The Effect of Storage Temperatures Below 100°C on the Viscosity of a Novolak Resin Propylene Glycol Solution

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ABSTRACT: The aging of a novolak resin solution used in iron-making blast furnace taphole clays is reported. The novolak resin propylene glycol solution was aged at temperatures between 2 and 80°C for up to 56 days. The viscosity was measured to evaluate the change in the resin's behavior. A cure reaction was found to occur with the addition of hexamethylenetetramine (HMTA) at temperatures lower than had previously been reported. Methods for handling and storage of taphole clay to avoid excessive increases in viscosity due to aging are discussed. An approach for estimating the long term aging at temperatures of 30 to 50°C was considered using shorter term aging data obtained at 70 and 80°C. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 267–276, 2004

Key words: resins; viscosity; curing of polymers

INTRODUCTION

Novolak resins are used extensively in industry. They are used in many different applications, such as molding compounds, heat and sound insulation, coatings, abrasive materials, adhesives, composite wood material, foundry resins, and refractories.[1] Blast furnace taphole clay is a type of plastic refractory that uses novolak resin solutions as binders. This paper examines how the conditions used to store taphole clay could affect the viscosity of the novolak resin it contains.

Taphole clays are used in integrated steel works to seal the iron making blast furnace's taphole between casts. The novolak resin hardens when the taphole clay is injected into the taphole, hence forming a seal. A ram extruder is used to inject the taphole clay into the taphole and problems sometimes arise due to unexpected changes in the extrusion behavior of the clay. The properties of the extruded taphole clay determine its ability to protect the blast furnace refractories and its ability to stop molten iron and slag or gases from escaping the furnace. The extrusion behavior of the taphole clay is highly dependent upon its viscosity and the viscosity of the taphole clay is dependent on the binder's viscosity. Understanding the viscosity variation in the novolak resin solution binder will assist in reducing the variability of the extrusion behavior of taphole clays, which can lead to significant improvements in the blast furnace operation.

Cure or hardening occurs when novolak resin reacts with hexamethylenetetramine (HMTA) (Scheme 1) to produce a nitrogen-containing crosslinked thermosetting resin. This cure reaction is believed to involve at least two steps. The reaction between novolak and HMTA has been found to produce various substituted benzoxazines and benzylamines intermediates.[2] Further reactions of these compounds generate methylene linkages between the phenolic rings resulting in crosslinking and cure (Scheme 2). The reaction of HMTA with novolak resins has been studied in some detail but there are still many uncertainties regarding the reaction. Much work has been done and the specific intermediates and structural composition depend on *ortho/para* sites, temperature, HMTA composition, molecular weight, and pH of the system.[2–6]

Previous investigations of novolak resins have generally focused on the rapid cure at temperatures above 100°C. Lemon,[7] when discussing the manufacture of foundry resins, states that novolak resins are crosslinked with HMTA when heated above 100°C. Examinations of the cure temperature of novolak and HMTA using both torsional braid analysis and differential scanning calorimetry have determined the cure temperature falls between 113 and 150°C.[8,9] Dargaville et al.[3] and Looney and Solomon,[6] when examining the cure reaction of novolak and HMTA with model compounds, chose 130°C as an appropriate cure temperature. Other studies of model compounds by Zhang et al.[2] and Lim et al.[5] have used 90°C as their lowest temperature for study. In a study by Zhang and So-

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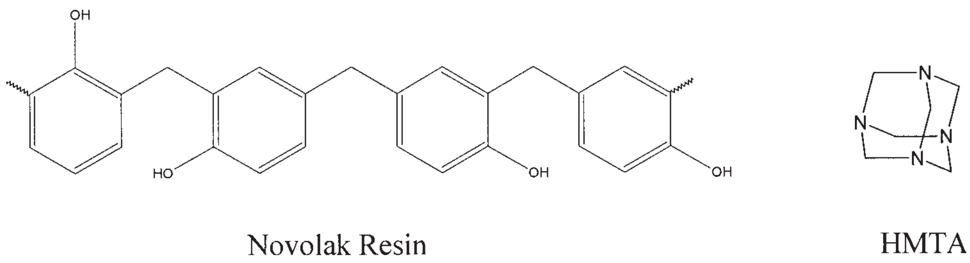


Scheme 1 Novolak resin and hexamethylenetetramine (HMTA).

lomon,[4] reactions between novolak resin and HMTA were found to have occurred when the sample was heated to 90°C. They concluded that the reaction was occurring at lower temperatures due to the addition of furfuryl alcohol, which acted like a solvent at these temperatures. In the case of the taphole clay materials being studied currently, the novolak resin and HMTA is mixed with a propylene glycol solvent and stored at temperatures well below 100°C for perhaps many weeks before the material is used.[10–12] Thus, the longer term and lower temperature cure reactions of novolak resins are important for the understanding of the behavior of taphole clays during extrusion.

This study has examined how extended storage affected the viscosity of a novolak resin with a propylene glycol solvent with and without the addition of HMTA. This comparison has allowed the observation of any reaction between novolak resin and HMTA at relatively low temperatures (below 50°C). Aging the novolak propylene glycol solution not only included a variation in time but different temperatures and compositions. From these data it is envisaged that guidelines for storage of novolak propylene glycol solution taphole clay could be established. Both long-term storage and short-term processing were studied. Viscosity data collected from short-term studies were also evaluated for predicting longer-term effects.

