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Viscosity and Surface Properties of Melamine-Formaldehyde Resin Composition

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The viscosity and wetting properties of aqueous melamine-formaldehyde resin (MFR) solutions for the decorative paper impregnation were investigated. It was determined that the flow behaviour of MFR solutions under different rotational speeds is close to that of Newtonian. The increase of temperature and the decrease of resin solid content decrease solution viscosity. The addition of titanium dioxide (TiO_2) suspension as filler increases viscosity of resin solution, but decreases intensity of viscosity anomalies. The dynamic wetting properties of MFR solutions depend on the solution solid content, TiO_2 and the amount of wetting agent. The dilution of MFR solution from 60 % down to the solid content of 52 % only insignificantly decreases MFR solution surface tension. The addition of wetting agent and TiO_2 suspension results on the wetting properties improvement. High intensity changes of the MFR solution wetting properties were found up to 0.2 phr of wetting agent.

Keywords: melamine-formaldehyde resin solution, filler, titanium dioxide, viscosity, wetting, surface tension.

1. INTRODUCTION

Resin impregnated paper is often used as a decorative and protective laminate for composite wood panels. The manufacture of such laminates commonly involves impregnation of paper in paper treater. Usually for these purposes compositions based on thermosetting resin, which exhibits high chemical and mechanical resistance together with hygienic properties, are used [1 – 5]. Nowadays one of the most popular materials conforming above listed requirements is melamine-formaldehyde resin (MFR) that turns into amino plastic after the thermo-curing [6, 7].

The development of the equipment and the demand for the faster technological process requires not only high thermo-curing reaction rate but also higher sorption rate of the resin solution into the internal layers of the paper backing [8 – 10]. Though there are some theories describing the possibilities of changing above mentioned parameters by the addition of various additives and varying of technological regimes, but up to now universal rules for selection effective composition and technological regimes in order to reach required properties of impregnated paper laminates have not been found.

It is known that the quality of the impregnated paper is highly dependent on the rheological and surface properties of resin solution [3, 4]. High viscosity solution slows down the impregnation process due to the low wetting and sorption properties. That is unacceptable for the modern high speed impregnation channels.

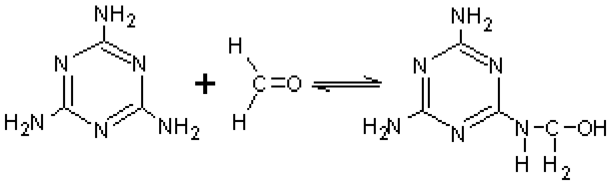
MFR composition is high solid content solution and the dilution in order to improve its sorption properties is necessary. Besides, the impregnation process proceeds at the temperature higher than ambient. That changes the rheological and surface properties of solution and they do not coincide with that stated in the material data sheets. For this reason it is often difficult to regulate impregnation process and achieve satisfactory wetting and sorption quality.

The modification of solution rheological and wetting properties can be achieved using different additives, e. g. wetting, release agents, fillers, etc. [11 – 16].

The goal of this investigation was to identify viscosity and wetting properties changes in dependence of the MFR solution composition and concentration.

2. EXPERIMENTAL

For investigations the commercially available melamine-formaldehyde resin aqueous solution PD-30 (purchased from ZTS ERG Pustkow, Poland) with solid content of 60 % was used. The melamine-formaldehyde resin was obtained via formaldehyde addition reaction with amino groups of the melamine with the formation of N-methylol groups [6]:



Wetting properties of MFR solution were changed via addition of the wetting agent (WA) *Deurol MA 5-F* (Deurowood, Austria), which represents mixture of anionic surfactants and does not include alkylphenol ethoxylates. This agent acts not only as water surface tension reducer, but also as anti-adhesive additive which prevents the undesirable adhesion between touching layers of coated material, such as occurs under moderate pressure and heat during curing and embossing procedure of impregnated paper laminate.

As filler titanium oxide TiO_2 water based dispersion *Tabersperse White* 1057 (Tabercolor, Spain) with solid content of 50 % was used to modify aesthetic properties of the composition. The stability of dispersion was ensured

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using <2.5 % of ester of monophenolmethylene poly(ethylene glycole) as dispersing agent.

The composition constituents and their contents are presented in Table 1.

