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All these contributions were presented at the 6<sup>th</sup> Central European Conference 2010, 13-14<sup>th</sup> September 2010, in Bratislava, Slovak Republic.

# THERMOMECHANICAL AND SORPTIVE PROPERTIES OF METALLOCENE POLYPROPYLENE FIBRES MODIFIED POLYVINYL ALCOHOL AND CLOISITE

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**Abstract:** *This work focuses on the study of the influences of polyvinyl alcohol (PVA) and nanoadditive Cloisite 15 A (C15A) in the system PVA/C15A to modified PP/PVA and PP/PVA/C15A fibres. These were determined thermomechanical and sorptive properties of prepared fibres.*

*Thermomechanical analysis (TMA) was using to evaluate of the dimensional properties of PP and modified PP/PVA and PP/PVAPC15A fibres. The evaluation was depending on the temperature and the temperature which leads to shrink of fibres was determined.*

*On the basis of results from thermomechanical analysis was found that the temperature of PP/PVA/C15a fibres increases causing fibre deformation. Dimensional stability was increased and it signifies by fibre reinforcing.*

*Determination of moisture sorption is important for assessing the effectiveness of modification fibres leading to increase hydrophilic (hydrophill) properties, as well as the wearing comfort of textile materials.*

*Chemical fibres take from the environment variable amounts of water vapor. Received amount depends on the chemical (attended by polar - hydrophilic groups) supermolecular and morphological structure of fibres as well as environmental conditions (temperature, water vapor pressure).*

*From obtained results it was detected that the addition of C15A improves sorptive and thermomechanical properties which leads to improving of dyeability.*

**Keywords:** *metallocene polypropylene, polyvinyl alcohol, Cloisite 15A, sorptive and thermomechanical properties*

## 1. INTRODUCTION

The PP is the most commonly used polyolefin polymer in production of staple fibres and filaments for applications such as textiles, nonwovens, high-tenacity yarns and films. The success of the polymer can be attributed to several interesting as well as advantageous properties, namely easy processability, a low specific gravity, a good chemical resistance as well as wide availability and a low cost [1]

In generally, the properties of polypropylene fibres make possible their practical use in many areas such as human and home appliances, automotive, construction, and other industrial applications [2].

The modification of polypropylene (PP) fibres during their production which helps to prepare PP fibres with improved properties, guarantees new opportunities for the

expansion of an assortment of PP fibres in the clothing and domestic textile industries.

In the present day introduction of single site catalyst for making superior polyolefin resins set another technological trend, marked with metallocene catalysts having a precise control over molecular architecture for highly tailored polymers: improved processing; and properties for all polyolefins [3].

Even though it is the modification of PP as well as of PP fibres very interesting and can be the basic for the preparation of fibres with improved properties. On the present, it is very extensively used modification PP with the inorganic nanoadditives. The nanoadditives influence the crystallization and the morphology of PP fibres as well as the thermal stability of PP fibres [2, 4].

Polymer-clay nanocomposites are a new class of materials which show improved properties at very low loading levels

compared with conventional filler composites. Among these improved properties are mechanical, dimensional, permeability, thermal stability and flame retardant engagements with respect to the bulk polymer [5].

Nanocomposites based on organic polymers and inorganic clay minerals consisting of silicate layers such as montmorillonite (MMT) have attract great interest because they frequently exhibit unexpected properties [6]. Smectic clays, such as MMT and surface modified MMT are valuable minerals and are widely used in many industrial applications because of their high aspect ratio, plate morphology, natural abundance and low cost [7].

This paper presents the effect of polyvinyl alcohol (PVA) and nanoadditive (Cloisite 15A) on the sorptive and thermomechanical properties of the modified PP/PVA and PP/PVA/C15A fibres.

## 2. EXPERIMENTAL

### 2.1 Material used

The following materials were used for preparation PP, PP/PVA and PP/PVA/C15A fibres:

- metallocene polypropylene Metocene HM562R (PP), produced by Basell Polyolefine, Italy, MFI = 26,6 g/10min,
- polyvinyl alcohol (PVA) Moviol 4-98, produced by Hoechst Specialities, Germany, viscosity = 4 mPa.s (4% aqueous solution, 20°C), degree of hydrolysis = 98% mol.
- nanoadditive Cloisite 15A (C15A), Southern Clay Product Co, USA, organosilicate which was modified alkylamine 2M2HT (dimethyl, dihydrogenated tallow, quaternary ammonium), concentration of modifier 125 meq/100 g of clay, water content < 2%, density 1.66 g/cm<sup>3</sup>
- compatibilisers - isotactic polypropylene PP, polypropylene-graft-maleic anhydride (iPP-g-MAH), the registered trade mark is Licomont AR504, Clariant, Germany, ( $M_n \sim 2900$  g/mol,  $M_w \sim 11890$  g/mol,  $M_w/M_n \sim 4.1$ ). Content of MA is 3.5 wt.%,

$T_m \sim 156^\circ\text{C}$  and density by 23°C is 0.89 - 0.91 g.m<sup>-3</sup>, 1.03 wt.% per amount PVA+GL+C15A in concentrate.

### Prepared fibres

For the preparation of PP/PVA concentrate, the PVA was plasticized in glycerine at a temperature of 130°C for 40 minutes. The PP/PVA/C15A concentrate was prepared by disperse of nanoadditive in glycerine and then PVA was plasticized by this blend at the temperature of 130°C, for 40 minutes.

The mixtures of PP/PVA and PP/PVA/C15A were mechanically mixed with PP and with compatibiliser iPP-g-MAH. Then the mixtures were dried at 80°C and melted using twin screw extruders LabTech Engineering Company Ltd. by the extruder temperature zones 170, 180, 190, 200 and 170°C.

The PP/PVA and PP/PVA/C15A concentrates have been used to the preparation of PP/PVA and PP/PVA/C15A fibres (Table 1).

**Table 1** The composition of the blend PP, PP/PVA and PP/PVA/CL fibres

PP/PVA/C15A concentrates [wt.%]	Fibres		
	PP [wt.%]	PVA [wt.%]	C15A [wt.%]
100/0/0	100	0	0
92.5/7.5/0	99.25	0.75	0
92/7.5/0.5	99.2	0.75	0.05
91.25/7.5/1.25	99.125	0.75	0.125
90.75/7.5/1.75	99.075	0.75	0.175
90/7.5/2.5	99	0.75	0.25

1. The concentrates were mixed with granulated polypropylene in ratio 1:10 and spinning, using the laboratory spinning machine TS-16 at the temperature 210°C.
2. The original mixtures of PP, PP/PVA and PP/PVA/C15A concentrates has been diluted by half with pure PP, mechanically mixed and spinning by using the laboratory spinning machine TS-16 at the temperature 240°C.

## 2.2 Method used

### *Sorptive properties*

The fibres have been prepared windings of the weight from 0.4 to 0.6 grams which were firstly drying in an oven at 80°C for one hour in an open weighing bottle. Then they were placed into desiccator saturated with NH<sub>4</sub>NO<sub>3</sub> solution. The sealed desiccator is expected to remain in equilibrium temperature 21.7°C and relative humidity of 65%. After 96 hours has been fixed the mass [m] of fibre and equilibrium moisture content. After drying in a hot air oven for 3 h at 105°C were fixed the mass [m<sub>0</sub>] of dry fibre. The quantity of water vapor - humidity is calculated from the relation:

$$\%H_2O = \frac{m - m_0}{m_0} \cdot 100\% \quad (1)$$

### *Thermomechanical properties*

Schimidzu Thermomechanical Analyzer TMA-50 was used for determination of thermomechanical properties of PP, PP/PVA and PP/PVA/C15A fibres.

There were used following measurements conditions: heating from the room temperature to 90°C, fibre length was 9.8 mm and the heating rate was 5°C/min.

TMA method was using for specified temperature of first fibre deformation at constant load. The whole deformation extension resp. shrinkage of fibre was evaluated at 90°C temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 Thermomechanical properties

In this part thermomechanical (TMA) properties of fibres were evaluated by Shimadzu Thermomechanical Analyzer TMA-50. In dependence on temperature there were evaluated dimension stability of pure PP and modified PP/PVA, PP/PVA/C15A fibres. From obtained dependences there were established temperature of first extension or shrinkage fibres and total shrinkage of sample at 90°C temperature.

At all prepared PP, PP/PVA and PP/PVA/C15A fibres were obtained shrinkage of fibres from 8.65 to 4.84% (Table 2).

The modification of PP fibres with PVA/C15A increase temperature of first deformation of fibres. Also the modification PP/PVA fibres with Cloisite 15A improve dimensional stability which relate with reinforcing effect of C15A in PP/PVA/C15A.

In spite of the lower content of crystalline phase of PP/PVA/C15A fibres compare with pure PP fibre is their dimensional stability better and temperature of the first deformation was increased.

**Table 2** Deformation temperature T<sub>1</sub> and shrinkage (I) of PP, PP/PVA and PP/PVA/C15A fibres

PP/PVA/C15A fibres	T <sub>1</sub> [°C]	I [%]
100/0/0	48.9	-6.54
99.25/0.75/0	47.9	-8.65
99.2/0.75/0.05	52.3	-6.9
99.125/0.75/0.125	50.7	-4.84
99.075/0.75/0.175	50.9	-5.15
99/0.75/0.25	48.9	-4.84

### 3.2 Sorption properties

In this part there were evaluated the sorptive properties of moisture sorption of PP and PP/PVA and PP/PVA/C15A fibres (Table 3).

There were studied the effect of PVA and PVA/C15A on sorptive properties. From the moisture sorption we can draw a conclusion that the addition of fibre with PVA increases the moisture sorption compared to pure PP. A follow-up modification with Cloisite the sorption values have increased compared with pure PP and PP/PVA (Table 3). Adding of C15A to PP increases the moisture sorption which may also be associated with better coloring of PP/PVA/C15A fibres.

**Table 3** Sorption of moisture of PP, PP/PVA and PP/PVA/C15A fibres

PP/PVA/C15A fibres	Sorption of H <sub>2</sub> O [%]
100/0/0	0.2
99.25/0.75/0	1.4
99.2/0.75/0.05	2.2
99.125/0.75/0.125	1.7
99.075/0.75/0.175	1.8
99/0.75/0.25	1.9

#### 4. CONCLUSION

In this work was studied effect of PVA and PVA/C15A with the different C15A content on their thermomechanical and sorption properties.

On the basis of the results obtained at the evaluation of thermomechanical and sorptive properties it can be stated shown, that:

- modification of PP with PVA and PVA/C15A improve the sorptive properties of modified fibres evaluated by measuring the moisture sorption;
- the temperature of the first deformation is lower for PP/PVA fibres and higher for PP/PVA/C15A fibres than for PP fibres;
- dimensional stability of the modified PP fibre by PVA/C15A was improved by addition of C15A

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## SURFACE DYEING OF POLYPROPYLENE FIBRES

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**Abstract:** At present polypropylene is one of polymers used the most frequently to manufacture such materials as textile, technical and bicomponent fibres, nonwovens, foils and tapes. Polypropylene fibres find wide application possibilities in textile and automotive industry due to their properties (low specific weight, good transport and insulation properties as well as low price). A disadvantage of polypropylene fibres is a fact that they are not surface dyeable. A solution can be chemical or physical modification of the polypropylene polymer. We would like to show in our paper a possibility of surface dyeing of polypropylene fibres using physical modification of the polypropylene polymer on spinning. Several modifiers were proposed and developed in the frame of our research works focused on study of properties of polypropylene polymer from a viewpoint of physical structure, surface dyeability and spinning with the aim to increase affinity of polypropylene fibre to dyestuff on surface dyeing of the fibre. Influence of new types of modifiers on improvement of surface dyeing of polypropylene fibres and workability of the modified polypropylene filaments was evaluated and compared with properties of polypropylene fibres modified using commercially available modifiers.

