Contributions to Forming and Analytical Investigations of Solutions of Cellulose and Cellulose Derivatives – A Research and Development Topic of the TITK eV

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Summary: Modification, forming and analytical characterisation of cellulose and cellulose solutions represents one of the most important research topics of the Thuringian Institute for Textiles and Plastics Research (TITK). The presentation provides information on the current capabilities of the institute and on the analytical methods developed in these fields.

Keywords: cellulose; degree of polymerisation; fibres; particle size distribution; rheology

Introduction

The industrial site of Rudolstadt-Schwarza is under the sign of cellulose forming for decades. One of the first and foremost viscose plants in Germany has been erected in the 30ties of the 20th century and the viscose fibre production has been terminated not before mid of the 90ties. Beside fibre production, research and development have ever been in the focus of attention. At the end of the 40ties the product assortment of the production site has been extended to man-made fibre manufacturing. In 1954 the Institute for Textile Technology of Chemical Fibres (ITC) was established as an additional facility for textile testing and further processing.

Since mid of the 80ties the alternative cellulose forming through the direct dissolution process using N-methylmorpholine-N-oxide (NMMO) is in the focus of the cellulose research at the Rudolstadt-Schwarza site. The ITC reestablished as the Thuringian Institute for Textile and Plastics Research (TITK) in 1991 as the first privately-owned, non-profit institute in the Free State of Thuringia has developed its own technology variant of the direct dissolution process to get shaped bodies under the brand name ALCERU. In cooperation with Zimmer AG, Frankfurt/Main in 1996 a pilot plant for the production of

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300 t per year cellulose staple fibres and 10 t per year cellulose filaments was erected at the site and run together until 2002.

Starting with its reestablishment the research activities of the TITK had been wide-spread and are always closely related to industrial demands. Important fields of research and development are currently :

- Structural materials

  Characterisation of native polymers and polymeric solutions; development of alternative processing methods for the forming of materials from natural polymers, preferably cellulose; manufacturing polysaccharide derivates; functional formed / moulded parts made of cellulose and protein derivates

- Textile and material research

  Development of fibrous composite materials and procedures of their production; fleeces, long fibre granulates, honeycomb composites; sort clean systems; long fibre recycling of Aramide and carbon fabrics

- Plastic compounds and their processing

  Nanoparticle and synthetic fibre reinforced composites; Flame-retardant thermoplastics; Polymers for electromagnetic impedance (EMI) applications; Polymer condensation

- Functional polymers

  Development of functional materials with special electronic characteristics and micro techniques of the polymer processing; modification of synthetic polymers, preferably based on polyamide (PA) 6, PA 66, polyethylene terephthalate, as well as liquid crystalline polymers and their processing to filaments, fibres and films

Used Methods and Equipment

The analytical procedures are subdivided into the topics

- pulp and cellulose analysis,
- characterisation of cellulose solutions and
- chemical analysis of shaped bodies.

Methods such as the determination of the intrinsic viscosity in Cuen[1] or Cuoxam[2] (capillary viscometer AVS 360, SCHOTT), of the α-cellulose content[3], the carboxyl[4] and carbonyl[5] content, ash[6], alkali, earth alkali or heavy metal content[7] (ICP-OES, OPTIMA

2000 DV, PERKIN ELMER), respectively, alkali consumption[8] as well as of the content of cellulose being soluble in 20% NMMO[9] are used for the characterisation of dissolving pulps.

Due to the substantial interest in cellulose shaping attention has to be focused on the analytical characterisation of cellulose solutions by thermal analysis, rheological methods (rotational/oscillational rheometer RHEOSTRESS 100, Gebr. HAAKE, Karlsruhe) and extensional rheometer (CABER 1, Gebr. HAAKE, Karlsruhe) as well as determination of particle size distribution (HELOS laser diffraction system, SYMPATEC, Clausthal-Zellerfeld). Long-term experiences could be accumulated especially concerning with the solvent system cellulose / NMMO monohydrate. Other cellulose solvents, e.g., ionic liquids such as butyl-methyl-imidazolium chloride, the influence of a hydrothermal or an enzymatic pre-treatment on the dissolving process as well as the influence of cellulose derivatives or the addition of secondary components to the cellulose solution are also in the focus of investigations.

