Solution Viscosity Increase in Fusion Synthesis of Ca/Mg-Resinates

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The effect of Ca/Mg-resinate concentration on solution viscosity was studied in toluene. The viscosity was observed to increase drastically above a specific concentration value. The change in viscosity dependence on concentration implies a transition from a dilute to a concentrated regime, where viscous dissipation is governed by resinate molecular interactions and excluded volume effects. The concept of critical resinate concentration, c_{crit}, was applied and used to explain the nonlinear solution-viscosity increase during the resinate synthesis. Ca/Mg-resinates were synthesized by the fusion method at 265°C in a laboratory-scale batch reactor. During the syntheses the increase in 50 wt. % toluene solution viscosity of the resinate turned almost exponential at a specific reaction time, denoted by t_{50}. Based on the apparent reaction kinetics, a semiempirical model with two estimated parameters was derived for the solution viscosity to be used for the prediction of the t_{50} time of resinate syntheses.

Introduction

Resinates are the rosin salts of polyvalent metals, such as calcium, zinc, and manganese (Figure 1). These kinds of resinates find wide application as dryers for paints and varnishes and as constituents of printing inks.

Resinates are produced by three different methods: fusion, solution, and the precipitation method. In order to improve the printing qualities of the resinate, rosin is generally first fortified by reacting with a dienophile, such as maleic acid or its anhydride or fumaric acid. The reaction products are tricarboxylic acids, which are referred to as maleopimaric or fumaropimaric acids. The rosin adducts have a high melting point, and their high acidity makes them reactive with many materials, such as metal hydroxides, to form resinates.

Pure calcium resinates synthesized from monomeric rosin by either the fusion method or solvent method are known to crystallize or otherwise solidify (block) during the reaction, especially at higher metal levels. However, when unmodified monomeric rosin is used, high metal contents are often needed to give sufficiently high viscosity to the resinate solution. The target value of the solution viscosity of the resinate varies, depending on the application. According to Jilek (1976), the solutions of the calcium resinates to be used as an ink vehicle should have a viscosity of about 500 mPa/s at 50 wt. % resinate concentration. In the present work the target value for the solution viscosity of the Ca/Mg-resinate is in the range of 50 to 100 mPa/s at 50 wt. % resinate concentration in toluene.

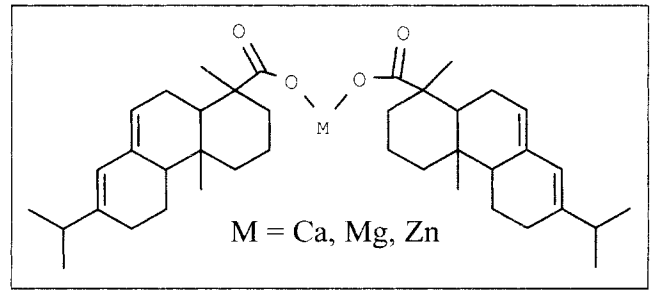

Figure 1. Resinate molecule scheme.

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The difficulty during the resinate-synthesis-by-fusion method is the change in the physical properties of the resinate, especially the increase in solution viscosity. During the synthesis the increase in solution viscosity at a given resinate concentration turns almost exponential at a specific reaction time. Therefore it is difficult to control a resinate process and to obtain a product with the desired solution viscosity.

In the resinate-synthesis-by-fusion method the main reaction is resinate formation. The most important side reaction is the decarboxylation of rosin acids forming neutral rosin oil. Other side reactions are the isomerization and polymerization (mainly thermal dimerization) of rosin acids. The isomerization and polymerization mechanisms of rosin acids have been studied by Sinclair et al. (1970) and Zinkel (1983). In this context, however, these side reactions have minor importance, because isomerization does not have a direct effect on the viscosity and polymerization occurs only to a small extent. Therefore, these side reactions are neglected in this study. The decarboxylation of rosin acids is not as well studied as the other side reactions, although its effect on viscosity is more important. It increases the resinate concentration in the reaction mixture when the neutral rosin oil vaporizes from the system.

Due to the lack of detailed knowledge of the phenomena on a molecular level, the chemical factors affecting the macroscopic properties of the reaction mixture, especially viscosity, are unexplained. The viscosity problems related to the blocking phenomenon have been observed by some authors (Petrone, 1971; Panda and Panda, 1985), but no explanation of the cause of this kind of behavior has been published. In this article, the reason for abrupt viscosity increase in the resinate solution after the critical resinate concentration is explained by resinate molecular interactions and excluded volume effects.

Simple kinetic measurements in the resinate synthesis are generally based on acid number determinations, conventionally by off-line titration with KOH. The titration gives the overall state of the system: the progress of the resinate reaction and the decarboxylation of rosin acids. In this article, an attempt is made to model the solution viscosity increase during resinate synthesis on the basis of acid number titration data. A simple mathematical model with two parameters is derived in order to be able to control the resinate process and the viscosity of the product.

Experimental Section

Synthesis procedure

Ca/Mg-resinates were synthesized by the fusion method in a 500-mL oil-heated batch-reactor vessel. The reaction mixture was stirred with a plate impeller. Nitrogen was continuously bubbled through the system. Syntheses were made from tall oil rosin (acid number 165 mg(KOH)/g) and from pure abietic acid (> 85%, Sigma, acid number 185 mg(KOH)/g). *Pro analysis* quality $Ca(OH)_2$, $Mg(OH)_2$, and $(CH_3COO)_2Ca$ were used as the reactive metal salts. The molar ratio 6.3:1 of Ca to Mg was used in the syntheses.

The rosin or the abietic acid was melted in the vessel at 235°C and the metal salts were gradually added to the rosin melt over 2 h. Then the temperature was increased to the reaction temperature, which was 245–265°C, depending on the synthesis. Reaction time was 5–6 h. Without taking into account the mass loss during the syntheses, the total theoretical metal contents calculated for the product were 3.4–3.5 wt. %.

