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The storage stability of melamine formaldehyde resin solutions: III. Storage at elevated temperatures

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Abstract

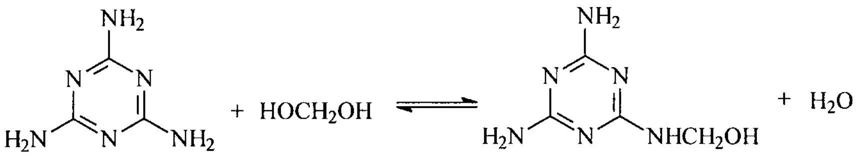
The possibility of storage of melamine formaldehyde (MF) resin solutions at elevated temperatures is examined. A series of MF resin solutions with various formulations were synthesised and storage stability was studied at room temperature and 50°C. In general, the stability at 50°C was higher over a much broader range of reaction times when compared with storage stability at room temperature. The storage of MF resin solutions at elevated temperatures offers many advantages like the ease of resin production on large scale and high reproducibility of storage stability. Further, it is shown, by means of ^{13}C-NMR and light scattering analysis, that the chemical structure and molecular weight are identical at the point of instability at 50°C irrespective of the initial degree of condensation i.e. reaction time. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: MF resins; C-NMR; Storage stability

1. Introduction

Melamine formaldehyde (MF) resins are one of the most important industrial adhesives used in a number of applications such as paper laminates or as moulding compound in dinnerware. Generally, MF resins are produced at a high solid content ($>$ 50%) in water as the reaction medium. The storage stability of aqueous MF resin solutions is limited at room temperature (RT); during storage of a transparent MF solution turbidity develops at a certain point in time and viscosity starts to increase. This phenomenon hampers the practical applicability of MF systems, for example, for paper impregnation purposes. In order to prolong the storage stability of MF solutions, it is a prerequisite to elucidate the mechanism of instability. In the first part of a series of publications on this subject, we reported on the processes that control the storage stability of MF resin solutions [1]. In the second part, we monitored the instability process with the aid of time resolved light scattering experiments combined with low-resolution relaxation ^{1}H-NMR measurements [2]. In the present article, we will discuss a noble approach to prolong the storage stability of MF resin solutions. Firstly a short summary of MF chemistry [3–6] is discussed below.

The reactions occurring during synthesis of MF resin can be roughly divided in two different stages; methylolation and condensation. At the start of the resin synthesis, melamine reacts with formaldehyde leading to the formation of a series of nine different methylolmelmaine. In reaction I, the first addition reaction of formaldehyde to melamine is shown.



Reaction I

The second step of reaction involves condensation, i.e. bridge formation, between the various (methylol)melamines leading to the formation of a large number of different oligomers. In principle, two different types of bridges may form during the condensation step, the ratio of which depends

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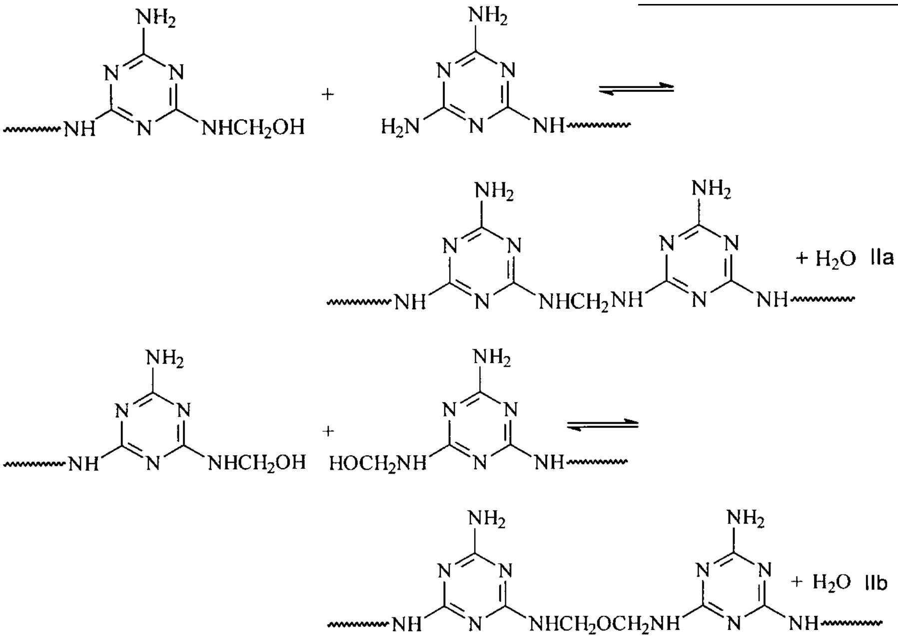
strongly on pH. At relatively low pH (7–8), methylene bridges are formed (reaction IIa) whereas at pH values above 9 the formation of ether bridges is favoured (reaction IIb) [7].



