CHAPTER 8

SUMMARY AND CONCLUSIONS
CHAPTER 8
SUMMARY AND CONCLUSIONS

The present work deals with improving the dyeability of cotton towards reactive dyes (containing various reactive systems) under neutral conditions by chemical modification via creation of innovative reactive sites on the cellulosic chain.

Extensive literature survey (Chapter 1) has revealed the possibility of modification of cotton by various chemical methods. The changes occurring due to such modification have also been studied thoroughly. From the study, possibility of modifying cotton with a polymeric material has been designed, keeping in mind possibility to achieve enhanced dyeing performance. Minimization of effluent load has also been critically decided by neglecting the utilization of chemicals and auxiliaries in the dyeing recipe.

The conclusion has been drawn in two portions – the first part deals with the structural behaviour of the fabric after treatment with a suitable polymer and cross-linking agent, while the second part is exclusively related with such polymer treated fabric and how it behaves during dyeing.

The modification of cotton has been achieved by utilization of a highly reactive polymer for pretreatment, which is, cross-linked with a suitable cross-linking agent. Three polymers have been selected for pretreatment – the first two, viz. Polyacrylamide (PAAm) and Polyacrylic acid (PAA) are water-soluble polymers [Chapters 2 and 3], while the third one being Polyacrylonitrile (PAN), which is water-insoluble. The first two polymers have been synthesized and characterized in the laboratory, in terms of solid content, variable viscosity measurements and infrared analysis. Furthermore, the third polymer used for the work is actually the polymer waste disposed off by the manufacturer. The main idea is to utilize this waste product by some sort of recycling technique to solve the environmental problems associated with it. The polymer is being converted into a water-soluble form after hydrolysis with caustic soda. The water-soluble form, i.e., hydrolyzed polyacrylonitrile (PANhyd) has a close resemblance with PAA polymer. However,
complete conversion of the nitrile groups (present in PAN polymer) into carboxylic acid groups involves a number of steps, with initial formation of amide groups from the nitrile groups. Therefore, there are chances that a few nitrile groups might have remained intact, while some amide groups may be present in the chain after hydrolysis along with the carboxylic acid groups [Chapter 4]. The cross-linking agents used for the pretreatment along with the polymer are selected from two categories – nitrogenous and non-nitrogenous types, and are of varied nature. One cross-linking agent, namely Glycerol 1, 3-dichlorohydrin (C III) has been synthesized in the laboratory. Epichlorohydrin (C I) and Glycerol 1, 3-dichlorohydrin (C III) are the non-nitrogenous cross-linkers, while Hydrazine hydrate (C II) and Hexamethylene diamine – Hydroquinone (C IV) belong to the nitrogenous category. The polymeric treatment has been recommended by pad-dry-cure technique. It is highly essential that optimum concentrations of pretreatment liquors should be preferred since higher concentrations of both polymer as well as cross-linking agent, particularly the cross-linking agent, show a noticeable declination in the tensile strength for the treated cotton sample, in the range of 1 – 40% for 15 gpl concentrations of various cross-linking agents [Chapter 6]. The optimum concentrations of the pretreatment ingredients have been quantified from the dyeing performance of the treated samples (in terms of their colour strength values) for Procion Brilliant Red M5B (DCT) and Procion Brilliant Red H7B (MCT) reactive dyes applied by exhaustion and pad-dry-cure dyeing processes under neutral conditions.