In the modified resinate syntheses, rosin was fortified to the acid number level 190 mg(KOH)/g using either maleic acid anhydride or fumaric acid. The fortification of rosin was carried out at 195°C and the reaction time was 2 h. In addition two different modifiers and their effect on the viscosity of the resinate were tested. Polyethenevinylacetate copolymer (EVA, $M = 50{,}000$ g/mol) was added in the amount of 1.5 wt. % and 5.0 wt. % of rosin to the fortified rosin melt after one hour at 195°C. Butyl-phenolformaldehyde resin (PFR) was added in the amount of 5.0 wt. % and 10 wt. % of rosin to the unfortified rosin melt at 180°C. The reaction time of PFR was 2 h. The modified resinate synthesis was also made from polymerized rosin (13 wt. % trimeric and 24 wt. % dimeric rosin acids) with a theoretical metal content of 1.8 wt. %.

Analysis

The number-average molar mass and the possible aggregation of the resinate molecules in toluene were examined with a vapor-pressure osmometer (VPO) (Knauer GmbH) using benzil as a standard. An infrared-spectrometer (NIC Nicolet 5DXC FT-IR Spectrometer) equipped with a ZnSe-cuvette (0.05 mm) was used to study the intermolecular hydrogen bonds between the two free carboxylic acid groups of the resinate in toluene. The density measurements (using Anton Paar KG DMA55 Calculating Precision Density Meter) were carried out at different resinate concentrations in toluene at 25°C in order to study the contribution of the resinate concentration to nonideal mixing. An attempt was made to determine the molecular size distribution of the resinate by GPC analysis (Waters 486, eluent: tetrahydrofuran (THF), column: Ultrastyragel 100 Å, flow velocity: 0.4 mL/min, detector: UV/VIS, $\lambda = 268$ nm).

The progress of the synthesis was followed by acid number titrations and viscosity measurements. The titration was carried out in a neutralized toluene–ethanol solution of the resinate with 0.2 M KOH using phenolphthalein as an indicator. The melt and solution viscosities of the resinate were measured by a Brookfield Digital DVII Viscometer.

Molecular Interpretation of Critical Resinate Concentration

Solution viscosity at different resinate concentrations in toluene

The toluene solution viscosity of the Ca/Mg-resinate was observed to be highly dependent on the mass concentration (Figure 2a). The increase in viscosity turned almost exponential after a specific concentration value. Therefore this concentration was determined as the critical concentration of the resinate, c_{crit}. The change in viscosity dependence on resinate concentration implies a transition from a dilute solution to a concentrated region, where molecular interactions have a stronger influence on viscosity.

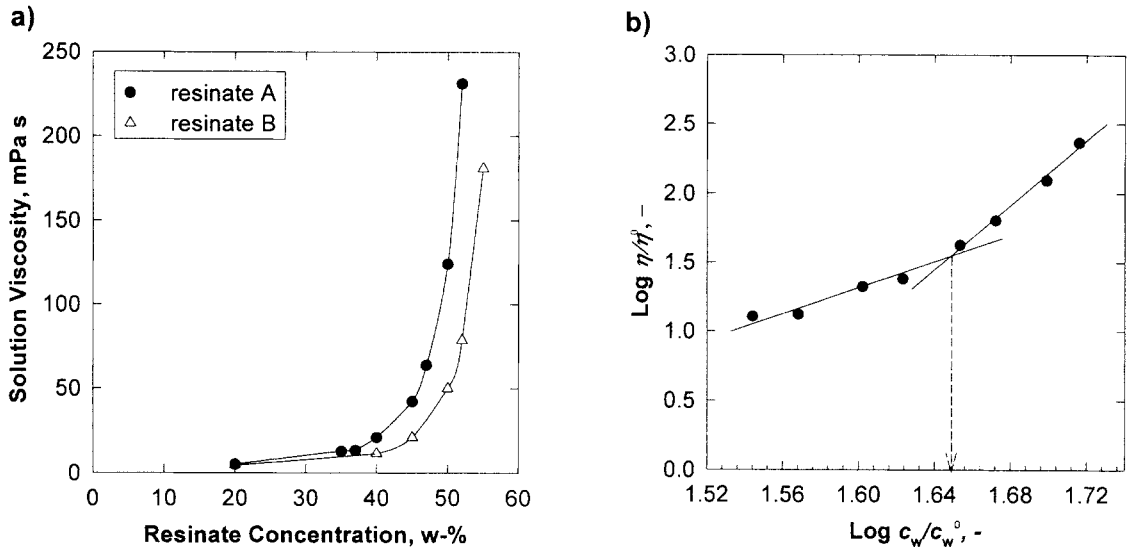

Figure 2. (a) Viscosity increase in toluene solutions of two different Ca/Mg-resinates; (b) determination of the critical concentration for resinate A.

The critical concentration value was determined based on a log-log plot of viscosity and concentration data for resinate A (Figure 2b). The intersecting lines were statistically calculated using least-square errors criteria to separate the points belonging to each line. The values of the critical concentrations for the resinates A and B with different acid contents were 44.6 wt. % and 48.1 wt. %, respectively.

Molecular interactions in the critical concentration region

Molecular interactions were studied at different resinate concentrations in toluene in the critical concentration region. The measurements were carried out using an FTIR, a vapor-pressure osmometer, and a density analyzer. The sample was the fortified Ca/Mg-resinate with an acid content of 1.22 mmol/g and $c_{crit} = 48.1$ wt. %.

FTIR Measurements. Free carboxylic acids tend to associate with another acid group forming intermolecular hydrogen bonds between molecules in nonpolar solvent. This is observed by FTIR measurements. FTIR analyses of the resinate were carried out in toluene solution at concentrations at 40–58 wt. %. There were no differences in the spectra of the resinates when the concentration of the sample increased. Even in the most dilute solution, almost all of the rosin acid groups in the resinate had formed hydrogen bonds. Because the molar absorbance of the acid groups did not depend on the concentration of the resinate, the association of rosin acids did not affect the critical resinate concentration value.

VPO Measurements. Another form of possible molecular interaction, in addition to association of acid groups through hydrogen bonding, is the molecular aggregation of different molecules in the reaction mixture. In order to observe possible aggregation of the molecules in toluene solution of the resinate the VPO measurements were carried out at two different temperatures, 25°C and 45°C. The vapor pressure of the resinate solutions was measured using pure solvent (toluene) as a reference system. The VPO method is based on accurate measurement of temperature difference, which is recorded as resistance difference, ΔR.