The residual NMMO content of the shaped cellulose bodies and its degradation products are detected by means of coupled HPLC-mass spectroscopy (Chromelion, DIONEX /Aqa, THERMOELECTRON) whereby the detection limit reaches up to 10 – 15 ppb for NMMO, N-methylmorpholine and morpholine, respectively.[10]

Characterisation of Cellulose Solutions

Because analytical methods for the characterisation of dissolving pulps have been well known for a long time the procedures for the characterisation of polymer dissolution developed by the TITK should be described more detailed.

A laboratory kneader system (HAAKE Rheocord 900 modified by a self-made vertical kneading chamber) is available and allows to prepare cellulose solutions with a solid content of up to 15 wt.-% cellulose in the named solvents and in quantities of 300 g up to 5000 g as well as to record the time-dependence of torque, pressure and temperature (Figure 1).

The characterisation of cellulose solutions has to supply information on the state of dissolution and solution quality especially regarding further processing to manufacture shaped cellulosic bodies. Rheological measurements are used to evaluate the state of dissolution. Figure 2 shows the rotary viscometer „HAAKE Rheostress 100".

Zero shear viscosity and its temperature dependence represent important measures for defining optimal spinning conditions. The creep test serves to the determination of the zero shear viscosity, that means, the deformation γ will be measured and recorded applying a load τ_0 ($\tau \rightarrow 0$) over a period of time.

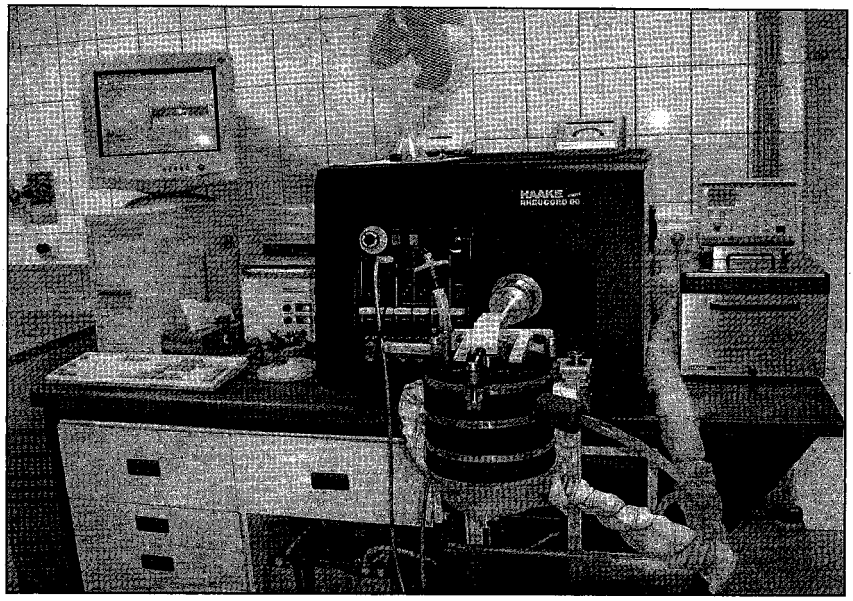

Figure 1. Laboratory kneader (HAAKE Rheocord 900) for preparation of cellulose solutions.

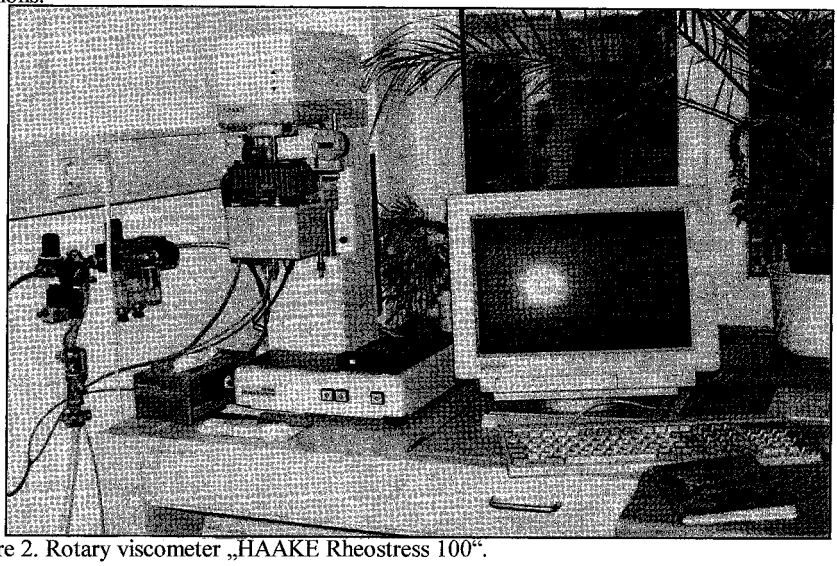

Figure 2. Rotary viscometer „HAAKE Rheostress 100".