**Keywords:** polypropylene, surface dyeing, modifier, dispersion dyestuff

### 1. INTRODUCTION

Dyeing of synthetic fibres is an important precondition for their application in blended textile materials. Physico-mechanical properties of synthetic fibres have their significance in designing construction of textiles. Colouristic properties are an important parameter for fashion designers creating design of a clothing product using further specific properties of the materials. Polyester and polyamide fibres are suitable for textile applications due to easy care; however their use is not suitable due to not always adequate physiological and functional properties of these fibres. Therefore, polypropylene fibres with excellent fluid transport properties, lower specific weight but also good thermal and insulation properties are used increasingly. Previous limitations decreased surface dyeability of polypropylene fibres are an objective of present research. Some results from this field are given also in this paper.

### 2. KNOWLEDGE FROM RESEARCH IN THE FIELD OF SURFACE DYEABILITY OF POLYPROPYLENE FIBRES

Polypropylene fibres belong to a group of polyolefines without functional groups in their structure on which dyestuffs could be bonded. Structure of their linear chain lacks molecules with different polarity unlike polyester and polyamide fibres where dyestuff shows high affinity to the polymer and therefore excellent colour fastness is achieved. One possibility how to achieve good colour fastness of polypropylene polymer was application of pigments into the polymer directly on spinning.

Therefore, some research works focused on incorporation of modifiers, suitable for dye take-up, into the polypropylene polymer. Application of polymeric mixtures is an efficient modification method. Modification of polypropylene is ensured by polyesters in blended polypropylene/polyester fibres with a majority share of polypropylene, where the polyester share is able to fix disperse dyestuffs and increase their exhausting.

At the same time it is necessary to optimize conditions of dispergation of the modifier and

create standard conditions of spinning of the modified polypropylene.

Several kinds of modifiers of our own were prepared under laboratory conditions in the frame of our research works focused on study of the problems of surface dyeing. They were applied to a mass of polypropylene fibre. Besides modifiers developed by our research team we applied commercial types of modifiers to the mass of polypropylene fibre as well. We have used products of the company BASF in a quantity of 10 wt.% of total polymer volume. Polyester polymers improving dyeability of the modified polypropylene fibres were used as modifiers. Commonly available commercial kinds of dyestuffs designed for dyeing of synthetic fibres were used to evaluate surface dyeability of the prepared types of modified polypropylene fibres. We have selected Bemacron dispersion dyestuffs from a wide assortment of various kinds of dyestuffs evaluated under laboratory conditions. The Bemacron dyestuffs exhibited good dyeing properties from a viewpoint of dye take-up and colour fastness. Therefore, E-type dispersion dyestuffs with a small molecule of the dyestuff and S-type dispersion dyestuffs with a big molecule of the dyestuff were used in further research focused on achievement of optimal dyeing.

### 3. CONDITIONS OF SURFACE DYEING OF THE MODIFIED POLYPROPYLENE FIBRES

#### 3.1 Laboratory evaluation of dyeing of knitted fabrics prepared from modified PP fibres

Several types of polypropylene fibres modified using Colorsvit 1 and Colorsvit 2 modifiers of our own and commercial BASF modifiers were evaluated in the frame of our research works. Description of the modified PP fibres with used modifier type is given in Table No. 1.

**Table 1** Parameters of the modified PP fibres

Sample No.	Fibre	Total fiber count [dtex]	Used modifier type
1	PP txh	56/33 × 1 FT*	Colorsvit 1
2	PP txh	56/33 × 1 FT	Colorsvit 2
3	PP txh	84/50 × 1 FT	BASF
4	PP txh	78/25 × 1 FT	BASF
5	PP txh	78/25 × 1 FT	BASF + TiO <sub>2</sub>
6	PP txh	50/50 × 2 FT	Colorsvit + TiO <sub>2</sub>
7	PP txh	50/50 × 1 FT	BASF
8	PP txh	50/50 × 1 FT	BASF
9	PP txh	56/33 × 1 FT	BASF

Notice: \* FT – frictionally crimped fibre

Tubular jersey knitted fabrics, surface dyed under laboratory conditions, were prepared from the fibres given in Table No. 1.

Dyeing procedure was selected in accordance with recommendations of the dyestuff manufacturer. As selection of an appropriate dyeing procedure, dyestuffs and auxiliaries can influence final dyeing of the knitted fabric, properties of the used dyestuffs, modified polypropylene fibres, pH of dyeing bath, properties of dispersants and dye levelling agents were considered on their selection so that uniform dyeing of the knitted fabrics could be achieved. Type of a dye levelling agent with an affinity to the dyestuff was specified on selection of the dye levelling agent.

8 E-type and S-type Bemacron dispersion dyestuffs were used for dyeing as given in Table No. 2.

**Table 2** Summary of the used dyestuffs

E-type BEMACRON	S-type BEMACRON
Bemacron Gelb E -3GI	Bemacron Gelb S -4G
Bemacron Rot E - FBL	Bemacron Rubin S - GFL
Bemacron Blau E – FBL	Bemacron Blau S –BGL
Bemacron Schwartz E – BC	Bemacron Schwartz S – 3L

Figure 1 shows time/temperature dyeing regime used on dyeing knitted fabrics prepared from modified PP fibres. Pretema Multicolor dyeing machine was used for dyeing under laboratory conditions with 1:50 fabric-to-liquor ratio.

Reductive washing after dyeing removed unfixed dyestuff from the samples of the knitted fabrics as it could affect adversely

colour fastness of the dyed knitted fabric. The dyed knitted samples were rinsed in clean water after reductive washing and flat dried.

### 3.2 Dyeing of knitted fabrics prepared from modified PP fibres tested under industrial operation

Modified PP fibre (sample No. 8), which achieved the best dyeability (Figure No. 3), was selected for testing of surface dyeing of polypropylene under industrial operation. Two types of tubular jersey fabrics were prepared from the selected modified PP fibre (sample No. 8) under industrial operation:

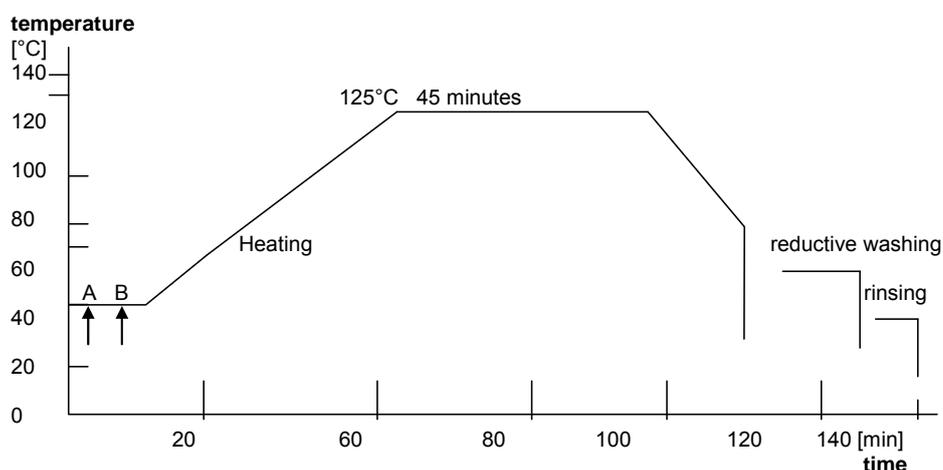
- one-component knitted fabric made of 100 % modified PP txh
- two-component knitted fabric made of PP txh (modified)/PES (standard)

Dyeing process with temperature regime evaluated under laboratory conditions was used to dye the knitted fabrics (the dyeing procedure is described in 3.1). Serilen Blau 2R-LS dyestuff and an auxiliary with affinity to the fibre were used to dye the knitted fabrics. Dyeing was performed on Brazoli R-jet H 2303 machine.

## 4. RESULTS OF THE EXPERIMENT

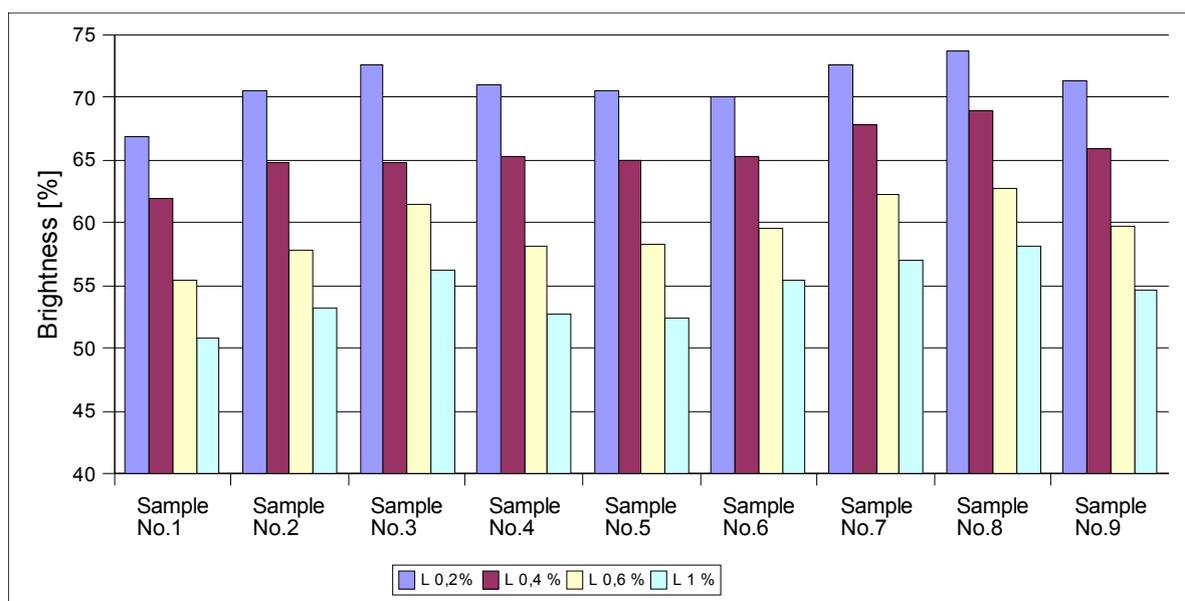
Samples of knitted fabrics prepared from the modified PP fibres dyed under laboratory conditions using Bemacron E dyestuffs were evaluated from a viewpoint of depth of dyeing using L, a, b colour co-ordinates. Method specified in *EN ISO-J01:2001 Textiles. Tests for colour fastness. Part J01: General principles for measurement of surface colour*, was used to determine depth of dyeing. Graphical comparison of depth of dyeing achieved using Bemacron E dispersion dyestuffs, expressed by brightness value in dependence on additive type and dyestuff concentration is shown in Figure No. 2.