Number-average aggregation numbers for the resinate solutions were calculated according to Eqs. 1 and 2 derived by J. Paatero (1975):

$$\bar{n} = \frac{K'' x_1}{2(1-x_1)\Delta R}\left(1 - \frac{2\Delta R}{K''} + \sqrt{1 + \frac{2\Delta R}{K''}}\right), \qquad (1)$$

where x_1 denotes the mole fraction of the sample, K'' is the calibration constant, and ΔR is the measured resistance difference, both expressed in mm. The calibration constant was measured by using benzil as a standard. The slope of the line (ΔR vs. mole fraction of benzil) gave the calibration constant.

The solution of $\bar{n}$ from Eq. 1 is iterative, because the sample concentration is dependent on the number-average aggregation number according to

$$x_1 = \frac{c_1/\bar{n}}{c_2 + c_1/\bar{n}}, \qquad (2)$$

where c_1 and c_2 denote the analytical concentrations of the solute and the solvent, respectively.

The number-average molar mass of the resinate was determined by VPO using THF as the solvent. THF is more polar than toluene, and therefore the use of THF hinders hydrogen bonding between acid groups, giving a more accurate value for the number-average molar mass of separate molecules. Compared to the theoretical value of the molar mass of calcium abietate (640 g/mol), the measured value for number-average molar mass of the resinate ($\bar{M}_n = 890$ g/mol) containing free rosin acids 1.22 mmol/g is relatively high. This is explained by possible resinate polymers in the reaction mixture. The polymeric resinate molecules may be formed when using fortified rosin with an acid functionality of three.

The molar mass of the resinate measured in THF was used to calculate mole fractions for Eq. 1 when calculating num-

Table 1. Number-Average Aggregation Numbers for Ca/Mg-Resinate in Toluene Determined by VPO

Resinate Conc. wt. %	Aggregation No.	
	$T = 25°C$	$T = 45°C$
5	1.29	1.36
10	1.38	1.30
45	1.34	1.25
50	1.41	1.30
55	1.49	1.37
58	1.51	1.36

ber-average aggregation numbers for the resinate at two different temperatures in toluene (Table 1).

The aggregation number differs from one even at the lowest resinate concentration. This is explained by considering the acid concentration of the resinate, which was 1.22 mmol/g. These acid groups associate through hydrogen bonds in toluene raising the aggregation number to greater than one.

In order to obtain high accuracy, the VPO method requires that the sample droplet placed in the thermistor should be of equal size. However, this requirement was difficult to fulfill for the measured series due to the large differences in viscosities at different concentrations. Therefore, the values differ when increasing the resinate concentration. However, increasing the concentration to the critical concentration region ($c_{crit} = 48.1$ wt. %) does not affect the aggregation number. On the basis of FTIR and VPO results, it is concluded that the viscosity increase is not due to any chemical association of the resinate molecules in the solution.

Density Measurements. The general mixing rule was applied to calculate the density difference in the mixing of resinate and toluene at different mass proportions,

$$\Delta\rho_{mix} = \rho_{measured} - \rho_{ideal} \tag{3}$$

$$\rho_{ideal} = \frac{\Sigma x_i M_i}{\Sigma x_i V^*_{m,i}}, \tag{4}$$

where M_i and $V^*_{m,i}$ denote the molar mass and molar volume of the pure component i, respectively, and x_i is the mole fraction of i in the mixture. The ideal density (Eq. 4) can also be calculated from the total mass and volume based on mass fractions and the densities of the pure components (resinate 952 kg/m^3 and toluene 862 kg/m^3).

The mixture behaves like an ideal solution when the mixing parameter $\Delta\rho_{mix} = 0$. In order to reveal the contribution of the resinate concentration to nonideal mixing, the value of the mixing parameter was proportioned to the resinate concentration (Figure 3). The figure implies that the relative mixing parameter is independent of concentration at low resinate concentrations in toluene. The increase after 20 wt. % resinate concentration implies a transition toward more dense packing of the molecules in the mixture.

Based on the FTIR, VPO, and density results it is concluded that there are two concentration regimes in studying the viscosity behavior of the resinates. The linear regime, where the resinate concentration is smaller than c_{crit}, and the nonlinear viscosity increase regime ($c > c_{crit}$), where the molecules form a sufficiently dense packing for increased molecular interactions.

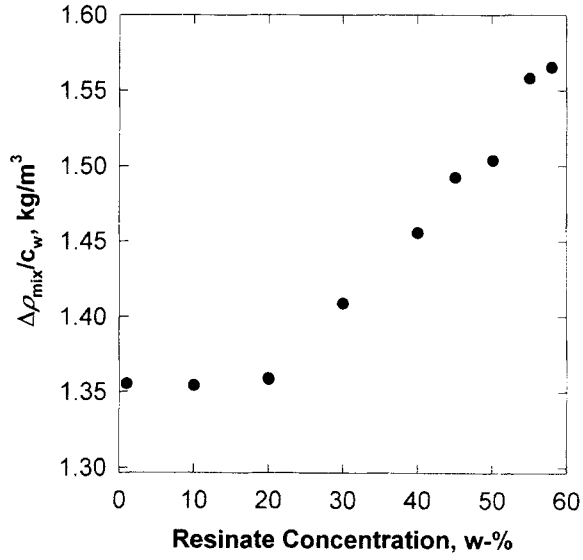

Figure 3. Relative mixing parameter in the density measurement of Ca/Mg-resinate in toluene at 25°C.

Kinetic and Viscosity Model for the Syntheses

General progress of the syntheses

Resinates were synthesized from pure rosin and fortified abietic acid and rosin. In addition EVA and PFR were used in order to control the increase in the viscosity to the target level.

It is not possible to synthesize Ca/Mg-abietate by the fusion method at 265°C using the theoretical metal content of 3.5 wt. % for the product due to the high viscosity, which prevents efficient mixing. Therefore the reference syntheses were made from fortified AA and from fortified rosin (Figure 4). In the abietate synthesis a strong viscosity increase was observed within a few hours of reaction time. With fortified rosin this phenomenon of viscosity increase was considerably weaker.