Reaction II

In contrast with the common practice, i.e. storage at RT, it is proposed that storage of MF solutions at elevated temperatures could be in a number of instances quite beneficial and result in longer storage times when compared with storage at RT. This idea has emerged from a fundamental understanding of the mechanism of instability of MF resin solutions. According to previous studies, the limitation of the storage stability is not caused by the continuation of the condensation reaction at RT, but by physical aggregation of MF species. In fact, within a certain range of degree of condensation, the process of aggregation leads to the formation of a physical gel. As revealed by relaxation ^{1}H-NMR, the MF aggregates will break up at a temperature above 50°C. At approximately 50°C, the turbid MF solutions will become clear and of low viscosity again. This is because of the fact that the intramolecular forces, operative in MF systems (mainly hydrogen bonds) are quite weak in nature and will be destroyed at elevated temperatures. Based on these findings it can be anticipated that, if MF solutions are stored at, for example, 50°C instead of RT, the aggregation process will not take place at all. Consequently, the MF resin solution would be, in principle, for an infinite time stable provided that no chemical conversion would take place. In reality, however, the condensation reaction will continue gradually at 50°C leading finally to the occurrence of the process of liquid–liquid phase separation [8] at this temperature. At the point of phase separation there is an equilibrium, i.e. equal chemical potentials, between a nearly pure water phase, containing a few chains, and a polymer-rich phase. Hence it follows that the ideal storage temperature should be high enough to prevent the aggregation process and sufficiently low to slow down the bridge formation for as long as possible.

Here we will compare the storage stability of a series of MF resins, with different formulations as a function of reaction time at room temperature and at 50°C. With the aid of ^{13}C-NMR measurements, the chemical structure of MF resins, with increasing degree of condensation, is analysed just before the occurrence of the process of liquid–liquid phase separation at 50°C. In order to determine the relative weight average molecular weights (M_W) of MF samples, light scattering measurement's were conducted.

2. Experimental

The resin synthesis and raw materials. The resin synthesis was carried out in a double wall reaction vessel, heated to 95°C with the aid of a water thermostat at 95°C. The reaction vessel was equipped with a condenser and a mechanical stirrer.

The quality of the melamine was standard DSM grade (99.8%). Neste supplied the formalin solutions. The pH of the formalin solution at RT was adjusted, in all cases, using a NaOH solution (1 N).

The resin solutions were stored in sealed bottles at both RT (22°C) and 50°C. The storage stability is defined as the time from resin preparation till the solution became opaque. The turbidity was judged by necked eye.