Various values of brightness of the knitted fabrics prepared from modified PP fibres dyed using Bemacron dispersion dyestuffs shown in the graphical presentation were influenced by modifier type used for modification. The best results from a viewpoint of dyeability were achieved with sample No. 8 prepared from PP fibre modified with a BASF additive



**Figure 1** Time/temperature dyeing regime used on dyeing the knitted fabrics prepared from modified PP fibres using Bemacron dispersion dyestuffs

Where: A is textile auxiliary: Kortamol NNO  
 Ammonium sulphate  
 Acetic acid  
 B is dyestuff: according to the colour



**Figure 2** Comparison of depth of dyeing of the knitted fabrics achieved using Bemacron E dispersion dyestuffs in dependence on additive type and dyestuff concentration

Colour fastness to rubbing and perspiration of the prepared samples of knitted fabrics were evaluated according to *EN ISO 105-X12: 2003 Textiles. Tests for colour fastness. Colour fastness to rubbing and EN ISO 105-E04:1999 Textiles. Tests for colour fastness. Colour fastness to perspiration*. Values of colour fastness of the prepared knitted samples dyed using Bemacron E dyestuffs were low and therefore conditions of dyeing of the knitted fabrics using Bemacron S dyestuff with a bigger molecule were evaluated as well. Conditions of dyeing of the knitted fabrics were the same as those of dyeing using Bemacron E dyestuffs. Average grey scale ratings of colour fastness in acid and alkaline perspiration of the samples of knitted fabrics dyed using the above-mentioned dispersion dyestuffs are given in Table No. 3. We can state, on the basis of achieved results of colour fastness of the

knitted fabrics prepared from modified PP fibres, that Bemacron S dyestuffs with a big dyestuff molecule show better colour fastness than Bemacron E dyestuffs with a small dyestuff molecule.

Samples of knitted fabrics surface dyed using Bemacron S dyestuffs with 0.1 - 0.5 - 1.0 - 2.0 wt.% concentration of the dyestuff are shown in comparison with dyed reference sample made of 100% PES in Figure No. 3.

An unsuitably selected levelling agent which caused fixation of the dyestuff on surface of the modified PP fibre showed itself on samples of knitted fabrics made of modified PP fibres (sample No. 8). Subsequent reductive washing influenced change of original colour, therefore further optimization of the process and technology of dyeing of the modified PP fibre is necessary

**Table 3** Comparison of grey scale ratings of colour fastness in acid and alkaline perspiration of the knitted fabrics achieved with Bemacron E and Bemacron S dispersion dyestuffs.

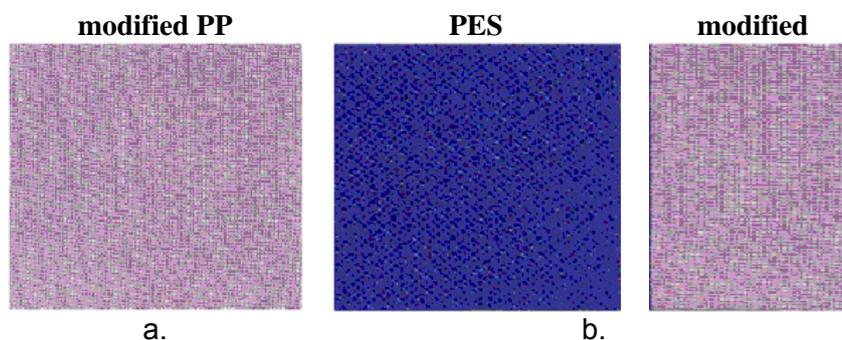
Dyestuff	Alkaline perspiration			Acid perspiration		
	Change in colour	Staining of adjacent fabrics		Change in colour	Staining of adjacent fabrics	
		cotton	polyamide		cotton	polyamide
Bemacron E	4-5	4	3-4	4-5	4	3-4
Bemacron S	4-5	5	5	4-5	4 - 5	4 - 5

Bemacron	PP 0,1%	PP 0,5%	PP 1%	PP 2%	PES 2%
Gelb S 4G					
Rubin S 2GLF					
Blau S BGL					
Schwarz S 3L					

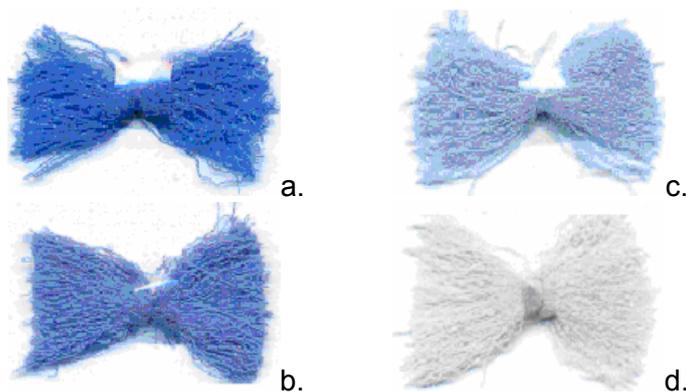
**Figure 3** Colour range: Comparison of depth of dyeing of a knitted fabric made of polypropylene modified using Colorsvit modifier and Bemacron dyestuffs and a knitted fabric made of 100 % standard polyester fibre

Dyeing was carried out using a routine procedure for dyeing of PES knitted fabrics with a levelling agent with affinity to the fibre and subsequent reductive washing. Figure No. 4 shows comparison of achieved colours of knitted samples made of 100 % modified PP fibre and two-component blended knitted fabric prepared of modified PP fibres and standard polyester dyed under industrial operation using the process described in chapter 3.2. A difference is visible mainly on the two-component knitted fabric, where PES

component is dyed in deep blue shade while the PP component has light violet shade. Dyeing without a levelling agent was repeated and it was found that dyeing does not change the shade. Change of the shade was caused by an unsuitable levelling agent used in the dyeing test under industrial operation. Comparison of dyeing of knitted fabrics made of polypropylene fibres, modified in different ways, using various dispersion dyestuffs is shown in Figure No. 5.



**Figure 4:** a) Knitted fabric made of 100% modified PP with BASF modifier;  
b) Knitted fabric made of 50% modified PP with BASF modifier and 50% standard PES.



**Figure 5** Comparison of dyeing of polypropylene fibres, modified in different ways, using various dispersion dyestuffs:

- a) Bemacron S BGL, PP fibre 70/50 x 1 FT, Colorsvit modifier, 10 wt.%
- b) Bemacron S BGL, PP fibre 70/50 x 1 S, BASF modifier
- c) Serilen blau 2R – LS, PP fibre 70/50 x 1 FT, Colorsvit modifier, 10 wt.%
- d) Serilen blau 2R – LS, PP fibre 70/50 x 1 S, BASF modifier

## 5.CONCLUSION

Conclusions resulting from comparison of the results achieved on surface dyeing of knitted fabrics made of modified PP filament using dispersion dyestuffs are as follows:

- it is evident from visual comparison of dyeing of the knitted fabrics that dispersion dyestuffs show sufficient yield as far as modified PP fibres are concerned
- a negligible difference was registered on comparison of colour fastness to washing and colour fastness to perspiration of the knitted fabrics dyed with dispersion dyestuffs in dependence on the used modifier type
- determined change in colour of all tested knitted fabrics is according to the grey scale on 4, 4-5 level

- it is important to optimize dyeing recipe for particular dyestuffs and auxiliaries from a viewpoint of the used dyestuffs
- it is necessary to assess purposefulness and conditions of reductive washing in the end of finishing cycle.

The performed research works and achieved results confirm purposefulness of application of modifiers based on PES polymer for surface dyeing of PP fibres. The achieved results confirm satisfactory affinity of the dyestuff, appropriate colour fastness and reproducible dyeing conditions.

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## POLYESTER FIBERS STRUCTURE AND HEAT SETTING

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**Abstract:** *The isothermal shrinkage kinetic of non stabilized and thermally stabilized PET monofilament for technical applications was studied in the temperature range from 70°C to 200°C. The maximum shrinkage rates were used for estimation of shrinkage rate thermal sensitivity SRTS. The SRTS parameter was rather sensitive for distinction between non stabilized and thermally stabilized PET.*

**Key Words:** *Polyester structure, shrinkage, thermal stabilization, shrinkage rate, temperature sensitivity*

### 1. INTRODUCTION

Thermal setting of synthetic fibers is mainly used for dimensional stabilization, improving of some properties and removing of internal stresses evolved during spinning and drawing. The main mechanism of setting is establishment of new conformation balances of polymeric chains in fibers deformed during their formation. In semi crystalline polymers is this process accompanied by re-crystallization leading to the more perfect crystallites with higher melting temperatures. In the loose state the chains retraction and disorientation in amorphous regions occurs. These processes are macroscopically visible as shrinkage.

PET has some properties that affect its processing behavior and also the fibers obtained from it. Firstly, it is a crystallizable polymer, but it has slow crystallization kinetics. Because of this combination of properties, PET can be obtained in various states of or PET, such as amorphous (as spun) "oriented mesomorphic" (drawn), and oriented crystallized (heat treated).

During spinning, due to the take up speed, the pre-orientation of amorphous PET occurs. The speed of the molten polymer emerging from the spinneret is much less than the speed at the godet wheel and this

stretching in the semi-molten state induces molecular order and orientation in the fiber. Stretching during spinning leads to the huge increase of the surface area per unit volume, which tends to reduce the chance of crystallization.

On the other hand, stretching by spinning results in a molecular orientation and therefore accelerates crystallization. It depends on the spinning conditions which effect will be dominated [16].

By proper drawing and heat setting the fibers structure and macroscopic shrinkage can be changed in wide range.

Main aim of this work is investigation of the isothermal shrinkage kinetic of non stabilized and thermally stabilized PET monofilament for technical applications in the temperature range from 70°C to 200°C. The maximum shrinkage rate is used for estimation of shrinkage rate thermal sensitivity SRTS. The SRTS parameter is rather sensitive for distinction between non stabilized and thermally stabilized PET [15].

### 2. PET FIBERS STRUCTURE

The polyethylene terephthalate (PET) fibers represent polyesters having rigid benzene ring in its backbone. These fibers were patented by Whinfield and Dickson in 1941.

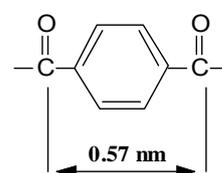
Cross-sectional area per single PET chain is relatively small, equal to the  $0.217 \text{ nm}^2$  only [18]. The cohesion of PET chains is a result of hydrogen bonds and van der Waals interactions, caused by dipole interaction, induction and dispersion forces among the chains. The total magnitude of secondary forces in a PET unit is  $1.37 \text{ kJ}\cdot\text{mol}^{-1}$ . Of this,  $1.02 \text{ kJ}\cdot\text{mol}^{-1}$  is due to the disperse forces induced by the benzene rings. Thus the strength of PET fibers is determined in the first place; by the rigidity of the benzene ring (the secondary van der Waals forces decrease with the sixth power of the distance) which form an angle of only  $12^\circ$  with the plane of the ester bonds. The partial flexibility in the macromolecule of PET is mainly due to the ethylene group. The interactive forces create inflexible tight packing among macromolecules, showing high modulus, strength, and resistance to moisture, dyestuffs and solvents. The unusually high melting point of PET (compared to aliphatic polyesters) is attributed to ester linkages. Due to this, PET is difficult to be crystallized.

