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RHEOLOGICAL PROPERTIES OF C9 PETROLEUM RESIN SOLUTIONS

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This paper investigates the rheological properties of C9 petroleum resin solutions, synthesized through different oligomerization methods. The research focuses on the behavior of resin solutions in terms of dynamic viscosity, shear stress, and shear rate with temperature, specifically between 293 and 343 K. The study shows that the viscosity of these solutions decreases with increasing temperature, which is typical of pseudoplastic, non-Newtonian fluids. The temperature coefficient for the resins ranges from −0.009 to −0.021 mPa·s/K, indicating that higher temperatures lead to a significant reduction in viscosity. The study examines the relationship between temperature and the density per unit viscosity, which increases in the observed temperature range. The density per unit viscosity at 293 K ranges from 507.0 to 1012.1 kg/m^3, and at 343 K, it ranges from 1083.7 to 2085.5 kg/m^3. These variations reflect differences in molecular structures and their influence on flow behavior under various temperature conditions. The flow index (n) ranges from −0.187 to −0.078, underscoring the strong pseudoplastic behavior of the resin solutions. The consistency constant, a measure of the material's resistance to flow, ranges from 2.1 to 5.55 Pa·s^n. These findings show that the viscosity of the solutions decreases with increasing shear rate, further confirming the pseudoplastic nature of the resins. These rheological characteristics indicate that C9 resins are suitable for use in high-temperature environments and in applications requiring stable flowability, such as paint coatings.

Keywords: rheology, viscosity, shear rate, shear stress, C9 resin, solution, oligomer.

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Introduction

Hydrocarbon resins, also known as petroleum polymer resins (PRs), are oligomeric products. Hydrocarbon resins are derived from petrochemical feedstocks. Their synthesis is based on the oligomerization of unsaturated hydrocarbons present in the liquid by-products of the pyrolysis of gasoline and diesel fractions, in particular the C9 fraction (422–473 K) [1,2]. The composition of such resins depends on the nature of the feedstock, pyrolysis and oligomerization conditions. Hydrocarbon resins are widely used in anti-corrosive coating, alkyd-based enamel, varnish, marine paint, offset ink, newspaper ink and rubber compounding.

C9 resins are produced by catalytic oligomerization [3], as well as high-temperature thermal and initiated oligomerization, low-temperature emulsion and suspension oligomerization methods [4,5]. The wide practical use of C9 resins is aimed at modifying resins and ensuring compatibility with plasticizing reagents [6,7].

Polymers (and oligomers) typically exhibit both viscous and elastic properties, displaying viscoelastic behavior [8]. It is clear from published studies that fluid viscosity is sensitive to the measurement environment. Therefore, it is essential to take the temperature and pressure of the fluid into account when studying them [9].

The results presented in ref. [10] demonstrate that the incorporation of C9 petroleum resins into modified bitumen leads to enhanced rheological properties. This improvement implies superior high-temperature performance and greater stability, attributes that are critical in the context of pavement engineering applications.

Varieties of methods are employed to study rheological properties, including capillary viscometers, which provide high measurement accuracy and allow for the study of liquids at different shear rates [8,11]. The operation of a capillary viscometer is based on the theory of fully developed flow. The length-to-diameter ratio has a significant impact on the capillary action. The hydrostatic head promotes the movement of the liquid through the capillary. The advantages of capillary viscometers are accuracy, low cost, and high shear rates. The disadvantage is the possible blockage of the capillary due to the formation of bubbles. Variable shear during flow changes the structure of the liquid and causes heating at high viscosities [12].

The knowledge of the viscous stability of hydrocarbon resin solutions in thermodynamic deformation regimes will provide, in addition to the practically necessary viscous characteristics, the basis for the thermodynamic deformation. Additionally, it will provide a basis for the development of a scheme for the evaluation of group contributions to the technical characteristics of the final products based on hydrocarbon resins.

The aim of this work is to investigate the change in the dynamic viscosity, shear stress and shear rate of viscous flow of C9 resin solutions as a function of temperature and resin synthesis methods.

Experimental

The research was conducted using a variety of hydrocarbon resins prepared by different methods (Table 1).

The composition of these resins differs depending on the method and temperature of oligomerization [4,5]:

Resins I–III are styrene-cyclopentadiene cooligomers obtained by high-temperature free-radical oligomerization;

Resins IV–VII, which are obtained by low-temperature emulsion and suspension oligomerisation, contain units of styrene and its derivatives;

Resin VIII is a cyclopentadiene resin, obtained from the C9 fraction, from which styrene and its derivatives were previously removed.

The dynamic viscosity of 10% resin solutions was determined using an Oswald viscometer with a 0.56 mm capillary diameter. The flow time was measured at 6 different temperatures ranging from 293–343 K in increments of 10 K.

