A COMPARATIVE RHEOLOGICAL STUDY OF SEVERAL COLLOIDAL SYSTEMS BASED ON CELLULOSE DERIVATIVES

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Aiming at diversifying the range of thickening products used in textile printing, several cellulosic ethers (methylcellulose, methylhydroxypropylcellulose and hydroxyethylcellulose) were tested. IR spectroscopy confirmed the chemical structures and the substitution degree of the commercial products Benecel, Benecel M and Tubicoat HEC. Rheological measurements were performed for systems with different concentrations, at temperatures in the normal working range and shear rates ranging from 1 s^{-1} to 243 s^{-1}. The rheological models elaborated on the basis of the resulted rheograms, allowed to calculate the viscosity of parameters' experimental domains. The present study leads to the conclusion that the colloidal systems consisting of 2% methylhydroxypropylcellulose and hydroxyethylcellulose have sufficient consistency to form pastes with adequate properties for textile printing.

Keywords: methylcellulose, methylhydroxypropylcellulose, hydroxyethylcellulose, textile printing

INTRODUCTION

Textile printing, the most versatile method used for introducing colour effects and design onto textiles, represents a local printing or dyeing processes under specific conditions. The printing paste, which transports and locates the colouring substance on the surface of the material, plays a very important role in textile printing. The quality of the printing paste depends on the presence of agglutinant substances, which are used as a carrying medium for the dyes. By dispersion in water, they will form colloidal systems or emulsions, the consistency of which depends mainly on the nature of the agglutinant, temperature and concentration.[1,2]

During the last decades, cellulosic ethers with good water solubility have been intensively studied, to identify new thickening products for textile printing.

The effectiveness of different substances as agglutinants in textile printing is evaluated by the rheological parameters of the printing paste. A rheological study is necessary to define some indices specific to the printing process,[3] such as flowing index, penetration degree, printing accuracy and process yield, to obtain faultless printing.

To select the adequate thickening agents, it is necessary to take into account some technological requirements (other than viscosity), such as print paste stability, good adhesion of the dried thickener film, minimum effect on the colour yield, ease of preparation and removal, acceptable cost. At first, considering several general characteristics (chemical stability, photo- and thermostability), methylcellulose-, methyl-hydroxypropylcellulose- and hydroxyethyl-cellulose-based products were selected.

In the past, the question how the required viscous properties can be achieved was answered on experimental grounds rather than as scientific understanding. Nowadays, when new materials are available, the need for improving productivity and repro-ducibility is increasing, since experience alone is inadequate, so that further rigorous rheological research is required.[4-10]

Based on such considerations, the present study develops a final analysis of the effects of some commercial cellulose ethers on the rheological behaviour of the textile printing paste.

To establish the thickening properties of the selected products, a rheological study was performed, mainly following the viscosity variation of pastes with different concentrations, as a function of the temperature and shear stress specific to the printing equipment.

The comparison of the rheological behaviour of the analysed substances aimed at discovering those with thickening properties corresponding to the printing process, for extending their sphere of applicability to the textile field.

EXPERIMENTAL
Materials and their characterization

The commercial agglutinants used in the experiments are presented in Table 1.

The Benecel-type products have high purity, being available both as granules and as powder. Due to their remarkable rheological properties, they have large applications in cosmetics, pharmaceuticals and food industry. At present, Tubicoat HEC, used as a thickening agent in the textile industry, was selected as reference, because it belongs to the same class of chemical compounds.

IR spectroscopy

As the studied products were available only in commercial forms, they were identified and rigorously characterized by IR spectroscopy, which confirmed their chemical structure.
Transmission spectra were registered with a FT-IR Digilab Scimitar spectrophotometer, in the 4000 cm^{-1}-400 cm^{-1} range, 48 scans being performed with a 2 cm^{-1} step. The spectra in electronic form were processed with a MERLIN-Bio-Rad and Galactic 32 software.

