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Rotational viscometry for the study of urea-formaldehyde resins

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Abstract. Rotational viscometry as a generally recognized method for rheological measurements of non-Newtonian liquids was used for the study of commercial urea-formaldehyde resins. The measurement results were analysed using the power law function with evaluation of the consistency and flow indices. The resins were observed during their storage until alkali-promoted polycondensation led to gelation. It is suitable to differentiate two periods in the course of the polycondensation process – the initial period of slow viscosity growth and the following period of fast structuration. Regularity in the change of values of the flow index, calculated from data obtained with two rotational viscometer models, permits to characterize the flow behaviour of urea-formaldehyde resins in the initial period of polycondensation. The results of the rheokinetic study were compared with the data obtained with standard methods. In the relationships trends were found, which are consistent with conceptions about the formation of the resin structure and processes, occurring during the initial period of polycondensation.

Key words: rotational viscometry, rheokinetics, urea-formaldehyde resins, polycondensation.

1. INTRODUCTION

In all technological processes, in which liquid materials participate, an important characteristic is flowability. For viscosity measurements, many methods and different devices have been used for a long time [1,2]. Both producers and researchers agree that viscosity as a characteristic of fluids is closely associated with the structure of the substance. Nevertheless, flow behaviour is an indirect measure of product consistency and quality. Single-point measurements, which are mostly used for quality control, cannot adequately characterize behaviour and structure–property relationships of non-Newtonian liquids. Therefore the use of multipoint techniques is strongly recommended in studies of materials with complicated structure such as adhesive resins, etc. Mathematical relationships between the viscosity parameters, chemical and physical structure and technological properties of liquid resins are the problems still worth to study.

Urea-formaldehyde (UF) plastics are known since 1915 (in production since 1928) and are till now widely used as adhesive resins in industry. A great progress has been made in the field of study of UF resins thanks to the application of the ^{13}C NMR spectroscopy [3–5]. However, there have been relatively few studies on the rheological behaviour of UF resins and much remains unclear in that field [6,7]. In earlier studies on rheological behaviour of UF resins, made in our laboratory, the industrial resins with a low F/U ratio (1.03–1.08) and laboratory resins with similar standard characteristics were investigated. Rotational viscometry as a generally recognized method for rheological measurements of non-Newtonian liquids was used in these studies. The measurement results were analysed according to the power law relationship between the shear stress τ and the shear deformation rate $\dot{\gamma}$

$$\tau = K\dot{\gamma}^{n}, \tag{1}$$

where K is the consistency index and n is the flow index.

The resins were observed during their storage until alkali-promoted polycondensation led to gelation [8,9].

The purpose of the present study was to examine the possibilities of rotational viscometry to characterize properties of UF resins from the standpoint of structure, molar mass and molar mass distribution. The latter is essential to know, but it is a very complicated phenomenon in case of step-growth polymerization. In this study, a more detailed interpretation of the meaning of the flow index n is presented. The results, obtained with two models of rotational viscometers of similar working principle but of different technical characteristics, are compared.

2. EXPERIMENTAL

Rheological measurements were performed for different batches of six UF resins indicated by numbers from 1 to 6. Resins 1a and 1b were synthesized in our laboratory (300–400 g), 2a, 2b, 3a, 3b, 3c, 4, 5 and 6 are commercial resins. A typical three-step procedure was used by the synthesis of resins 1, 2, 3, 5 and 6, the synthesis conditions (pH, temperature and time) could be different. For comparison, the resin 4 was synthesized without the first hydroxymethylolation step. All resins had the F/U molar ratio within limits of 1.04–1.06. Standard characteristics (Table 1) were obtained by methods described previously [9] and lie in the limits required for low-toxic resins for producing adhesively-bonded wood particleboards (PB).