To maintain the desired controlled conditions, the viscometer containing the solution was placed in a water bath, where the temperature was kept constant. Prior to commencing each new measurement, the temperature of the solution was allowed to stabilize within the water bath for a period of 10 minutes. The flow time of the solution through the capillary of the viscometer was determined by measuring the time interval during which the volume of liquid between

Table 1

Production conditions and properties of hydrocarbon resin

Resin	Production conditions	Molecular weight	Softening point, K
I	Initiated oligomerization, *tert*-butyl hydroperoxide as an initiator, reaction temperature of 453 K, and reaction time of 6 hours	640	354
II	Initiated oligomerization, oligoperoxide (obtained by condensation of pyromelite dianhydride with polyethylene glycol-35 and *tert*-butyl peroxymethanol) as an initiator, reaction temperature of 473 K, and reaction time of 6 hours	600	352
III	Thermal oligomerization, reaction temperature of 453 K, and reaction time of 8 hours	690	358
IV	Emulsion oligomerization, initiating system Sn stearate–hydrogen peroxide, reaction temperature of 313 K, and reaction time of 3 hours	670	356
V	Emulsion oligomerization, potassium persulfate as an initiator, reaction temperature of 323 K, and reaction time of 3 hours	690	358
VI	Suspension oligomerization, benzoyl peroxide (6 dosages) as an initiator, reaction temperature of 353 K, and reaction time of 3 hours	500	348
VII	Suspension oligomerization, tert-butylpiperidinomethylperoxide as an initiator, reaction temperature of 323 K, and reaction time of 3 hours	505	347
VIII	Initiated oligomerization of fraction C9 after suspension oligomerization, isopropyl benzene hydroperoxide as an initiator, reaction temperature of 453 K, and reaction time of 6 hours	650	354

two marks on the viscometer moved under the influence of gravity. Leakage time measurements were conducted with an accuracy of 0.1 seconds. At each temperature point, a minimum of three flow time measurements were performed. The mean flow time was employed to calculate the relative and dynamic viscosity.

The density of the resin solution in gasoline and the density of pure benzene at varying temperatures were determined using the dilatometric method.

In the capillary viscometer, the pressure drop created by the weight of the liquid column was calculated as the product of the liquid density, the height of the column, and the gravitational acceleration. The shear rate was calculated as the ratio of the volume flow rate of the liquid to the geometric parameters of the capillary (capillary diameter (d) of 0.56 mm, and height of 32 mm). Shear stress was calculated as a function of pressure drop and capillary diameter [12,13].

Results and discussion

The rheological behavior of eight solutions of hydrocarbon resins obtained by different methods was studied. The temperature dependence of the density change of the solutions was determined experimentally, and the flow time of the solutions at different temperature conditions was measured. The viscosity, shear stress and shear rate were calculated from the experimental data.

The dynamic viscosity varies from 0.39 to 1.77 mPa·s (Fig. 1). The viscosity of the resins studied decreased with rising temperature. These findings confirm the temperature dependence of viscosity, which is typical of pseudoplastic non-Newtonian fluids. The largest alterations in viscosity were observed in resins IV and VIII, which demonstrated the greatest changes. At 293 K, resin IV exhibits the highest initial viscosity (1.77 mPa·s), which decreases to 0.71 mPa·s at 343 K. The correlation between temperature and dynamic viscosity for different resins is in the range of −0.95 to −0.99. The critical temperature (the temperature corresponding to the largest change in viscosity) is 303 K in all cases. The values of the temperature coefficient when the temperature changes from 293 to 343 K are shown in Table 2.

The density of 10% resin solutions in benzene in the temperature range of 293–343 K varies from 1012 to 810 kg/m^3 (Fig. 2). In the temperature range under consideration, the greatest variation in density was observed in the case of a resin solution of V (66 kg/m^3), while the lowest value was recorded for resin VII (38 kg/m^3). A decrease in resin solution density is invariably accompanied by a decrease in viscosity. While the nature of this relationship is consistent across all cases, the rate of change varies.

