

Semester: 4th Semester

Subject: Textile Fibre II

Topic : Acrylic & Modacrylic Fibres

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Definitions:

Acrylic. A manufactured fibre in which the fibre-forming substance is any long chain synthetic polymer composed of at least 85 per cent by weight of acrylonitrile units ($-\text{CH}_2-\text{CH}(\text{CN})-$).

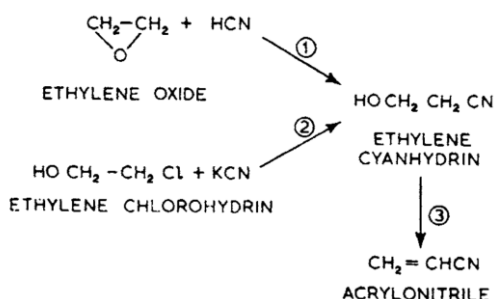
Modacrylic. A manufactured fibre in which the fibre-forming substance is any long chain synthetic polymer composed of less than 85 per cent but at least 35 per cent by weight of acrylonitrile units ($-\text{CH}_2-\text{CH}(\text{CN})-$), except fibres qualifying under subparagraph (2) of paragraph (j) (rubber) of this section and fibres qualifying under paragraph (q) (glass) of this section.

The early types of polyacrylonitrile fibre, e.g. 'Orlon' Types 41 and 81, were spun from 100 per cent polyacrylonitrile, but almost all modern types of acrylic fibre are spun from copolymers. These may be the 'normal' type of copolymer in which the second component is polymerized with the acrylonitrile, or they may be of the 'graft' copolymer type, in which the second component is incorporated by grafting on to the polyacrylonitrile.

Vinyl acetate, vinyl chloride, methyl acrylate and 2-vinyl-pyridine are among the monomers which are probably used commercially.

High Bulk Fibre

Acrylic fibres are unusual in their ability to attain a metastable state on hot stretching. When hot-stretched fibres are cooled, they will remain in their stretched state until subsequently heated, when they revert to their unstretched dimensions. High shrinkage fibres may be made in this way, with shrinkages of 30 per cent and higher, and by blending these high-shrink fibres with normal staple, followed by subsequent steaming, high bulk effects are obtained.

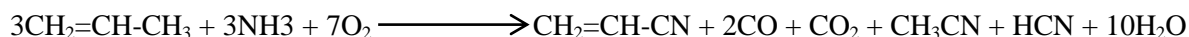


Acrylonitrile can be manufactured from propylene, acetylene, ethylene, ethylene -oxide.

However, the currently used practice is to manufacture it from propylene using the Sohio process.

This is a heterogeneous vapor-phase catalytic process that uses selective oxidation of propylene and ammonia, commonly referred to as the propylene ammoxidation process:

Catalyst, ~400-500°C, 50-200kPa



Polymerisation

The comonomers most commonly used are neutral comonomers (in the sense that they are not intended to participate in any chemical reaction), such as MA and VA to increase the solubility of the polymer in spinning solvents, modify the fiber morphology, and improve the rate of diffusion of dyes into the fiber.

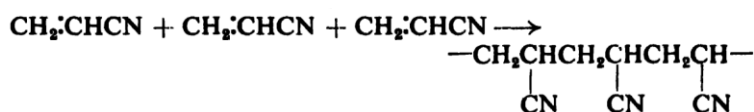
Sulfonated monomers, such as sodium styrene sulfonate (SSS), sodium methallyl sulfonate (SMAS), and sodium sulfophenyl methallyl ether (SPME) are used to provide dye sites or to provide a hydrophilic component in water-reversible crimp bicomponent fibers. Halogenated monomers, usually vinylidene chloride, vinyl bromide, and vinyl chloride, impart flame resistance to fibers used in the home furnishings, awning, and sleepwear markets. Modacrylic compositions are used when the end use requires high flame resistance. Almost all of the modacrylics are flame-resistant fibers with very high levels of halogen monomers.

Acrylonitrile and its comonomers can be polymerized by any of the well-known *free radical methods*.

The conditions under which *radical polymerizations* are carried out are of both the *homogeneous* and *heterogeneous* types. This classification is usually based on whether the *initial reaction mixture* is *homogeneous* or *heterogeneous*. Some *homogeneous* systems may become *heterogeneous* as polymerization proceeds as a result of insolubility of the polymer in the reaction media. **Mass and solution polymerizations** are homogeneous processes; **suspension and emulsion polymerizations** are heterogeneous processes.

1. Bulk polymerization is the most fundamental of these, but its commercial use is limited by its autocatalytic nature.
2. Aqueous dispersion polymerization is the most common commercial method, while solution polymerization is used in cases where the spinning dope can be prepared directly from the polymerization reaction product.
3. Emulsion polymerization is used primarily for modacrylic compositions where a high level of a water insoluble monomer is used or where the monomer mixture is relatively slow-reacting.

