STUDIES IN

STRUCTURE AND DYEING OF SYNTHETIC-POLYMER FIBRES

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CERTIFICATE

This is to certify that the thesis entitled "STUDIES IN STRUCTURE AND DYEING OF SYNTHETIC-POLYMER FIBRES", submitted by Mr. Rajesh Kumar Saxena to the Indian Institute of Technology,Delhi, for the award of degree of DOCTOR OF PHILOSOPHY is a record of the bonafide research work carried out by him. Mr. Rajesh Kumar Saxena has worked under my guidance for the submission of this thesis, which to my knowledge has reached the requisite standard.

The thesis or any part thereof, has not been submitted to any other University or Institution for the award of any Degree or Diploma.

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ABSTRACT

The pseudo-stable nature of the physical structure of the synthetic-polymer fibres has given rise to many theories of the fibre structure to explain the physical arrangement of the polymer chains in the fibre and to correlate the effect of chemical, thermal and mechanical agencies on the physical structure of the fibre.

During dyeing, the fibres are subjected to a thermo-chemical treatment. The uptake of dye is considered to begin when the fibre undergoes a change in the structure. The free volume theory has been formulated to explain the diffusion of dyes into these thermoplastic fibres. According to this theory, at the glass transition temperature, the segmental motion sets in and the diffusion of the dye takes place by "jumping" from one site to another.

In actual practice it has been observed that, in many cases, practically no dye is sorbed at the T_g of the fibre. Furthermore, the diffusion of the different dyes (differing in size, shape, etc.) does not start at the same temperature i.e. T_g of the fibre.

In Part I of the thesis, an endeavour has been made to assess the effect that the dye has on the temperature at which the diffusion starts i.e. T_D.

In the first chapter, a method for determining T_D has been established. The T_D of six dyes, differing in their size, shape and interaction with the fibre, has been determined and it has been established that the temperature at which the dye starts diffusing into the fibre is different for different dyes and it is higher than the T_g of the fibre (determined by the shrinkage method). Furthermore, the normally used surface active agents, such as ~~Lyogen DFT (S)~~ Ekalene F (S), has practically no effect on the temperature at which the diffusion starts. Change in pH from 4.5 to 7 also does not seem to affect T_D.

The carriers lower the T_g. The T_D of the fibre is also lowered to the same extent (as the T_g) irrespective of the dye used. These observations not only establish the validity of T_D, but also show that the carriers enhance the dye-diffusion by their action on the fibre and have practically no effect on the dye.

Measurements of T_D, of polyester fibres having different T_g, show that the difference in T_D and T_g for any one dye remains the same irrespective of the dye used.

On the basis of this and the previous observations, it is established that T_D and T_g are interrelated. An empirical equation of the type

$$T_D = T_g + \Delta T_{Dye}$$

where ΔT_{Dye} is the contribution of the dye

has been proposed. Furthermore, it is shown that by substituting T_D in the WLF equation, in place of T_g, more meaningful results are obtained.

An analysis of the visible light absorption spectra of the polyester fibres dyed in the absence or presence of the dispersing agent shows that the dye diffuses into the fibre in the monomeric form and, in the case of dyeings carried out in the absence of dispersing agent, dye-aggregates seem to be sorbed in the 'holes' or 'cracks' on the surface of the fibre.

Studies on the concentration dependence of the diffusion coefficient show that the diffusion coefficient increases with concentration of the dye, thereby showing that the dye initially entering the fibre makes the diffusion of the subsequent dye molecules easier. Assessment of the changes brought about by the dye in the physical structure of the dyed fibres opens a new area of investigation and forms Part II of this thesis.

Part II of the thesis deals with the methods of assessment and extent of the changes brought about by the dyes in the physical structure of the fibres. The changes brought out in the structure have been investigated by measuring the critical dissolution time (CDT) and the mechanical properties of the dyed fibres.

Initially, the CDT technique, used to detect the changes in the physical structure of the fibre, was standardized by studying the effect of temperature (of the dissolution bath) and the tension (on the fibres) on the dissolution time. A mechanism of dissolution has also been proposed.

Optimum conditions for investigating the changes in the mechanical properties of the dyed fibres were established by measuring the mechanical responses of the fibres under different r.h. and loading conditions.

Having established the tools for investigating the subtle changes brought about by the dye in the mechanical properties of the dyed fibres, the effect of various dyes and varying dye concentrations on the tensile properties of the polyester fibres was investigated. After determining the CDT of these fibres, it has been

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PART II : DYE INDUCED CHANGES IN THE FIBRE

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CHAPTER 2B DYE INDUCED CHANGES IN THE PROPERTIES OF THE DYED NYLON 6 FIBRES

postulated that the dyes do stimulate the structural rearrangements in the fibre during dyeing. The changes in the mechanical properties of the dyed fibres have been attributed to the physical hindrance (by the dye molecules) offered to the polymeric chains during stretching. Specific dye-polymer interactions do not seem to be responsible for the increase in initial modulus, yield point, etc.of the dyed fibres. This hypothesis is further substantiated by investigating the mechanical properties and CDT of the nylon fibres dyed with the dyes having specific interaction with the polymeric chains, namely, acid and reactive dyes. For comparison, the effect of a disperse dye has also been investigated.