Turn the chains about the C--O--C bonds in the ethylene glycol moiety of the repeat unit, results in the formation of two conformers, a planar trans-conformer and a spatial gauche conformer. Trans-conformation corresponds to the arrangement with the longest elementary unit. It is the state at which the so-called van der Waals distances between the chains and the individual groups in the chains are maintained. The activation energy for transition between these conformers is  $92 \text{ kJ}\cdot\text{mol}^{-1}$  [18]. The amorphous PET is assumed as molecular network with entanglements as knots. The PET repeat unit contains six flexible units, the average length of which is  $L = 0.268 \text{ nm}$ .

The amorphous orientation in PET fibers is rather low (orientation factor 0.34-0.40), Total trans-conformation fraction in PET fibers is nearly 0.80. Trans-conformation fraction in amorphous regions is typically about 0.64. Typical PET has 40% crystallinity. Another factor for crystallization is the position of the benzene rings. If benzene rings are placed

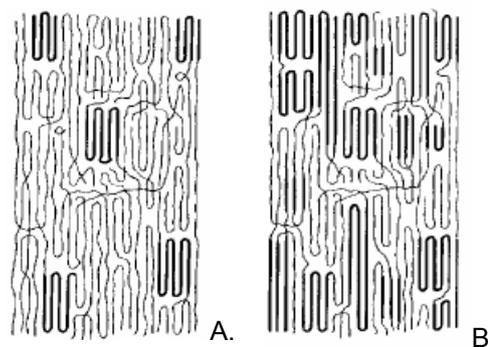
on the chain axis, then close packing of the molecular chains eases polymer crystallization. The elastic modulus of crystalline regions of PET in direction parallel with chain axis is 108 GPa. The calculated Poisson ratio is around 0.34.

PET exhibit glass transition  $T_g$  (about  $77-80^\circ\text{C}$ ), crystallization temperature ( $180-190^\circ\text{C}$ ) and melting point ( $256^\circ\text{C}$ ). The elastic modulus of crystalline regions of PET in direction parallel with chain axis is 108 GPa. PET fibers are well known for their high performance properties, resistance and good tensile properties. The geometrical structure of the terephthalate unit is shown in the Figure 1.



**Figure 1** Dimensions of terephthalate unit

The molar volume of PET  $V_{\text{PET}} = 144 \text{ cm}^3/\text{mol}$ . The amorphous density of PET  $\rho_{\text{aPET}} = 1333 \text{ kg}/\text{m}^3$ . The crystalline density of PET  $\rho_{\text{cPET}} = 1440 \text{ kg}/\text{m}^3$ . Total energy of secondary bonds is  $1.37 \text{ kJ}/\text{mol}$ . Undrawn fibers are practically amorphous. The semi crystalline structure appears mainly during thermal setting in isometric or isotonic state. Changes of PET structure after setting are schematically shown in Figure 2.



**Figure 2** Structure of PET before (A) and after (B) setting

Fibers after setting have degree of crystallinity about 0.4, orientation factor of crystalline phase is  $f_c > 0.95$  and orientation factor of amorphous phase is  $f_a = 0.6$ . Basic structural units are relatively strong **micro fibrils** having diameter 10 - 15 nm and length 103 nm. These units are assembled into **fibrils** having diameter 30 - 45 nm.

Very important role plays oriented non crystalline phase (TTM) – „taut tie molecules“. Portion of TTM is around 0.1 - 0.05. This phase is responsible for mechanical properties of PET fibers.

### 3. SHRINKAGE AND HEAT SETTING

The purpose of heat setting is stabilization of fibers dimensions (reduction of shrinkage caused by chains retractions), relaxation of internal stresses in the fiber, and creation or stabilization of the crystalline structure (the melting of small imperfect crystallites and the formation of more perfect larger ones) Basically, there is a competition between two separate processes i.e. crystallization, starting in the oriented amorphous mesophase (extended chain crystallization) and then extending into low oriented amorphous phase (folded chain crystallization) and shrinkage due to chain disorientation via bond rotation in amorphous regions i.e. changes of amorphous chains conformation from the trans to gauche form. Shrinkage is generally defined as an irreversible shortening of fiber length. The energy needed to cause shrinking is called the shrinkage work and the stress developed during the shrinking is called the shrinkage stress. Fibers are made to shrink by the effect of elevated temperature in the atmosphere, in water or in another medium. Shrinkage in fibers, yarns and fabrics can be determined by a great number of different methods in which the changes in length after contraction are measured under defined conditions [1]. For instance, the shrink forces can be determined by direct measurement of the stress generated in fibers of constant length by the effect of shrinking conditions (temperature, etc.) [2]. Shrinkage and

shrinkage stress can be observed through the measurement of the change of the sample length with free ends and through the measurement of the force exerted on the constraints with fixed ends, respectively, both as a function of time or temperature [8].

Shrinkage or shrinkage stress is generated caused by an entropic retraction. When the internal energy of an oriented polymer is elevated by an increase in ambient temperature, polymer molecules tend to relax the orientation by retracting from an ordered, extended conformation to a disordered, random coil. This eventually produces a change of length or contraction force [8].

Ludewig [9] showed that boiling water-shrinkage of PET multifilament yarn decreases on drawing from about 50% in the as-spun state to 12% in the drawn state. The shrinkage behaviors of PET up to a temperature of 130°C were extensively investigated in the work [10].

In polyester fibers two basic contraction mechanisms leading to macroscopic shrinkage can be distinguished. These are amorphous and crystalline contractions. The amorphous phase in drawn PET fibers that have not yet been thermally treated comprises more than 90% of the volume. Amorphous phase consists of a "frozen" physical network with chain entanglements forming knots in it. When heated above the glass transition temperature (for amorphous PET it is about 70°C in the dry condition and 50°C in the wet) the mobility of the physical network is released. The result is an amorphous contraction in which the individual chains in the network take up a steric configuration which is energetically the most convenient for them. But simultaneously crystallization takes place. Oriented PET fibers have half-time of crystallization shorter than 0.01 s [4]. Complete shrinkage is therefore obtained by shock heating only.

In semicrystalline PET fibers "amorphous" shrinkage takes place only partially. The amount is determined by the orientation in the amorphous phase and the mean relative molecular mass of the polymer. Amorphous

shrinkage can occur at low temperatures (less than 100°C) only. The corresponding shrinkage forces are in the region 10 to 20 mN.tex<sup>-1</sup>.

The other shrinkage mechanism is the crystalline contraction. It occurs especially in differential shrink fibers. This type of contraction is provoked by rearrangement of the crystalline phase, connected with the formation of "perfect" crystallites with folded chains. The rearrangement of the crystalline phase can occur at relatively high temperatures only (above 200°C for PET) and its prerequisite is the presence of a greater number of less than perfect crystalline structures [3]. The latter are formed during setting under tension or in copolyesters [5, 6]. In copolyesters the decrease in the temperature of maximum crystallization results in the crystalline contraction taking place at temperatures distinctly below 200°C. The maximum shrinking forces in crystalline contraction are three to six times lower than in amorphous contraction. Under similar drawing and setting conditions crystalline contraction does not depend on the type of comonomer but only on its content [3, 7]. At higher temperatures, the shrinkage due to recoiling of chains and crystallization processes is concurrent [11]. Fast crystallizing conditions restrict shrinkage.

Excessive shrinkage of textiles containing synthetic fibers is eliminated by heat-setting. By this means the crystalline phase is "improved" by recrystallization, which is connected with conformation changes to the chain in amorphous regions under defined external geometrical proportions. Standard are isometric (TA) or tension free (FA) states during heat-set [12]. The fibers heat-set at temperatures in the 180-220°C range show in both cases shrinkage of less than 2%. The TA samples have significantly higher shrinkage than the FA samples [13]. When the fiber is allowed to shrink during heat-setting, there are no external constraints to structural reorganization and a significant part of the residual stresses present in the non heated drawn yarns relax. When the

PET is held at constant length, a shrinkage force develops and only a part of the residual stresses is able to relax through limited structural reorganization. Thus, the higher shrinkage of TA samples is primarily due to the presence of greater residual stress in these fibers.

The deformation energy to break characterized by factor  $SF = \sigma \cdot \sqrt{\varepsilon}$ , (where  $\sigma$  is tenacity and  $\varepsilon$  is fiber breaking elongation) is used as indicator of thermal stabilization. It was found that SF factor increases with the increasing of setting temperature [17].

It was shown [14] that in oriented PET yarns shrinkage is a unique function of the product of amorphous volume fraction and amorphous orientation factor.

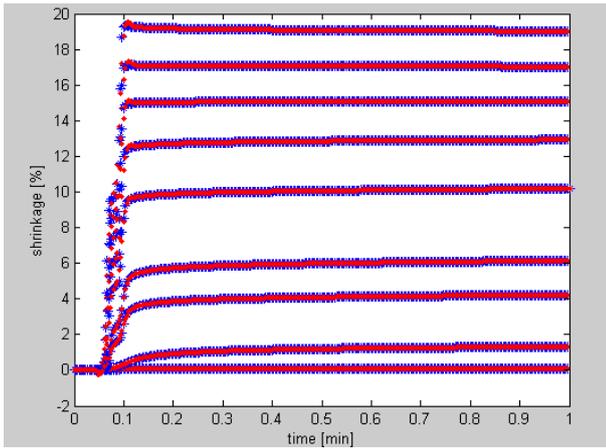
The fiber shrinkage is generally considered indicative of the shrinkage of the textile products. The structure of the yarns and fabrics and its effect on the resulting dimensional changes should be taken into consideration as well.

#### 4. EXPERIMENTAL PART

PET non stabilized and stabilized monofilaments for technical applications with measured fineness 33.84 dtex were prepared. Shrinkage experiments were realized on the TST2 shrinkage tester (Lenzing) under standard conditions. The pre-stress 0.7g was selected. Measurements were realized at temperatures 70, 90, 100, 120, 140, 160, 180 and 200°C. All measurements were investigated in the time interval till 1 min which was sufficient for effective (maximum - equilibrium) shrinkage  $S_e$  reaching. All measurements were repeated 20 times and mean values were used for curves creation and parameters estimation.

#### 5. RESULTS AND DISCUSSION

The shrinkage kinetic curves (dependence of shrinkage on the time) for non stabilized monofilaments are shown in the Figure 3. The experimental data (marked as cross) are replaced by cubic smoothing splines  $g(t)$ .



**Figure 3** a) Time dependence of non stabilized monofilaments shrinkage at various temperatures (50, 70, 90, 100, 120, 140, 160, 180, 200°C), red dots are smoothed values  
b) Shrinkage curve at 100°C (empty circles are experimental points, dot are smoothed values)

Function  $g(t)$  is twice differentiable (i.e. from class  $C^2$   $[a, b]$  where  $a = t_1$  and  $b = t_N$ ). The criterion of smoothness can be described by the integral [15]

$$I(g) = \int_a^b [g^{(2)}(t)]^2 dx \quad (1)$$

where  $g^{(2)}(t)$  is the second derivative of the smoothing function.

The integral  $I(g)$  is called the smoothness measure in the curvature of function  $g(x)$ . The corresponding least-squares criterion has the form [15]

$$U(g) = \sum_{i=1}^n w_i [y_i - g(t_i)]^2 \quad (2)$$

where  $w_i$  denotes the weight of individual points; this depends on their "precision" or scatter only.

The goal is to find a function  $g(t)$  with a sufficiently small value of  $U(g)$ ; i.e. it should be close to the experimental data, and have a small value of  $I(g)$ . Finding the best smoothing function  $g(t)$  leads to the minimization of the modified sum of squares [15]

$$K_1 = U(g) + \alpha I(g) \quad (3)$$

where  $0 \leq \alpha \leq \infty$  is a smoothing parameter which "controls" the ratio between the smoothness  $g(t)$  and its closeness to the experimental points.