Figure 4b shows (note that $t = 0$ h is the time when the temperature had reached 265°C) that during the synthesis from fortified abietic acid the acid number values were much lower than the theoretical value. In the case of rosin the theoretical acid value is not reached until 4½ h reaction time, because the resinate reaction is not completed at time $t = 0$ h. The theoretical value is based on the stoichiometric reaction (1:2) between the metal salt and the rosin acid without taking into account the decarboxylation reaction. Thus the difference between the theoretical and measured values gives the relative amount of decarboxylated rosin in the reactor, when the neutral rosin oil has almost completely vaporized from the system.

Gel permeation chromatography (GPC) analysis shows (Figure 5) that abietic acid polymerizes more than rosin during the synthesis. Thermal dimerization was observed only to a small extent in the resinate synthesis from rosin. The rosin acid content and the amount of abietic-type rosin acids affects the dimerization of rosin acids through double bonds. The high content of dehydroabietic acids in rosin prevents dimerization, because these acids do not have a conjugated

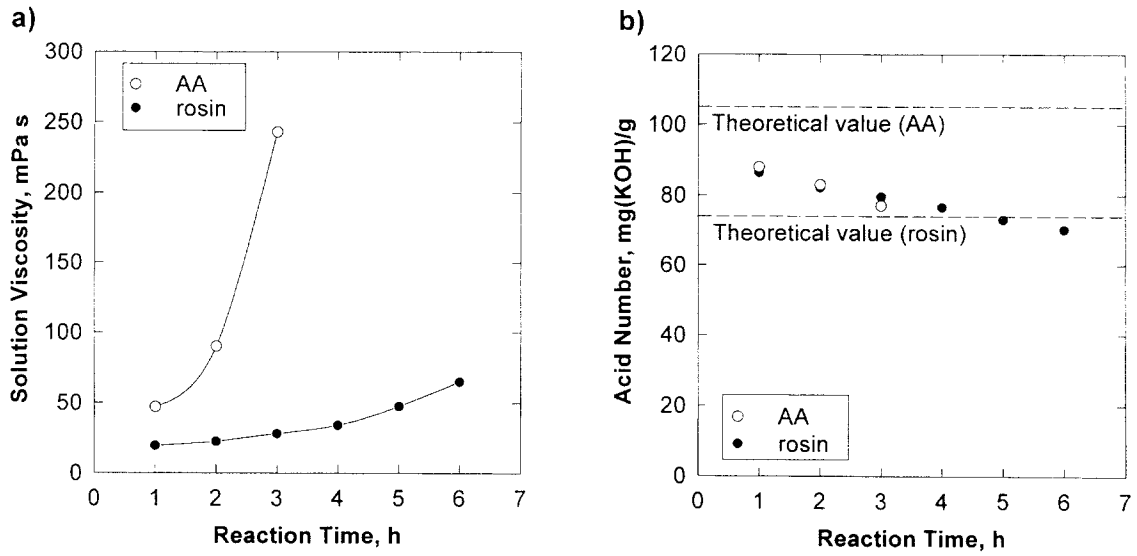

Figure 4. Syntheses of Ca/Mg-resinates from fortified abietic acid (AA) and fortified rosin at 265°C.

(a) Viscosity of 50 wt. % resinate toluene solution. (b) Acid number of the resinate.

diene structure. Only a relative amount of decarboxylated rosin acid is observed in GPC grams, because the neutral rosin oil has almost completely evaporated from the system.

Melt Viscosity Increase During the Synthesis. The viscosity of the 50 wt. % toluene solution of the resinate is usually measured when monitoring the progress of the reactions. The relation between the melt viscosity (measured at 200°C) and the toluene solution viscosity (at 25°C) was studied for the fortified Ca/Mg-resinate (Figure 6). Increase in melt viscosity of the resinate indicates the growth of molecular size.

Effect of Fortification of Rosin. The rosin is fortified in order to stabilize the viscosity increase and to obtain a higher softening point for the resinate to be used as an ink vehicle.

The more complete resinate reaction when using fortified rosin was observed from the acid number values (Figure 7b). The values did not reach the theoretical value during the synthesis without fortification in 6 h, which was probably due to dispersion problems with the slaked lime in the reaction. Similar behavior was reported by Oldring and Hayward (1987), when the value of the theoretical acid number was low (below 40 mg(KOH)/g). Calculated from the measured acid number values after 15-min reaction time, only 75% of the added metal salts had reacted, assuming that decarboxylation had not occurred. When fortified rosin was used, the resinate reaction was 90% completed after 15 min.

In the synthesis using fortified rosin the critical concentration value was 47.7 wt. % after 6 h, and without fortification it was 46.2 wt. %.

Effect of Reaction Temperature. In the syntheses at lower reaction temperatures it was observed that the viscosity increase remained almost linear during the 6 h reaction time (Figure 8). This was due to the hindering effect of the lower

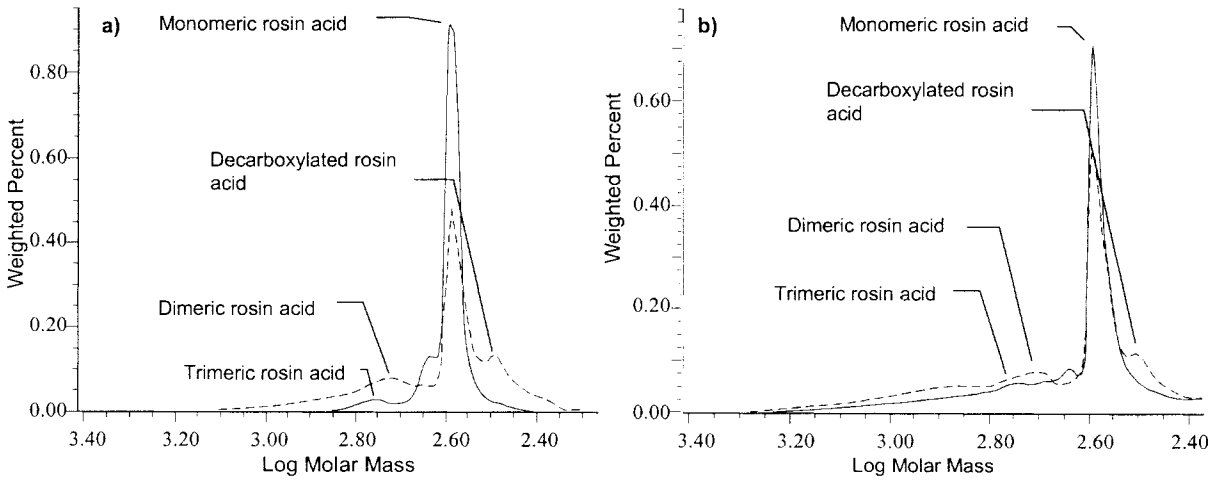

Figure 5. Effect of polymerization of rosin acids on molar-mass distribution of the resinate measured by GPC.