The pH measurements. The pH electrode (METTLER

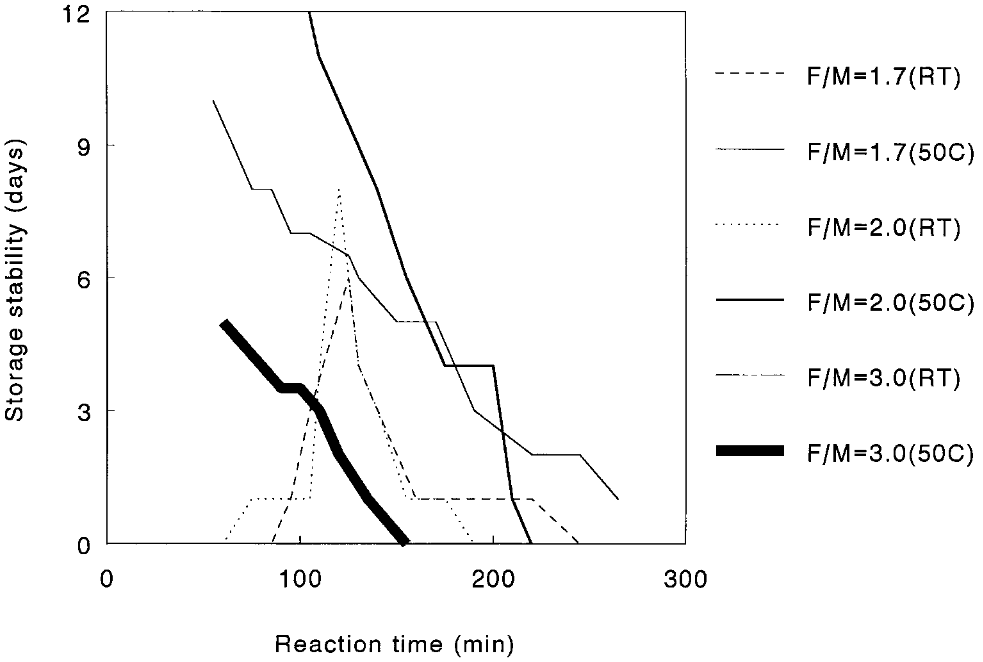


Fig. 1. Storage stability data at RT and 50°C for a series of resins with F/M = 1.7, 2.0 and 3.0. (pH = 9.0, SC = 50%, $T = 95$°C).

TOLEDO 465-50-57) was calibrated at the operational temperature, i.e. RT or 95°C, using two buffer solutions; pH = 7 and 9. The pH was monitored automatically on a Kip recorder,

Water tolerance measurements. The water tolerance (WT) measurements were conducted at RT by titrating a certain amount of resin solution with water till sustainable turbidity was observed. WT is then equal to the amount of water (in grams) divided by the weight of the resin solution (in grams).

Light scattering measurements. These experiments were conducted using a Sofica 50.000 apparatus at a wavelength of 546 nm. The apparatus was equipped with a high-pressure mercury lamp (Osram HBO 100W). The solutions were made in DMSO at a concentration of 27.5 g/l.

^{13}C-NMR experiment. The spectra were recorded on a Varian unity 300 using DMSO as the solvent. Spectra with complete decoupling by ^{1}H noise irradiation were measured with a pulse (90° width) repetition time of 11 s (1 s acquisition plus 10 s delay). The NMR spectra were analysed according to the assignment of the peaks presented by Tomita and Ono [9].

3. Results and discussion

3.1. The analysis of the storage stability at RT and elevated temperatures

Fig. 1 shows the storage stability data as a function of reaction time for MF resins with three different F/M ratios. In general, the storage stability profile at RT consists of ascending and descending branch. As was described in earlier publications, the storage stability in the ascending part is controlled by the low solubility (crystallisation) of (methylol)melamines whereas in the descending region physical gelation dominates. The maximum in stability is regulated by the interplay (trade-off) between these two processes and is located generally within a very narrow range of reaction times. As a result, the production of MF solutions with the maximum achievable stability is not a trivial task.

In contrast with the MF solutions at RT, the samples at 50°C seem to be stable over a much wider range of reaction time. The points on the stability curve at 50°C marks the initiation of the process of liquid–liquid phase separation. All samples independent of the initial degree of condensation must reach a critical molecular weight (conversion) before phase separation sets in. We will provide evidence for this behaviour in Section 3.2. For samples drawn too early, like in the case of resins with F/M = 2, low solubility of (methylol)melamines will limit the storage stability. Generally, it is our experience that in order to prepare MF resins with the highest storage stability at 50°C, the reaction mixture should be heated 10–20 min after the dissolution of all melamine. In all cases, this point is far before the could point [10].