Rheological experiments

Rheological studies were performed on a rheoviscosimeter with concentric cylinders, working at shear rates ranging from 1 s^{-1} to 243 s^{-1}. The flowing properties were set out under conditions of external shear stress, for concentrations between 1 and 10%, and temperatures from 20 to 35 °C. To verify the thixotropy phenomenon, the measurements were performed during the increase and decrease of the shear rate.

Viscosity variation as a function of shear rate was studied at concentrations of 1, 1.5 and 2% for Benecel 424, 324 and 363, at concentrations of 6, 7, 8, 9 and 10% for Benecel M011 and Benecel M021, at temperatures of 20, 25, 30 and 35 °C. The concentrations of 2, 2.5 and 3% and the temperatures of 20, 25 and 30 °C were selected for Tubicoat HEC.

Table 1
Materials

No.	Commercial product	Chemical compound (prospectus)	Manufacturing company	Application fields
1	Benecel 324	methylhydroxypropylcellulose		
2	Benecel 363	methylhydroxypropylcellulose		thickening agent (cosmetics, pharmaceuticals, food industry)
3	Benecel 424	methylhydroxypropylcellulose	*Aqualon*, USA	
4	Benecel M 011	methylcellulose		
5	Benecel M 021	methylcellulose		
6	Tubicoat HEC	hydroxyethylcellulose	Tubingen, Germany	thickening agent (textile industry)

RESULTS AND DISCUSSION
IR spectroscopic characterization of cellulose ethers

For a better identification, characterization and comparison, the absorption spectra of the studied substances and of cellulose have been superposed in the same graph.

All samples have bands characteristic of polysaccharides and of the glucopyranosic ring, respectively.[11-15] The bands specific to cellulose are: 3450-3225, 1620, 1160, 1065-980, 900, 670-665 and 610 cm^{-1}. For the etheric derivatives of cellulose, the characteristic bands are:[16,17]

- for *methylcellulose*: 1320, 1160, 1125, 1075 and 945 cm^{-1};
- for *hydroxyethylcellulose*: 3330, 1355, 1200, 1110-1020 and 910-885 cm^{-1}.

The products based on *methylhydroxypropylcellulose* (Benecel 324, Benecel 363 and Benecel 424) show similar spectra, therefore only the spectrum for Benecel 363 is plotted in Figure 1, the conclusions regarding the assignment of bands and structure being also applicable to the other two products.

The spectra for the products based on *methylhydroxypropylcellulose* (Fig. 1) permit the following observations:

- the amount of absorbed water is lower; the band at 3474 cm^{-1} decreases and the peak at 1620 cm^{-1}, specific to cellulose, disappears simultaneously;

- the number of OH groups decreases, with the same effect of decrease of the band at 3474 cm^{-1};

- two peaks appear: one at 1445 cm^{-1} for δ_{asim} (CH$_3$) and one at 1360 cm^{-1} for δ_{sim} (CH$_3$);

- the peak at 900 cm^{-1}, specific to cellulose, has shifted to 930 cm^{-1} in the case of the studied products.

The products based on *methylcellulose* (Benecel M 011 and Benecel M 021) have similar spectra. Figure 2 presents the spectrum for Benecel M 021, the conclusions on the assignment of the bands and structure being applicable to both products.

The spectra of the products based on methylcellulose (Fig. 2) show the following changes:

- several shifts of bands appeared, such as the band for the OH groups at 3415 cm^{-1} (cellulose) has shifted to 3466 cm^{-1} (studied product); the band for absorbed water at 1620 cm^{-1} (cellulose) has shifted to 1645 cm^{-1} (studied product);

- the amount of absorbed water is lower; the band at 3466 cm^{-1} decreases;

- after etherification, the number of OH groups decreased, as well as the band at 3466 cm^{-1};