The deformation reaches constant values after a certain time period, whereas dγ/dt corresponds to the zero shearing $\dot{\gamma}_0$. Following this the zero shear viscosity η_0 is defined as: $\eta_0 = \frac{\tau_0}{\dot{\gamma}_0}[Pas]$.

The function of the deformation of the storage modulus G' and the loss modulus G'' taken at dynamical load over a sufficiently large range of shearing ω (WLF-transformation) allows the calculation of the inverse relaxation function lg H = f (lg λ) and the weighted relaxation time spectrum H*λ = f (lg λ) there from. At the state of a complete solvation the relaxation time λ is directly proportional to the logarithm of the molecular mass according to $\lambda = K_\lambda \cdot M^a$.[11,12]

If the slope of the deformation function becomes tan δ = 1, then G' = G'' and the so-called "cross-over" is characterised by $G'^{\#}$ and $\omega^{\#}$. The unevenness $U_\eta = \frac{\eta_o}{\eta^{*\#}} - 1$ may be calculated from the zero shear and complex viscosity at "cross-over" $\eta^{*\#} = \frac{\sqrt{2} \cdot G'^{\#}}{\omega^{\#}}$.[12]

The elastic behaviour increases with the width of the molecular mass distribution.[11-13]

Figures 3 and 4 display graphical presentations of storage and loss modulus as well as the complex viscosity as a function of the shear rate ω and additionally a relaxation time spectrum of a 12 wt.-% solution of a wood pulp in NMMO monohydrate.

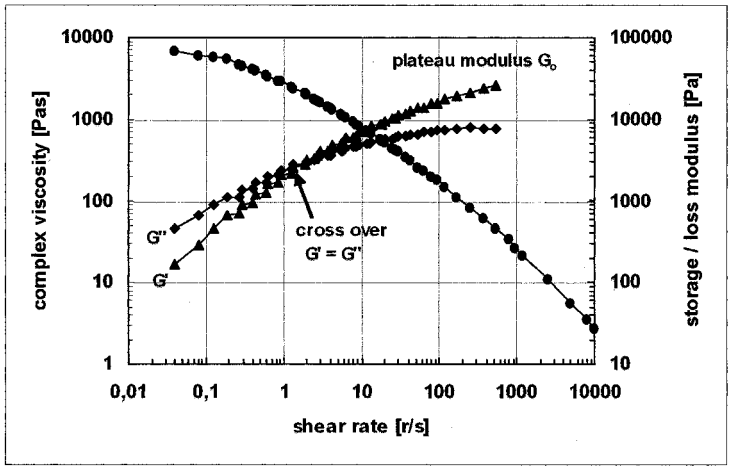

Figure 3. Graphical presentation of storage (▲) and loss modulus (◆) as well as the complex viscosity (●) depending on the shear rate.

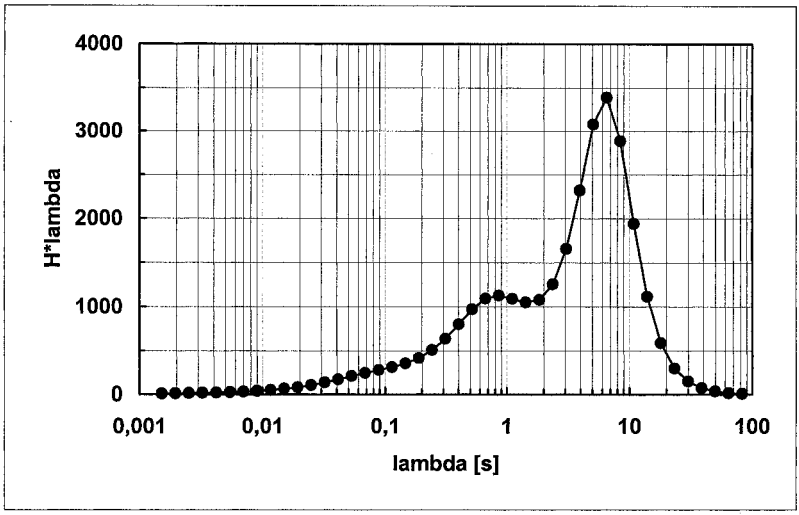

Figure 4. Relaxation time spectrum of a wood pulp solution (12 wt-% in N-methylmorpholine-N-oxide monohydrate).