Notably, the maximum of storage stability is for all F/M ratios higher at elevated temperatures in comparison with RT. In fact, in the case of resins with F/M = 3, for some unknown reasons, the solutions did not have any stability at all at RT. Usually, a maximum storage stability of at least 5 days can be obtained at RT for resin solutions with F/M = 3. This phenomenon demonstrates clearly one of the most

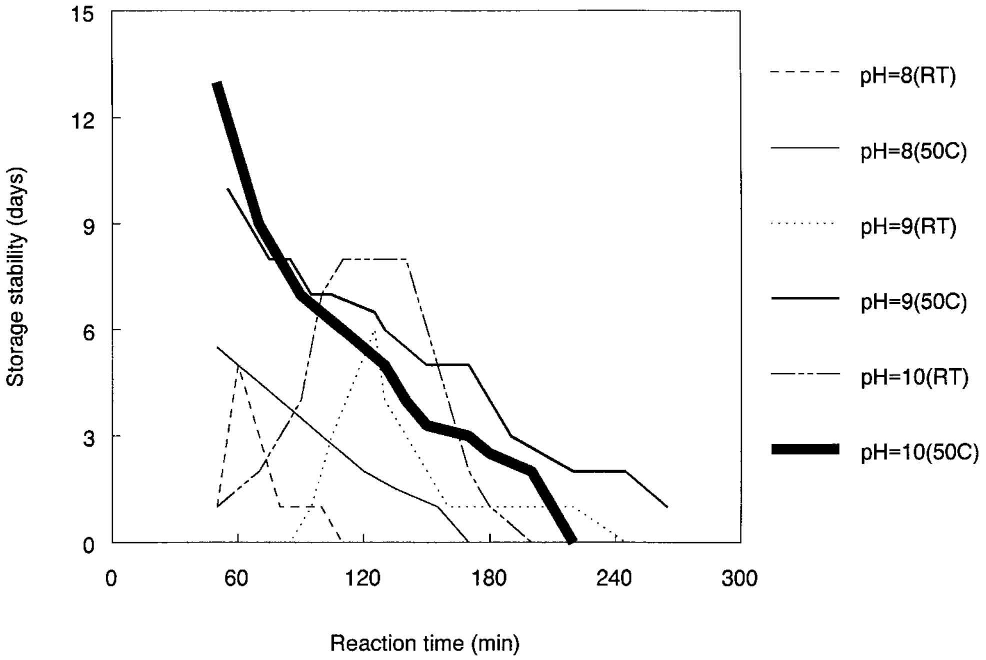


Fig. 2. Storage stability data at RT and 50°C for a series of resins with various pH of the formalin solution. (F/M = 1.7, SC = 50%, $T = 95$°C).

important advantageous of storage at higher temperatures, i.e. the reproducibility of the stability. The storage stability at RT is governed by such delicate processes that can be triggered by slight changes in storage conditions, like undercooling or rigours shaking. In contrast, the process of liquid–liquid phase separation is hindered hardly (especially for low molecular weight systems such as MF solutions) by kinetically controlled processes like nucleation and growth occurring prior to liquid–liquid phase separation. As a result, provided the chemistry is well controlled, the stability data at elevated temperatures can be easily reproduced.

Fig. 2 shows the storage stability data for a series of MF resin solutions with a F/M of 1.7 but different initial pH of the formalin solutions. Identical remarks, as for previous experiments (Fig. 1) can also be made here regarding the storage stability at RT and 50°C. Comparison of stability data at 50°C reveals that MF solutions with pH of 9 seem to have the highest stability reached after a longer reaction time. The sample with initial pH of 8 has the lowest storage stability. The analyses of these data is hampered by the fact that the reaction mixtures with various initial pH values of formalin solutions have followed a different pH profiles (see Fig. 3). Consequently the initial degree of condensation and the type of bridges is different for MF resins at the same reaction time. In order to compare the stability results, shown in Fig. 2, the reaction time must be converted into some measure of the degree of condensation. In practice, water tolerance is used as a widely accepted tool for monitoring the reaction of MF resins [11]. For this purpose a certain amount of resin solution is titrated by water till turbidty is observed. This marks the point of the occurrence of liquid–liquid phase separation. As the reaction proceeds, i.e. as the degree of condensation increases, the could point (binodal) curve shifts for a typical MF formulation to higher temperatures. As a consequence, still lower amount of water is needed to cause phase separation in a MF solution with