- new bands appear: the band at 2837 cm^{-1}, more evident, corresponds to δ_{sim} (CH$_2$), another band specific to δ_{asim}(CH$_3$) at 1456 cm^{-1}, and one for δ_{sim}(CH$_3$) at 1375 cm^{-1}.
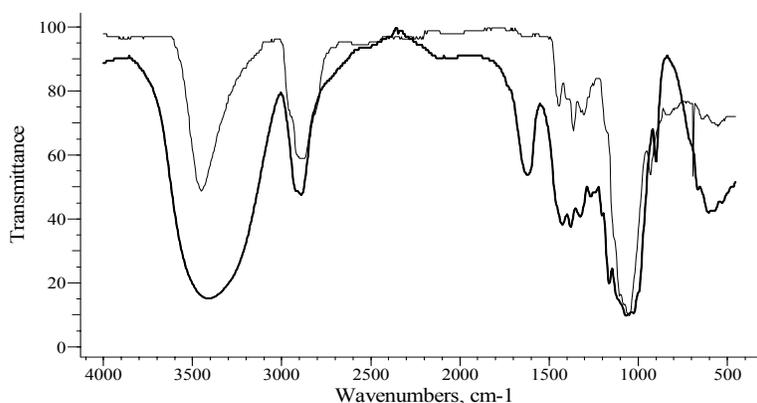
Figure 1: FT-IR absorption spectra for Benecel 363 product (thin line) and cellulose (thick line)
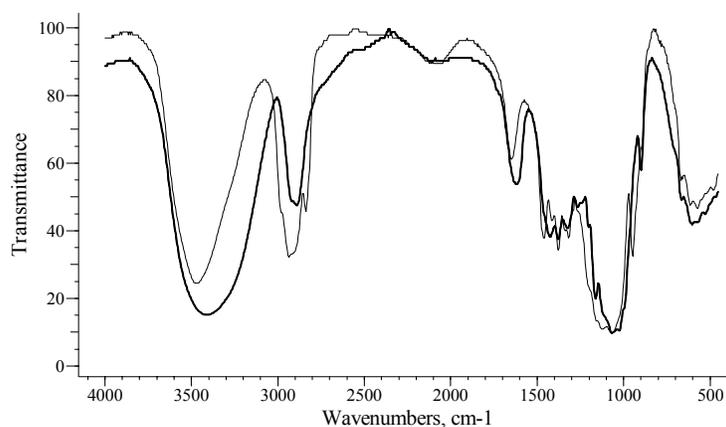
Figure 2: FT-IR absorption spectra for Benecel M 021 product (thin line) and cellulose (thick line)
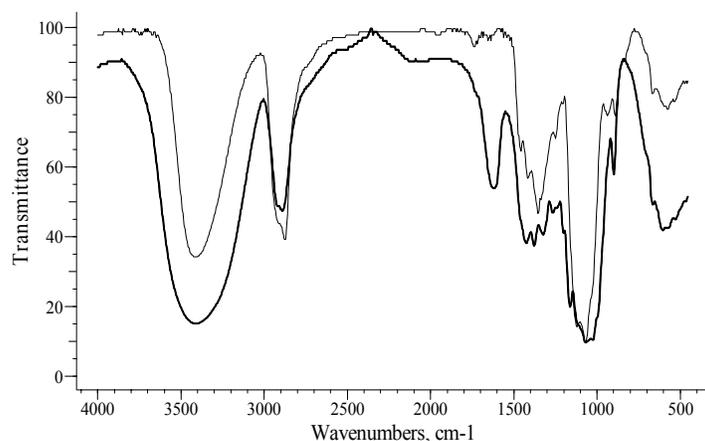
Figure 3: FT-IR absorption spectra for Tubicoat HEC product (thin line) and cellulose (thick line)

The spectra for *Tubicoat HEC* plotted in Figure 3 have the following characteristics:

- the amount of absorbed water is lower; the band at 3410 cm^{-1} decreases and the peak specific to cellulose at 1620 cm^{-1} disappears simultaneously;

- after etherification, the number of OH groups decreases, as well as the band at 3466 cm^{-1};

- a band specific to *hydroxy-ethylcellulose* appears at 932 cm^{-1}; the weak band at 1745 cm^{-1} is due to a mild degradation, leading to C=O groups;

- a weak but distinct band appears at 1456 cm^{-1}, for deformation vibration, for scissoring vibration δ_{sim} (CH$_2$) and a prominent peak may be observed at 2876 cm^{-1}, for ν_{sim} (CH$_2$).