Such pretreatment brings about some chemical as well as morphological changes in the treated sample. The mass add-on for the cotton substrate due to polymeric treatment indicated the attachment of the polymer along with the cross-linking agent to the cotton material. The mass add-on for the treated cotton varies greatly depending upon the combination of the polymer and cross-linking agent used for the pretreatment. The combination of C IV agent with any of the three polymers is claimed to have offered the best performance during the subsequent neutral dyeing application of the reactive dyes. The nitrogen content and FTIR studies also reveals
the occurrence of cross-linking reaction. There is a tremendous increase in the nitrogen content for the treated cotton sample by 1.106% and 1.867% for C II and C IV agents respectively in combination with the PAA polymer, which indicates the incorporation of the nitrogen atom into the macromolecular cellulosic chain. The PAAₘₙ polymer also has its own contribution towards the nitrogen content values due to the presence of amide group in its polymeric chain. FTIR studies have also exhibited the presence of ~N—H stretching through the occurrence of absorption bands at 3380 cm⁻¹ and 3390 – 3395 cm⁻¹ for the samples treated with PAAₘₙ polymer and various cross-linking agents. However, for PAA polymer, the appearance of absorption bands at 3368 – 3375 cm⁻¹ and 3370 – 3390 cm⁻¹, which are respectively due to the presence of C II and C IV agents in the treatment liquors. The incorporation of C I and C III agent in the pretreatment liquors has virtually shown no ~N—H stretching vibrations in the infer-red spectra — this observation is further confirmed by the nitrogen content value, which is found to be 'nil' in either case. A similar behaviour identical to that of PAA polymer, as far as FTIR spectrum is concerned, has also been with PANₜₚₙ polymer and various cross-linking agents. However, for its treatment on the cotton substrate along with C I and C III agents, there is a little contribution to the nitrogen content values due to the presence of residual ~CN groups in the PANₜₚₙ polymer even after hydrolysis.

DSC thermographs have supported the occurrence of cross-linking, which is clearly visible from the change in the degradation peak temperature for the modified substrate. The smoothness of the curve for the native cotton is hampered due to such treatments and it also widens the limits of decomposition. For instance, the final decomposition of PAAₘₙ/C IV treated sample occurs at about 368 – 370° C, which is higher than that of the original cotton sample.

The extent to which the polymeric treatment offers modification to the cotton substrate is adjudged from the dyeing performance of the treated samples with reactive dyes under neutral conditions. All dyed samples have been compared with those dyed by the conventional dyeing methods. It has been revealed from the concentration study (at different concentration levels/depth of shade) as well as the
sequential studies (for different dyeing sequences) of commercial reactive dyes that there is a good opportunity for such polymer-aided neutral dyeing of reactive dyes for successful commercialization. Except for the admixture of PAA as well as PAN_{hyd} polymers with CI agent individually, all other combinations have offered acceptable dyeing performances at different levels, the performances offered by the polymers and cross-linking agents also depend to a great extent on the dyeing sequence and the type of reactive dye selected for application.

Among the three polymers used, PAA has extensively given extremely good performance with C II, C III and C IV agents, whereas performance with C I agent has been shown by only PAA_m polymer since possibility of using C I agent along with other polymers (PAA and PAN_{hyd}) is almost negligible as illustrated in the reaction mechanism schemes 3.1. The overall study of the three polymers with various cross-linking agents and different dyeing sequences has suggested that PAA/C IV admixture in the pretreatment bath has performed with great excellence offering enhanced dyeing results with most of the reactive dyes for nearly all the three dyeing sequences utilized. Some results obtained on such pretreated samples are even higher than the conventionally dyed sample. This particular combination has shown up to 33.20% improvement in the colour yield for Procion Black HE-BL (HE) reactive dye for simultaneous treatment and dyeing applied by pad-dry-cure process. The same dye has exhibited 24.37% enhancement in the colour yield when the pretreatment and dyeing processes are conducted separately for pad-dry-cure dyeing procedure. However, the best performance has been shown by PAA_{m}/C IV combination when it is simultaneously treated with the cotton fabric along with Remazol Brilliant Violet 5R reactive dye in the same bath by pad-dry-cure process. Here the colour yield is enhanced by 64.57% (K/S = 20.16) as compared to the conventionally dyed sample (K/S = 12.25).

The pad-dry-steam dyeing process has also given good performance and it always runs at par with pad-dry-cure (One-step, simultaneous) process, as far as dyeing behaviour is concerned, for the application of reactive dyes by neutral dyeing technique on various pretreated samples.
Commercial reactive dyes have performed according to their nature and reactivity. However, among the same group of dyes also, the performance varies from dye to dye. In general, DCT, MCT and VS dyes have shown excellence in the padding processes, while HE and ME dyes have done extremely well during their application by neutral technique.