Two different rotational viscometer models with defined shear rate were used for measurements: Brookfield RVDV-II+ programmable viscometer with small sample adapter and Rheotest-2 (Prüfgerätewerk Medingen). Both viscometers are

Table 1. Standard characteristics of UF resins

Characteristics	Resin									
	1a	1b	2a	2b	3a	3b	3c	4	5	6
pH at 25 °C	8.6	8.2	9.2	8.8	8.8	8.8	8.9	8.8	8.3	9.1
Dry solids, % 105 °C, 3 hours	67.7	70.4	70.1	70.5	69.9	69.6	69.7	69.9	69.5	68.7
Density at 25 °C, kg/m^3	1276	1290	1288	1291	1280	1280	1293	1285	1289	1278
Viscosity at 25 °C, mPa$\cdot$s	417	487	483	377	437	345	382	292	326	451
Gel time at 100 °C, (1% NH_4Cl), s	61.6	63.6	65.5	47	56.2	56.5	54.4	53.4	68.3	54.2
Water tolerance at 25 °C*	3	3	2	2	4	3	3	6	2	2
Solubility in water at 25 °C, % of resin	47.5	54.2	47.8	49.2	53.2	50.0	50.0	58.5	47.6	48.0
Methylol groups, % of dry solids	19.6	17.9	17.3	19.7	18.5	18.1	21.4	20.9	18.2	18.5

* Parts of water to 1 part of resin.

of coaxial-cylinder-type devices but technical parameters, including the size of cylinders, the shape of rotor and the shear rates used are different (spindles No. 21 and 27 with shear rates of 0–186 s^{-1} and 0–68 s^{-1}, respectively, for Brookfield; shear rates of 1–437.4 s^{-1}, for Rheotest-2). Viscosity was measured at 25 ± 0.1 °C. Particular attention was paid to the method of ageing the resin samples [9]. During measurements, requirements of ISO 3219:1993 [10] were followed.

Viscosity change during resin storage was measured and described by a power law function (1) between shear stress and shear deformation rate, which enables direct evaluation of the consistency index K and power law index n [1,8]. The viscosity values extrapolated to zero and to infinite shear rates, $\eta_0\,(\eta_{\max})$, and $\eta_\infty\,(\eta_{\min})$, were also obtained on the basis of the power law

$$\eta = \tau/\dot{\gamma} = K\dot{\gamma}^{n-1}, \tag{2}$$

$$\log\eta_0 = \log K + (n-1)\log\dot{\gamma}, \tag{3}$$

$$\log\eta_\infty = \log K + (1 - n\log(1/\dot{\gamma})). \tag{4}$$

Viscosity value, marked η_{50} and named midpoint viscosity, is the interpolated value of viscosity to torque 50% [8]. All calculations are performed using Microsoft Excel common applications.

3. RESULTS AND DISCUSSION

According to technical requirements, immediately after production the resins have rather similar characteristics (Table 1). It is generally known that some reactions, occurring during resin synthesis, continue at lower temperatures at which they are stored [5]. The result is a change in the macromolecular structure of the resin, which usually is expressed in an increase of the viscosity and leads finally to the loss of flowability (gelation). It has been found that the stability of various types of resins during storage is different [9]. In the present study, the gelation of the resins took place within about 26–42 days (Fig. 1).

The dependence of the viscosity on time is often used for characterization of storage stability of resins. In [6,9,11] the time of gelation was calculated using the dependence of the storage time on reciprocal viscosity η^{-1} by linear extrapolation it to 0. We have found that in the case of storage at 25 °C, the linear dependence seems not to be a good approximation. A better result can be achieved when the straight line is plotted only through the points from the end period of the storage, and the points from the initial period of storage, which deviate from this dependence, are not considered. In Fig. 2, calculation of the gelation time with the same method for resins 3b, 4, 5 and 6 is represented. It is clearly seen that the difference in gelation time among studied resins depends mainly on the duration of the period of storage when the viscosity growth is slow. The same conclusion was drawn in [8,9].