The spectral analysis of the studied thickening products confirmed their structures previously known either from literature or from the documentation of the companies, respectively cellulosic ethers methylcellulose, ethylhydroxypropylcellulose and hydroxyethylcellulose.

Rheological behaviour

Figure 4 plots the rheograms for each experimental temperature value, at all studied concentrations. To assess correctly the type of rheological behaviour, the graphical representations were realised in double logarithmic coordinates.

In all studied cases, viscosity varies linearly with the shear rate increase in logarithmic coordinates. The pronounced decrease (even up to two orders of magnitude), recorded as stress increases, is specific to pseudoplastic bodies.[18-21] The superposition of rheograms, obtained when increasing and decreasing the shear rate, shows the absence of thixotropy.

For this type of rheological behaviour,[22-25] the mathematical Ostwald–de Waele model was considered the most appropriate, as expressed by the equation:

$$\eta = k \cdot (\dot{\gamma})^{n-1} \qquad (1)$$

where η is viscosity (measured in Pa·s), $\dot{\gamma}$ is shear rate (measured in s^{-1}), k is the consistency index (in Pa·s^n), and n is the flowing index (dimensionless).

The model contains two material coefficients. To establish the way in which the considered parameters – temperature and concentration – influence the two indices, the numerical values of the consistency index and of the flowing index from each rheogram were calculated. Data correlation was realized by simple regression, so that the equations with the highest correlation coefficient – either linear equations or second-degree polynomials – were selected.

The flowing index, which expresses the deviation from the ideal behaviour of a Newtonian fluid (n = 1), is highly influenced by concentration and far less by temperature (Fig. 5). For solutions of hydroxy-propylmethylcellulose, the flowing index depends only on concentration. In all studied cases, the variation is linear. The highest deviation from the ideal situation, *i.e.* the lowest value of the flowing index, appears at high concentrations and low temperatures.

For all studied substances, the consistency index, *k,* is influenced by both temperature and concentration, as presented in Figure 6.

Generally, it decreases linearly with the decrease in temperature and increases polynomially as a function of concentration. As this material index offers data on sample consistency, the hydroxymethylcellulose-based pastes (Benecel 324, 363 and 424) can be considered as having a consistency close to the one of the pastes containing the reference Tubicoat HEC, at the same concentration – of approximately 2%. By contrast, the methylcellulose-based pastes (Benecel M011 and M021) reach the reference values at a concentration of approximately 10%.

For a correct assessment of the rheological behaviour, a regression equation was established, expressing the variation of the consistency index and of the flowing index as a function of temperature and concentration, for all studied substances. The equations were meant to be, mathematically, as simple as possible and to have a correlation coefficient very close to 1.

The studied products are part of the same class of chemical compounds (cellulose derivatives), therefore the rheological behaviour appeared as similar, in all cases being possible to maintain the same form of the regression equation for the variation of both indices. The general form of the equation is:

$$z = a + b \cdot x + c \cdot y + d \cdot x^2 + e \cdot y^2 + f \cdot x \cdot y \quad (2)$$

where x = temperature (°C); y = concentration (wt%); z = k (Pa·s^n) or n (dimensionless).

The correlation coefficients for the equation applied to each substance are given in Table 2.