EXPERIMENTAL

A RVTCP Wells-Brookfield cone/plate viscometer was used to measure the viscosity of the polymer. The cone used was a CP-51 with a radius of 1.2 cm and a cone angle of 1.565°. The full-scale torque on the viscometer was 7.19×10^{-4} Nm. A PT100 temperature probe was mounted into the bottom of the cup so the temperature of the resin at the time of measurement was known (± 0.5°C). The viscometer had a shear rate range of 1.92 to 384 s^{-1}.

The novolak resin solution was provided by Huntsman Chemical Company Australia Pty. Limited and was known as Resinox FV1637 Phenolic Resin Solution. The novolak resin solution contained 55% novolak phenolic resin with the remainder being propylene glycol. Hexamethylenetetramine, also provided by Huntsman Chemical Company Australia Pty. Limited, was used as the curing additive. The same batch of material was used for all of the experimental work.

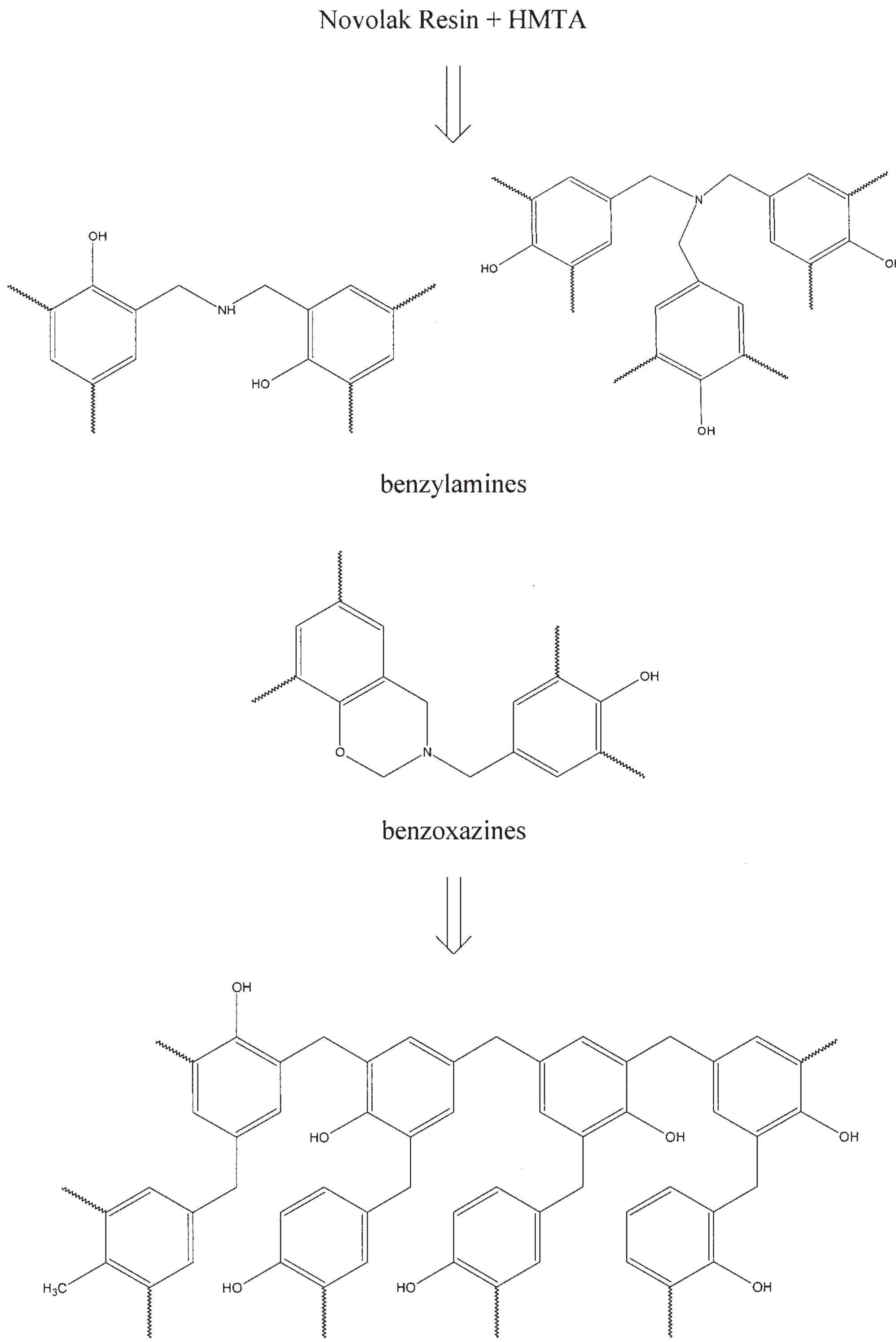
The experimental work was performed to determine the effect of aging time, temperature, and composition on the viscosity of a novolak resin solution. The program was a three-factor, three-level factorial design experiment. Each of the conditions were performed in triplicate. The factors and levels used are given in Table I.

The aging time levels were selected to replicate the times that are important in production conditions.[10] It is common to store taphole clays prior to use in the blast furnace.[11,12] The 1-day storage time was selected to determine any initial effects, while 14 days is the preferred storage time used in production. Fifty-six days was used to represent a long storage time. The samples were stored in sealed containers in closed conditions away from sunlight.

The aging temperature of 2°C was used to determine the baseline at which it was assumed that little if any aging would occur. The temperatures of 30 to 50°C reflect the types of temperatures that can occur during storage.