Table 1. Composition of the modified MFR

Component	Content, phr
MFR PD-30	100
Dilutant (water)	5 – 15
Wetting agent MA-5F	0.1 – 0.5
TiO_2	2 – 7

Viscosity measurements were carried out using rotational viscometer Brookfield DV-II, which enables to measure fluid viscosity in the range of rotational speed from 0.1 rpm up to 200 rpm. This device measures Brookfield viscosity at fixed rotational speed by driving a measurement tool standard spindle LV-1, immersed in the test fluid, through a calibrated torsion spring. The temperature of MFR solution varied from 20 °C up to 40 °C. Rotation speed of the axis varied from 10 rpm up to 200 rpm.

Dynamic surface tension of liquids γ_s was measured as a function of time. For this purpose tensiometer DCAT 21 (DataPhysics Instruments GmbH, Germany) was used and Wilhelmy Plate method was applied (Fig. 1). It employs a microroughened platinum iridium plate (19.90 mm in width and 0.20 mm in thickness), attached to a microbalance. The surface tension measurements were based on weight determination. As a result of test, the average value of six measurements was used.

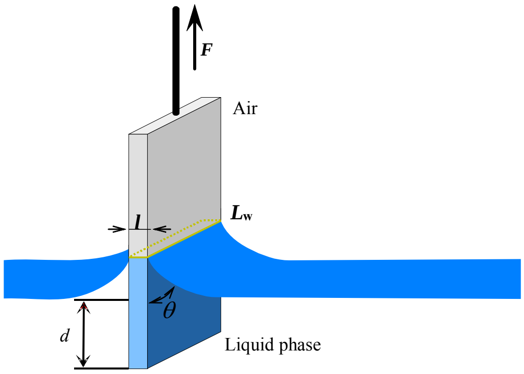


Fig. 1. Schematic representation of Wilhelmy plate method

In this technique the plate is suspended at the interface and maintained in this position by a force that balances the weight of the plate and the meniscus force of the liquid acting on the lower edge of the plate. This force is proportional to the interfacial tension as described by:

$$\gamma_l = \frac{F}{p \cdot \cos\theta}, \quad (1)$$

where F is force measured by using a microbalance, p is perimeter of the three-phase contact line $l \cdot L_w$, θ is the contact angle measured for the liquid meniscus in contact with the object surface. Repeated cycles of immersion and emersion were performed at a rate of 1 mm/s. Immersion depth of the plate was $d = 10$ mm.

The analysis of the adsorption curves is based on the change of the concentration of liquid molecules in the *gas-liquid* interface during the certain period of time. Modifying additives enabled to change the dynamic surface tension of the composition. The phenomenon is observed more clearly when the interaction forces between the dissolved substance (e. g. resin) and the solvent are strongly different [17].

3. RESULTS AND DISCUSSIONS

The influence of rotational speed of the viscometer spindle and solid content of the MFR composition at various temperatures on the solution viscosity is presented in Figure 2. As it can be seen, the increase of test temperature and the decrease of solution solid content decreases solution viscosity. The decrease of the solid content from 60 % down to 52 % at 20 °C decreases the dynamic viscosity η in 3.3 times (Fig. 2, a). This tendency remains when temperature was increased from 20 °C up to 30 °C, also. In this case the Brookfield viscosity of the 52 % solution is 2.6 times lower than that of 60 % (Fig. 2, b). Comparing the dynamic viscosity curves plotted in Figure 2 (a – c) it is evident that an increase of temperature decreases viscosity of a liquid. Besides, increase of the solution temperature decreases influence of solid content. As shown in Fig. 2, c, viscosity curves are plotted close to each other.

The observed changes can occur not only due to the decrease of intermolecular interaction after solution dilution, but due to the increase of molecules thermal motion after increasing of test temperature also [14].