Tables 3 and 4 present coefficients a, b, c, d, e, f, specific to each substance, as well as the variation domains of concentration, temperature and shear rate (in which the rheological equations are valid).
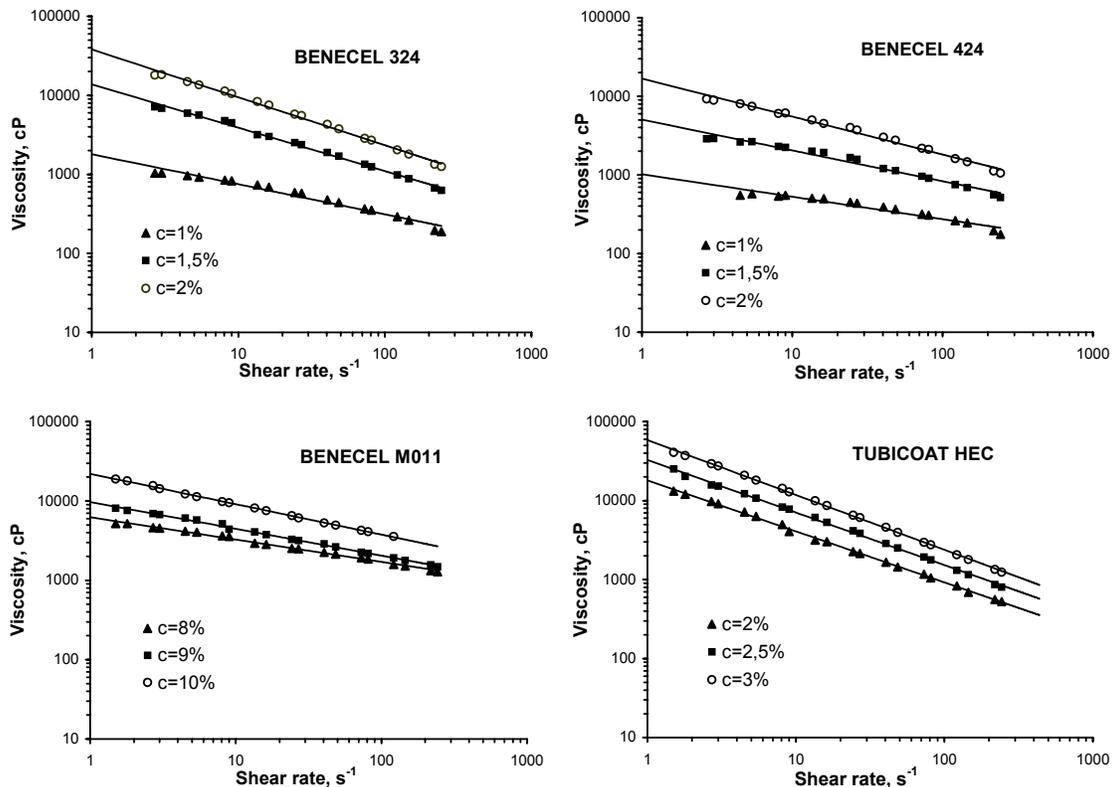
Figure 4: Viscograms obtained at the temperature of 20 °C
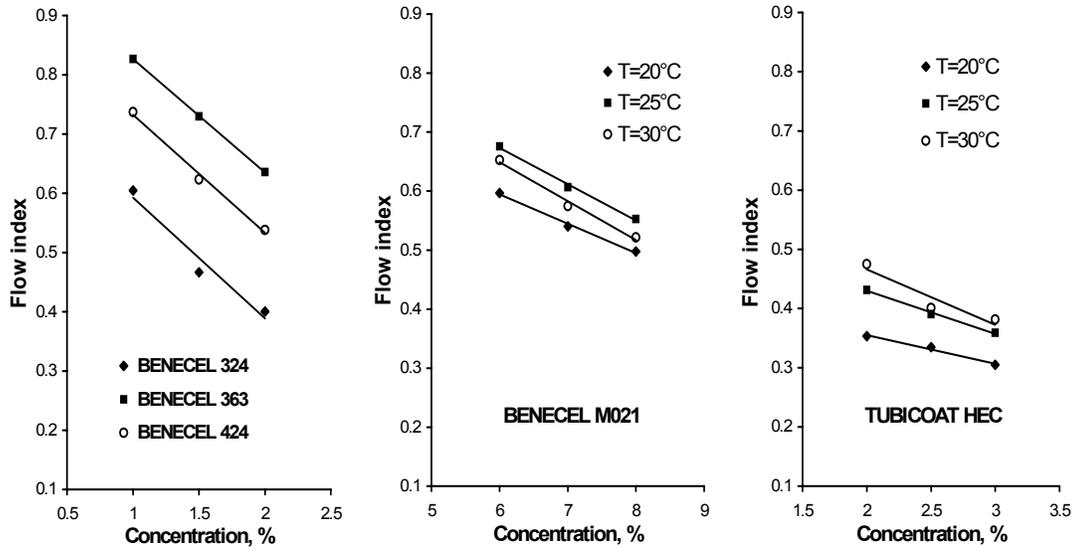
Figure 5: Variation of flowing index n depending on concentration
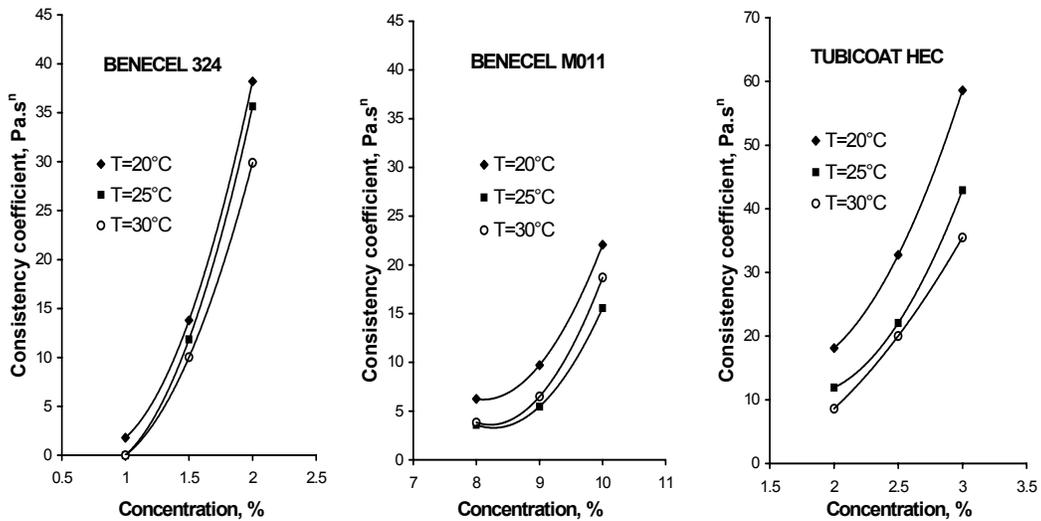
Figure 6: Variation of consistency index k depending on temperature and concentration

