Clean and Innovative Textiles Strategy
for Circular Economy

MODULE 6
Sustainable Chemical Processes and Textile Care

Unit 6.2
Sustainable pre-treatment, dyeing and printing

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6.2.1 Waterless pre-treatments

Textiles need to be properly prepared to absorb dyes or finishing agents. The conventional wet pre-treatments involve excessive use of water and toxic and harmful chemicals. The purpose of waterless pre-treatments is preparation of textiles before dyeing, printing and/or finishing while eliminating the use of water and chemicals.
This can be performed by using:

- Plasma pre-treatment,
- UV radiation,
- Gamma radiation,
- laser.

Plasma is a fourth state of matter or a partially ionised gas produced by an electrical discharge at atmospheric or low pressure.
The particles of the ionised gas collide with the textile surface and different effects can be obtained depending on the process gas and treatment time:

- Activation or functionalisation of the textile: use of non-polymerising gas for producing plasma (oxygen, air, nitrogen or ammonia) and short treatment times.
- Surface etching: use of non-polymerising gas and longer treatment times which leads to micro to nano rough surface.
- Activation and surface etching: use of non-polymerising gas and shorter plasma treatment time.
- Polymerisation: use of polymerising gas or monomers in vapour phase, which leads to formation of thin and uniform film on the surface of textile.

The effectiveness of plasma pre-treatments:

- Increased hydrophilicity to natural and man-made textiles,
- Increased dyeability of textiles,
- Increased functionality of textiles due to higher adsorption and adhesion of dyes, nanoparticles and coatings.

Ultraviolet (UV) radiation is electromagnetic radiation with a wavelength from 400 to 100 nm. The textile surface must be able to absorb UV radiation directly (through the presence of UV absorbing species or through a previously applied photoinitiator) to generate a large number of highly reactive free radicals in order for the UV radiation to have some effect on the textile material. The photoinitiator must be odourless, nontoxic, inexpensive, and easily removed by washing with water.
Surface modification with UV radiation is known as photosensitized oxidation process. One limitation to the use of UV radiation is the treatment of textiles that are highly susceptible to UV degradation.
The effectiveness of UV radiation:

- Increased dyeability,
- Increased bonding in fiber-reinforced composites.

Gamma radiation is an electromagnetic, penetrating ionizing radiation produced by the radioactive decay of the atomic nucleus. The limitations of using this technology are primarily the safety of the method and the high cost of the technology. Gamma radiation can be very harmful to humans if not properly controlled.
The treatment of textiles leads to the breaking of bonds. The effects are the formation of excited states, short-lived radicals and the formation of new bonds.

The effectiveness of Gamma radiation:
- Increased dyeability,
- Enhanced linkage between textile and different coatings.

LASER (Light Amplification by Stimulated Emission of Radiation) can be used as a pre-treatment to change the chemical properties of textiles or in post-treatment for cutting, engraving and applying fading effects.
Lasers are optical devices designed to produce very strong, coherent, and single-colour light.
Carbon dioxide (CO_2) lasers with wavelengths of 10.6 µm are commonly used to modify textiles.

The effectiveness of Laser pre-treatment:
- Increased dyeability,
- Changes of surface morphology,
- Changes of wettability of textile (hydrophilic/hydrophobic).

6.2.2 Sustainable pre-treatments

The purpose of sustainable wet pre-treatments is to prepare textiles for dyeing, printing and finishing using non-toxic and ecologically friendly chemicals, such as:
- Enzymes,
- Chitosan,
- Cationic agents,
- Bio-mordants.

Enzymes are biocatalysts, chemically complex 3D proteins with high molecular weight that can accelerate chemical processes. Enzymes are relatively sensitive substances that can be degraded by high temperatures, ionising radiation, light, acids, alkalis, and biological factors. They are also biodegradable and environmentally friendly and are derived from animal tissues, plants and microbes. Enzymes are classified and named according to the chemical reaction they catalyse.
Two models of enzyme action mechanism:
- Lock and key: early theory; Enzyme and substrate have a specific shape to fit exactly into another.
- Induced fit: modern theory; Enzymes are regarded as flexible structures; the active site can change the shape to fit with substrate.

Application of enzymes:
- Desizing (amylase, lipase)
- Scouring (pectinase, cellulase, cutinase)
- Bleaching (oxidoreductase, xylanase)
- Shrinkproofing of wool (proteinase, lipase)

Chitosan is a natural polysaccharide source derived primarily from the waste products of the crab and shrimp industry, but can also be produced from mushrooms. The unique natural properties of chitosan include its cationic, biocompatible, biodegradable, non-toxic, non-immunogenic and antimicrobial properties.

The application of chitosan as a pre-treatment is usually done to achieve higher adsorption of dyes on textiles. The cationic nature of chitosan forms positive sites on the textiles and consequently the anionic dyes bind more easily to the textile. The colour yield is greatly increased on pre-treated textiles. Chitosan can be used to increase the dyeability of natural and synthetic textiles.

During **cationization**, positive (cationic) sites are created on the textile surface with the help of cationic agents such as CHPTAC (3-(Chloro-2-hydroxypropyl) trimethylammonium chloride) and EPTAC or GTA (2,3-epoxypropyltrimethylammonium chloride or glycidyltrimethylammonium chloride).