An investigation of the extensional properties of cellulose solutions is feasible by means of the extensional rheometer CABER 1 (Figure 5) and includes a tensiometric investigation of the surface tension of the solutions.

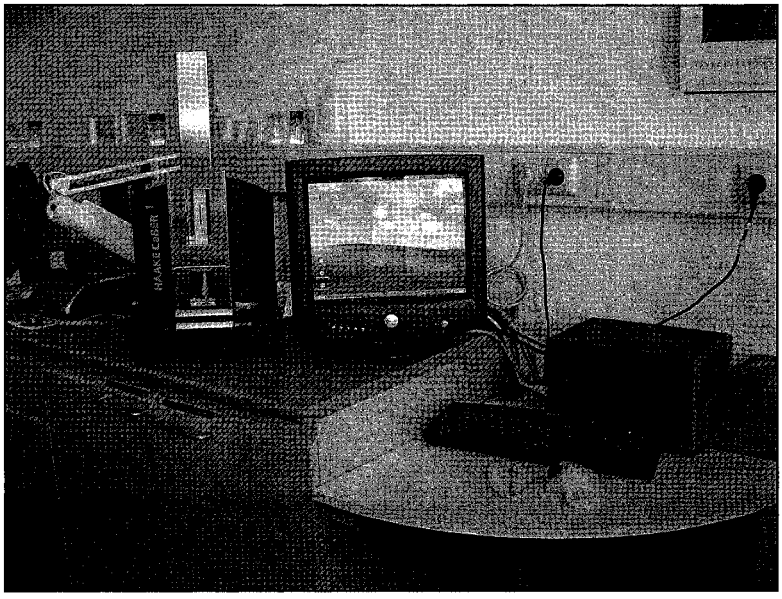

Figure 5. Extensional rheometer Haake CABER 1.

Especially under the perspective of forming cellulose solutions to produce fibres and filaments the characterisation of the solution quality is required and is performed by optical methods.[14]

Beside microscopic observations applying transmitted and reflected light in combination with coloured and polarised filters, phase-contrast and fluorescence microscopy are available for microscopic investigations of the state of dissolution.

Figure 6 shows the start of the dissolution process of a cellulose fibre in NMMO monohydrate by means of transmitted light observed through a polarised filter. Figure 7 shows the dissolving state of a multi-phase polymer solution (cellulose : starch = 3 : 1).

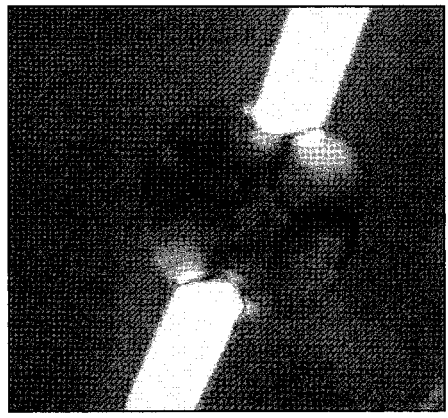

Figure 6. Microscopic image (200-fold) of pulp fibre during dissolution in N-methylmorpholine-N-oxide monohydrate.

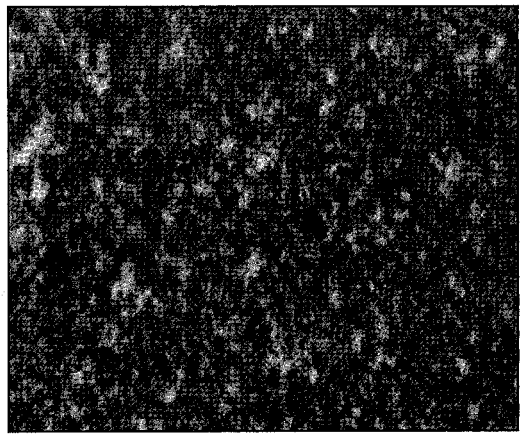

Figure 7. Microscopic image (200-fold) of Multi-phase polymer solution (cellulose : starch = 3 : 1).

Laser diffraction has to be used to determine particle size distribution in the range between 0.5 and 175 µm and particle content of the cellulose dope, as it can be found typically in cellulose solutions.[14]

Figure 8 shows the HELOS-Laser diffraction instrument that has been applied for the investigation.

