



# Factors influencing the stability of man-made fibers: A retrospective view for historical textiles



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## ARTICLE INFO

### Article history:

Received 3 September 2013  
Received in revised form  
31 January 2014  
Accepted 4 March 2014  
Available online 19 March 2014

### Keywords:

Synthetic  
Regenerated  
Chemical  
Mechanical  
Conservation  
Aging

## ABSTRACT

Modern textiles in historical collections have been manufactured from some of the earliest commercial man-made polymers, but unlike their plastic and film counterparts with the same composition, aged fibers appear more physically stable. The main reasons for this lie in the different chemical and mechanical properties conferred on fiber polymers during their production. With a focus on domestic textile fibers manufactured before 1960, polymer factors such as orientation, crystallinity and chain length are considered for viscose rayon, cellulose acetate, regenerated protein, nylon, poly(acrylonitrile), poly(ester) and elastane (spandex). Viewed from past and recent polymer science literature, this paper offers an introduction to polymeric contexts for the current condition of historical textiles, especially those with a user life-time, and considerations for their preservation.

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## 1. Introduction

Materials are expected to change their chemical and mechanical properties given long enough exposure to air, light, humidity, temperature and pollutants, but some modern polymers are destabilizing over a relatively short time-span. Since the 1980's, museums, galleries and archives have been increasingly aware of active degradation with plastics, foams, films and paints in collections of decorative arts, contemporary arts, social history, science and technology, and costume dating from the mid nineteenth century onwards. The most unstable historical polymers are found to be cellulose nitrate, cellulose acetate, poly(urethane) and poly(vinyl chloride). Conservation scientific research has been aimed at investigating the causes and effect of degradation, and identifying acceptable approaches to active and passive conservation measures for stabilization [1–11].

To date, man-made fibers in historical textiles appear relatively more stable compared to plastics and film. Textile conservators are noticing some effects of aging, like yellowing and low wet strength, but relatively few conservation science studies exist in this field compared to plastics and film [12–19]. The expectation is that modern textiles will need more attention in the coming years as

they age and as more are collected and exhibited, but for the moment conservation is in a fortunate position of having time to understand better the aging of man-made fibers to prepare for preventive measures rather than reactive ones, as has been the case with plastics. At this point in time, textile conservators are perhaps less concerned about synthetic or regenerated fibers degrading to a state of lost structural integrity than fiber misidentification, especially when imitations or substitutes for natural fur, silk, cotton and wool are present [15,20], or when mixed man-made fibers or mixed man-made and natural fibers are in one object where an invasive treatment, like aqueous wet cleaning, could affect the mechanical and chemical properties of the fibers differently [14].

For these reasons, a retrospective look at the chemical and physical properties for the polymers of important man-made historical fibers is timely. This paper focusses on man-made fibers for domestic textiles made between 1891 and 1960, a heyday era for modern fiber development. This is an increasing period of historical interest for institutional and private collectors, which consequently leads to more textile exhibitions and loans of such collections. It is in the course of preparation for these events that conservation decisions for handling, treating and mounting will have the most impact on the care and protection of historical textiles. Being able to anticipate materials failure through aging or the potentially detrimental action of a conservation decision before it actually happens is therefore advantageous for textile preservation. That said,

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modern textile conservation approaches take a minimal interventive stance, with limited and carefully considered use of any treatment or stabilization method involving chemicals [21,22], and with controlled environmental conditions that exclude ultraviolet radiation and detrimental pollutants in storage and display spaces [23]. However, man-made textiles such as furnishing fabrics and clothing tend to enter collections with a user life-time behind them and past exposure to everyday environments. Also those made pre-1960 would have had more daily exposure to atmospheric pollution than today as well as having been manufactured in a period of improving quality and technical understanding of fiber properties and performance for different applications [18]. This paper considers aspects of quality for these early fibers with regard to their polymeric properties alongside potential factors contributing to their current and future condition relating to manufacturing quality and a history of use.

## 2. General polymer properties determining textile fiber stability and degradation

Fibers are defined as filaments with a high ratio of polymer chain length to linear density. To achieve this, fibers must possess three fundamental and interrelated polymer properties: orientation, chain length and crystallinity. These have impact on the mechanical properties of fibers in terms of strength, stretch and flexibility [24] as well as chemical and biological resistance. The significance of these polymer properties have been known from the early days of man-made fibers, at the latest by 1935 [25]. In the following sections, each of these three polymer properties is considered in turn and then related to the mechanical properties of tenacity and extensibility.