The amount of HMTA added to novolak resin to achieve cured results generally falls between 5 to 15 wt % for many refractory materials.[8] Taphole clay materials typically have less than 5 wt % HMTA added.[13] The lower percentage addition allows for a slower cure when exposed to the heat of the blast furnace. In the current study, three conditions were studied using different amounts of HMTA. The three proportions of HMTA used were 0, 1.65, and 5.5%. These figures were based on the total amount of novolak resin solution and HMTA. If they were related to the novolak resin component only, they would be 0, 3, and 10%, respectively. These figures were chosen to reflect taphole clay percentages as well as possible higher percentages used in the refractory industry.

In addition to the factorial experiments, two samples, each of 1.65% HMTA addition novolak resin solution material, were stored at a temperature of



Scheme 2 The two-staged cure reaction of novolak with HMTA showing examples of the intermediates found and the formation of the cured structure.

40°C for periods of 14 and 56 days. These extra samples were provided to examine the behavior of material aged between 30 and 50°C.

The viscosity of all the specimens was measured using progressively higher shear rates. The specific shear rate depended on the particular viscosity of the material being tested. The samples were measured at four different temperatures 30, 40, 50, and 60°C. The material was contained and dispensed from a 5-mL syringe. A new sample was used for each of the temperatures and the material was not exposed to light between testing.

TABLE I
Factors and Levels Used in the Experimental Design

Factor	Level
Aging time (days)	1
	14
	56
Aging temperature (°C)	2
	30 ± 2.5
	50 ± 1
Composition (% HTMA)	0
	1.65
	5.5

Examination of the effect of shorter-term aging at higher temperatures was also studied. Novolak resin solution with and without HMTA addition was held at 70 and 80°C for 6 h. The viscosity of the material was obtained initially and then hourly throughout this period. The material that was tested contained 0% HMTA and 1.65% HMTA. The testing was performed three times for each composition.

For each specimen an Arrhenius relationship for viscosity, η, was determined [eq. (1)[rsqb]. η_0 is an empirical parameter that is constant over a small range of temperatures. The activation energy is E_α with R as the gas constant, T as the absolute temperature, and F as a structural factor. A plot of the log of viscosity versus the inverse of absolute temperature was obtained and from this the gradient and the intercept were calculated. The standardized viscosity at 50°C was predicted using the calculated gradient and y-intercept values. The standard error for this predicted value was also calculated.

$$\eta = \eta_0 \exp(E_\alpha RTF \quad (1)$$

RESULTS AND DISCUSSION

The novolak solution was found to be a Newtonian fluid in the range of shear rates tested. The Arrhenius equation also provided a good model for the temperature variation of viscosity. Figure 1 is an example of the data obtained from varying the test temperature. Figure 1 also shows the Arrhenius model fitted to the data. The standardized viscosity at 50°C was obtained using this model. The standardized viscosity was used to compare the novolak resin solutions and eliminated the need for experimental temperature precision. The temperature of the novolak resin solution was accurately known at the time of testing but it was often impossible to obtain exactly 50°C.

The standard errors associated with each of the viscosities were calculated from the Arrhenius data and, generally, the results were precise, although the deviation between different samples aged using the same conditions could be quite high. The largest variation was observed for the samples stored at 50°C with HMTA added. These variations may have occurred due to HMTA addition or mixing. It is less likely that the variation occurred from raw material contamination because all the materials tested were obtained from the same source batch. If these materials or the storage conditions allowed contamination, variation would be expected to be observed throughout all the measurements. In this study the variation occurred in only a few samples. The variation in the 1.65% HMTA samples aged for 56 days shows how the amount of variation depended on the amount of viscosity increase. The samples stored at 2°C with no increase in viscosity varied between 0.75 and 0.94 Pa.s (22% of average) compared to the much higher variation observed in the samples stored at 50°C, which varied between 2.99 and 5.18 Pa.s (54% of average). Small variations in the addition HMTA and the initial mixing and thus contact between the HMTA and the novolak resin may have resulted in the variability observed. These variations, although significant, do not affect the fundamental analysis as they are not sufficient to affect the comparisons between the conditions tested.

A summary of the results is given in Figures 2, 3, and 4. These graphs show the viscosity data of the novolak resin solution calculated at 50°C testing temperature. All the data points are plotted using the three different levels employed in the experiments:

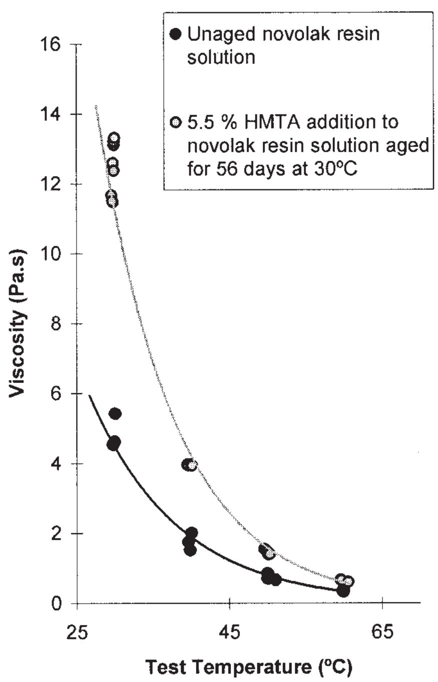
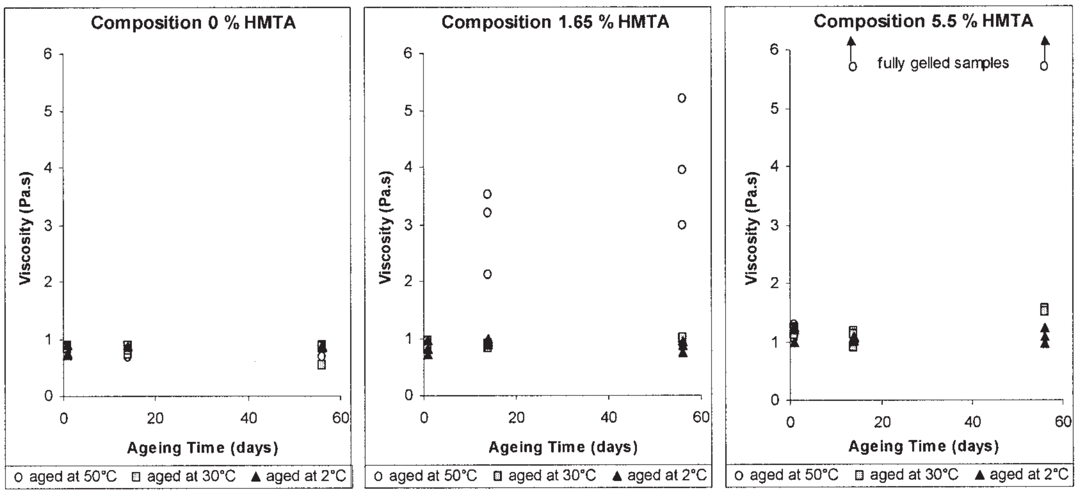


Figure 1 Viscosity change with test temperature for unaged pure novolak resin solution samples and 5.5% HMTA samples aged for 56 days at 30°C. Solid lines are the Arrhenius model fit.



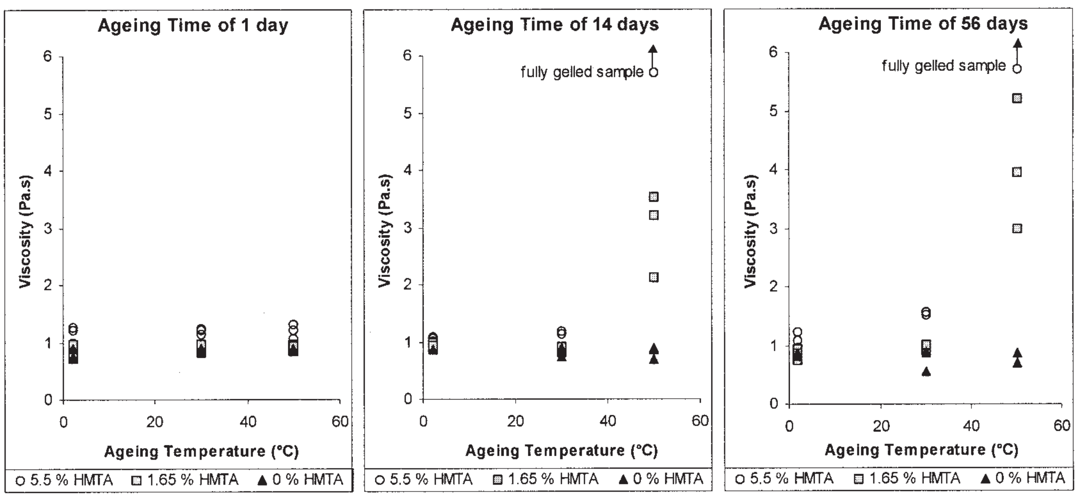
(a) (b) (c)

Figure 2 Viscosity of novolak resin propylene glycol solution (calculated at 50°C) plotted against aging time at different aging temperatures containing (a) 0% HMTA, (b) 1.62% HMTA, and (c) 5.5% HMTA.

aging time, aging temperature, and HMTA composition.

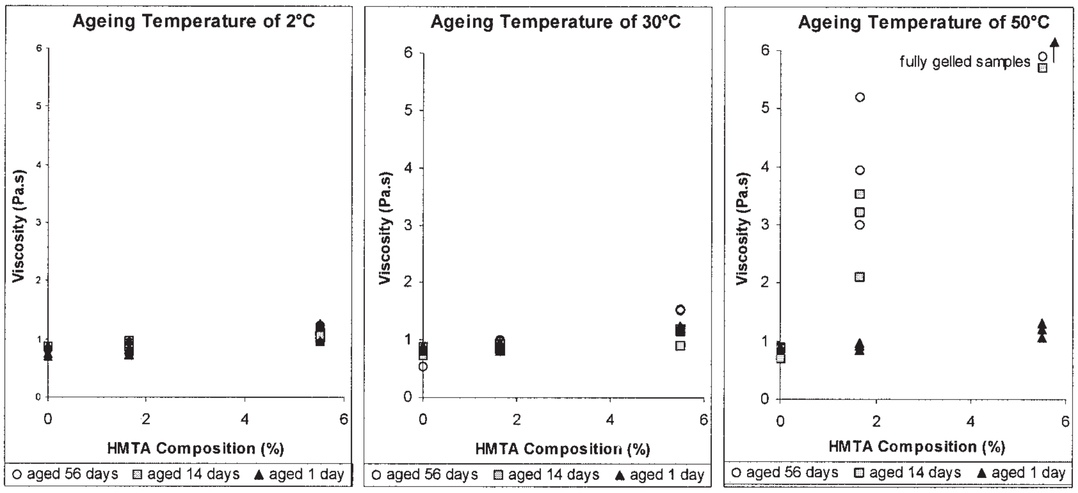
Figure 2(a) shows the variation in the viscosity of novolak resin solution containing no HMTA. There is no significant change in viscosity with either time or aging temperature. The constant viscosity also shows that there is negligible loss of solvent at these temperatures. From Figure 4(a) it can be seen that the effect of aging on the viscosity for the material stored at 2°C was insignificant.