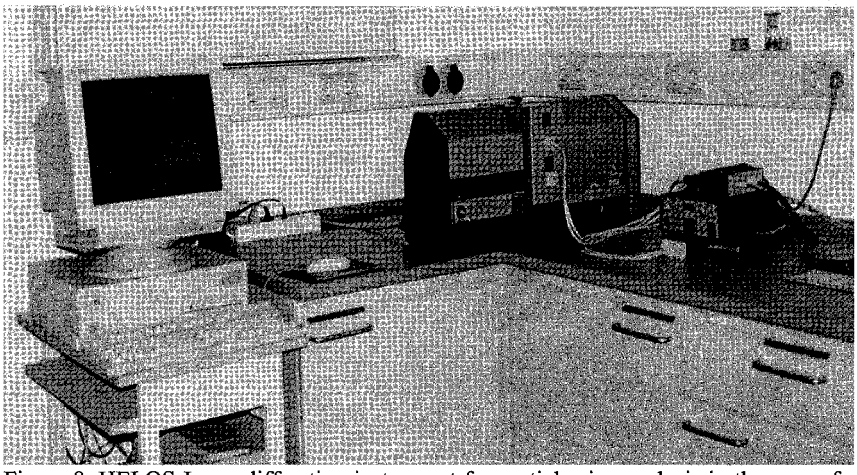

Figure 8. HELOS-Laser diffraction instrument for particle size analysis in the range from 0.5 and 175 µm.

The characterisation of cellulose solutions is performed by means of a home-made manufactured, temperature-controlled measuring chamber with a defined layer thickness of 2 or 4 mm, respectively and using a He-Ne-laser with a wave length of 633 nm. Following the measuring principle of light diffraction at interfaces of optically distinguishable media, gel particles that show only slightly different indices of refractivity can be detected by laser diffraction. They are not detectable microscopically.

The assessment of particle analysis of cellulose solutions covers the particle distribution and its optical concentration. After calibration with titanium dioxide and considering the inherent solution colouration, the optical concentration provides information on the particle content.[14]

Figure 9 shows a graphical presentation of the particle size distribution of a 12 wt.-% solution of a wood pulp in NMMO monohydrate.

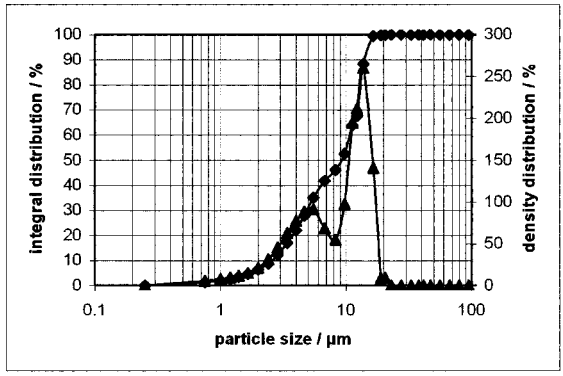

Figure 9. Particle spectrum as a function of cumulative (◆) and density distribution plotted versus particle size (▲) of a 12 wt.-% solution of wood pulp in N-methylmorpholine-N-oxide monohydrate.

The particle distribution between 0.5 and 175 µm is measured and presented in 31 classes. The figure shows both, the cumulative distribution as well as the density distribution that means a distribution standardised to the corresponding class width for one particle size.

The filter value has turned out to be favourable for the complex characterisation of the measured the particle size distribution and the particle content, respectively. The semi-logarithmic presentation of the quantity of particle N calculated from content and distribution versus the particle diameter X can be substituted by a straight line with sufficient precision. The filter value F_p may be determined then from the maximum particle diameter X_m and the logarithm of the particle number N_{10} in the size class 10 µm. It represents a decisive value in the spinning process [13]:

$$F_P = 10 \cdot \frac{X_m}{\lg N_{10}}.$$

Forming of Cellulose Solutions

An extraordinary and flexibly applicable equipment (self-made by TITK) covering laboratory and semi-technical scale production capabilities to produce fibres, filaments and films is available for the investigation of the forming parameters of pure and modified cellulose solutions.

It allows a wide variation of the spinning conditions concerning temperature (75 – 150°C), pressure (5 – 100 bar), nozzle geometry (discharge diameter, length/diameter-ratio 0,5 – 2, round or profile nozzle), capillary density (15 – 375 capillaries/cm^2), drafting conditions in

nozzle and air gap, air-conditioning of the air gap, take-up speed (10 – 750 m/min), after-treatment.