All functions satisfying these conditions are cubic splines  $g(t)$  with knots  $t_i$ . For known  $\alpha$ , the smoothing cubic spline results [15]. For determination of parameter  $\alpha$ , the mean quadratic error of prediction MEP ( $\alpha$ ) was used [18].

The shrinkage rate curves were obtained by using of first derivatives of spline smoothing function  $g(t)$  with optimized smoothing parameter  $\alpha$  [15]. The maximum shrinkage rates  $R_s$  for all investigated temperatures were then simply evaluated. The dependence of  $R_s$  on the temperature was in both cases nearly linear. The slope of corresponding regression line is called shrinkage rate thermal sensitivity coefficient SRTS. For the non stabilized monofilaments is **SRTS = 4.89 % min<sup>-1</sup>.°C<sup>-1</sup>** and for stabilized monofilaments is **SRTS = 0.11 % min<sup>-1</sup>.°C<sup>-1</sup>**.

It is clearly demonstrated that the SRTS is sensitive on the degree of stabilization due to heat treatment.

## 6. CONCLUSIONS

The investigation of thermal shrinkage is very good tool for investigation of quality of fiber heat stabilization. It is simple to check the shrinking tendency by using of shrinkage rate thermal sensitivity coefficient SRTS. The SRTS is also the sensitive indicator of the degree of stabilization due to heat treatment.

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# METHODS FOR TESTING OF ANTIBACTERIAL ACTIVITY OF TEXTILE

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**Abstract:** *Antibacterial treatment of textiles became very popular in last few years. Many producers of underwear, socks, sportswear, shoes and other textile products announce the presence of antibacterial finishing in their goods as significant added value, increasing users comfort by limiting unpleasant sweat odour and by preventing him from dermal problems caused by perspiration. Antibacterial and antifungal finishes could be also present in other textile applications like beddings or upholstery and in many non-textile applications (building materials, paintings, floorings etc.).*

*For the consumer can determine those effects only subjectively, there are several different international microbiological standards for measurement of antibacterial activity of textiles, based on two main principles: agar plate tests (qualitative) and dynamic tests (quantitative).*

*This contribution is an overview of different methods for determination of antibacterial activity of textiles and, especially, meaning and interpretation of their results, which is absolutely crucial in considering of real effect of finishing.*

## 1. INTRODUCTION

Nowadays, producers of textiles utilize many different finishes of textile product in order to provide some novel functions and make them therefore more attractive for costumers. Antibacterial finishing of garments represent one of most interesting and faster-growing areas of textile treatment. Many new antibacterial agents like silver [1] or chitosan [2] are subject of scientific works and they also appear in many applications.

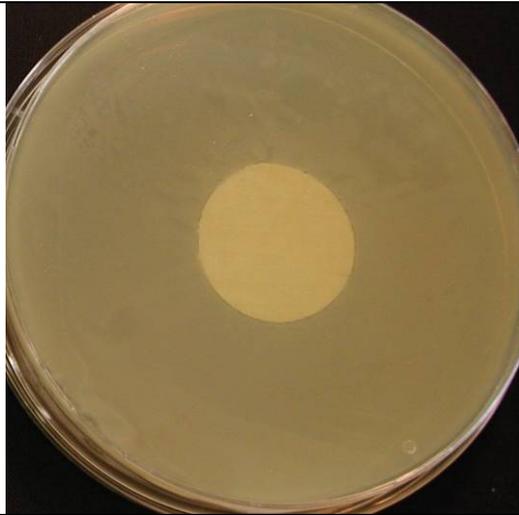
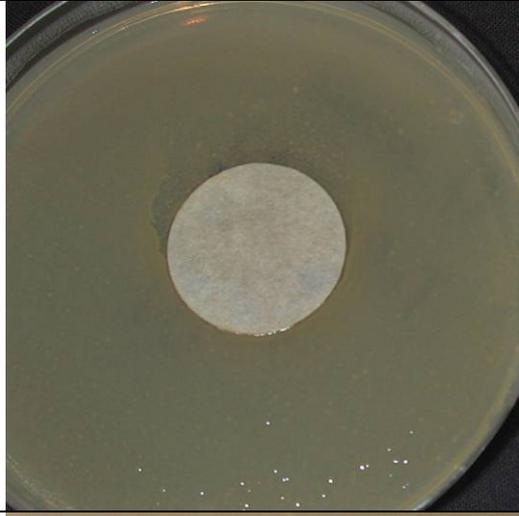
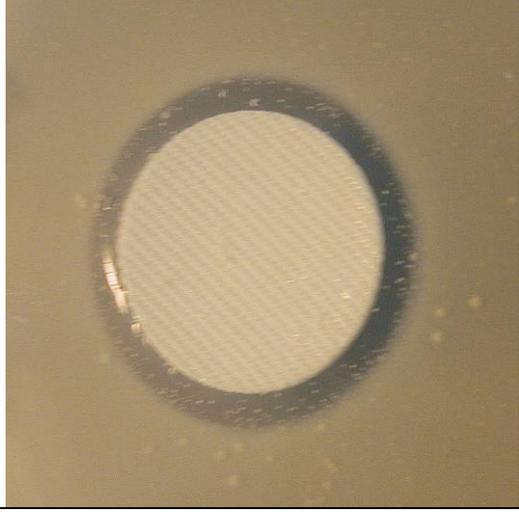
Problem is, that consumer himself isn't able to determine real effect and is limited only to subjective evaluation of secondary effects (lesser smell or positive dermal effects in comparison with untreated products). Proper assessment of antibacterial activity of textiles must be done in specialized microbiological laboratories, using methods, described in one of many different international standards. Because methodologies of determination are various and results should be obtained in different forms, knowledge of their proper interpretation is necessary for understanding the behaviour of final product.

Basically, there are two types of antibacterial activity tests: qualitative tests (where result says if treated material inhibits bacterial growth and, very approximately, how much) and quantitative tests (results are obtained as number of CFU - colony forming units, or percentual reduction of living bacteria).

## 2. AGAR PLATE TESTS (QUALITATIVE)

This kind of tests is based on the principle of diffusion of antimicrobial agent. It's used for determination of antibacterial and also antifungal properties. Textile sample is placed on the agar surface which is inoculated with the test microorganisms. Afterwards, microorganisms are left to grow. When incubation time passes, appearance of plate with sample is assessed. Usually, three types of results are considered (see Table 1). *Staphylococcus Aureus*, *Escherichia Coli* and *Klebsiella Pneumoniae* are the most frequently used testing bacteria, stated in agar plate test-based standards, but standards usually allow the laboratory to use any other bacteria, if order party wishes so.

**Table 1** Examples of results given by agar plate antibacterial activity test

Appearance	Result	Picture
Sample is overgrown by bacterial colonies	no antibacterial activity	
Sample isn't overgrown by bacterial colonies, but no inhibition zone is present	moderate antibacterial activity	
Sample isn't overgrown by bacterial colonies and inhibition zone (zone of no bacterial growth) is present around sample	good antibacterial activity	

Sometimes, samples show good antibacterial effect only after “pre-treatment” by gently brushing or rubbing them (for example on Martindale device), so the antimicrobial

agent can easily diffuse to the surface. This treatment actually imitates behavior of the material in practical use. It means that e.g.

antibacterially treated socks may work better after some time of use.

Most used standards utilizing agar plate tests are:

EN ISO 20645: Textile fabrics - Determination of antibacterial activity - Agar diffusion plate test

AATCC 147: Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method

JIS-L 1902: 2002 Testing for antibacterial activity and efficacy on textile products.

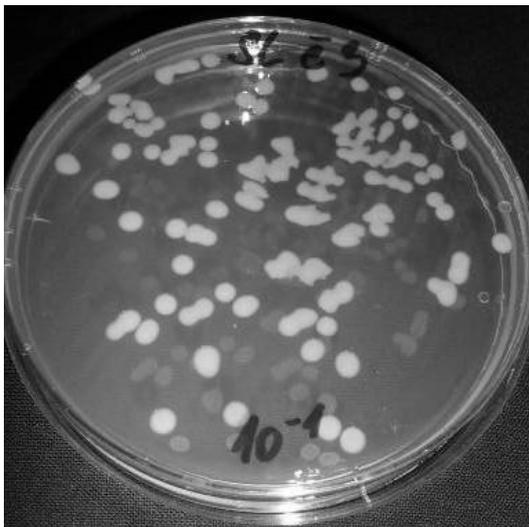
### 3. SHAKE FLASK DYNAMIC TESTS (QUANTITATIVE)

Apart from agar plate methods, results of dynamic tests are expressed quantitatively, in numbers of colony forming units (CFU). During testing, small sample of textile is cut into very tiny pieces and then subjected to prepared bacteria solution of specific concentration. Then, solution with sample is shaken for specific period of time to enable proper contact between sample and whole volume of solution. Then, small amount of solution is inoculated onto agar plate, where it's left to form circular colonies (see Figures 1 and 2). Afterwards, colonies are counted and their number (together with number

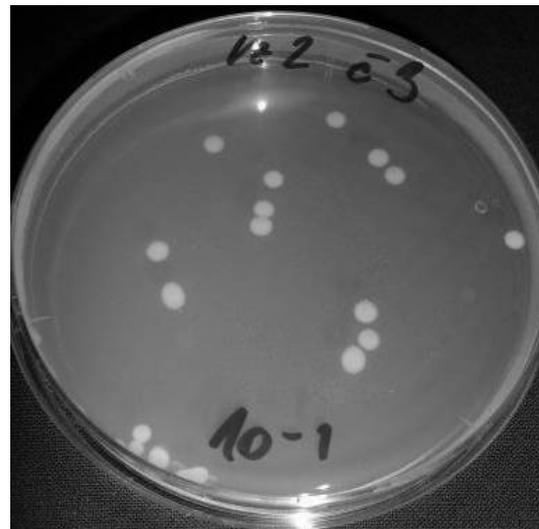
given by "blank" sample or number claimed from initial bacterial solution) represents base for expression of test results.

Results are expressed usually as a percentage reduction of bacteria in testing solution, caused by sample, less frequently as logarithm of fraction CFU on untreated sample/ CFU on treated sample. Accuracy of this principle is limited by maximal number of colonies, which can be clearly recognized on the surface of agar as standalone circles, not split together into indifferent mass. According to the praxis of our microbiological laboratory, this critical number lays somewhere around 300 colonies. On the other hand, too small number of colonies (less than 15) is undesirable too, because of quite high deviation of microbiological test's results. In order to obtain right amount of CFU for expression of results, several different dilutions of bacterial solution, taken from flask after shaking, are made, and all inoculated onto the agar plates. Then, the one with appropriate number of colonies is used as a result.

As in agar plate tests, *Staphylococcus Aureus*, *Escherichia Coli* and *Klebsiella Pneumoniae* are the most frequently used testing bacteria. Standards usually allow the laboratory to use any other bacteria, if order party wishes so, too.