The substitution of functions k = f (c, T) and n = f (c, T) in equation (1) leads to the rheological model of each thickener. From a quantitative point of view, the resulted rheological models emphasize the influence of external stress, temperature and concentration, on the viscosity of the printing paste.

The resulted rheological models were verified by comparing them to the experimental data. In Figure 7, the values calculated by equation (1) and those measured at 20 °C, for different concentrations and shear rates, are presented by a continuous line.

The high conformity of the calculated and experimental values proves the adequacy of the rheological model. Therefore, the proposed equations can be used to calculate the viscosity of printing pastes at different temperatures, concentrations and external stress, as required by modern technologies.

Table 2
Correlation coeffcients of specific regression equations

Benecel 324		Benecel 363		Benecel 424		Benecel M 011		Benecel M 021		Tubicoat HEC	
K	n	K	n	K	n	K	n	K	N	K	n
0.997	0.960	0.997	0.999	0.996	0.993	0.985	0.987	0.986	0.977	0.974	0.958

Table 3
Coefficients of equation (2) characteristic of consistency index k

	Benecel 324	Benecel 363	Benecel 424	Benecel M 011	Benecel M 021	Tubicoat HEC
a	-20.72326	3.091292	1.685953	366.34319	158.80843	169.32736
b	2.55466	0.088253	0.4240422	-4.343041	-5.674835	-8.112557
c	-24.7486	-7.578787	-12.887892	-74.296607	-36.650016	-53.8261
d	-0.040986	0.006344	0.0016439	0.0890436	0.134537	0.1320287
e	23.51293	8.26782	12.90493	4.5904824	4.7395886	17.324867
f	-0.55336	-0.389458	-0.501703	-0.048775	-0.312567	0
Concentration, %	1-2	1-2	1-2	8-10	6-8	2-3
Temperature, °C	20-30	20-30	20-30	20-35	20-35	20-30
Shear rate, s^{-1}	3-243	3-243	3-243	1-243	1-243	1-243