In [8], the dependence of the viscosity on the storage time was described by the power law, using the classical rate equation for the description of the polymer network formation. The viscosity η, the kinetic factor k and the average order of non-linear polycondensation n' were the parameters considered in this approach:

$$\mathrm{d}\eta/\mathrm{d}t = k\eta^{n'}, \tag{5}$$

$$\log(\mathrm{d}\eta/\mathrm{d}t) = \log k + n'\log\eta. \tag{6}$$

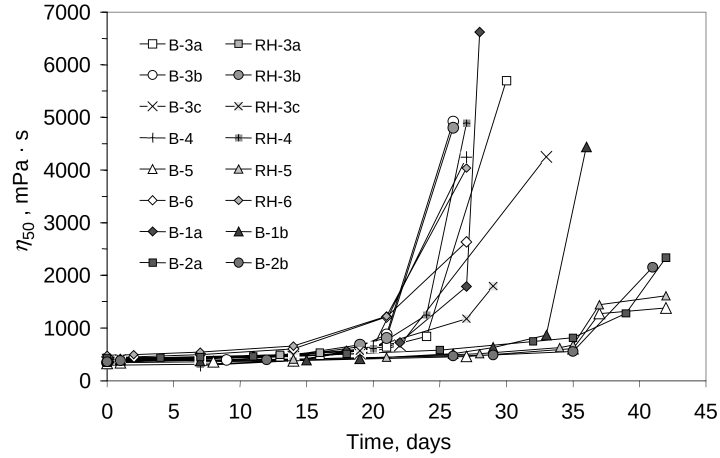

Fig. 1. Dependence of the midpoint viscosity η_{50} on the storage time; B denotes the Brookfield and RH the Rheotest-2 viscometer.

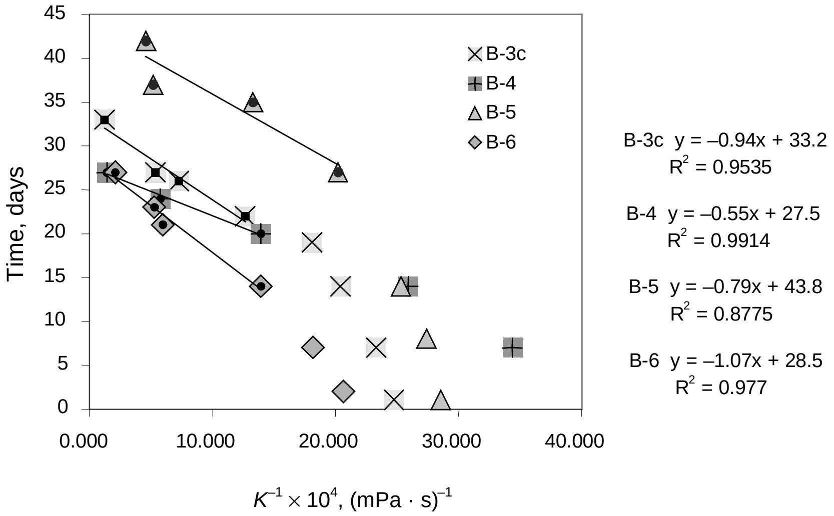

Fig. 2. Dependence of the storage time on K^{-1}; measurements were made with the Brookfield viscometer.

A conclusion was drawn that the behaviour of a resin can be described by power law, but not starting from viscosity values typical for fresh resin (300–450 mPa·s). In this initial period of ageing, the viscosity growth in time is slow, which leads to a great deviation from the power law. Paper [9] confirms the conclusions drawn.

In this study we are concerned with the rheokinetic behaviour of the resins during the initial period of storage, when the viscosity growth is slow. In Table 2, rheokinetic data n, $K(\eta_0)$ and $\eta_{\min}(\eta_\infty)$ are presented.

The flow index n (power law index) is known as “the measure of the degree of non-Newtonian behaviour”. For Newtonian liquids n has the value of 1, and the smaller it is the more non-Newtonian is the liquid [1]. Because of the complicated structure of UF resins it is far from easy to interpret the physical-chemical meaning of n, whereas their non-Newtonian behaviour depends both on chemical reactions and physical interactions between molecules of very different size and reactivity. In the initial period of storage, when the midpoint viscosity η_{50} is less than 1000 mPa·s, the value of n deviates slightly from 1. It means that the non-Newtonian character of the resins is weakly expressed immediately after production and during some time at storage. As one can see from Table 2, data obtained with Brookfield and Rheotest-2 viscometers differ from each other, depending on the differences in shear deformation conditions (the size of cylinders, the shape of the rotor and the shear deformation rates used).