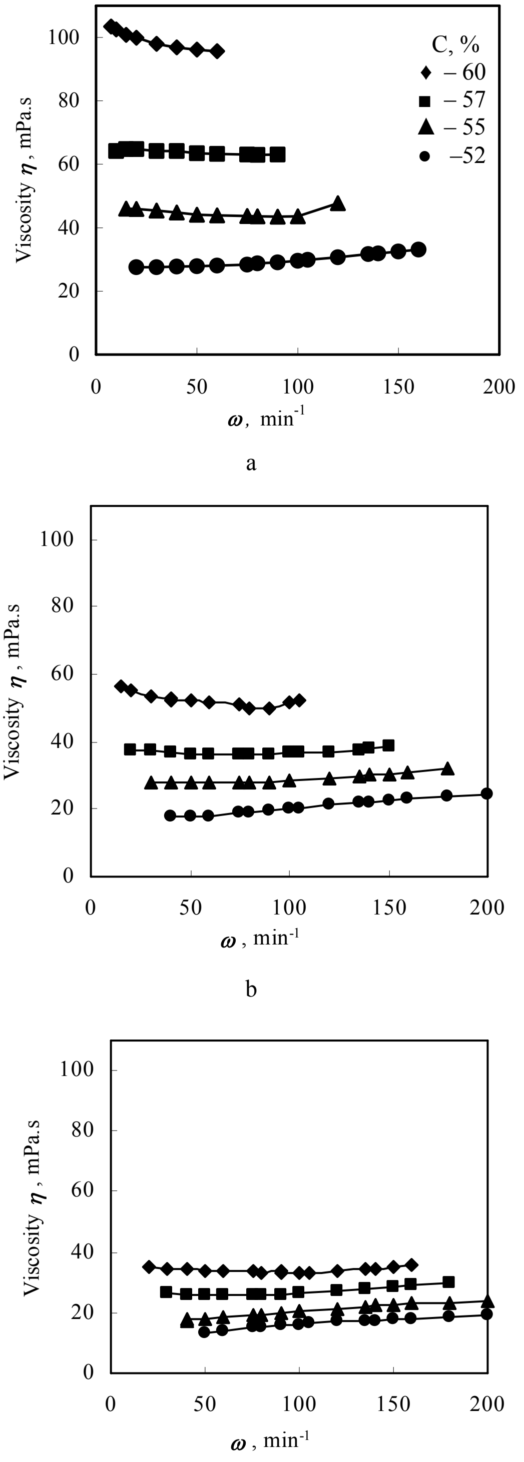
Therefore, it can be presumed that increasing the temperature and decreasing the solid content can enhance the sorption ability of the resin into the paper substrate.

Only insignificant viscosity anomalies were found for MFR solutions. In Table 2 viscosity index values for MFR solutions calculated as viscosities ratio at high rotational speed (100 s^{-1}) and two times lower (50 s^{-1}) are presented. As it can be seen index values for higher solid content solutions (55 % – 60 %) are close or equal to 1. That indicates that MFR solution structure is stable under different loading conditions that are typical for Newtonian fluids. The viscosity of lower solid content ($C = 52$ %) solutions increases when rotational speed increases. This effect intensifies with the increase of temperature that suggests the existence of some weak associations in the solutions.

The viscosity dependence on the rotational speed is also observed in MFR solution modified by TiO_2 suspension (Fig. 3). However, the effect of TiO_2 content on the viscosity changes is insufficient. It may be supposed that observed viscosity enhancement is due to the induction of structural reinforcements of the association complex, i. e. increase of local alignments and large number of favourable interactions [18 – 20].

The addition of TiO_2 suspension and the increase of rotational speed also can lead to the creation of aggregates and clusters of filler particles. Insignificant changes in viscosity indicate that size of over all created structures is only slightly influenced by the TiO_2 content. Another reason of the viscosity increase can be appearance of friction between MFR molecules and filler particles surfaces [21].

Data presented in Table 3 indicates that the viscosity behaviour for filler modified is similar to that of unfilled solution with solid content of 52 %. At rotational speed of 100 rpm the increase of viscosity is not higher than 5 %, but the increase of rotational rate for two times increases viscosity for about 26 %. That indicates on the decrease of intensity of viscosity anomalies.



a

b

c

Fig. 2. Brookfield viscosity at different rotational speed *vs* melamine-formaldehyde resin solution solid content and temperature T, °C: a – 20; b – 30; c – 40

Table 2. The influence of solid content C and temperature T on the MFR solution viscosity index

Temperature T, °C	$VI = \frac{\eta_{\omega=100\,\mathrm{min}^{-1}}}{\eta_{\omega=50\,\mathrm{min}^{-1}}}$, at C, %:			
	52	55	57	60
20	1.07	1.09	1.00	1.00
25	1.04	1.00	0.96	0.96
30	1.11	1.00	1.03	1.00
35	1.20	1.04	1.03	0.86
40	1.24	1.17	1.00	0.97

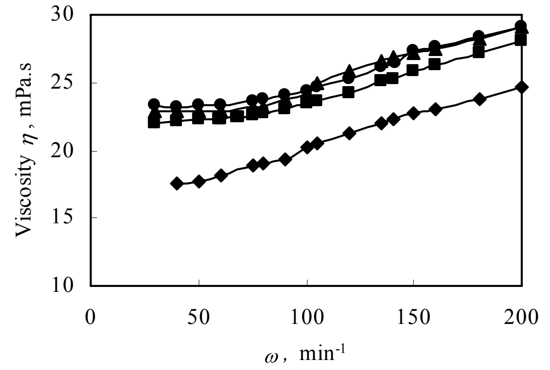


Fig. 3. Brookfield viscosity of resin solution at different rotational speed ω *vs* TiO$_2$ content φ, phr (♦ – 0 , ■ – 2, ▲ – 5; ● – 7) at C = 52 % and T = 30 °C