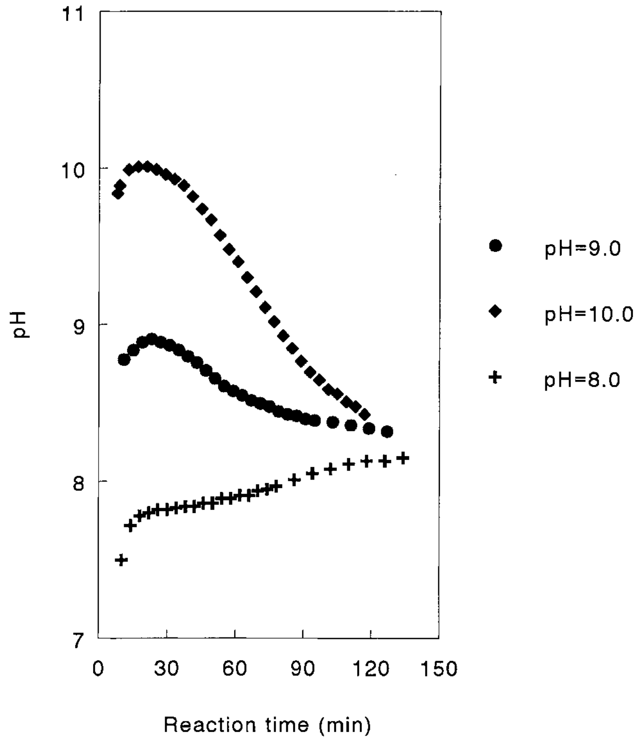


Fig. 3. pH as a function of reaction time for a series of resins. (F/M = 1.7, SC = 50%, $T = 95$°C).

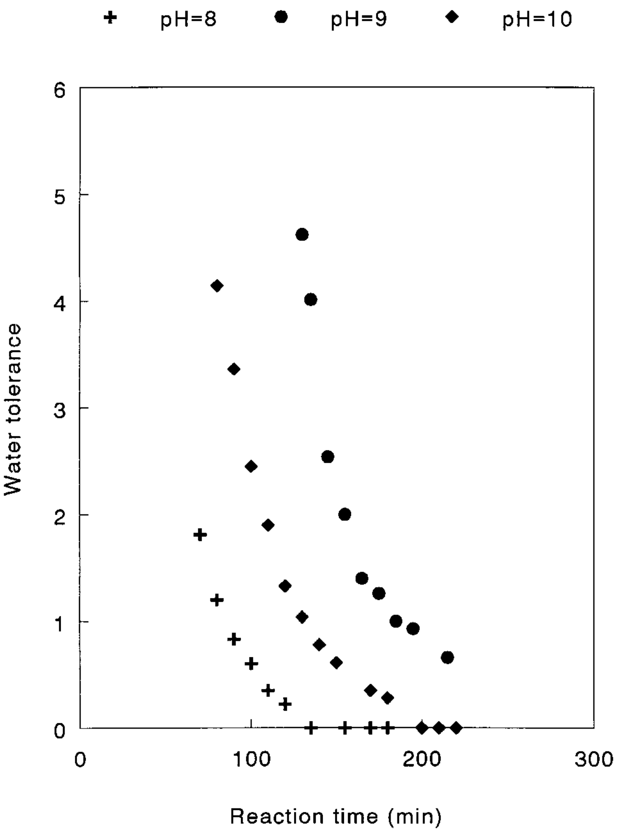


Fig. 4. Water tolerance (WT) values as function of reaction time for a series of resins. (F/M = 1.7, SC = 50%, T = 95°C).

increasing degree of bridging; WT decrease with reaction time until it reaches a value of zero [12]. Indeed, it appears that WT is inversely proportional to the total number of bridges irrespective of the type of bridge [13]. In Fig. 4, the evolution of WT as a function of reaction time is shown for MF resins with different pH of formalin.