The cationization of the textile surface enables electrostatic attraction between the textile and the negatively charged dye molecules. The use of cationic agents in pre-treatment eliminates the need for electrolytes in the cotton dyeing process to increase dye exhaustion and colour yield of the fabric. We can use the cationization process for dyeing with synthetic and natural dyes.

Bio-mordanting is a wet pre-treatment to dyeing with natural dyes with the aim to achieve higher dye adsorption, to change the hue of dyed textile and to increase the fixation rate of natural dyes on textiles. Bio-mordants are derivates from biowastes, biomaterials and different by-products:

- Tannin from tree bark, leaves and gulls,
- Cream of tartar from by-product of fermenting grapes into wine,
- Chitosan from waste products of the crabbing and shrimp industry,
- Soy milk from soya bean seed waste.

6.2.3 Water-free and water-low dyeing

Large quantities of water are used for dyeing textiles. To reduce water pollution and to reduce or even eliminate the use of water for dyeing, water-free and water-low dyeing methods are available:

- Dyeing in carbon dioxide,
- Foam dyeing,
- Spun dyeing.

Dyeing in CO_2 instead of water saves both water and processing chemicals. However, only polyester fabrics can currently be dyed using this method.

In **foam dyein**g, fabrics are dyed with foam instead of water. Foam is a gas dispersed in a liquid. For dyeing, the foam is formed from an aqueous solution of dye, foaming agent and dye carrier. The fabric is padded with a foam and treated at a high temperature to allow the dye to fix to the fabric.

Spun dyeing (mass dyeing / dope dyeing / gel dyeing / solution dyeing) is a water-less dyeing process in which the dyeing of the fibres takes place during the spinning of man-made fibres. Pigments or insoluble dyes are introduced into the melt or spinning solution before extrusion. Coloured filaments are thus produced instead of white ones. This technique is mainly used for coloration of very hydrophobic fibres such as polypropylene. Spun dyeing significantly reduces water consumption in the dyeing process, cuts energy consumption and greenhouse gas emissions, and considerably reduces the amount of dyes and fixing agents required. The colours of the textiles are also more durable to washing and UV fading.

6.2.4 Dyeing with sustainable dyes

Sustainable dyes are from natural sources or synthetic. Not all natural dyes follow the sustainable path. Therefore, when we choose a natural dye, we must consider all aspects: what is the source of the dye, how does it affect the environment and health, and how is the dye applied to textiles. Sustainable synthetic dyes are produced by dye manufacturers and controlled by the standards OEKO TEX 100, GOTS and other ecological standards about regulated substances.

The origin of natural dyes are cultivated plants (indigo, madder, sappan) or cultivated insects (cochineal). In recent years, research has increased on the use of plant materials from food waste and invasive alien plant species as sources of dyes. Both plant materials are considered biowaste and are therefore considered highly sustainable and environmentally friendly. Using plant waste to produce dyes is one of the Achroma Group's goals. In addition to traditional synthetic dyes, it also produces dyes synthesised from plant waste from the food and herb industries. At Huntsman, sustainable para-chloro-aniline (PCA)-free reactive dyes for cellulosic textiles and their blends have been developed, reducing the consumption of water, energy and time. The cleanest, most sustainable and ECO rewarded indigo dye on the market is produced by DyStar.

6.2.5 Digital printing

Textiles can be coloured using digital printing method which also enables:
- detailed patterns,
- tonal transitions,
- graphically complex designs.

Digital printing is a specialized form of roll-to-roll wide-format inkjet printing, which was developed as sampling method. Digital printing reduces the water and energy consumption, waste, and water pollution associated with traditional textile printing.

Evolution and development of digital printing contributed to the creation of the two main types of digital textile printers:
- Multi-pass (smaller, very flexible, lower cost; can print 4 metres of fabric per minute): printheads are mounted to a carriage that moves from left to right and right to left over the width of the fabric.
- Single-pass (bulk, not flexible, very expensive; can print 40 metres of fabric per minute): carriage is not moving, the printheads are mounted over the full width of the fabric on a fixed printbar, one for each colour. The fabric moves under those bars with a constant speed.

Before digital printing, fabrics must be cleaned and pre-treated to help fix the dye in the ink to the fibres, control the spread of ink droplets, optimise the intensity of the colours, and help absorb the ink for faster drying. After the fabric absorbs the ink, it must be dried and/or coated to prevent the inks from rubbing or washing off. Advances in pigment inks are enabling apparel manufacturers to skip the post-print steaming and washing processes to reduce water and energy consumption.

Different combinations of inks, pre-treatments, and fixation processes are used with different types of synthetic and natural fabrics:
- Direct-Disperse Inks are used for printing directly onto polyester and polyester blends. A post-print heat process is required.
- Acid dyes are used on pre-treated nylon and silk fabrics. The printed textiles must be steamed to set the inks and washed to remove any residue. Post-print heat processing is used to permanently set the dye.
- Reactive inks for linen, rayon, nylon create a chemical bond with the cellulose fibres in these fabrics. The printed textiles must be steamed to fix the inks and washed to remove any residues.
- Textile pigment inks include binders that enable the pigments to adhere to the surface of cotton and other natural fabrics. A rotary heat calendar is used to fix the pigments to the fabric.

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