Polymerisation Reaction:

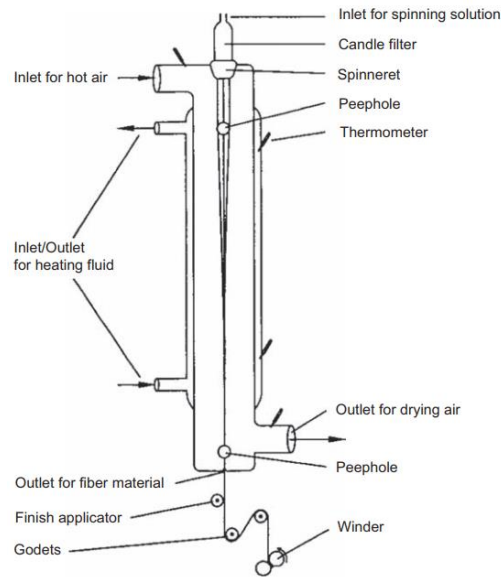


Orlon DP: 2000, MW - 100000

Dry Spinning

The polymer is dissolved in an organic solvent, such as dimethyl formamide(DMF), to form a solution containing 25-40 per cent of polymer. This is degassed, filtered and heated almost to boiling point, and then extruded through spinnerets. The fine jets of solution emerge into a vertical tube or spinning cell, through which air or other gas at high temperature (e.g. 400°C.) is flowing. As the jets fall through the tube, the solvent evaporates to leave solid filaments of polymer.

The filaments are brought together at the base of the spinning cell and stretched hot to many times their original length. If continuous filament yarn is being produced, the filaments are oiled, twisted and then wound on to bobbins. If staple fibre is required, a number of yarns are brought together into a tow. This is then crimped and cut into staple of the desired length. Uncut tow is used for conversion.



Schematic presentation of dry spinning

The spinning dope is carried forward towards the spinning tube, it goes through a number of filtration steps, and is heated to 90 to 130e140 deg C. The spinneret used in dry spinning is made from stainless steel and contains up to 2800 holes with the diameter lying in the 0.1-0.3 mm range. The preferred hot gas to dry the extrudate is air mixed with nitrogen, the latter for reducing the fiber's tendency to yellow as well as to increase the explosion threshold. The resulting fibers are taken up by a godet and given a finish prior to their collection in spin cans, if tow, or winding up at high speed, if filament yarn. The second step in the case of tow is drawing in hot water bath at 98 deg C. Draw ratios used range from 2 to 10X. After washing, the drawn fibers are dried at 120 -170 deg C, which can affect shrinkage, dyeability, and crimping potential of fibers.

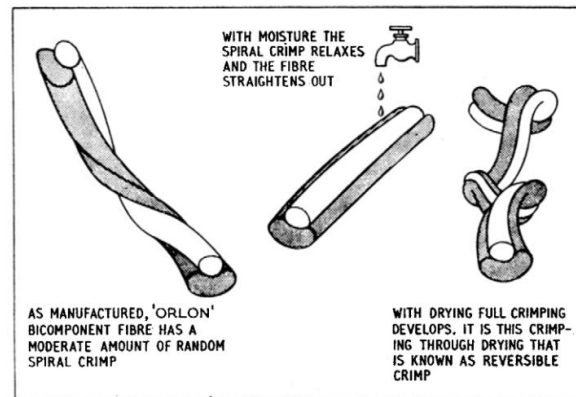
When acrylic fibers, normally in the form of a heavy tow, are hot-stretched (**e.g., by being drawn over a hot plate**) and then cooled under tension, they are converted to a labile state. Upon immersion in hot water, such fibers contract considerably, but not to their prior unstretched length. In practice, this characteristic is used to produce a bulky yarn resembling the woolen yarns long accepted for use in sweaters.

Using a “stretch-break” process, the stretched labile (readily undergo change or breakdown) fibers are further cold-stretched to their breaking point so that the fibers break at different points leading to a distribution of lengths, similar to the lengths found in wool. These are crimped by a crimping process

and then mixed with thermally stable stretched and relaxed acrylic fibers. The blend is converted to a spun yarn by the long staple process, and knitted into sweaters and other woolen type products. When such garments are dyed in hot water, the labile fibers in the blend contract lengthwise and carry the stable ones by friction. Because the latter do not change their overall lengths, the yarn as a whole decreases in length and becomes more voluminous or “hi-bulk” structure.

The other method for making enhanced bulk yarns is the use of side-by-side bicomponent acrylic fibers containing two polymers with different shrinkage potentials.

'Orion Bicomponent Fibre. The crimp in this fibre is an inherent property resulting from the bicomponent structure of the fibre. Two filaments of differing chemical composition are fused during spinning, forming a double filament in which each component behaves differently with respect to its swelling characteristics. This results in a three-dimensional crimping effect. The effect is similar to that shown by wool, in which the fibre crimp results from the bi-component nature of the protein forming the cortex of the fibre.