In Fig. 5, the stability data of MF solutions with different pH of formalin are plotted against WT values. As can be seen, the data points overlap roughly. Based on these results, it can be stated that the stability of MF solutions with equal degree of condensation is the same at 50°C independent of the pH of the formalin solution. As mentioned earlier, the ratio of the ether over methylene bridges is strongly dependent on the pH of the formalin solutions. Therefore, the storage stability at 50°C seems to be hardly influenced by ratio of the ether over methylene bridges. In other words, the type of bridges does in the first approximation, not affect the process of liquid–liquid phase separation. We have shown in previous publications that the storage stability at RT is modified by the ratio of ether over methylene bridges [1,2].

3.2. The analysis of chemical structure and molecular weight at the point of liquid–liquid phase separation

The complex chemical structure of MF resins may be well studied with the aid of ^{13}C-NMR [14]. We have investigated the chemical structure of MF resins of two F/M ratio's at the point of liquid–liquid phase separation during storage at 50°C. The NMR data are presented in Tables 1

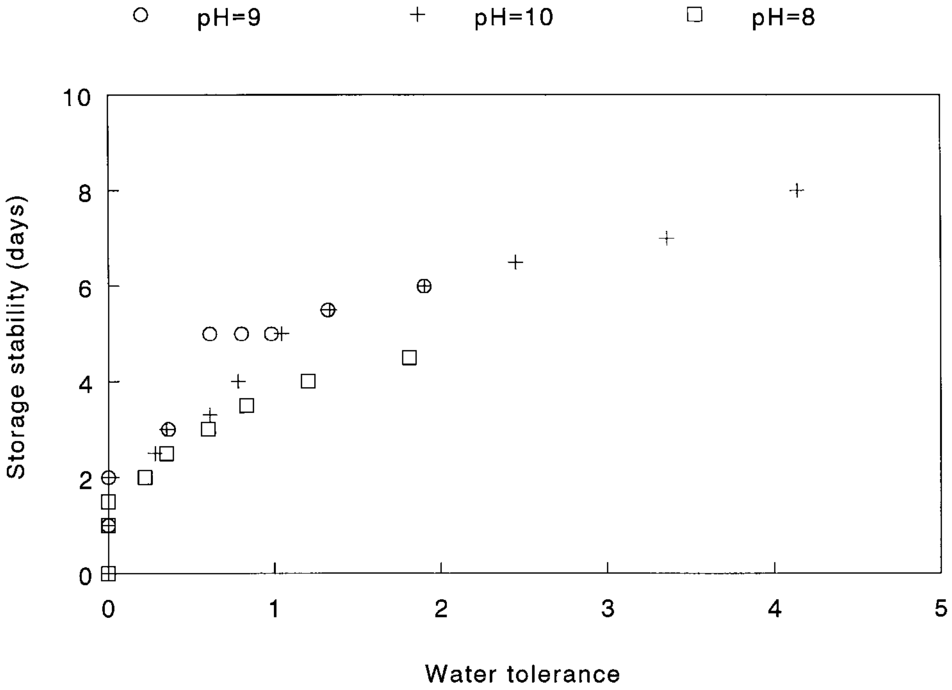


Fig. 5. Storage stability data at 50°C as a function of WT for a series of MF resins. (F/M = 1.7, SC = 50%, T = 95°C).

Table 1
^{13}C-NMR results of a series of MF resins with different reaction times just before initiation of the liquid–liquid phase separation during storage at 50°C. The values represent the percentage of each specific group (%) relative to the total amount of carbon originating from formaldehyde. (pH = 9.0, $T = 95$°C, SC = 50%)

t(min)[a]	-NR-CH2-OR	-NR-CH2-OH	-NH-CH2-OR	-NH-CH2-OH	-NR-CH2-NR	-NH-CH2-NR	-NH-CH2-NH	E/M[b]
65	2.0	12.7	8.9	58.4	1.4	5.3	10.9	0.31
85	2.5	11.8	9.4	58.2	1.9	5.0	10.8	0.34
105	1.8	12.8	8.5	59.1	1.7	4.8	10.7	0.30
170	1.4	12.7	8.7	58.4	1.7	5.3	11.3	0.28

[a] These are the reaction times in minutes.
[b] This is the ratio of ether over methylene bridges.