### 2.1. Orientation

Linear polymer chains need to align to maximize intermolecular interactions for stability and flexibility [26]. Alignment through orientation of the polymer chains is a key fiber property and an essential stage in the processing for all man-made fibers. Orientation is achieved by extruding the solvated or molten polymer through small-holed spinnerets, then pulling and stretching the resulting filaments. This physical action orientates the polymer chains along the longitudinal axis in the direction of the fiber axis [26]. This orientation is the fundamental difference between fibers and their more polymerically-disorientated plastic counterparts. Polymers with a high degree of polarity and evenly spaced polar groups can withstand this induced orientation because of cohesion through intermolecular interaction, like hydrogen bonds between hydroxyl groups. The extrusion process induces an ordering of orientation from the outer layer of the fiber (skin) to the inner core where the skin is more orientated than the core [26]. This 'skin-core' structure is a consequence of the physical action of extrusion and is prevalent in all extruded man-made fibers. It was observed by polarized and unpolarized fluorescence spectrometry of viscose rayon and cotton in 1935 [25] and has been confirmed with recent studies of viscose fibers by microdiffraction techniques and transmission electron microscopy [27]. These studies also reveal that the surface skin has a higher crystallinity index than the core. The amorphous core is susceptible to reactions like water absorption, which in the case of viscose results in swelling of the fiber [28].

Orientation is not confined to the ordering of crystalline sections of the fiber polymer. The more random amorphous sections also need to orientate along the fiber axis [26]. This can impart strengthening qualities, as in the case of viscose rayon where increased orientation improves the wet strength of these fibers which have relatively high amorphous composition. The rate of

orientation between the different sections can differ between fibers, for example the amorphous orientation of nylon polymer chains happens more slowly than crystalline orientation [29], which has implications for production processes like spinning rates when forming the filament.

### 2.2. Crystallinity

All polymers are part crystalline, part amorphous. For fibers, the crystalline regions need to dominate because they are necessary for fiber strength through intermolecular interaction between polymer chains. As a rule, as a polymer becomes more crystalline, the resulting fiber will become less flexible and stiffer. Regular bi-functional repeating units in the polymer help crystallization, but not tri-functional groups which tend to cross-link to form more rigid networks [29]. This is why cellulose triacetate fibers make a stiffer-feeling fabric than cellulose diacetate. Crystalline and amorphous regions need to align along the fiber axis in the direction of orientation to give strength. In a highly orientated fiber, crystallinity may decrease towards the core of a fiber with a concurrent increase in amorphous fibrillation but this does not affect orientation [27]. Changes in crystallinity put stress on fibers and significant levels of unwanted impurities or side reactions during processing can disrupt crystallinity and cause weakening [26].

Crystallinity is associated with the glass transition temperature,  $T_g$ , which is the temperature threshold between a polymer existing in a rigid glass-like state and a visco-elastic state with more chain movement. Intermolecular interactions and flexibility affect  $T_g$  as a consequence of the aging effects of oxidation. An advantage with synthetic fibers like nylon, poly(acrylonitrile) and poly(ester) is that different monomer groups can be utilized to change properties like  $T_g$ . Chain freedom can also be influenced by the chemistry of the side group, for instance poly(ester) has aromatic groups in its polymer, resulting in less flexible segments along the chain and a stiffer fiber. Bonds in the chain backbone and the side group chemistry affect the potential energy to change conformation, while intermolecular bonds that are stronger than van der Waals, i.e. dipole and hydrogen bonding, increase bond strength, affecting fiber strength and fiber stiffness [26]. The accessibility of hydroxyl groups and their distribution along cellulose diacetate polymers both influence the moisture regain of the resulting fiber and these two properties can be controlled by the method of production.

The impact of  $T_g$  is seen when the polymer chain behavior of broken fibers of nylon 6,6 and poly(ester) is considered. Their polymers behave in one of two ways when fractured: chain scission across amorphous regions, or plane slip and shear involving amorphous and crystalline regions. When the polymers experience chain scission in their glass-like crystalline state below their  $T_g$  (47 °C for nylon 6,6 and 70 °C for polyester), free radical form near fracture sites. Above  $T_g$ , when the polymers have more amorphous character, chain scission induces breakage with more shear and slip but fewer free radicals [30]. This has implications for old nylon that becomes more crystalline with aging as this would lower its  $T_g$  and put it at risk of free radical formation if fibers are broken during handling or movement.

### 2.3. Chain length

One parameter reflecting the length of a polymer chain is the degree of polymerization (DP), which is the average number of repeat units in a polymeric chain. Their DP range for fibers is from around 500 to 10,000 [26]. The polymer chains need to be of the same appropriate mean length to allow sufficient intermolecular chain bonding to achieve desirable effects. In terms of processing, if the chains are too short, either the polymer can't be extruded or the extruded filaments are too weak. However, if the chains are too

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