – –, 15% graft yield.

3.5 Relative apparent activation energy of diffusion

The relative apparent activation energy of dye diffusion (E) as calculated from the Arrhenius equation ($2{\cdot}3 \log D = E/RT + \text{constant}$) gives a numerical indication of the effect of the temperature of dyeing on the changes in the dye diffusion coefficient. The relative apparent activation energy of dye diffusion (E') into the modified fibres (ratio of E for grafted to E for untreated fibres) can be considered as the energy necessary for the dye molecule to move within the modified fibre matrix with respect to the case of untreated fibres dyed under the same conditions. E' was found to be the order of $\sim$0·25 and $\sim$10 for C.I. Acid Blue 23 and C.I. Basic Red 2 respectively in polyamide fibres bearing a 15% graft yield.

3.6 Affinity and heat of dyeing

Dyeing of the grafted polyamide fibres with cationic as well as anionic dyes (5% o.w.f.) at 80°C was carried out for a prolonged period to establish an equilibrium with the adsorption and desorption taking place at similar rates. The partition coefficients (k) were first determined and the affinity of a dye for the substrate ($-\Delta\mu^0$) as well as the corresponding heat of dyeing ($-\Delta H^0$) were thus derived.[17,22]

Calculations of the affinity and heat of dyeing revealed negative values, indicating that the dyeing processes of the untreated and grafted polyamide fibres with both anionic and cationic dyes were exothermic. Generally, increasing the temperature of dyeing caused a noticeable decrease in affinity values where the equilibrium was shifted in favour of the external phase (Table 1). It was observed that the heats of dyeing of anionic dyes decreased as the graft yield of acrylic acid onto the polyamide fibre increased. The contrary was true using cationic dyes (Table 1). These results are in accord with the heat of dyeing being a measure of the strength of attraction between the dye moiety and the fibres.

3.7 Entropy change

The average entropy change values ($-\Delta S^0$) of dyeing grafted polyamide fibres with anionic and cationic dyes at 70°C and 90°C were also estimated. In the case of anionic dyes it was found that the average values were ~0·148, ~0·132 and ~0·07 kJ mol^{-1} K^{-1} for untreated, modified polyamide fibres of 5% graft yield and modified polyamide fibres of 15% graft yield respectively. In the case of cationic dyes, the average values were ~0·045, ~0·073 and ~0·23 kJ mol^{-1} K^{-1} for the untreated and for modified polyamide fibres bearing 5% and 15% graft yield respectively.

It is apparent that grafting of polyacrylic acid to the polyamide fibre backbone imparted a decreased randomness of the anionic dyes within the substrate matrix during dyeing, which may be ascribed to the repulsion between the acidic groups of the modified substrates and the anionic dyes. The tendency of attraction between cationic dye moieties and induced functional groups in grafted polyamide backbone served in promoting the average entropy change values of cationic dye molecules within the modified polyamide fibre macrostructure. Similar findings were also reported elsewhere.[19,33]

3.8 Organicity and inorganicity of the dyes

Fujita[24] has proposed the concept of organicity and inorganicity properties in the characterization of organic compounds. The ratio of the organicity to inorganicity character (A) of the dyestuffs can be utilized to denote numerically the primary properties of the dyestuff molecules.[25] Polar interactions in the cationic and anionic dye molecules contribute to the

TABLE 1
Affinity and Heat of Dyeing of the Anionic and Cationic Dyes Used in Dyeing Grafted Polyamide Fibres

Dyestuff	*Ratio of organicity to inorganicity*,[20] *A*	*Affinity*, $\Delta\mu^0$ ($kJ\,mol^{-1}$)						*Heat of dyeing*, $-\Delta H^0$ ($kJ\,mol^{-1}$)		
		Control sample		*Graft yield*				*Control sample*	*Graft yield*	
				5%		*20%*			*5%*	*20%*
		70°C	*90°C*	*70°C*	*90°C*	*70°C*	*90°C*			
C.I. Acid Blue 23	0·211	20	17·2	16	13·65	13·5	12	68·2	56·4	39·3
C.I. Acid Blue 3	0·511	25	21·4	23·9	21·0	22·0	20	86·9	73·8	56·4
C.I. Basic Brown 1	1·086	6	5·2	26	24·6	48·0	44·6	20	50·1	110
C.I. Basic Blue 1	2·560	8	7·1	31·4	29·9	55·4	49·9	24	57·2	150

inorganicity, whilst non-polar interactions contribute to the organicity. Dyes having low *A* values, irrespective of whether they are cationic or anionic, tend to form ionic bonds with the functional groups in the substrate. An anionic dye having a higher *A* value has higher affinity for the substrate. This tends to interact via Van der Waals forces with the polymeric substrate.[26] It was also observed that on increasing the *A* value of the cationic dyes, increase in the affinity values as well as of the heat of dyeing occurred, essentially ionic bonds being formed with the modified substrate during dyeing. The ratio of organicity to inorganicity character of the dyes expresses their tinctorial behaviour for untreated and modified substrates grafted to various graft yields.

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