**Figure 1** CFU – untreated „blank“ sample



**Figure 2** CFU - antibacterially treated sample

Most used standards utilizing shake flask tests are:

AATCC 100 Antibacterial Finishes on Textile Materials: Assessment of

ASTM E 2149-01 Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents Under Dynamic Contact Conditions

#### 4. DISCUSSION

Agar plate tests can give very good results (i. e. forming of inhibition zone around sample) only if antibacterial agent is able to migrate well from the sample. Otherwise, only partial effect is observed (only agar surface under the sample is free of bacteria). Sometimes, agar plate tests are carried on as a first basic test (because they are very simple to make), giving information whether the sample has any antibacterial effect. When positive, shake flask tests subsequently specify level of efficiency.

Results of shake flask-based tests aren't such dependent on migrating ability of antibacterial agent. They are more popular among scientists, because they can give more precise information about level of antibacterial activity of product.

In general, both types of tests describe the same properties of textiles and using specific one depends on situation and decision of experienced microbiologist.

To provide antibacterial effect, there must be certain level of migration of antibacterial agent to the surface of the product. But too rapid migration in wet environment (water, sweat) can also point to bad fastness of antibacterial finishes to washing. Moreover, migration of antibacterial agent to the contact with the body surface in higher

concentrations can cause natural bacterial protection of skin. All mentioned positives and risks are very dependent on nature of antibacterial agent and technology of incorporation of agent into the textile. For better prediction of antibacterial behaviour of product, antibacterial activity tests should be complemented by other analysis (dependence of additive amount on number of washing cycles, dermal tests, microscopic pictures etc.).

#### 5. CONCLUSION

Antibacterially additivated textile products are more and more common nowadays. To responsibly determine their real efficiency, we can choose one of several different standard methods. Methods can be divided into two main groups: agar plate tests (which are easy to carry on, qualitative and strongly dependent on ability of antibacterial agent to migrate from sample) and shake flask tests (more time consuming to make, quantitative, less dependent on leakage of agent from sample). This paper brought overview of such methods, their basic description and comparison, which can contribute to better understanding of their results and meaning.

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# MEASUREMENT OF POROSITY AND THE CHOICE SELECTION OF THE THRESHOLD VALUE THROUGH THE IMAGE ANALYSIS

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**Abstract:** Pores are characterized as small air holes among the weave points in the fabric. Pore size is expressed by the indicator of porosity. Fabric porosity has a decisive influence on the properties and utilization of fabrics. Therefore it is necessary to be identified and measured in several ways. In this work one possibility of porosity measurement of the fabrics has been studied. Picture analysis NIS Elements consisting of Nikon microscope, CCD camera and related software were used for measurement. During porosity measurement the fabric surface was compared to that of pores. Scanned picture was divided into the surface of pores and that of a fabric. For division it was necessary to choose the correct threshold value of a scanned picture. The result of experimental measurements was the choice of the threshold value of a scanned binary picture, which will ensure a bigger objectivity and repetition of porosity measurements.

## 1. INTRODUCTION

The pores determine how much air is contained in the fabric. They are expressed by an indicator of porosity which determines proportion of the internal volume of a fabric filled by the air [1]. Reversed value of porosity is the measure of fabric packing density by weave points. Some special fabrics such as filter fabrics, bed ticking and fabrics for parachutes must have a low porosity. Because of their utilization this property is dominant with above mentioned assortment. On the other hand, clothing and furnishing fabrics have a higher porosity compared to special fabrics. Statistically closed air in pores of such fabrics is the representative of a thermal insulation. In fact fabric porosity affects all its properties.

Also the arrangement of fibers in a yarn and sort of yarn influence the final porosity [4]. It is necessary to take into consideration that the shape, division and size of fabric pores are changed, for example by deforming in its processing, in its final exploitation and common up keeping. The structure of a fabric with a particular weave and used material should have a certain optimal value of porosity. This porosity value can be theoretically calculated and experimentally

measured. The whole group of measurement methods exists for porosity measurements. Classical methods use the measurement of air transfer through a fabric. The basic of the measurement is the amount of air passing through the fabric at the set value of a pressed air [8]. Such measurement is not a sufficient indicator of how the pores are large and how they are placed in fabric.

Therefore it is appropriate to complete the classical method of porosity measuring by using picture analysis consisting of microscope Nikon, CCD camera and NIS-Elements software. Measurements realized at this equipment display are enlarged, real picture with a high distinguishing ability. They are able not only to get a picture but also to process and archive it. The main aim of the wide exploitation of this equipment is the possibility of different dimensions measuring on the scanned picture. Each dimension can be measured after system calibration. During porosity measurement a lot of transigrate light over the hole in a fabric have been scanned.

Types of measurements on picture analysis [3]:

- fast measurement using ocular measure which operates like a floating ruler (can

be put to the measurement object and subtract its distance)

- interactive measurement suitable for direct measurement of objects immediate output of measured data with the actual distances using calibration constants
- objective measurement defined like picture points group of the binary layer suitable for measuring surface, lengths and so on.
- textural measurement of the whole surface screen or the surface bounded by a measuring frame suitable for measuring the surface, the number of objects and so on.

Measurements can be performed on the following types of pictures:

- color picture for measuring the intensity or a typical shade of color picture
- binary picture for measuring the shape and size
- the picture of mask for measurements restricted on the measurement field (it means the point of intersection of the measuring frame and picture mask).

Typical linear morphological operations are following:

- space filtering, erosion that removes one layer of pixels from the object surface
- dilatation is adding one layer of pixels on the surface of the object by which the objects enlarges
- opening (combination of erosion and dilatation) leading to the connection of the objects
- filling the holes in the objects
- selecting it is replanting of the object by its contour.

The result of these operations is a binary picture and the elements of this field are pixels. Processed objects are created by connection of pixels of one type (black color) and the background is created by variety of supplements (white color). The technique of the nearest neighbors-where the smallest structural element contains 9 pixels (3 lines and 3 wholes around the central pixel) - is

usually used for the final connection of pixels.

The shape of the surface division of the scanned picture on the white and black objects was influenced by the threshold value. By the measurements of porosity was searched the best threshold value (of the range from 60 to 220) of the scanned binary picture. Experimental measurements with different threshold value were introduced in the Figures 3 and 4.

## 2. EXPERIMENTAL PART

### 2.1 Used materials

The porosity measurements were realized on taw cotton fabric with its production name Mirabell. The fabric was made of a cotton yarn, raw carded group AI on the length weight of 29.5 tex (the warp and in weft) woven in a tabby weave. The manufacturer stated the basic parameters of fabrics:

- sett of fabrics (warp/weft) 230/195
- surface weight 125 [g.m<sup>-2</sup>]
- shrinkage (warp/weft) 6/4 [%]
- 

### 2.2 Used methods

A binary picture (black, white) was created from the original picture. There were white objects (those are the areas transmitting light) and other shades have been transferred to black (that is the area of building weave points in the fabric). A binary picture represents the set of pixels the value is of which is 1 - for white areas and 0 for background - black area. System NIS uses so called square grid with 8 connectives where 2 neighboring pixels are considered to be one object, and then all the pixels object neighboring diagonally are evaluated as a one object [3]

The work procedure on picture analysis was divided in to the following parts [5]:

- creation of the actual picture itself through a digital camera connected to optical member with a wide possibility of picture enlarging
- picture analysis supported by a software

- analysis of selected parts of the picture and measurement of selected indicators.

exported directly into the application QC Expert and statistically evaluated.

As the visual characteristics of appearance irregularity was calculated [2]:

$$AP = \sum A_i \tag{1}$$

where  $AP$  is the surface of pores (the real surface of transparent parts in the grid cells)  $A_i$  surface pores

$$AE = x_i * y_i \tag{2}$$

where  $AE$  is the total surface of pores,  $x_i, y_i$  data position measured on picture surface

Then ratio of pores surface to picture surface is calculated as follows:

$$AF = AP/AE \tag{3}$$

Setting the picture analysis during porosity measurements were as follows:

- calibration of size 1.51 (mm x pixel) with the objective Alpha 4 x
- setting the format of camera shooting 8-bit 1280 x 1024
- setting illumination of light by camera 40 ms
- to set camera intensity – for red color 1, green color 1.3, blue color 2.4
- measured surface picture 2.98312 e +006 [mm x mm].

Based on the set macro consisting of the above mentioned orders there were made 100 measurements of porosity with different threshold value. Measurements were

### 3. RESULTS AND DISCUSSION

Before the porosity measurement basic analysis of the fabric was realized. Here were measured indicators of sett of fabrics, basic weight and of fabric shrinkage. As it results from experimental measurements in Table 1, these differ from the introduced by manufacturer values. The measurement of porosity itself necessary for the selection of threshold binary picture was made on tow cotton fabric design 172.221th. Threshold binary picture was selected in the range from 60 to the 220. The results of the measured values are listed in Table 2.

Pictures 1 of different alternatives of color picture threshold value provide the possibility of visual selection of the best threshold value. Pictures 2 show the binary picture of a selected part of pores group. The threshold value from 140 to 160 has been selected as the most objective. Changes in the quality of scanned picture are influenced by the work of laboratory worker who on the basis of his own experience suggests the microscope setting. Setting the camera and the work with NIS Elements software is more objective and in this work specified precisely. Statistical evaluation of porosity is introduced in the Table 2.

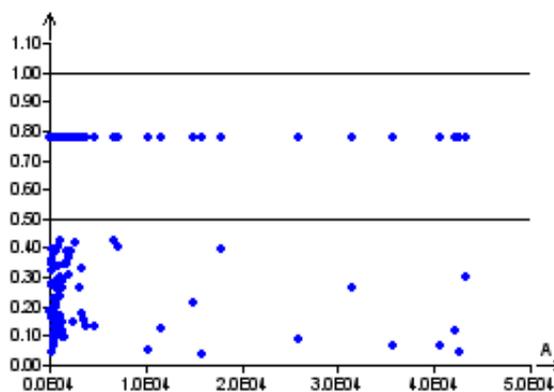
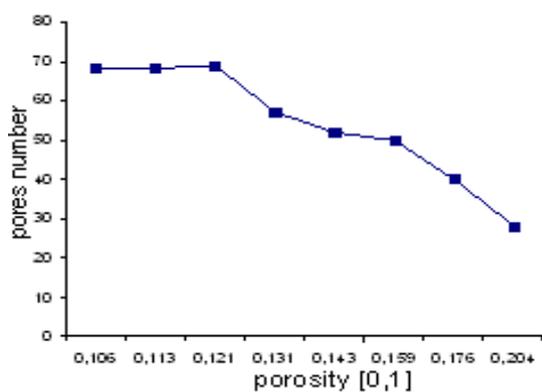
Dispersion and density of pores distribution is evident from picture 5. Porosity measurements show that with the growth of threshold value the number of pores on the measured surface is reduced. Pores mutually merge and their number is reduced - see picture 4.