Table 2
2. Similar results as in Table 1 for MF resin with F/M of 3

t(mim)[a]	-NR-CH2-OR	-NR-CH2-OH	-NH-CH2-OR	-NH-CH2-OH	-NR-CH2-NR	-NH-CH2-NR	-NH-CH2-NH	E/M[b]
60	10.0	44.7	9.6	22.8	2.0	5.4	1.0	1.17
80	9.5	45.4	9.6	22.4	2..7	5.44	0.9	1.10
110	10.0	43.6	10.0	22.6	2.3	5.6	1.0	1.12
135	10.2	44.3	10.2	22.3	2.3	5.2	1.0	1.20

[a] These are the reaction times in minutes.
[b] This is the ratio of ether over methylene bridges.

and 2 showing the concentration of various chemical groups.

As was predicted, the chemical structure seems to be generally the same at the point of phase separation independent of the reaction time. Also, the ratio of ether over methylene bridges is identical [15].

In addition to the chemical structure, we have also studied the molecular weight of MF resins at the point of liquid–liquid phase separation. The classical method of determining the weight-average molecular weight is light scattering. Here, the intensity of scattered light is measured as a function of scattering angle for a series of solutions with different concentrations. By extrapolating to zero angle and zero concentration, the light scattering intensity can be related to the weight average molecular weight (M_W) according to a method developed by Zimm [16]. Unfortunately, for relatively low molecular weight species, such as MF resins, the determination of the scattered light in dilute solutions is cumbersome, because of the lack of sufficient contrast, as a result of which the complete Zimm-plot could not be

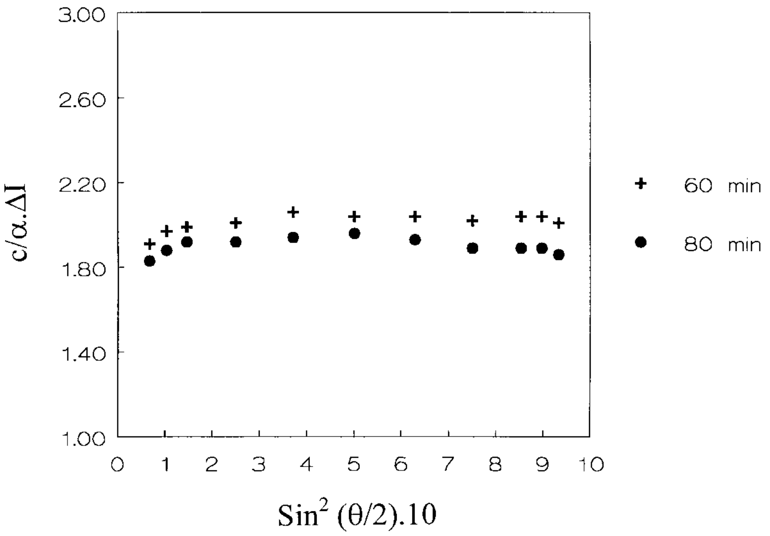


Fig. 6. The measurements of the light scattering intensity (I) as a function of scattered angle, conducted on two MF resin solutions of the same formulations but different reaction times (F/M = 3.0, pH = 9, $T = 95$°C) just before the occurrence of liquid–liquid phase separation at during storage at 50°C, α = factor correcting for effective volume changes as a function of the scattering angle.

constructed with sufficient accuracy. Nevertheless, information concerning relative differences in M_W values between two MF resin solutions can still be extracted. For this purpose, the scattered intensity as a function of the scattered angle is compared for two MF solutions at equal and relatively high concentration of resins using DMSO as the solvent. At such high concentrations, the measurements can still be conducted accurately. In Fig. 6, the light scattering results are displayed conducted on two MF resin solutions of the same formulations but different reaction times at the point of liquid–liquid phase separation during storage at 50°C. In this figure, the lower the curve is positioned the higher is the molecular weight. As can be seen, only a small difference in M_W is measured between the two MF solutions.

4. Conclusions

It is shown that the storage of MF resin solutions at 50°C offers a number of advantages in comparison with storage at RT. These include the ease of production of stable MF resin solutions and high reproducibility of stability data. Further, it is demonstrated that the chemical structure and molecular weight of MF resins with different reaction times is identical before the instability process, i.e. liquid–liquid phase separation, sets in at 50°C.

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