The largest increase in the resin's viscosity was found to be the samples that had the longest storage times and that were exposed to the highest temperatures. The samples containing 1.65% HMTA showed an increase in their viscosity when exposed to high temperatures for long periods [Fig. 2 (b)]. The increase



(a) (b) (c)

Figure 3 Viscosity of novolak resin propylene glycol solution (calculated at 50°C) plotted against aging temperature at different HMTA % after aging for (a) 1 day, (b) 14 days, and (c) 56 days.



(a) (b) (c)

Figure 4 Viscosity of novolak resin propylene glycol solution (calculated at 50°C) plotted against HMTA % composition at different aging times at aging temperatures of (a) 2°C, (b) 30°C, and (c) 50°C.

in viscosity after storage at 50°C was substantial, while a much less significant change in viscosity was observed when the novolak resin solution was stored at 2 and 30°C [Figs. 3(b) and (c)]. The samples containing 5.5% HMTA aged for longer than the initial day at 50°C were not able to be determined because these samples had fully gelled [Figs. 2(c) and 4(c)]. The long exposure time of 56 days and the highest storage temperature of 50°C were found to have the greatest effect on the viscosity, whereas the samples with 0% HMTA addition and those stored at 2°C show negligible increase.

Between 30 and 50°C there is a rapid increase in the viscosity for samples containing HMTA [Figs. 3(b) and (c)]. Figure 5 shows the viscosity of a novolak resin solution containing 1.65% HMTA material as it varies with temperature after storing for 14 and 56 days. This graph includes the samples aged at 40°C as well as those performed in the factorial experiments. After 14 days there was a minimal increase in the viscosity of the samples aged at 40°C, but after 56 days there was a substantial increase in viscosity.

Figure 6(a) shows the difference in aging the material for short times at 70 compared to 80°C. The differences in the initial viscosities of the materials are due to the viscosity of the resin being lower at higher temperatures. Both samples exhibit a steadily increasing viscosity with time. The 80°C sample was found to have a much greater rate of increase compared to the 70°C sample. The viscosity of the sample held at 80°C sample exceeded that of the sample held at 70°C after around 4 h.

In Figure 6(b) a comparison is made between two samples held at 80°C. One sample contains 1.65% HMTA and the other is pure novolak resin solution. The 1.65% HMTA sample was found to exhibit a 400% increase in the viscosity, whereas when there is no HMTA addition the viscosity increased by around 100%.

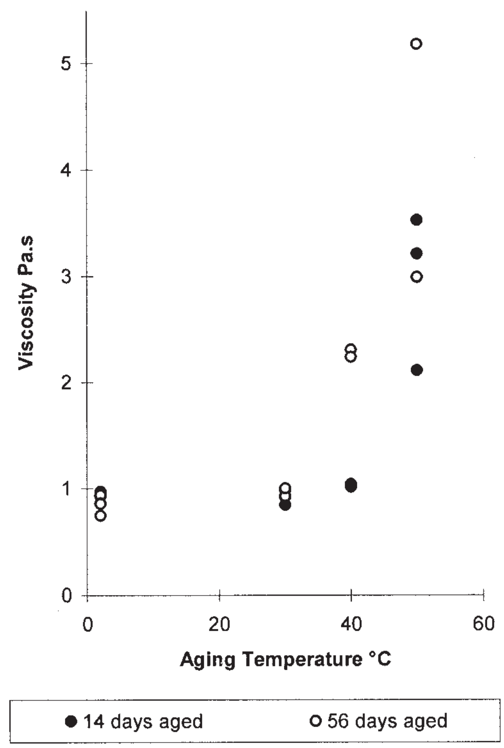
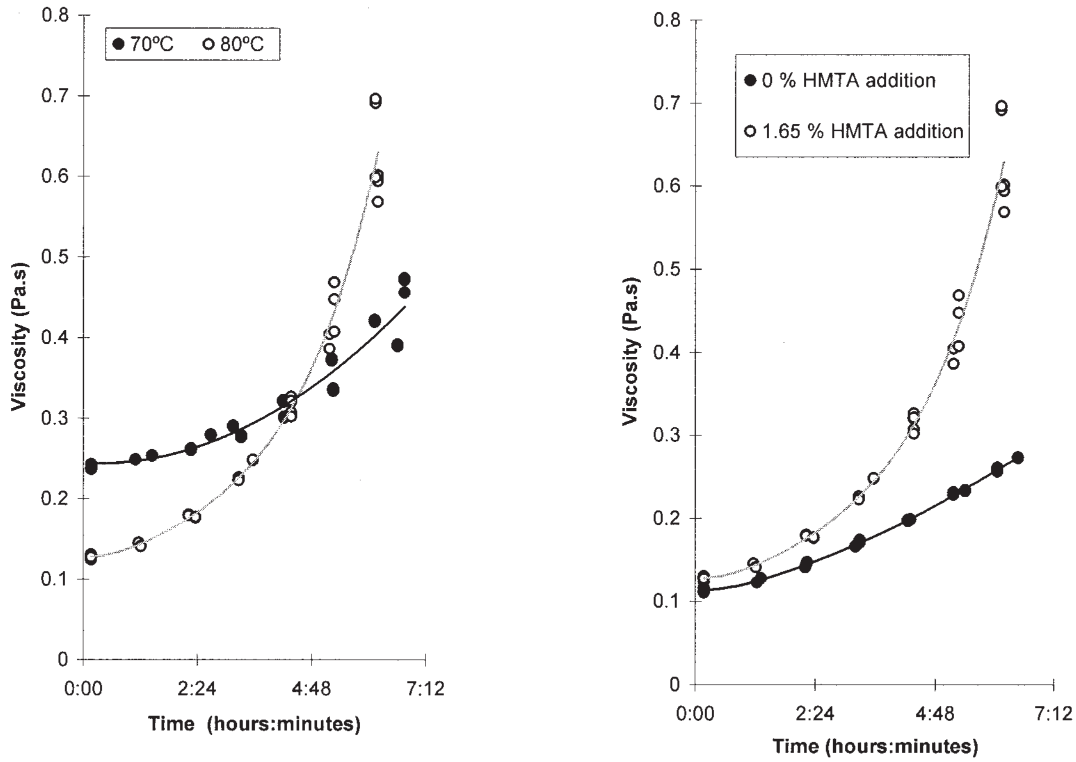