**Table 1** Values of sett of fabrics, basic weight and shrinkage of cotton fabric Mirabell

Design	Sett of fabrics warp-weft [0,1m]	Basic weight [g.m <sup>-2</sup> ]	Shrinkage warp-weft [%]
17221-tow	230/190	150	8/6

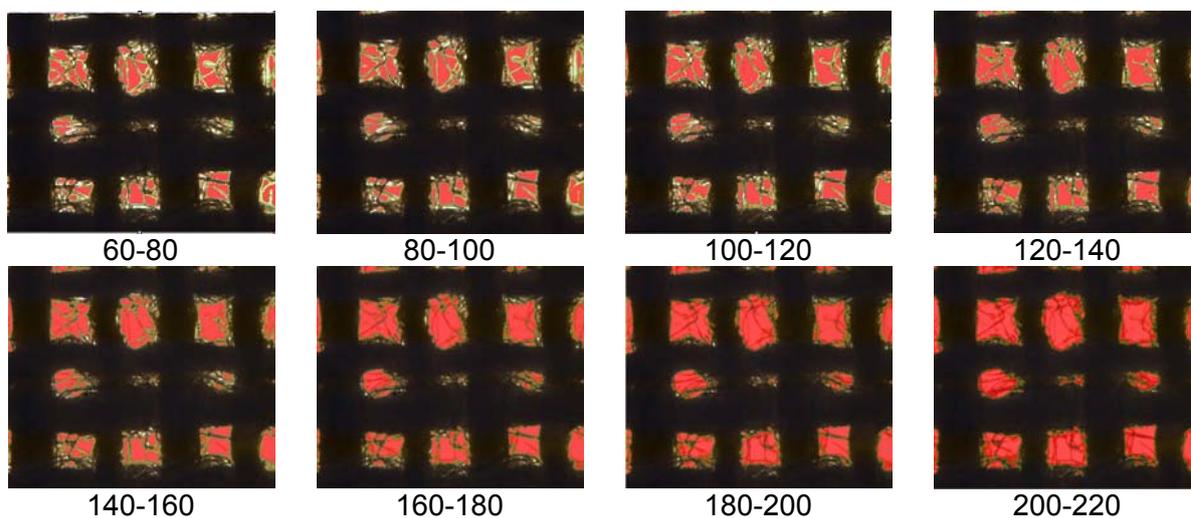
**Table 2** Porosity measurements of tow fabrics Mirabell in different threshold values (with probability 0.95)

Threshold value	Amount pores (0.1)	Porosity [%]	Average surface of pores AP [ $\mu\text{m} \times \mu\text{m}$ ]	Variation coefficient of porosity [%]
60-80	68	10.6	4650	38.0
80-100	68	11.3	4972	36.1
100-120	69	12.1	5248	34.0
120-140	57	13.1	6833	36.9
140-160	52	14.3	8213	38.7
160-180	50	15.9	9478	40.2
180-200	40	17.6	13140	47.2
200-220	28	20.4	21767	60.9

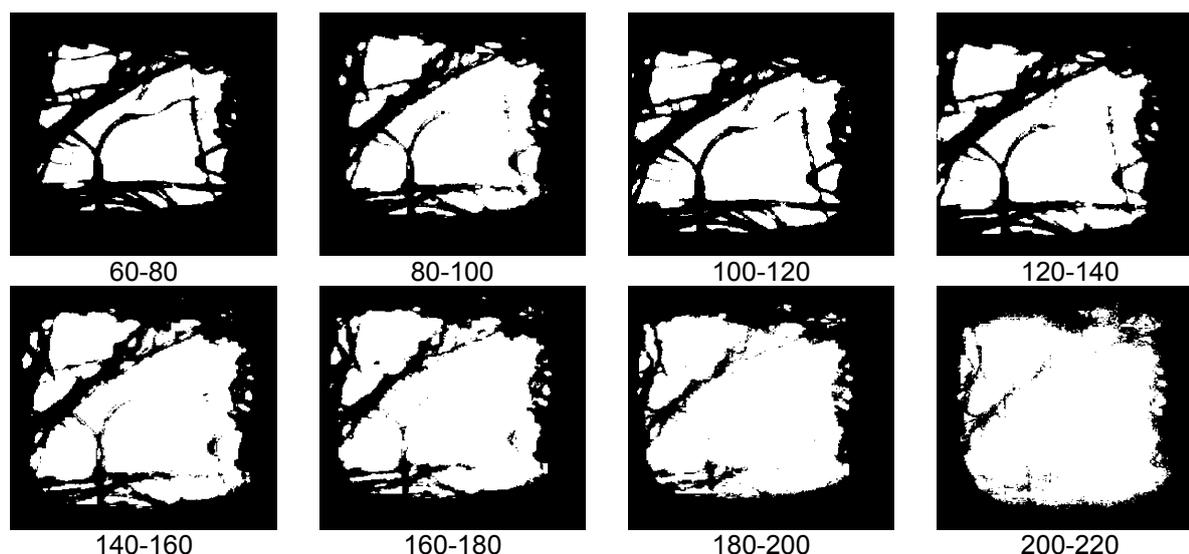


**Figure 1** Comparison of pores number

**Figure 2** Diagram of dispersion pores in the fabric



**Figure 3** Pores in the fabric with a threshold value from 60 to 220



**Figure 4** Binary pictures

#### 4. CONCLUSION

1. The method of fabric porosity was developed using picture analysis with a special program NIS Elements, which is necessary complement to existing method of porosity measurement.
2. It was found that with the increasing of the threshold value porosity is increasing as well. As the most objective was selected a suitable threshold value of scanned binary picture from 140 to 160.
3. Using this value the porosity measurements were realized and the characteristics of the location and dispersion were statistically evaluated.
4. We came to the conclusion that with an increasing threshold value pores merge and their number on the monitored area of the picture is reduced.
5. Statistical evaluation confirmed that the pores area is different. It can be concluded that the porosity variance is a sign of uneven structure of the yarn used for weaving. The weave influences the structure and segmentation of pores.
6. For a complex evaluation of textile structures, picture analysis is getting more important place not only in the textile laboratory. It serves suitably as a complement to existing methods of measurement. It is possible that some

methods of measurement in the future will be replaced by this picture analysis, which from our point of view appears to be faster, more accurate and more universal. Measurement of porosity using picture analysis NIS - Elements will be necessary to take as one of the methods for measuring this property and about its suitability will be determined by the structure of the fabric and by the purpose of its exploration.

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# NEW EMULSIFYING AGENTS BASED ON O-(CARBOXYMETHYL) CELLULOSE

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**Abstract:** *The new emulsifying agents were prepared from carboxymethylcellulose (CMC) by esterification of cinnamic acid. The chemical modification was performed in different reaction media DMF/TSA and H<sub>2</sub>O/DMF with 4-DMAp as catalyst and N, N-dicyclohexylcarbodiimide as activator of cinnamic acid, at various reaction conditions. The obtained CMC esters were characterized by FT-IR spectroscopy and surface-active and associative properties. Some of the prepared derivatives were water-soluble and showed excellent emulsifying power. Results from the studying of the associative properties of cinnamic esters of CMC showed existence of macromolecular interactions. Prepared cinnamic esters of CMC can be applied in chemical, pharmaceutical, food industry as well as in other industries.*

**Keywords:** *carboxymethylcellulose, cinnamic acid, surface-active properties, emulsifying efficiency*

## 1. INTRODUCTION

During the last years, there has been a growing urgency to develop novel biodegradable and renewable resource-based polymers, which can compete with synthetic polymers in performance and thus reduce our dependence on fossil resources, and to develop new or modified technologies by applying environmentally-friendly chemical processes. Considerable attention has been devoted to polysaccharide-based surfactants, since they show potential use in environmental protection, pharmaceutical, detergent, textile and other industries. Recently, considerable number of studies report on polymeric surfactants prepared by partial hydrophobization of commercial and non-commercial polysaccharides such as hydroxyethyl cellulose [1,2], pullulan [3] and dextran [4], carboxymethyl starch [5] and beechwood xylan [6].

As a further commercially available anionic cellulose derivative carboxymethyl-cellulose (CMC) was used for targeted hydrophobic modification in order to prepare ionic polymeric surfactants. CMC is commercially available in large quantities and known to act

as water binder, thickener, emulsion stabilizer, suspending agent and antiredeposition agent in detergents [7]. Polymeric surfactants with efficient emulsifying and performance properties were prepared from CMC by etherification [8] as well as esterification using conventional [9] and unconventional microwave assisted methods [10, 11]. The prepared derivatives are potentially applicable in cosmetics as stabilizers of oil-in-water emulsions and in detergent industry as co-surfactants and co-builders.

The aim of this research work was the partial hydrophobization of CMC by esterification with cinnamic acid, which can lead to preparation of new biopolymers with interesting surface-active, associative or antioxidant properties. Unsubstituted cinnamic acid is a good inhibitor making the excellent antibacterial, antimicrobial, antiparasitic and anticancer effects [12]. Cinnamic acid has no industrial use. The prepared cinnamoyl CMC derivatives were characterized by FT-IR spectroscopy and their surface-active and associative properties were determined.

## 2. EXPERIMENTAL

### 2.1 Materials and analytical methods

CMC, Lovoza T20 ( $\text{Na}^+$  salt,  $\text{DS}_{\text{CM}} = 0.5$ ) was gift from Lovochemie (Lovosice, Czech Republic). Cinnamic acid (CA) was a commercial product from Merck Chemicals Ltd. (Bratislava, Slovak Republic). N,N'-dicyclohexylcarbodiimide (DCCI), 4-dimethylaminopyridine (4-DMAp), 4-toluenesulfonic acid (4-TSA) and Tween 20 were from Aldrich Chemical Co. (Steinheim, Germany). All chemicals were used without further purification. Fourier-transform infrared (FT-IR) spectra were obtained on the Nicolet 6700 spectrometer with a ATR extension piece (SMART ORBIT DIAMOND) with using 128 scans at a resolution of  $4 \text{ cm}^{-1}$  (Bratislava, Slovak Republic).

### 2.2 Synthesis of cinnamoyl esters of carboxymethylcellulose

- (i) CMC (1.0 g) was activated in 22 ml DMF containing 4-TSA (0.6 g) by stirring at  $50^\circ\text{C}$  for 30 min to yield the 'gel suspension' consistence [13]. CA (0.5-2 g) dissolved in 10 mL DMF, DCCI (1.4 g) and 4-DMAp (0.05 g) was added to the gel suspension of CMC. The reaction mixture was stirred at  $50^\circ\text{C}$  for 0.5-1 h and subsequently poured into 4-6 volumes of ethanol. The precipitated derivative was separated by filtration, thoroughly washed with ethanol, and extracted in a Soxhlet apparatus with ethanol for 8 h. The product was obtained in the non-ionized form and they needed to be transformed to the carboxylate form, as previously described [9].
- (ii) CMC (1.0 g) was solubilized in 35 ml  $\text{H}_2\text{O}$  under stirring at room temperature for 1 h. CA (0.5-1.0 g) dissolved in 20 ml DMF, DCCI (0.35 g) and 4-DMAp (0.05 g) was added to the CMC solution and mixture was stirred at  $50^\circ\text{C}$  for 0.5-2 h. The recovery and purification of the esters were the same as described in method (i).

### 2.3 Surface-active properties of cinnamoyl esters of carboxymethylcellulose

The emulsifying efficiency was tested on emulsion of the 'oil in water' (O/W) type. The emulsion was prepared by mixing 9 ml of water containing 0.05 g of the polysaccharide and 1 ml of paraffinic oil dyed with SUDAN IV, in the laboratory mixer (Heidolph DIAX 600) at 20 500 rpm for 1 min. The stability of the emulsion was estimated at three time intervals after the emulsions had been prepared, i. e. 5 min ( $h_1$ ), 1 h ( $h_2$ ) and 24 h ( $h_3$ ), and expressed in terms of the height (mm) of the oil and cream layers formed on the surface of the emulsion.