(a) ——— fortified AA; – – – – Ca/Mg-abietate (T = 265°C, reaction time 3 h). (b) ——— fortified rosin; – – – – Ca/Mg-resinate (T = 265°C, reaction time 4 h).

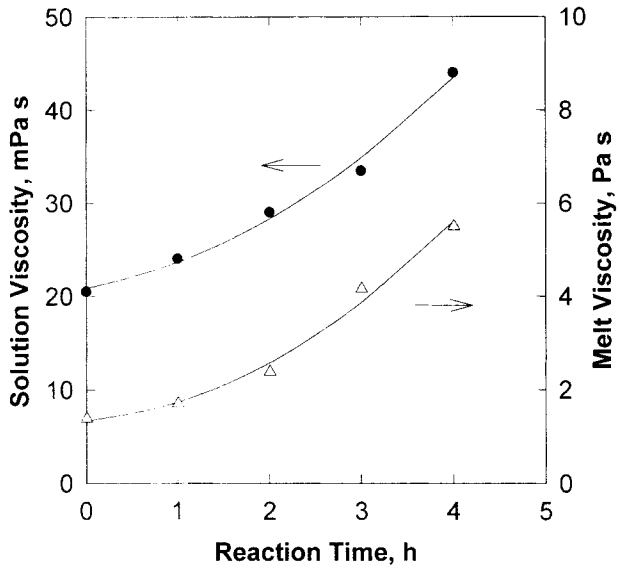

Figure 6. Melt viscosity and 50 wt. % toluene solution viscosity of fortified Ca/Mg-resinate; melt viscosity was measured at 200°C and solution viscosity at 25°C.

reaction temperature on the resinate reaction and on the decarboxylation of rosin acids observed from the acid number values of the synthesis.

The critical concentrations of the resinates synthesized at different reaction temperatures were determined from the log-log plot of viscosity data at different concentrations. At the reaction temperature 265°C the critical concentration value was 47.7 wt. %, at 255°C the value was 51.6 wt. % and at the lowest temperature (245°C) the critical value was 52.5 wt. %. Because the critical resinate concentration value was greater than 50 wt. % at the two lower reaction temperatures, the viscosity increase remained linear in Figure 8a.

Modeling of viscosity increase

Reactions Affecting Acid-Number Value. Kinetic studies were carried out by conventional method using acid-number titration, which gives the result of the overall state of the system: the progress of the resinate reaction and decarboxylation of rosin acids.

Reactions of the acid groups during the resinate synthesis are resinate formation (5–7) and decarboxylation (8):

$$2\,RCOOH + Ca(OH)_2 \rightarrow Ca(OOCR)_2 + 2H_2O\uparrow \quad (5)$$

$$2\,RCOOH + Mg(OH)_2 \rightarrow Mg(OOCR)_2 + 2H_2O\uparrow \quad (6)$$

$$2\,RCOOH + (CH_3COO)_2Ca \rightarrow Ca(OOCR)_2 + 2CH_3COOH\uparrow \quad (7)$$

$$RCOOH \rightarrow RH\uparrow + CO_2\uparrow \quad (8)$$

By assuming that water and acetic acid are completely removed from the reaction mixture due to the relatively high reaction temperature ($T = 265$°C), the rate laws (Eq. 9) and (Eq. 10) are written for the irreversible resinate and decarboxylation reactions, respectively:

$$r'_A = -k'c_A^2 c_B \quad (9)$$

$$r''_A = -k''c_A, \quad (10)$$

where A denotes a carboxylic acid group and B is $Ca(OH)_2$, $Mg(OH)_2$, or $(CH_3COO)_2Ca$.

Mass Balance of the Reaction System. The loss of mass during the synthesis affected the kinetic study. The loss, which was observed to be about 20% of the total mass, was mainly caused by the decarboxylated rosin vaporizing from the open reaction vessel with nitrogen. In the experimental setup the neutral rosin oil could not be collected and weighed because it either escaped through or solidified and blocked the distillation column. Calculated from the overall mass balance, it

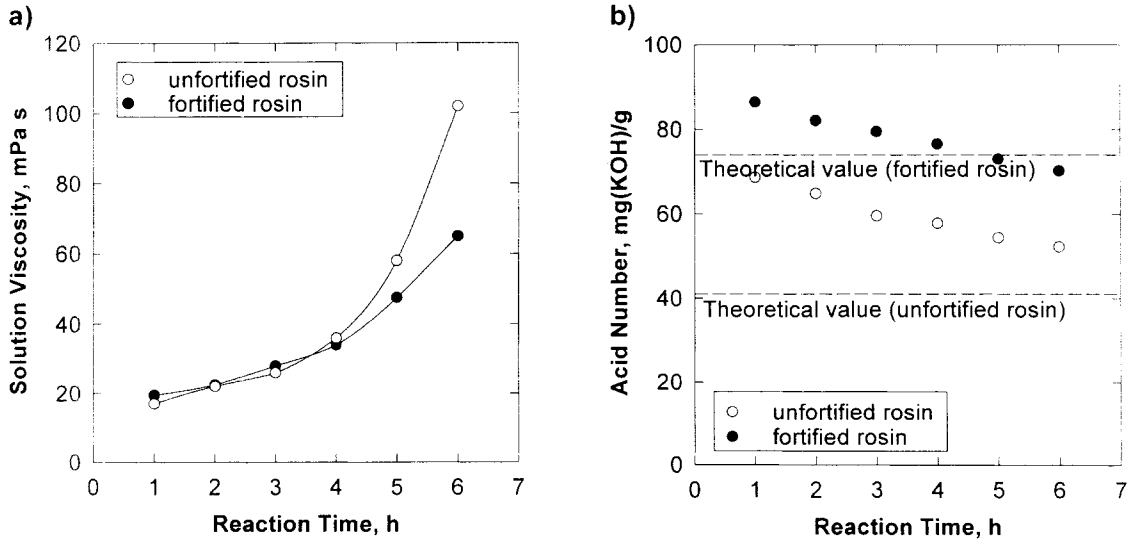

Figure 7. Syntheses of Ca/Mg-resinates from rosin and fortified rosin at 265°C.