Figure 5 Viscosity of a novolak resin solution samples containing 1.65% HMTA (at a temperature of 50°C) versus aging temperature after 14 and 56 days storage.



(a) (b)

Figure 6 Viscosity of novolak resin solution versus time (a) containing 1.65% HMTA and held at 70 and 80°C, and (b) containing 0 and 1.65% HMTA and held at 80°C.

The aim of this investigation was to establish the effect of aging on the viscosity of a novolak resin solution. The addition of HMTA curing agent to the novolak resin was performed to ascertain whether curing would occur at temperatures lower than previously reported. Specimens were also aged without the addition of HMTA to determine whether any other reactions or physical changes were occurring. The specimens aged for shorter periods at higher temperatures were used to predict the behavior of the samples aged for the longer period at lower temperatures. The objective of this study was to determine the factors that may have the largest effect on the extrusion performance of blast furnace taphole clays containing novolak resin solutions.

There appears to be no change in the viscosity of the novolak resin solution when there is no addition of HMTA. This suggests that the only aging that occurs is due to a reaction between the novolak resin solution and the HMTA. The greater the amount of HMTA added to the novolak resin solution the greater the observed viscosity increase. The longer the aging time for any novolak resin HMTA combination, the greater the resultant viscosity increase. These observations clearly indicate a low temperature crosslinking reaction occurs upon aging.

It has been found in studies of novolak and HMTA reactions that initially there are various substituted benzoxazines and benzlamines formed.[2,4] These intermediates then react to form methyl crosslinkages resulting in cure (Scheme 2). Given the extended times used in the current study and the large increase in the viscosity observed it can be hypothesized that some or all of these reactions occurred resulting in crosslinking and an increase in the viscosity of the system.

Effect on taphole clays

The novolak resin solution mixed with 1.65% HMTA is a common binder combination used in taphole clays. These results suggest that taphole clay material containing novolak resin solution is able to be stored at temperatures of 30°C and less with little change in the behavior of the clay for up to 56 days. However, when the novolak resin solution was aged at 40°C for extended periods, a significant viscosity increase was found, which may result in a significant variation to the taphole clay's expected behavior. Close control of storage temperature is therefore needed to maintain constancy in the performance of taphole clay.

It is generally accepted that the cure of novolak phenolic resins occurs around 100°C and above.[4,7]

Much of the work performed on novolak resins was concentrated on the cure behavior in applications in which the HMTA is added to the novolak at the time of cure and rapid cure is required.[1] Taphole clays are mixed well before they are used. The HMTA is added to the novolak resin solution and combined with refractory material to produce taphole clay at least 1 week prior to use in the blast furnace and can be stored for much longer. From these experiments, it is clear that a slow cure reaction can occur over long periods of time at temperatures far less than 100°C. After 56 days of aging a cure reaction was found to have occurred at temperatures as low as 40°C. It is possible that the solvent added to the novolak resin provides the mechanism for lower temperature cure reaction to occur. Zhang and Solomon[4] also found that the addition of a solvent reduced the novolak HMTA cure temperature. The solvent would allow greater mobility of the polymer chains and thus greater interaction between the novolak molecules and the HMTA. This greater interaction would allow faster reaction of the materials at comparatively low temperatures.

Viscosity prediction

In an attempt to predict the change in viscosity, an isothermal empirical model proposed by Roller[14,15] for thermosetting resins was used to examine the curing behavior of the novolak resin solution aged at 70 and 80°C. The empirical model has the form:

$$\ln \eta(t) = \ln \eta_\infty + \Delta E_\eta/RT + tk_\infty \exp(\Delta E_k/RT) \quad (2)$$

where $\eta(t)$ is the viscosity as a function of time t at absolute temperature T; η_∞ is the calculated viscosity at T = ∞; $\Delta E\eta$ is the Arrhenius activation energy for viscosity; R is the universal gas constant, k_∞ is the kinetic analog of η_∞; and ΔE_k is the kinetic analog of $\Delta E\eta$. The empirical parameters were determined using the data from the 70 and 80°C samples in the first 3 hours of aging. This was the period prior to the material becoming excessively viscous and variable. The parameters that were determined are listed below.