Table 4
Coefficients of equation (2) characteristic of flowing index n

	Benecel 324	Benecel 363	Benecel 424	Benecel M 011	Benecel M 021	Tubicoat HEC
a	0.9317	1.0173	0.7968	-1.17241	0.12582	0.10244
b	0	0	0	0.113618	0.081224	0.04585
c	-0.1992	-0.191	-0.2041	0.167209	-0.111925	-0.247233
d	0	0	0	-0.001872	-0.00127	-0.00074
e	0	0	0	-0.009868	0.007127	0.035133
f	0	0	0	-0.002125	-0.00189	0
Concentration, %	1-2	1-2	1-2	8-10	6-8	2-3
Temperature, °C	20-30	20-30	20-30	20-35	20-35	20-30
Shear rate, s^{-1}	3-243	3-243	3-243	1-243	1-243	1-243
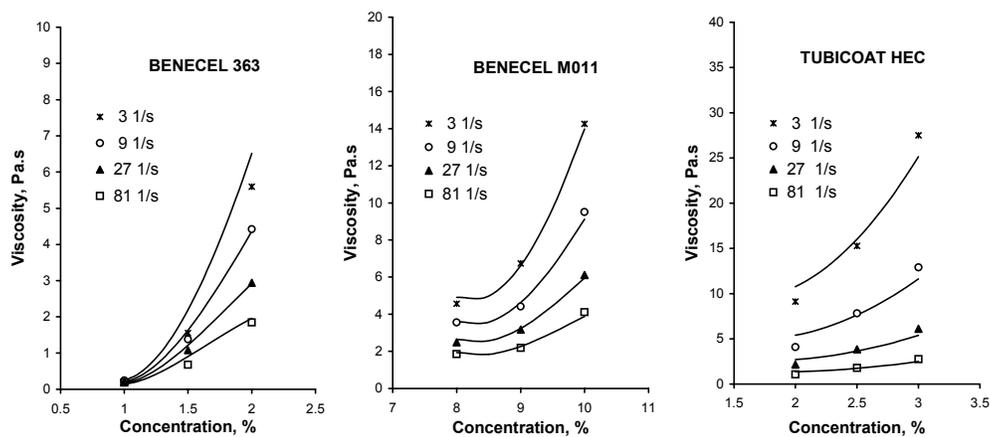
Figure 7: Checking of rheological models for the temperature of 20 °C

CONCLUSIONS

• IR analysis confirmed the chemical composition of the studied substances, respectively methylcellulose, methyl-hydroxypropylcellulose and hydroxyethyl-cellulose.

• The rheograms of all studied pastes evidenced their pseudoplastic-like behaviour:

viscosity decreases with the shear rate increase, its decrease becoming more significant with increasing product concentration.

• The samples underwent continuously increasing, then continuously decreasing stress, yet no hysteresis loops of the significant areas were obtained, which demonstrates the absence of thixotropy.

• The Ostwald–de Waele model was adopted to describe the rheological behaviour. For each paste, at the mentioned temperatures and concentrations, the equations of viscosity variation were found and the values of the consistency index and flowing index were calculated, for obtaining the most simple regression equations with a correlation coefficient very close to 1.

• The regression equations allow the calculation of the optimum concentration of the printing pastes as a function of the working parameters: temperature and stress value, respectively. Moreover, the obtained models can be applied for a quantitative comparison of the different classes of agglutinants used in textile printing.

• Analysis of the obtained rheograms led to the conclusion that the Benecel products with a methylhydroxypropylcellulose structure (Benecel 324, 363, 424) evidence an adequate rheological behaviour for the agglutinant systems used in textile printing, while the methylcellulose-based products (Benecel M 011 and M 021) have moderate viscosities, even if concentration is increased above the economically and ecologically acceptable limits.

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