(a) Viscosity of 50 wt. % resinate toluene solution. (b) Acid number of the resinate.

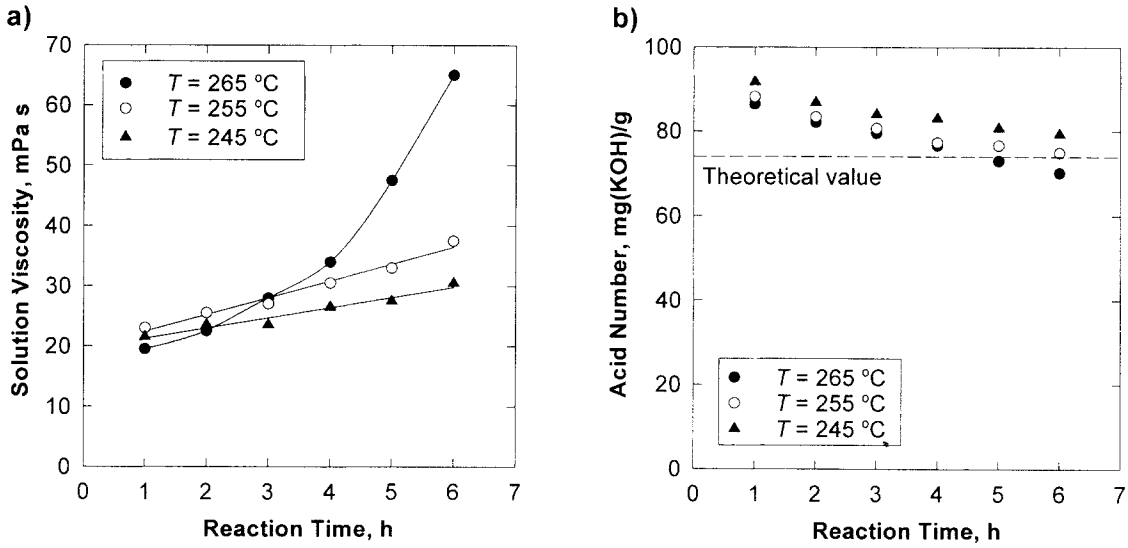

Figure 8. Syntheses of Ca/Mg-resinates from rosin at different reaction temperatures.

(a) Viscosity of 50 wt. % resinate toluene solution. (b) Acid number of the resinate.

was concluded that almost all (> 95%) decarboxylated rosin acids evaporate from the system, and it was assumed that the total molar flow from the reactor consisted only of the decarboxylated rosin and carbon oxides vaporizing from the system. This simplification was done by neglecting water and acetic acid in the vaporizing flow. The total amounts of water and acetic acid are less than 5% of the total mass and it is assumed that most of them have already been vaporized when the temperature has reached 265°C ($t = 0$ h). The kinetic study of the resinate synthesis is similar to polyesterification kinetics followed by acid number titrations (Paatero et al., 1994), despite the fact that the water of the reaction is of minor importance in the resinate synthesis.

During the synthesis of the resinates in the fusion method, the mass balances of the compounds in the reaction vessel can be written as

$$r_i m = \dot{n}_{i,v} + dn_i/dt, \tag{11}$$

where r_i denotes the generation rate (i = RCOOH) expressed in mol/(min kg solution), m is the mass of liquid in the reactor, n_i is the amount of compound i in the reactor, and $\dot{n}_{i,v}$ is the molar flow of i leaving the reactor by vaporizing. The amounts and flows of substance are expressed with the concentrations (c_i), the mass of the liquid (m), and the vaporizing mass flow ($\dot{m}_v$):

$$n_i = c_i m \tag{12}$$

$$\dot{n}_{i,v} = c_{i,v}\dot{m}_v, \tag{13}$$

where c_i and $c_{i,v}$ denote the concentrations in the reactor and vaporizing stream, respectively. Furthermore, the mass in the reactor, the mass of the vaporized substance (m_v), as well as the mass and molar flow ($\dot{n}_v$) are related by

$$-dm/dt = dm_v/dt = \dot{m}_v = \dot{n}_v M_v, \tag{14}$$

where M_v is the molar mass of the vaporized substance. It is the molar mass of rosin acid (302 g/mol) according to the decarboxylation reaction (Eq. 8). By assuming that the total molar flow from the reactor equals the decarboxylated rosin and carbon dioxide evaporating from the system, the molar flow is expressed as

$$\dot{n}_v = m r''_A, \tag{15}$$

where A denotes the acid group. After inserting Eqs. 12–15 into the balance equation (Eq. 11) and performing the differentiation, the following equation is obtained

$$dc_A/dt = r'_A + r''_A + c_A r''_A M_v. \tag{16}$$

Because resinate reaction is fast, it is assumed that $r'_A \approx 0$ when the temperature has reached 265°C ($t = 0$ h), and so Eq. 16 is written by inserting Eqs. 9 and 10 as

$$dc_A/dt = -k'' c_A - k'' M_v c_A^2, \tag{17}$$

which is rewritten as

$$dc_A/dt = -k'' c_A(1 + M_v c_A). \tag{18}$$

According to Eqs. 17 and 18, the total reaction order is between one and two depending on the $M_v c_A$, the value of which was between 0.5 and 0.3 during the different syntheses. Since the final aim is to obtain a viscosity model, it is sufficient to include the kinetic model in a simplified form. The simplified model is tested by fitting the data to the first- (Eq. 19) and second-order (Eq. 20) rate equations linearized by integration:

$$\ln(c_{A,0}/c_A) = k''t \tag{19}$$

$$c_{A,0}^{-1} - c_A^{-1} = k'''t. \tag{20}$$

The experimental kinetics fit reasonably well into both of the preceding linear rate equations, but the average fit was better when using the second-order rate law (Eq. 20). Figure