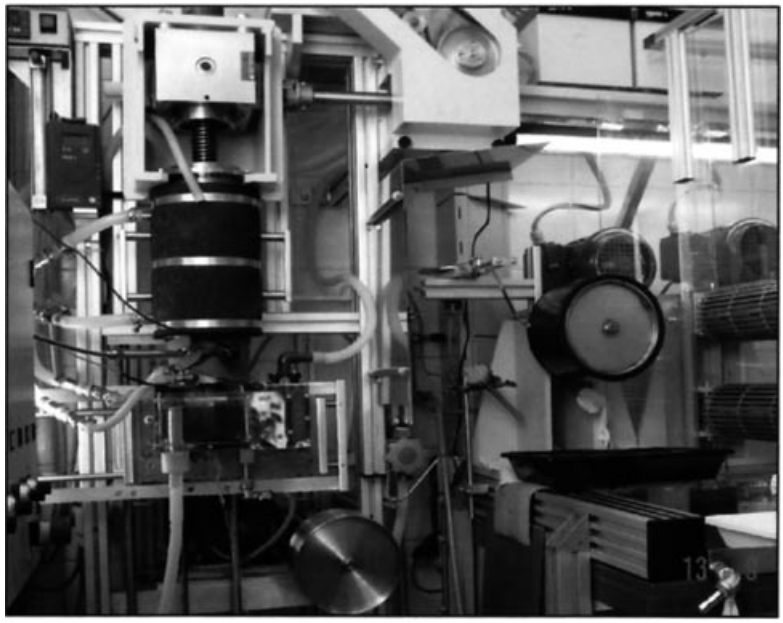

Figure 10. Laboratory spinning setup for the preparation of cellulose fibres and –filaments.

By measuring of throughput, pressure and temperature of the spinning solution, speed, tension and shrinkage of the fibre, temperature and relative humidity of the blowing air, temperature and flow rate of the spinning bath at different spinning configurations, the parameters of shear and extensional deformation can be investigated widely quantitatively. Washing, drying, finishing and winding of filament yarns are carried out continuously at defined yarn tension.

By means of blending the cellulose-NMMO-mixture with additional components before the preparation of cellulose solutions or by a dynamic mixing procedure shortly before the spinning machine respectively, modified cellulose fibres with a broad variability of functional and structural properties can be generated (Figure 11).

A differential scanning calorimeter (DSC 25, METTLER-TOLEDO) is used to characterise the thermal stability of cellulose solutions.[15] Information on the onset-temperatures, which

is this temperature where thermal decomposition of the solvent used starts, as well as on the long-term stability of spinning dopes is available by calorimetric investigations in a small-scale autoclave.[16]

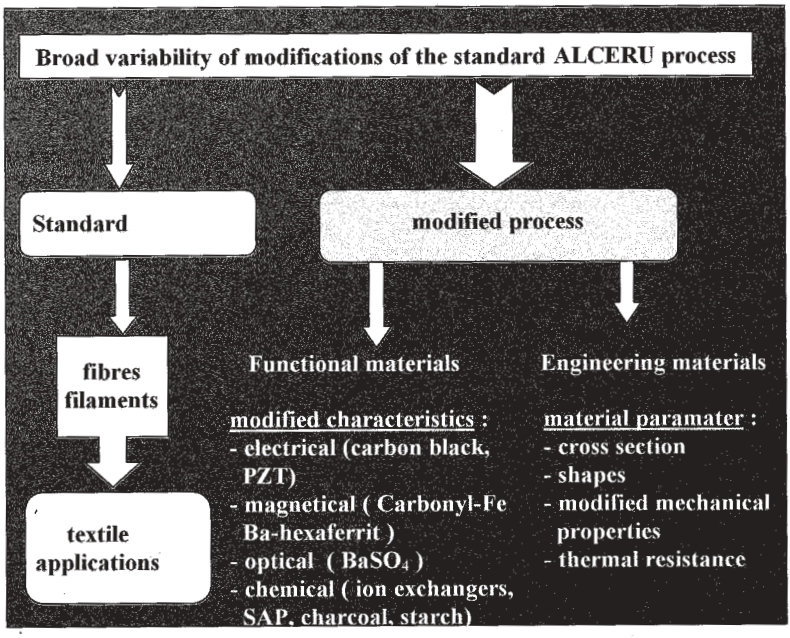

Figure 11. Different paths of modification of the standard spinning process by incorporation of functional additives as well as different nozzle cross section and shaping technique, PZT, plumbum zircon titanate ceramics, SAP, superabsorbent polymers.

Acknowledgement

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