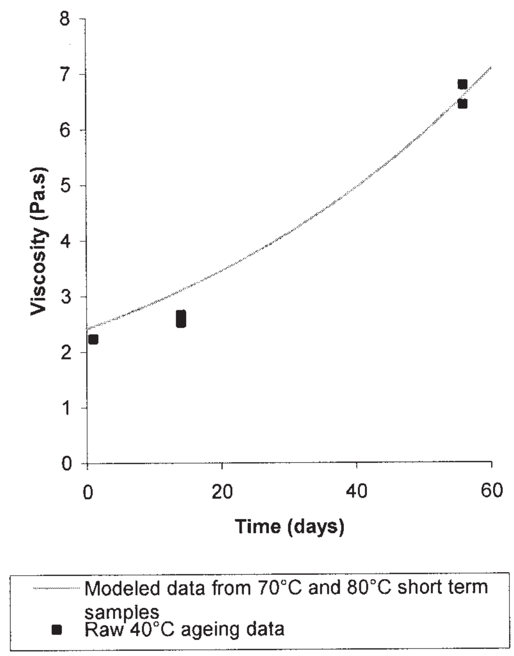
$$\eta_\infty = 7.02 \times 10^{-12}\text{Pa.s}$$

$$\Delta E_\eta = 69.1\text{kJ/mol}$$

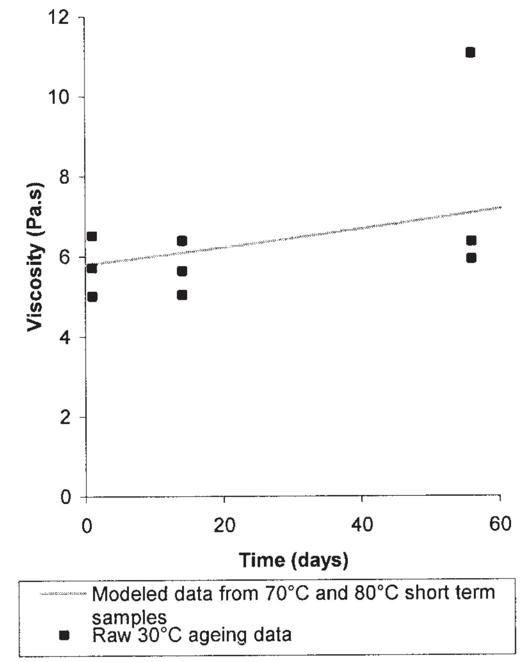
$$k_\infty = 3.62 \times 10^{14}\text{s}^{-1}$$

$$\Delta E_k = 127\text{kJ/mol}$$

Using the empirical equation determined from the short-term 70 and 80°C data it is possible to apply the model to predict the viscosity increase at aging temperatures of 30 and 40°C. Figures 7(a) and (b) show the raw data obtained from the samples aged at 30 and 40°C and the model results determined by the empirical equation. There is very good correlation between the raw data and the model even to very long aging



(a)



(b)

Figure 7 Viscosity versus time of the modeled data compared with the raw data for (a) 40°C samples and (b) 30°C samples containing 1.65% HMTA.

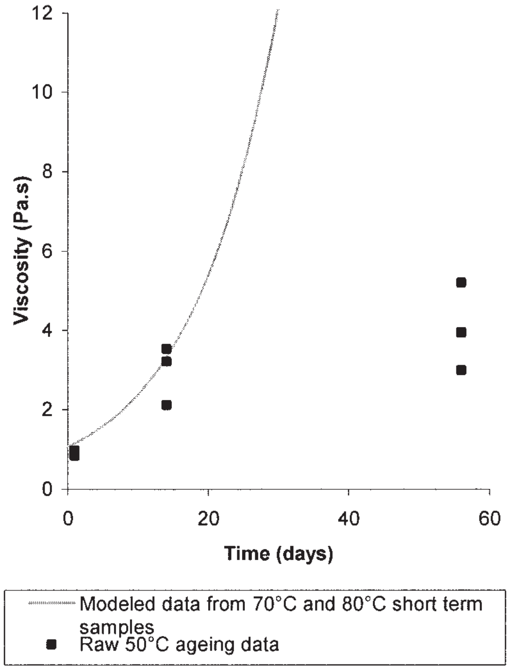


Figure 8 Viscosity versus time of the modeled data compared with the raw data for the 50°C samples containing 1.65% HMTA.

times. Using this model, the short-term curing reaction data could be used to predict the behavior of the longer lower temperature aging.

Unfortunately, the model used does not fit when the material was aged at 50°C (Fig. 8). The predicted results agree well with the raw data for 1 and 14 days of storage at 50°C. However, the model grossly overestimates the viscosity for 56 days of storage. There appears to be a new process operating at long times at 50°C that slows the increase in viscosity and is not detected in the short-term experiments. The mechanism that allows curing at temperatures lower than 100°C may have been due to the increase in mobility of the novolak polymer chains after the addition of a propylene glycol solvent. An increase in the viscosity and crosslinking of the novolak resin solution would reduce this mobility. If the amount of crosslinking in the novolak resin solution became too high, it may have inhibited the mobility of the polymer chains, which would reduce the expected viscosity increase. The higher temperatures at 70 and 80°C may not have been aged for long enough to allow the reaction to reach the point where the viscosity increase slows. Further work would be required to prove this theory, as the viscosity data are extremely variable under these conditions.