Values of the flow index n, calculated from the data obtained wiht Brookfield and Rheotest-2 viscometers differ from each other by about 0.1 unit. It can be explained by different conditions of deformation. The better or worse agreement

Table 2. Rheokinetic data of UF resins stored at 25 °C (until $\eta_{50} < 1000$ mPa·s and for the last sample before gelation)

Resin	Days	n	$K(\eta_0)$	$\eta_{\min}(\eta_\infty)$	Resin	Days	n	$K(\eta_0)$	$\eta_{\min}(\eta_\infty)$
Brookfield					Rheotest-2				
3a	13	0.992	469	452	3a	7	0.905	662	428
	21	0.984	682	634		13	0.907	721	469
	24	0.968	936	808		16	0.900	793	501
	30	0.773	9305	3270					
3b	9	0.994	407	396	3b	7	0.933	546	401
	14	0.989	492	466		14	0.912	891	463
	21	0.928	1112	792		21	0.883	1229	715
	26	0.677	9820	2222		26	0.644	9230	1789
3c	7	0.995	429	419	3c	7	0.927	615	440
	14	0.986	490	458		14	0.921	690	478
	22	0.953	790	637		22	0.881	1067	622
	33	0.722	8087	2246		29	0.749	3644	1147
4	7	0.998	291	289	4	7	0.882	538	313
	14	0.995	386	377		14	0.880	638	372
	20	0.966	718	619		20	0.856	1083	557
	27	0.768	6988	2397		27	0.680	8561	1963
5	8	0.997	365	360	5	14	0.909	616	405
	14	0.991	395	379		21	0.898	680	425
	27	0.981	495	454		28	0.890	793	479
	35	0.950	752	603		35	0.840	1250	597
	42	0.862	2180	1156		42	0.743	3396	1037
6	2	0.982	484	446	6	2	0.907	721	471
	7	0.974	550	488		7	0.902	798	508
	14	0.954	718	579		14	0.861	1121	591
	27	0.789	4727	1791		27	0.681	7598	1775

between the viscosity values η_0 and η_∞, computed from Brookfield and Rheotest-2 viscometers' data, is partly due to methods used to compute them (see Eqs. (3) and (4)). There is a better agreement between calculated values of η_∞. This value of viscosity, using a simplified explanation, does not involve chain interactions, associative interactions with water and entanglement effects in branched and crosslinked polymer clusters [8]. As an example, the dependence of η_∞ on time in the initial period of storage for some resins is depicted in Fig. 3. From the relationship between η_∞ and flow index n (Fig. 4) we can draw conclusions about changes in the structure of resins due to polycondensation during storage, which are related to the changes in the degree of non-Newtonian properties. Graphs from data of parallel measurements with the two viscometers demonstrate that despite different values of n, trendlines of linear relationships have similar slope. Difference in the trendline slopes of the resins studied is comparatively small but characteristic (Table 3). The greater is the absolute value of the slope, the bigger is the change in non-Newtonian properties of the resin occurring with the rise of viscosity during polycondensation reactions.

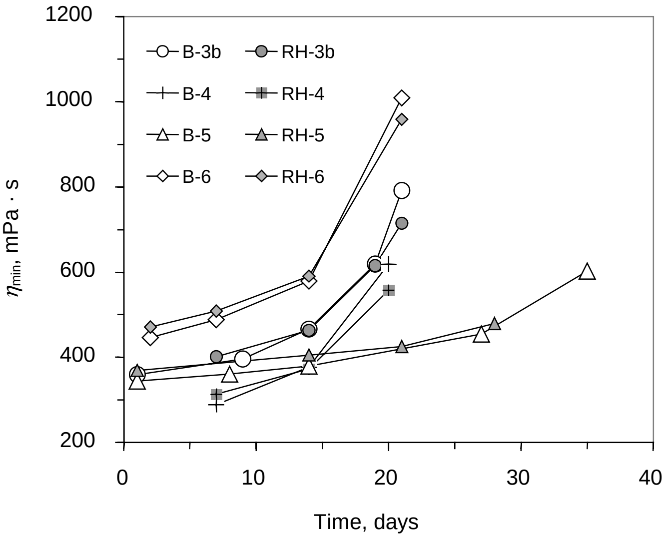

Fig. 3. Dependence of the minimal viscosity η_{min} on the storage time during the initial period of slow viscosity growth for resins 3b, 4, 5 and 6; B denotes the Brookfield and RH the Rheotest-2 viscometer.