In the temperature range studied, the shear stress of resin solutions exhibited a range from 1.11 to 1.39 Pa (Fig. 3). A decrease in shear stress is observed with increasing temperature for solutions of all resins. This is consistent with the fact that increasing the temperature reduces the viscosity of liquids, resulting in a decrease in the shear stress. The shear stress for

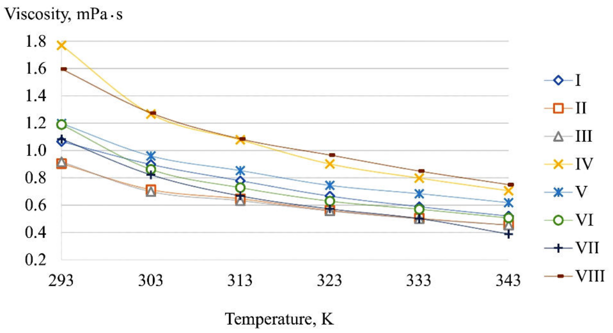

Fig. 1. Resin solution dynamic viscosity as a function of temperature

Table 2

Rheological properties of hydrocarbon resin solutions

Resin	Temperature coefficient, mPa·s/K	Density per unit viscosity, $m^{-1}·s^{-1}$		Flow index	Consistency constant, $Pa·s^n$
		293 K	343 K		
I	–0.011	909.1	1760.0	–0.129	3.49
II	–0.009	964.0	1832.0	–0.140	3.53
III	–0.009	1012.1	1958.0	–0.144	3.07
IV	–0.021	507.0	1201.5	–0.111	2.70
V	–0.012	845.4	1529.1	–0.187	5.55
VI	–0.014	727.6	1620.9	–0.110	2.71
VII	–0.014	783.3	2085.5	–0.078	2.10
VIII	–0.017	539.3	1083.7	–0.143	3.29

all series shows similar trends with a smooth decrease within each series. Solutions VI and VII have the lowest initial shear stresses, while solutions V and I have the highest initial shear stresses.

The resin solutions displayed a high elastic response, exhibiting flow at a shear stress that was three orders of magnitude higher than their dynamic viscosity (Fig. 1 and 3).

In all cases, an increase in shear rate is observed with rising temperature (Fig. 4), which correlates with the dynamic viscosity. At 293 K, resin V demonstrates the highest initial shear rate (1675.53 s^{-1}), which subsequently increases to 2298.79 s^{-1} at 343 K. Resin VII exhibits the highest shear rate at 343 K (3660.38 s^{-1}), representing the highest value among all series. This indicates that this series exhibits the highest fluidity at high temperatures. Resin IV demonstrates the lowest shear rate (1166.30 s^{-1} and 2016.31 s^{-1} at 293 K and 343 K, respectively).

The viscosity of resin solutions decreases with increasing shear rate (Fig. 5), indicating the pseudoplastic nature of these fluids. The most significant decrease in viscosity is observed in the speed range of 2000–3000 s^{-1}, where it decreases from 1.07 to 0.50. The correlation between the shear rate and the resins solutions viscosity is −0.89.

The relationship between shear rate and shear stress (Fig. 6) was found to be nonlinear for all samples, thereby confirming their non-Newtonian nature. The decrease in shear stress with increasing shear rate indicates the shear thinning effect, which is characteristic of non-Newtonian pseudoplastic fluids. At high velocities (over 2000 s^{-1}), the shear stress for all samples approaches similar values, indicating a decrease in their viscosity and more similar behavior. Therefore, all samples can be classified as pseudoplastic non-Newtonian fluids that exhibit liquefaction under shear.

The temperature coefficient indicates the extent to which the dynamic viscosity changes in response to a one–degree temperature increase [13]. All resins exhibit negative values of the temperature coefficient, indicating a reduction in viscosity with increasing temperature from 293 K to 343 K. Resins II and III demonstrate the lowest temperature coefficient, with a value of −0.009. These resins exhibit enhanced stability in viscosity across a broad temperature range, rendering them suitable for use in a diverse range of temperatures. Resin IV exhibits the greatest reduction in viscosity, with a coefficient of −0.021, indicating a