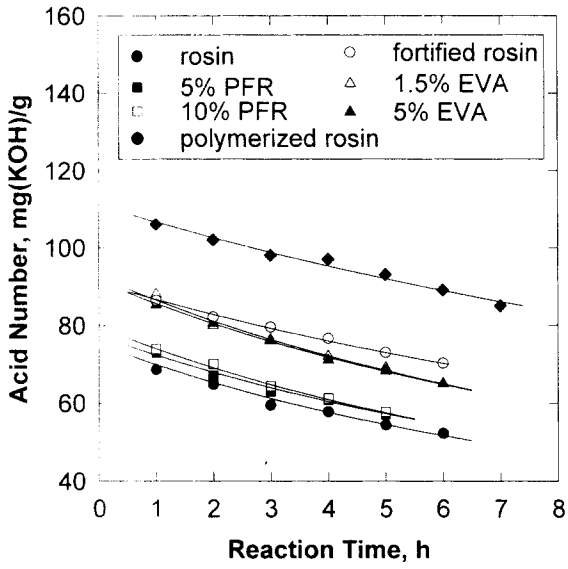

Figure 9. Empirical values and fit of the second-order rate model for acid numbers in the syntheses of Ca/Mg-resinates at 265°C from rosin, from PFR-modified rosin, from polymerized rosin, and from fortified rosin with EVA additions.

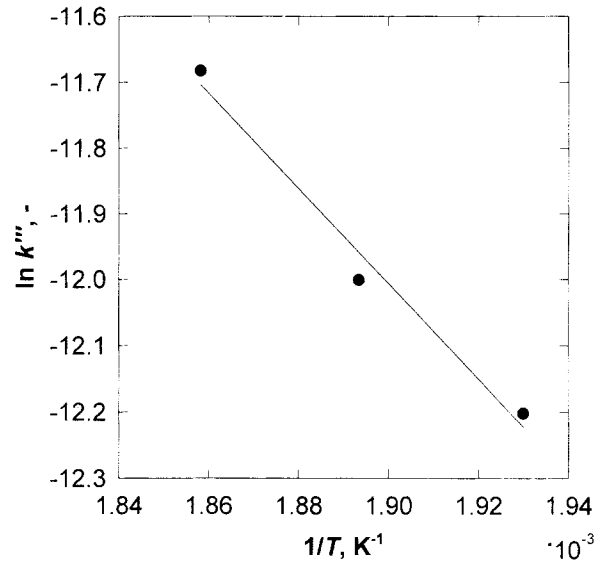

Figure 10. Determination of apparent activation energy for reactions in the synthesis of Ca/Mg-resinate from fortified rosin.

9 shows the data fit for the second-order rate equation. The lowest acid number values for resinates are obtained using rosin without fortification, because the fortification of rosin affects the initial acid number in the syntheses. The highest values are in the synthesis using polymerized rosin, because the theoretical metal content of the synthesis was only half that used in the other syntheses.

From Eq. 20 the apparent reaction-rate constants were determined for the resinate synthesis made from fortified rosin at different temperatures. The corresponding Arrhenius plot is shown in Figure 10, from which the obtained apparent activation energy was 60.1 kJ/mol.

Viscosity Dependence of Acid Concentration. The empirical correlation between the viscosity of 50 wt. % toluene solution of the resinate and the acid concentration in the reaction vessel was derived as

$$\frac{1}{\eta} = a' + b' c_A^{-1}. \tag{21}$$

By combining Eqs. 20 and 21, Eq. 22 is obtained:

$$\frac{1}{\eta} = \left(a' + b' c_{A,0}^{-1}\right) + (b' k''')t, \tag{22}$$

which can be rewritten by lumping the constants as

$$\frac{1}{\eta} = a + bt. \tag{23}$$

This simple two-parameter model provides a good description for the viscosity of the resinate solution as a function of reaction time. Parameter a describes the viscosity level at the reaction time $t = 0$ (the smaller the value of a is, the bigger the initial value of the viscosity). Parameter b includes the rate constant from the kinetic model, thus illustrating the rate of the viscosity increase. Figure 11 illustrates the fit of the model (Eq. 23) for the resinate syntheses with different modifications.

The fortification of the rosin affects the shape of the viscosity curve (Figure 11a). In EVA additions rosin was fortified, and in modification with PFR the fortification was not done. Viscosity increase is weaker with fortified rosin independent of the viscosity level.

Figure 11a indicates that the resinate syntheses from unmodified rosin and fortified rosin, as well as those of slightly modified rosin, have good correlations. It is obvious that severe modifications (Figure 11b) change the viscosity increase in resinate syntheses, because factors other than resinate reaction and decarboxylation also affect viscosity. In the synthesis using polymerized rosin, the high viscosity values were partly due to the rosin dimers present in the reaction mixture. PFR can react with rosin acids and hence increase the viscosity. Addition of EVA changes the relation of viscosity to acid concentration because of the higher viscosity level due to the macromolecules being added to the reaction mixture.

The models (Eqs. 21 and 23) can be used in process control. The independent parameters a', b', a, and b can be calculated based on acid number and viscosity samples at two different reaction times during the progress of the reactions. Parameter determinations can be done for several process batches, with different amounts of Ca and Mg being added and with different grades of raw material (rosin) being used. So the viscosity increase of the resinate solution and the total reaction time of the batch can be estimated.