Table 3. The influence of filler content on viscosity index *VI* of the resin solution

VI	TiO$_2$ content			
	0	2	5	7
$\frac{\eta_{\omega=100\,\mathrm{min}^{-1}}}{\eta_{\omega=50\,\mathrm{min}^{-1}}}$	1.11	1.05	1.04	1.04
$\frac{\eta_{\omega=200\,\mathrm{min}^{-1}}}{\eta_{\omega=50\,\mathrm{min}^{-1}}}$	1.39	1.27	1.26	1.26

Generally, impregnation involves dynamic wetting process. In this study this process was analyzed according to the changes of time dependent surface tension-time curves (adsorption curves), obtained by Wilhelmy balance method. The influence of both resin solid content and composition on the dynamic surface tension γ_1 was investigated. From the data presented in Table 4 can be stated that surface tension is constant as the solid content of MFR changes from 52 % up to 60 %. However, as will be shown later influence of wetting agent and TiO$_2$ or both of them is remarkable.

Table 4. The influence of solid content on the surface tension γ_1 of MFR aqueous solution

MFR solution concentration C, %:	52	55	57	60
Surface tension γ_1, mN/m	64.27	61.34	62.39	64.37

Figure 4 shows the changes of dynamic surface tension of aqueous resin solutions in dependence on the WA content in 0 s – 100 s time period. As aqueous resin solutions are multi-component composition, dynamic surface tension γ_1 exhibits a sigmoidal character of time dependence.

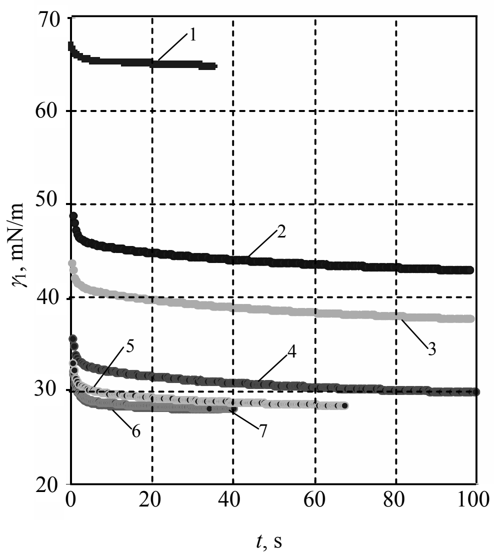


Fig. 4. The changes of resin solution ($C = 52$ %) surface tension γ_1 in time *t vs* wetting agent amount (phr): 1 – 0; 2 – 0.05; 3 – 0.1; 4 – 0.2; 5 – 0.3; 6 – 0.5; 7 – 0.7

The change in surface tension can be divided into two phases: the initial phase (up to 10 s) shows a very intensive rate of surface tension change, which tapers off in late phase. It can be presumed that interaction forces between the resin molecules are higher than the forces between the water and the resin molecules. Consequently, the molecules of the water expel the molecules of the resin to the surface. That is why the latter resin molecules concentrate in the air/liquid interface over the time during the process of adsorption. After the certain period of time the adsorption process slows down with the increase of resin molecules concentration on the surface. New molecules find it more difficult to get to the surface at higher viscosity of the surface layer. Unmodified resin solution with solid content of 52 % the surface tension equilibrium ($\gamma_1 = 61.4$ mN/m) reaches after 35 s – 70 s.

For the given resin solid content (52 %) $\gamma_1(t)$ curves display significant dependence on the WA content ϕ_{WA}. The equilibration time vary from approximately 100 s at lower WA content (0.05 phr – 0.2 phr) up to 40 s – 70 s at the higher one. The results of surface tension versus time show that curves at WA content of 0.05 phr – 0.7 phr are plotted under curve for WA content of 0 phr.

The remarkable effect on the equilibrium surface tension was observed after the addition of 0.05 phr of WA. In this case the surface tension decreases from 64.64 mN/m down to 43.06 mN/m. Further increase of the WA up to 0.3 phr markedly decreases the surface tension values (down to 28.27 mN/m). Higher amounts of WA do not have considerable influence on the surface tension. As can be seen, resin composition containing 0.5 phr – 0.7 phr of WA show very similar surface tension behaviour in time. It is evident that the surface tension of the resin solution can be lowered using effective amount (0.2 phr – 0.3 phr) of WA. Therefore, the use of higher amounts of wetting agent is unreasonable.