Various reaction mechanisms have been developed indicating the interaction of the polymer with the cross-linking agent to form a condensate and thereafter attachment of this product with cellulose macromolecule (Articles 2.3.6, 3.3.6 and 4.3.5). The plausible dyeing mechanism for monochlorotriazine and vinyl sulphone dyes (as depicted in various reaction schemes in the above-mentioned Articles) reveals covalent bond formation with such modified cotton substrate as no dye strips from the dyed fabric when it has been treated with pyridine (100%) as well as its admixture with water (50:50).

The fastness properties of the dyed samples are quite adequate and in accordance with the conventional dyeing results. The results of the washing fastness test has assured the stability of the modified samples towards washing and showed excellent fastness. However, there is a slight impairment in fastness to light (by 1 – 2 grades) and rubbing (particularly wet, by 1 grade) for a few reactive dyes.

The degree of fixation of selected reactive dyes from DCT, MCT, VS, HE and ME series has also been studied extensively [Chapter 5]. For exhaust dyeing process, the percentage exhaustion of the dyebath has also been determined. Depending upon the type of polymer used, different cross-linking agents have give varying degree of dyebath exhaustion for various reactive dyes. The utilization of nitrogenous cross-linking agent in the pretreatment bath has assured better exhaustion of the reactive dye during exhaust dyeing process. The exhaustion for the dye for C IV agent (used in the treatment liquor) has reached to a value of 96.12% with PAA/C IV combination for Benzafix Orange ME-2RL (ME) dye, thereby allowing minimum amount of dye to have remained in the dye liquor, which assure minimization of the colour value in the effluent liquor. The fixation of the reactive dyes onto the modified cotton substrate is also quite good for a few polymeric admixtures. When the above-mentioned ME reactive dye has been
applied by the pad-dry-cure (one-step, simultaneous treatment and drying) process, fixation to an extent of 98.48% has been achieved, which is nearly total fixation of the adhered reactive dye to the modified substrate. Thus, the polymeric treatment assists to a great extent in the fixation of the reactive dye on the substrate via partial cross-linking (as also explained in the mechanism schemes in Chapters 2, 3 and 4).

The padding techniques have been of great help in giving not only good fixation of the reactive dye but also higher colour yields and adequate fastness properties (as visualizes for 18 commercial reactive dyes in Chapter 7). Moreover, these techniques can be successfully utilized in the industry in a continuous manner and the effluent generated for such techniques is almost negligible since maximum amount of padding liquor is utilized until the last metre of the fabric to be dyed. The remaining liquor can be reused again for a fresh lot of fabric since it does not contain any chemical/auxiliary, which may affect its stability.

The dyed fabric also exhibited very encouraging wrinkle recovery, which may even replace the subsequent wash-n-wear treatment. The crease recovery of the cotton fabric is improved largely when PAA polymer is applied to the cotton fabric in the presence of C IV (HMTA-HQ) agent. The Dry crease recovery angle is found to be 122° for the treated sampled dyed by pad-dry-steam and pad-dry-cure (two-step) processes. This value is 38.27% and 40% more than the respective conventional dyeing processes.

Effluent liquors exhibit neutral pH values since no addition was done in the dyeing liquors. Other effluent parameters, such as BOD, COD, TS, TDS, etc. are also quite below the limit prescribed by Gujarat Pollution Control Board; and need not require any further treatment before discharging.

Appropriate mill trial has also given comparable dyeing results and also shown better opportunity for using this technique on commercial scale. The dyeing of cotton with reactive dyes using polymer aided dyeing may be considered as a novel approach as there is no risk of pollution. Improved dyeings and better fixation of reactive dyes are attained, thereby opening a new horizon for successful acceptance by the cottage as well as composite textile industries.