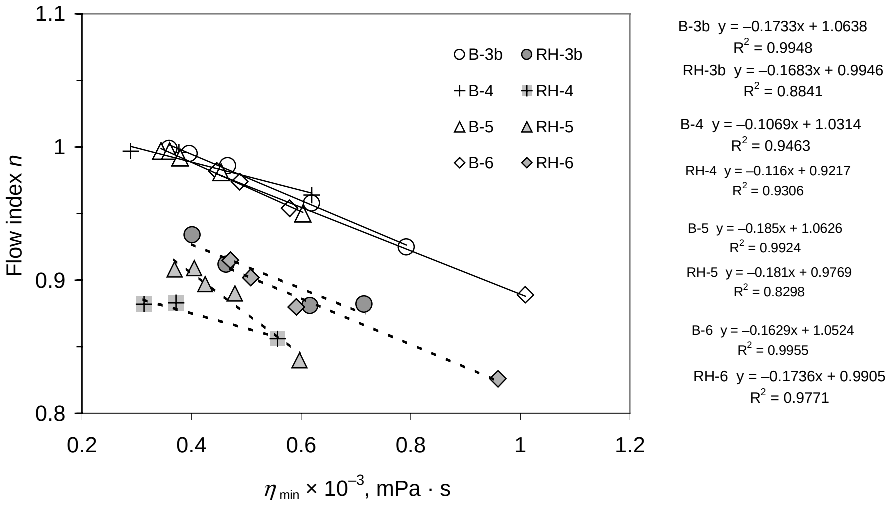

Fig. 4. Relationship between the flow index and the minimal viscosity η_{min} for resins 3b, 4, 5 and 6; B denotes the Brookfield and RH the Rheotest-2 viscometer.

Table 3. Calculated rheokinetic parameters

Resin	Slope of the trendline of the function $n = f(\eta_\infty)$, absolute value	Slope of the trendline of the function $n = f(\eta_0)$, absolute value	Gel time, days
3a	0.060	0.046	30.1
4	0.111	0.064	27.6
6	0.168	0.119	28.5
3b	0.171	0.088	25.5
5	0.183	0.110	43.6
3c	0.204	0.106	32.5

In analogous to Figs. 3 and 4 graphs, where η_0 is used in place of η_∞, the difference in the behaviour of the resins is not so distinctly expressed. Great differences in η_0 values, obtained with different viscometers, disturb finding regularity in rheological properties of resins. The average slope of the function $n = f(\eta_0)$ was calculated for six resins (Table 3). The zero shear viscosity η_0 can be taken as the maximum viscosity of the resin at the determined conversion degree [8] and it includes therefore the maximum influence of physical interactions. This approach seems to be suitable for explanation of the great variation in viscosity measurement results at small shear deformation rates.

As it is seen in Fig. 4, the relationship $n = f(\eta_\infty)$ relates non-Newtonian behaviour of the resin to the rise in viscosity during the polycondensation reaction. Therefore we preferred to use the slope of the linear trendline of the function $n = f(\eta_\infty)$ as an additional rheokinetic parameter for more profound study. Its correlation with values of some standard characteristics of the resins was examined using Fig. 5.

In Fig. 5, the relationship between the values of some characteristics of the resins (Table 1) and absolute value of the slope of the trendline of the function $n = f(\eta_\infty)$ is presented. As the units and values of the characteristics in Fig. 5 are different, the slopes of the trendlines are not absolutely comparable. The positive or negative tendency in the variation of different standard characteristics can be observed with the growth of the slope of the trendline of the function $n = f(\eta_\infty)$. For instance, properties of the resins were selected, which should characterize the structure of the resins more expressively.