The surface tension of polysaccharide solution in water in the concentration range  $0.15\text{-}5.0 \text{ g}\cdot\text{l}^{-1}$  was determined at  $25^\circ\text{C}$  using the Du Nouy ring apparatus. Surface tension data were plotted against the logarithm of polysaccharide concentration in order to obtain the critical micelle concentration (c.m.c.) and the corresponding surface tension ( $\gamma_{\text{min}}$ ), as described in previous papers [10].

### 2.4 Viscometry of cinnamoyl esters of carboxymethylcellulose

The solution behavior of CMC derivatives in the dilute regime was studied by viscometric measurements of CA-CMC solutions in aqueous 0.1 M NaCl using an Ubbelohde-type capillary viscometer (0.64 mm diameter). The concentration of the CA-CMC solutions ranged between 0.32 – 0.065 g/dl. The flow times were measured at  $25^\circ\text{C}$  maintained by a circulating bath. Prior to the measurements, the polymer solutions were filtered through paper filter (Whatman Schleicher & Schuell 589/1). Based on the ratio of flow times of the solution and solvent ( $t/t_0$ ) representing the relative viscosity ( $\eta_{\text{rel}}$ ) was used to calculate the specific viscosity as  $\eta_{\text{sp}} = \eta_{\text{rel}} - 1$  and there from calculated intrinsic viscosity as  $[\eta] = \eta_{\text{sp}} / c$  at  $c \rightarrow 0$  [14].

The concentration dependence of the reduced viscosity  $\eta_{\text{red}}$ , was described by the

Huggins relationship (1) in order to determine the Huggins constant ( $k_H$ ).

$$\eta_{red} = \eta_{sp} / c = [\eta] + k_H \cdot [\eta]^2 \cdot c \quad (1)$$

### 3. RESULTS AND DISCUSSION

The esterification reaction was performed using the cinnamic acid (CA) activated by DCCl, in two different reaction media: (i) DMF/4-TSA and (ii) H<sub>2</sub>O/DMF with addition of 4-DMAp as catalyst. Variations of the CMC/CA mass ratio and reaction time at 50°C were served to prepare water-soluble CA-CMC derivatives. The reaction conditions and characteristics of the derivatives are summarized in Table 1.

In order to obtain the derivatives in the water-soluble form necessary for FT-IR analysis and surface-active testing, the carboxymethyl substituent was transformed into carboxylate form similarly as [9]. In this way the vibration of the COO<sup>-</sup> groups at ~1600 cm<sup>-1</sup> is well separated from that of the protonated and ester forms absorbing at ~1730-1740 cm<sup>-1</sup>. Partially soluble and water soluble CA-CMC derivatives at concentrations of 0.5% wt were prepared. FT-IR spectroscopy was used for qualitative estimation of the extent of esterification. The FT-IR spectra of the CMC

derivatives show a pattern of absorption bands similar to that of the starting polysaccharides (Figure 1). In the case of CMC derivatives modified by cinnamic acid a signal at ~1702 cm<sup>-1</sup> indicated the presence of the ester function shifted from typical 1740 cm<sup>-1</sup> location by the double bound conjugated with aromatic ring structure [15]. However, the FT-IR spectra of some CA-CMC derivatives did not show absorption band at 1702 cm<sup>-1</sup> attributed to the  $\nu(\text{CO})$  vibration of the ester groups. Only derivatives CA-CMC I prepared in DMF/4-TSA with addition of 4-DMAp as catalyst appeared as a shoulder (~1699 cm<sup>-1</sup>) and CA-CMC V prepared in H<sub>2</sub>O/DMF appeared as a shoulder (~1702 cm<sup>-1</sup>), indicating a low extent of esterification (Figure 1). The absorption band appeared at 1740 cm<sup>-1</sup> maybe attributed to the free acid.

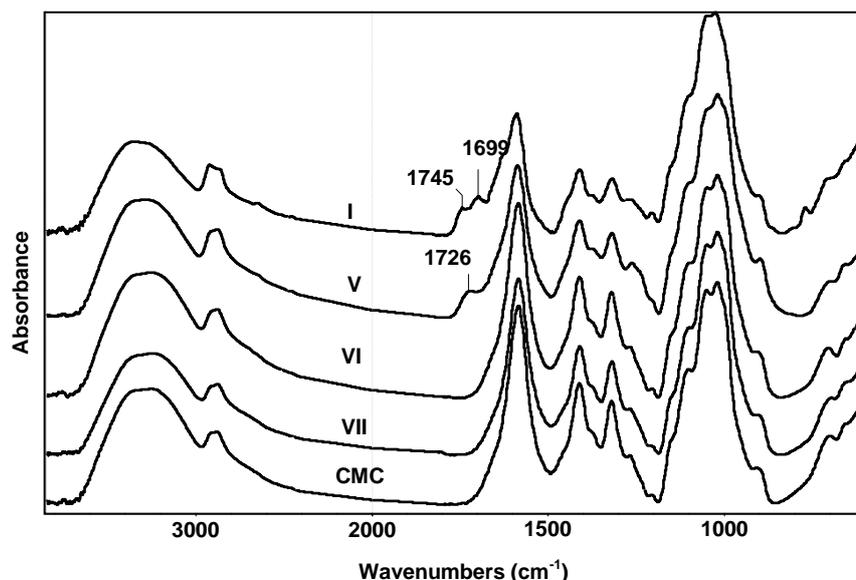
Differential FT-IR spectra were used to provide further proof of esterification (not showed), too. The presence of ester groups was confirmed by the intensity increase of the absorption bands at ~2924 cm<sup>-1</sup> and 2860 cm<sup>-1</sup>, respectively, attributed to the  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  vibrations of the CA substituent.

**Table 1** Results of esterification of CA with CMC at temperature 50°C and their characteristic spectral data

Sample CA-CMC	CMC:CA [Mass ratio]	React. time [h]	React. medium	Yield [g/g] <sup>a</sup>	$\nu(\text{CO})$ [cm <sup>-1</sup> ]	$\nu(\text{CH}_2)$ [cm <sup>-1</sup> ]
I <sup>c</sup>	1:2	0.5	DMF/4-TSA	0.43	1699	2924, 2871
II <sup>b,c</sup>	1:2	0.5	DMF/4-TSA	0.41	-	2921, 2871
III <sup>c</sup>	1:1	1	DMF/4-TSA	0.39	-	2923, 2869
IV <sup>c</sup>	2:1	0.5	DMF/4-TSA	0.54	-	2922, 2860
V <sup>d</sup>	2:1	0.5	H <sub>2</sub> O/DMF	0.33	1702	2922, 2855
VI <sup>d</sup>	1:1	1	H <sub>2</sub> O/DMF	0.20	-	2924, 2879
VII <sup>d</sup>	2:1	2	H <sub>2</sub> O/DMF	0.26	-	2921, 2860

<sup>a</sup> Expressed as g of the recovered derivative per g CMC (on dry mass basis), <sup>b</sup> without 4-DMAp,

<sup>c</sup> partially soluble in H<sub>2</sub>O, <sup>d</sup> soluble in H<sub>2</sub>O.



**Figure 1** FT-IR spectra of CMC and selected CA-CMC derivatives (I, V, VI, VII)

Regardless the low degree of esterification, the CMC derivatives displayed surface-active properties. The surface-active properties of the CA-CMC derivatives were first tested by surface tension. The critical micelle concentration (c.m.c.) and the corresponding minimum surface tension ( $\gamma_{min}$ ) of the selected CA-CMC derivatives were assessed from the logarithmic concentration dependence of surface tension:  $\gamma = f(\log c)$ . The  $\gamma_{min}$  and c.m.c. values are summarized in Table 2. As seen, CA-CMC derivatives do not substantially lower the surface tension of water, because they lowered the  $\gamma_{min}$  from 72.8 only to 61.32 mN/m similarly as unmodified CMC. Moreover, they don't form the micelles in concentration range, except derivatives CA-CMC IV and V. The c.m.c. values ranged between 0.36-1.25 g/l, what is lower as compared with unmodified CMC (2.51 g/l). The hydrophobization effect achieved by the esterification reaction of CMC is expressed by the emulsifying efficiency of the presented derivatives. Emulsifying efficiency of CA-CMC derivatives was evaluated by observing of stability of emulsions of the oil in water (O/W) type during 24 hour measuring the height of oil and cream layer formed on the top of the emulsion (Table 2). In contrast to the unmodified CMC, in none of the derivatives

oil was separated from the emulsion during 24 h. Most of them showed considerable emulsifying properties comparable to that of the control-Tween 20, what related with substitution of CMC by hydrophobic substituents.

**Table 2** Surface-active properties (surface tension,  $\gamma_{min}$ , critical micelle concentration, c.m.c., emulsifying efficiency) of CA-CMC I-VII derivatives and controls

Sample CA-CMC	$\gamma_{min}$ [mN/m]	c.m.c. [g/l]	Oil / Cream layers <sup>a</sup> [mm/mm]		
			$h_1$	$h_2$	$h_3$
I	72.30	none	0/40	0/38	0/33
II	-	-	0/0	0/1	0/13
III	72.52	none	0/38	0/33	0/31
IV	61.32	1.25	0/74	0/47	0/43
V	67.49	0.68	0/0	0/0	0/27
VI	72.68	none	0/0	0/0	0/9
VII	72.26	none	0/0	0/0	0/18
CMC	65.53	2.51	0/7	1/6	6/1
Tween 20			0/0	0/0	0/11

<sup>a</sup> Height of oil and cream layers formed on the surface of the emulsion after 5 min ( $h_1$ ), 1 h ( $h_2$ ) and 24 h ( $h_3$ ); (-) Not determined.

Associative properties of prepared water-soluble derivatives were investigated by viscometric experiments in dilute range. The intrinsic viscosity and Huggins constant were determined for unmodified CMC and

selected CA-CMC derivatives (Table 3). In general, these quantities provide insight to molecular structure and interactions of the polymers in solution. The Huggins constant is generally around 0.4 for non-interacting macromolecules in solvents and can reach values above 5 for highly interacting macromolecules [16]. As seen in Table 3, for each solution of CA-CMC derivatives in dilute range, the intrinsic viscosities are distinctly higher than for the unmodified CMC and  $k_H$  remains relatively high, suggesting hydrophobic intramolecular interaction. These results suggest the existence of intra- and/or intermolecular associates formed, the most probably, due to intramolecular interactions of the hydrophobic substituents [17]. The further studies of CA-CMC derivatives will be focused on antioxidant properties, too.

**Table 3** Intrinsic viscosity  $[\eta]$  and Huggins constant ( $k_H$ ) of CMC and selected CA-CMC derivatives in aqueous chloride medium at 25°C

Sample CA-CMC	$[\eta]$ [dl/g]	$k_H$
V	5.71	0.99
VI	6.93	0.76
VII	3.75	2.00
CMC	3.01	0.10

#### 4. CONCLUSIONS

The presented result confirmed that CA-CMC derivatives can be prepared by esterification of CA with CMC in DMF/4-TSA and H<sub>2</sub>O/DMF media under mild reaction conditions. The achieved degree of esterification of CA-CMC derivatives was rather low. However, it was sufficiently high enough to impart surface active properties of derivatives. All exhibited excellent emulsifying efficiency, which were comparable or even better than that of the commercial synthetic emulsifier Tween 20. The viscometric measurement indicated that the incorporation of cinnamic substituents induces intramolecular associations in dilute solutions. The novel CMC esters represent biosurfactants with potential applications in

manufacture of consumer products and in industrial processes.

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