Determination of t_{50} from the Viscosity Model. The reaction time at which the viscosity increase changes is denoted by t_{50}. This critical time can be predicted from the viscosity model by dividing Eq. 23 by time t, obtaining function $f = \eta/t = [t(a + bt)]^{-1}$, which has an inflection point at t_{50}. By forming the first time derivative (f') of this function and by calculating t_{50} from the zero point of f', the following equation (Eq. 24) is obtained:

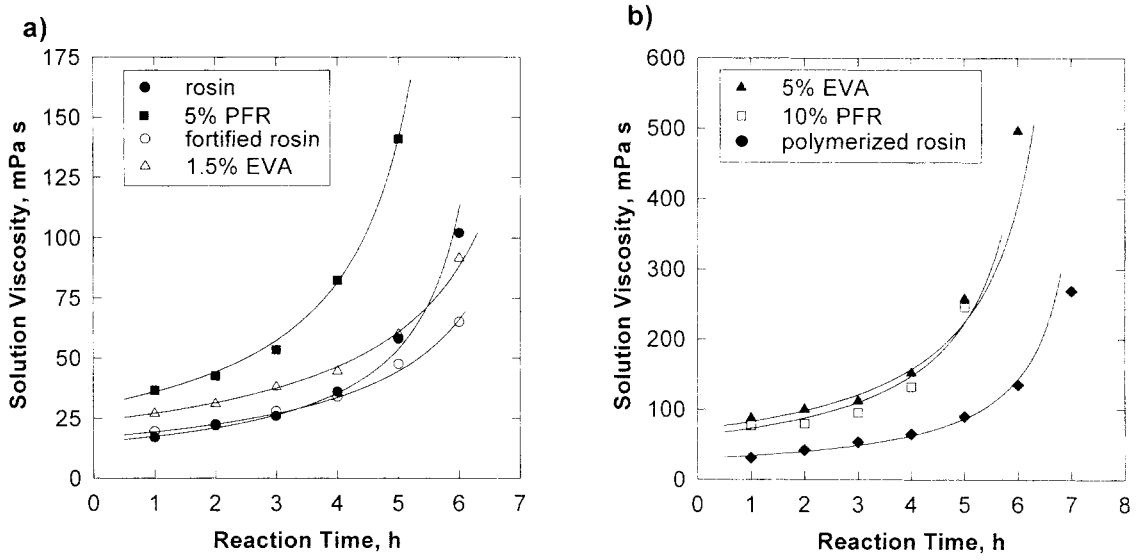

Figure 11. Viscosity increase in 50 wt. % toluene solution of Ca/Mg-resinates and modified resinates during synthesis at 265°C.

Lines are calculated according to the viscosity model (Eq. 23).

$$t_{50} = -\frac{1}{2}\frac{a}{b}, \tag{24}$$

which includes the parameters a and b from the viscosity model (Eq. 23). The t_{50} values in Table 2, calculated according to Eq. 24, indicate that fortification of rosin tends to increase the critical reaction time.

Conclusions

To study the molecular background for the abrupt solution-viscosity increase during the fusion synthesis of Ca/Mg-resinates, the solution viscosity of resinates was studied at different concentrations in toluene. It was observed that the viscosity increase turns almost exponential at a critical resinate concentration, denoted here by c_{crit}. This phenomenon is explained by resinate molecular interactions and excluded volume effects, when molecules are packed sufficiently densely in the solution.

The concept of critical resinate concentration was applied to explain the nonlinear viscosity increase in 50 wt. % toluene solution of the resinate during the syntheses. The abrupt solution-viscosity increase indicates the time, denoted by t_{50}, when the critical concentration of the resinate has reached the value of $c_{crit} = 50$ wt. %. A simple mathematical model with two parameters was derived from apparent reaction kinetics for the solution viscosity increase in the resinate syntheses (Eq. 23). The model provides a good description for the viscosity increase, not only for the synthesis of Ca/Mg-resinates made from rosin but also for the syntheses of slightly modified resinates with higher viscosity. The viscosity model can be applied to control the resinate process and to predict the t_{50} time (Eq. 24) of the syntheses.

Table 2. Critical Reaction Times of the Resinate Syntheses

Resinate Synthesis Using	t_{50}
Rosin	3 h 27 min
5% PFR modified rosin	3 h 12 min
10% PFR modified rosin	3 h 35 min
polymerized rosin	3 h 45 min
Fortified rosin	4 h
1.5% EVA addition to fortified rosin	4 h 10 min
5% EVA addition to fortified rosin	3 h 42 min

Notation

a' = parameter in Eqs. 21 and 22, $(\text{Pa}\cdot\text{s})^{-1}$
b' = parameter in Eqs. 21 and 22, $\text{g/kg}\ (\text{Pa}\cdot\text{s})^{-1}$
c_w = resinate mass fraction in toluene, wt. %
c_w^0 = unit concentration, wt. %
E = activation energy, J/mol
k' = reaction-rate constant of the resinate reaction, kg/(mol·min)
k'' = reaction-rate constant of the decarboxylation reaction, min^{-1}
k''' = apparent reaction-rate constant, kg/(mol·min)
η^0 = unit viscosity, Pa·s

Literature Cited

Jilek, J., "Calcium Salts of Tall Oil Rosin," *J. Coat. Technol.*, **48**, 83 (1976).

Oldring, P., and G. Hayward, eds., *Resins for Surface Coatings*, Vol. 1, SITA Technology, London (1987).

Paatero, E., K. Närhi, T. Salmi, M. Still, P. Nyholm, and K. Immonen, "Kinetic Model for Main and Side Reactions in the Polyesterification of Dicarboxylic Acids with Diols," *Chem. Eng. Sci.*, **21**, 3601 (1994).

Paatero, J., "Phenomenological Study on the System Aliquat 336 in Xylene-Nickel(II) in Aqueous Chloride Solutions," Rep. No. 106, Institute of Industrial Chemistry, Åbo Akademi, Turku, Finland, p. 10 (1975).

Panda, H., and R. Panda, "Modifications of Rosin for Printing Inks —Part 1," *Paint Resin*, **55**, 25 (1985).

Petrone, J. P., "Synthetic Resins for Inks I: Limed and Zinc Resinates, Rosin Esters," *Amer. Ink Maker*, **49**, 27 (1971).

Sinclair, R. G., D. A. Berry, W. H. Schuller, and R. V. Lawrence, "Influence of Reaction Conditions on the Dimerization of Abietic Acid and Rosin," *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 60 (1970).

Zinkel, D. F., "New Developments in Rosin Ester and Dimer Chemistry," *Nav. Stores Rev.*, **93**, 12 (1983).

Manuscript received Nov. 10, 1997, and revision received Mar. 24, 1998.