The quantity of water needed for coagulation of a colloidal solution is undoubtedly connected with the structure of the system. It is not easy to find exact mathematical relationships due to the complicated structure of the UF resin. At the same time, it is quite understandable that the less is the solubility of the resin in water and water tolerance, the greater is the polycondensation degree and the degree of non-Newtonian behaviour. Graphs in Fig. 5a show the logical trend of this relationship. In practice, water tolerance is one of the characteristics which is often avoided for low accuracy of measurement, but it is worth to pay more attention to the improvement of accuracy of the measurement method.

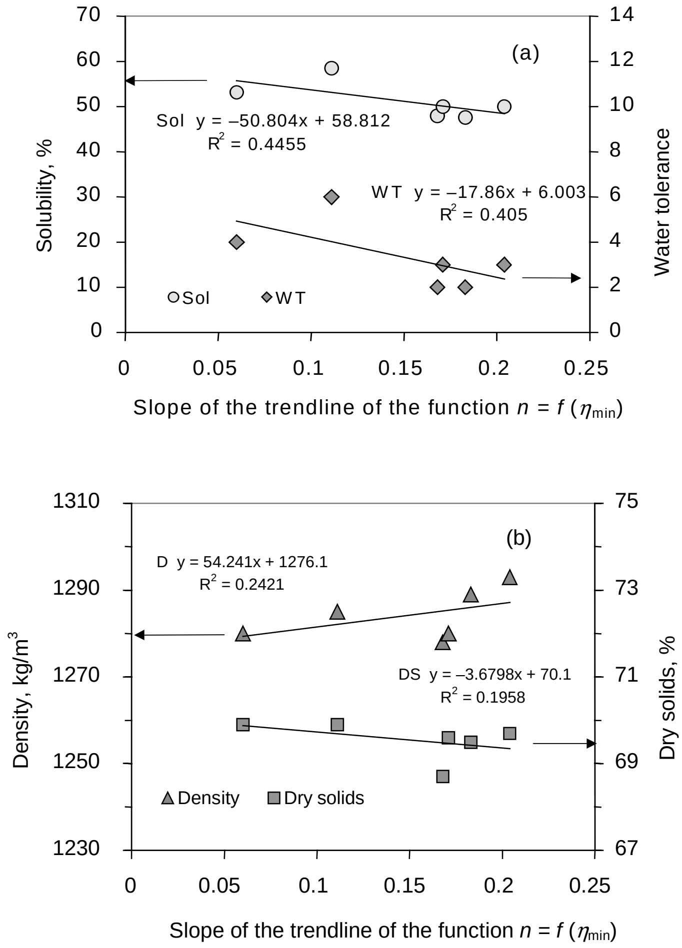

Fig. 5. Relationship between standard characteristics of the resins and the slope of the trendline of the function $n = f(\eta_{\min})$, computed from rheokinetic data; Sol – solubility in water, % of resin; WT – water tolerance, parts of water to 1 part of resin; D – density, kg/m^3; DS – dry solids, %.

For rheological measurements, a particularly important characteristic is the content of dry solids, which has a great influence on the value of viscosity. For this study resins were used with similar content of dry solids, if possible. In Fig. 5b relationship between the slope of the trendline of the function $n = f(\eta_\infty)$ and dry solids and density is presented. Positive trend of density, plotted against the slope of the trendline of the function $n = f(\eta_\infty)$, shows that the more non-Newtonian is the resin, the greater is the value of density (the lower is the concentration of low-molar-mass components, for example, of unbound urea). Contrary to our presumption, the trend of dry solids is negative. From the plot of density against dry solids (Fig. 6) we can see that values of dry solids of the resins 3, 4 and 5 really lie in the limits of the permissible error of measurements (±0.25%), there-