As can be seen from Fig. 5, $\gamma_1(t)$ curves of MFR with TiO_2 are situated below this for the resin solution without filler. It is evident that the surface tension equilibration duration insignificantly increases (from 38 s up to 43 s), when the amount of the filler TiO_2 is not higher than 2 phr.

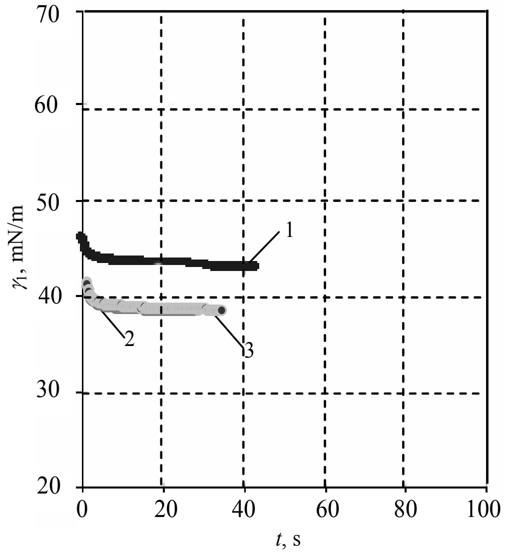


Fig. 5. The changes of resin solution ($C = 52$ %) surface tension γ_1 in time *t* vs TiO_2 content, phr: 1 – 2; 2 – 5; 3 – 7

At the higher filler amounts the equilibration duration decreases, and reaches 25 s at 7 phr of TiO_2.

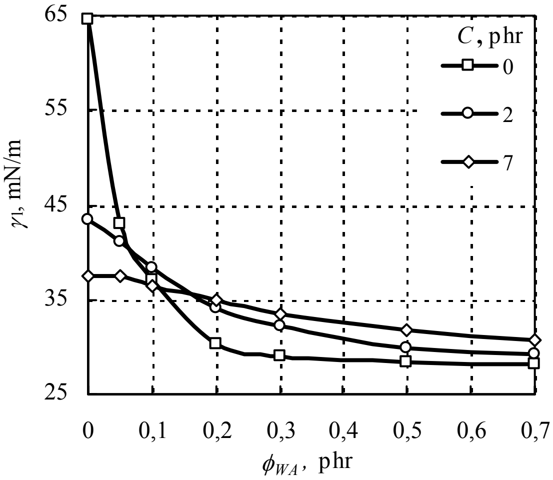


Fig. 6. The influence of the wetting agent and TiO_2 content on MFR solution surface tension γ_1

The investigation of the TiO_2 content influence on the MFR equilibrium surface tension values showed that the filler decreases the equilibrium tension values (Fig. 6).

It can be seen that 2 phr of TiO_2 decreases the surface tension from 64.4 mN/m down to 43.4 mN/m. The further increase of TiO_2 lowers the surface tension insignificantly. The addition of 7 phr of the filler decreases surface tension approximately down to 37.47 mN/m.

Thus, it is possible to use TiO_2 suspension not only for the improvement of the decorative properties, but also for the optimization of wetting properties of the resin.

The investigation of the influence of both additives (WA and filler) on the surface tension values showed that WA marginalizes the influence of the TiO_2 (Fig. 6). The optimal content of WA and TiO_2 is 0.7 phr and 7 phr, respectively. In this case the surface tension values are marginally higher than that of MFR modified only with WA.

4. CONCLUSIONS

The viscosity of the melamine-formaldehyde resin composition depends on the solid content, temperature, composition, and deformation speed of the solution. Unmodified resin solutions behaviour is similar to Newtonian liquids. The viscosity decreases with the decrease of the solution concentration and test temperature. The addition of TiO_2 emulsion increases the viscosity of the solution, but decreases intensity of viscosity anomalies.

The influence of resin solid content on the dynamic surface tension is negligible. Modifying additives changes the dynamic surface tension of the resin solution. Both wetting agent and TiO_2 filler decrease the surface tension and improve wetting properties of resin solution. The efficiency of wetting agent on the wetting properties of unmodified resin is higher than that of obtained for only TiO_2 modified and both wetting agent and TiO_2 modified. The best wetting properties has MFR solution composition consisting of 0.2 phr of WA. Filled composition shows best wetting properties when contents of both WA and TiO_2 are 0.7 phr and 7 phr, respectively.

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