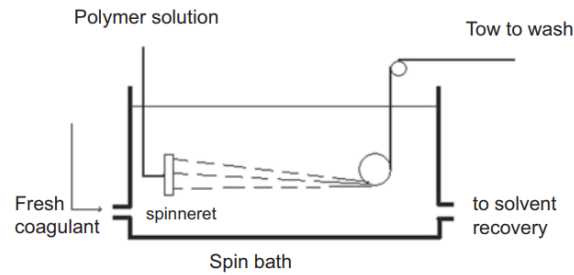
Wet Spinning

Polymer is dissolved in dimethyl formamide or other solvent, and the solution is degassed and filtered. It is then pumped through spinnerets into a coagulating bath containing a liquid in which the solvent is soluble but the polymer insoluble. The jets of solution coagulate into fine filaments, forming a tow which is washed after emerging from the bath. The tow is heated and drawn, dried, oiled and crimped. It may then be heated to relax the fibre before being cut into staple.

In the wet spinning process polymer comes out of the solution into the bath and forms a gel-state solid, or coagulates, after exchange takes place between the polymer solvent and the nonsolvent. Two conceptually distinct phase transitions are thought to occur during coagulation: gelation and phase separation (precipitation). If coagulation happens without gelation, then the strength of filament is low due to the lack of interconnectivity between chains. Polymer microcrystallites form during gelation, which serve as physical cross-links between chains. When the gel undergoes phase separation and the solid filament is formed, the cross-links provide internal cohesion needed for the drawing step.

The spinnerets are usually made of precious metal alloys, with the hole-diameters ranging from 0.05 to 0.38 mm and hole numbers varying from few thousand up to 360,000. The ratio of hole-

diameter/hole-length (aspect ratio) is critical in fiber formation as it governs the quality of spinning and the resulting tensile properties.



Schematic presentation of wet spinning

Melt spinning

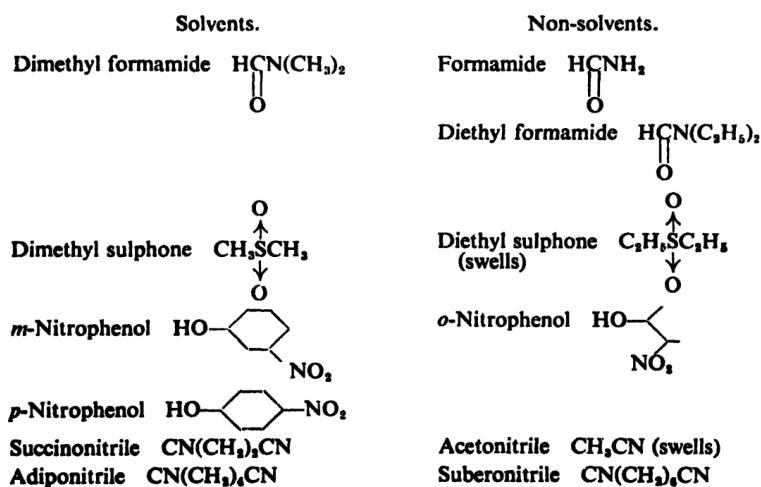
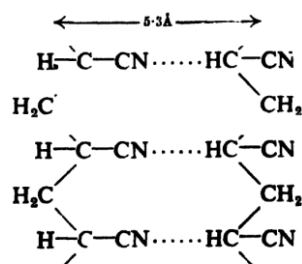
Polyacrylonitrile degrades before reaching its melting point (320 deg C). Water, on the other hand, has a plasticizing effect on acrylic polymer and blocks the polar interactions between nitrile groups, and causes a lowering of melting point (~180°C at 33%W water), thus making melt spinning possible.

Physical properties of acrylic fibers

Acrylic and modacrylic fibers are sold predominantly as tow and staple products with only a limited quantity of continuous filament as special product. The linear densities of fibers lying between 0.84 and 17 dtex are produced, with the most common values being 1.7 for staple and 3.3e5 for tow to top conversion. Typical values of some of the physical properties of acrylic and modacrylic fibers are given in Table.

Property	Acrylic	Modacrylic
Specific gravity	1.14-1.19	1.28-1.37
Tenacity (N/tex)		
Dry	0.09-0.33	0.13-0.25
Wet	0.14-0.24	0.11-0.23
Loop/knot tenacity	0.09-0.30	0.11-0.19
Breaking elongation (%)		
Dry	25-45	25-45
Wet	29-61	
Initial modulus (N/tex)		
Dry	3.5-4.9	2.6-3.5
Wet	3.1-4.9	

Chemically Orlon fibres are very stable because of the H – bonds between Nitrogen and α Hydrogen atoms represented by dotted line. Long molecular chain shown vertically and hydrogen bonds are shown as formed horizontally, distance 5.3Å as detected from the x-ray diagram distance between the polymer chains due to presence of nitrile groups.



Solvents for PAN fibre should be strongly polar as listed in the table slight change in constitution/polarity mean a difference between a solvent a nonsolvent.

1. [Man-Made Fibers by Moncrieff, R. W.](#) (click to download)
2. Handbook of Textile Fibre Vol II by G. Cook