Aging conditions

Small changes in the storage temperatures were found to have a significant effect on the viscosity of the novolak resin solution. When the novolak resin solution was mixed with 1.65% HMTA and stored at 50°C the increase in the viscosity was substantial. Furthermore, increasing the HMTA percentage at this aging temperature resulted in fully gelled material. To demonstrate the critical effect of temperature, the short-term samples were again compared to the long-term samples. The Arrhenius plots for the 1.65% HMTA samples, stored at 50 and 40°C for 56 days, were extrapolated to determine the approximate viscosities that would have been obtained if the material had been tested at 70 and 80°C. An example of this extrapolation showing the samples stored at 50°C for 56 days is shown in Figure 9. These viscosities were then compared with the short-term studies at 70 and 80°C (Figs. 6 and 7). The time required in the short-term studies to reach the same viscosity that had been determined using the extrapolated viscosities in Figure 9 was noted. The time required to reach these levels of cure (characterized by the expected viscosities: 3.91 and 2.27 Pa.s at measuring temperature of 50°C) after being stored at different temperatures is shown in Figure 10.

From Figure 10 it can be seen that small variations in temperature can have a very significant effect on the rate of cure of the novolak resin HMTA solution and the rate of change of viscosity. Graphs like this could be used as a method for determining the maximum time that taphole clay containing novolak resin HMTA solution could be stored at a particular temperature before the taphole clay became unsuitable for use. These graphs resemble the S-N charts used to predict the fatigue resistance of structural material and could

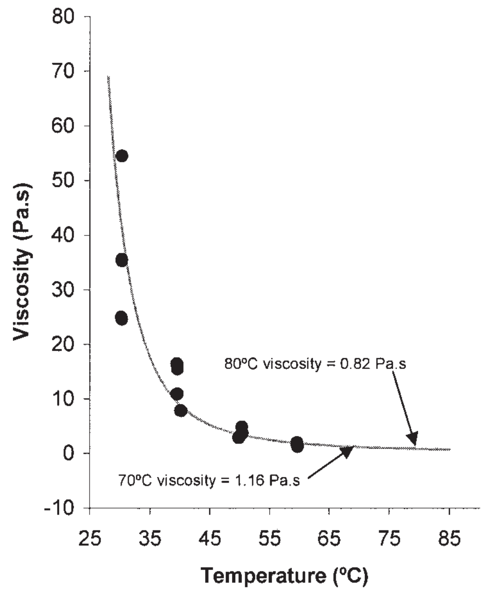


Figure 9 Extrapolation of the Arrhenius plots for a novolak resin solution containing 1.65% HMTA aged for 56 days at 50°C to include the viscosities at 70 and 80°C.

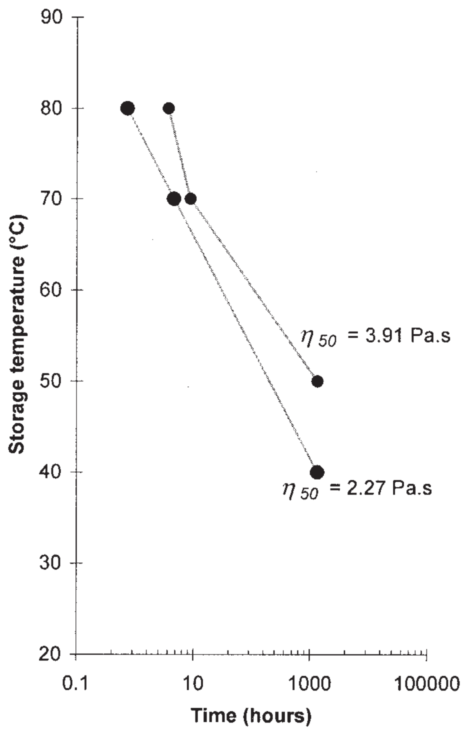


Figure 10 The storage temperature versus the average time required for 1.65% HMTA novolak resin solution sample to reach various viscosities: 3.91 and 2.27 Pa.s viscosity at testing temperature of 50°C (η_{50}).

be used in the same way to predict the storage lifetime of novolak resins. More samples of different compositions and storage temperatures, along with further understanding of the effect of evaporation of the solvent, would be required to build up a complete assessment of the nature of this reaction.

CONCLUSION

It was established that novolak resin in propylene glycol solution underwent an aging reaction when mixed with HMTA. The aging was found to be due to a cure reaction between the novolak solution and the HMTA leading to chain extension and an increase in solution viscosity. This curing reaction occurred at temperatures well below 100°C. From the aging data it was concluded that long-term storage of taphole clay at 30°C would have no major effect on the novolak resin propylene glycol solution binder. However, if the taphole clay material were stored at temperatures of 40°C and above, the resultant increase in the viscosity could significantly affect the extrusion behavior.

It is possible to predict the long-term behavior of novolak resin propylene glycol solution held at 30 and 40°C from shorter-term testing of samples aged at 70 and 80°C. However, this was not found to be the case for samples stored at 50°C, due to the viscousness of these samples. Further study is required to accurately model these viscosity changes. A graph has been developed that may be able to predict the maximum storage period for novolak resin propylene glycol solution held at various temperatures. This graph could be used to predict the shelf life of taphole clay at various storage conditions.

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