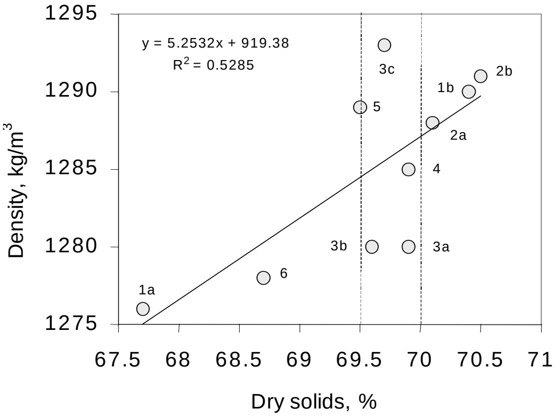

Fig. 6. Plot of the density versus dry solids.

fore variation of density values is not caused by the content of dry solids and may be related to non-Newtonian properties. Content of dry solids of other resins differs appreciably.

In Fig. 7 the relationship between the absolute value of the slope of the trendline of the function $n = f(\eta_\infty)$ and gel time is presented. Neither the gel time evaluated from rheokinetic data nor the gel time measured at 100 °C with 1% NH_4Cl, show noticeable dependence on non-Newtonian behaviour. The same we can say about the concentration of methylol groups, measured iodometrically.

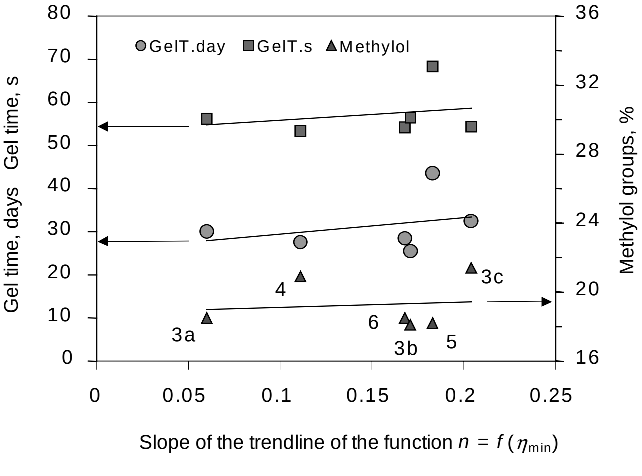

Fig. 7. Relationship between standard characteristics and the slope of the trendline of the function $n = f(\eta_{\min})$ computed from rheokinetic data; GelT.d – gel time evaluated from rheokinetic data, days; GelT.s – gel time at 100 °C and with 1% NH_4Cl, s; Methylol – methylol groups, % of dry solids.

Measurement data shown in Fig. 7 can be expressed as:

GelT.s: $y = 26.72x + 53.17$, $R^2 = 0.066$

GelT.days: $y = 38.28x + 25.58$, $R^2 = 0.101$

Methylol: $y = 3.266x + 18.78$, $R^2 = 0.014$

For comparison, relationships between the gel time, calculated from rheokinetic data and some standard characteristics of the resin are presented in Fig. 8.

Functional relationships are as follows:

GelT.s: $y = 0.300x + 47.75$, $R^2 = 0.126$

Methylol: $y = -0.060x + 21.06$, $R^2 = 0.117$

Viscosity: $y = 1.942x + 333$, $R^2 = 0.051$

Dry solids: $y = 0.052x + 67.81$, $R^2 = 0.228$

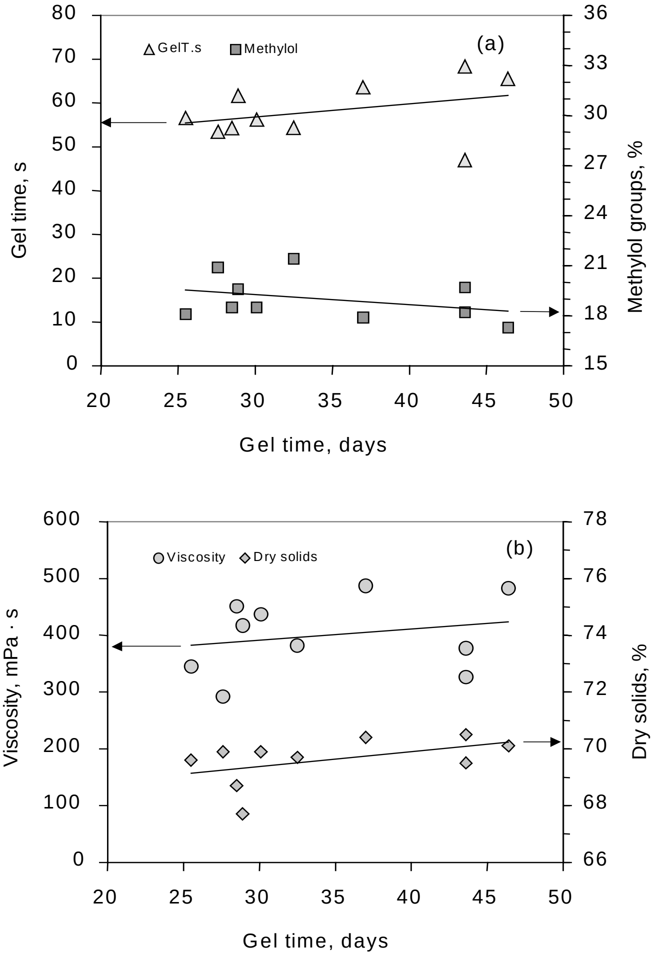

Fig. 8. Correlation of the gelation time, computed from rheokinetic data, and standard characteristics of the resin.

Trends of graphs in Fig. 8a are logical, but correlation is not good, maybe because of great deviation of some resins (gel time at 100 °C), or by too low accuracy of the measurement method (methylol groups). Values of viscosity seem to have no essential meaning on the duration of gelation (stability of the resin). The role of the value of dry solids (or, concentration of water in the resin), needs more profound study.

The fact that in rheokinetic calculations the data from the initial period of storage deviate from regularities, which are valid for the data from the main period of polycondensation, was discussed in a previous study [8]. It was explained by linear polycondensation reactions, proceeding in the initial period mostly in the low-molecular part of the resin. The polycondensation of urea with hydroxymethylurea, formed due to the migration of formaldehyde from the resinous part, is the best example. The reaction mechanism of urea-formaldehyde resins during room temperature storage is analogical to the mechanism of alkaline polycondensation in UF synthesis [4].

4. CONCLUSIONS

Using rotational viscometry for study of different urea-formaldehyde resins, measurement data were systematized using power law functions with the evaluation of the consistency index K and flow index n. It was found that immediately after manufacture, when according to the requirements of users the viscosity of resins is in the limits of 300–450 mPa·s, the rheological characteristics give insufficient information, because in the case of most resins studied the non-Newtonian behaviour, e.g. shear thinning, is weakly expressed. During storage of the resins in alkaline conditions, where both, chemical and physical, structures change, their rheological characteristics become more differentiated.

It is suitable to differentiate two periods of the gelation process – the initial period of slow viscosity growth and the following period of fast structuration. The change in the values of the power law index n of resins in the initial period is not great. Values of n, calculated from data obtained with two models of rotational viscometers, may be different, but the regularity in their variation is similar. It gives the opportunity to characterize the non-Newtonian behaviour of the resins using measurements during a relatively short time.

Rheological characteristics are mostly useful for the comparison of UF resins, which have relatively similar standard characteristics, particularly the F/U molar ratio and content of dry solids. For rheokinetic calculations, measurement data of controlled accuracy are needed.

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Rotatsiooniviskosimeetria karbamiidformaldehüüdvaikude uurimiseks

Aime Suurpere, Peep Christjanson ja Kadri Siimer

On kirjeldatud rotatsiooniviskosimeetria kasutamist tööstuslike karbamiid-formaldehüüdvaikude vanandamise uurimisel. Mõõtmistulemusi on töödeldud astmefunktsiooni abil, arvutades konsistentsi ja voolamise indeksid K ja n. On näidatud, et polükondensatsiooniprotsessis on otstarbekas eristada esialgset aeglast viskoossuse tõusu järgnevast kiirest struktureerumisest. Reokineetilise uuringu tulemusi on seostatud karbamiidformaldehüüdvaikude standardanalüüsi näitajatega.