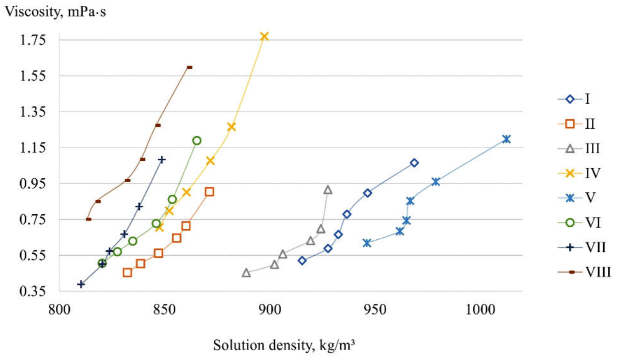

Fig. 2. Resin solution dynamic viscosity as a function of density

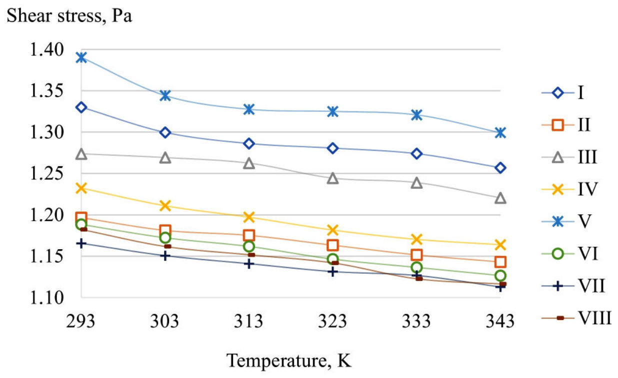

Fig. 3. Shear stress as a function of temperature

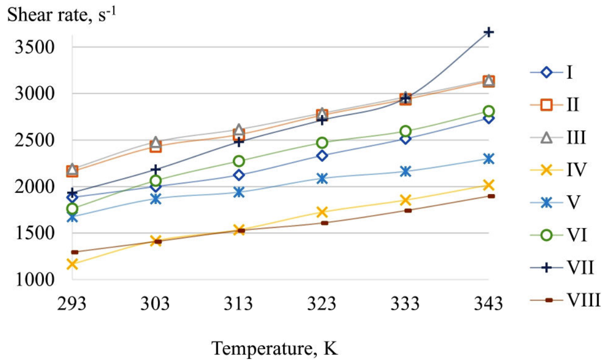

Fig. 4. Shear rate as a function of temperature

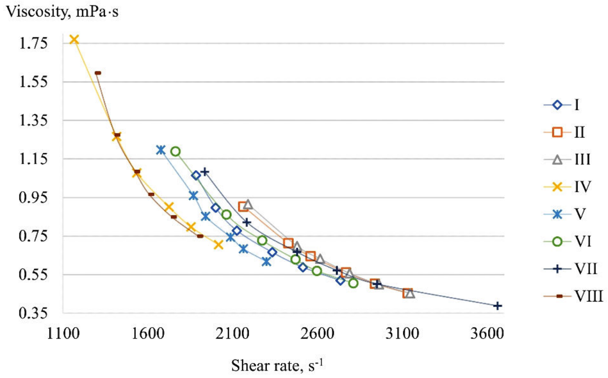

Fig. 5. Viscosity as a function of shear rate

pronounced temperature–dependent effect on this resin solution.

It was observed that an increase in temperature from 293 K to 343 K resulted in an increase in density per unit viscosity for all resins. This trend is consistent with a decrease in viscosity with increasing temperature (Fig. 1). The highest value of density per unit viscosity at 343 K was observed for resin III (1958.0), indicating its high stability at this temperature. The lowest value for the change in density per unit viscosity was observed for resin VIII (1083.7–539.3=544.4), which indicates greater stability of the rheological properties of this resin, and thus greater stability in industrial conditions.

The flow index (n) determines how shear stress varies with shear rate. Resins with a lower n value show a stronger dependence of viscosity on shear rate. All samples have a value of n<1, which indicates their pseudoplastic behavior.

Styrene resin IV and cyclopentadiene resin VIII, which exhibit the most significant viscosity alterations in response to temperature fluctuations, can be utilized in applications where rapid adjustments to rheological characteristics are necessary, particularly in paints and coatings designed for high-temperature environments. Styrene resin V has the highest consistency and is recommended for use in environments with high shear stress, such as in rubber compounds or bitumen modifiers. Styrene-cyclopentadiene resin III is produced by thermal oligomerization and exhibits high temperature stability, rendering it suitable for use in conditions requiring a stable viscosity, such as in anti-corrosion coatings and marine paints.

Conclusions

The dependence of the change in dynamic viscosity of hydrocarbon resin solutions on temperature, solution concentration, and method of their synthesis has been studied. It was found that with increasing temperature the properties of resin solutions approach those of non–Newtonian fluids, which is confirmed by their pseudoplasticity. It was determined that the dynamic viscosity of resin solutions is contingent upon the temperature and composition of the solution.

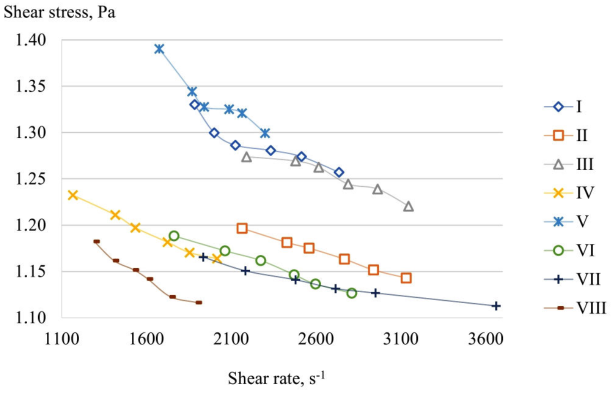

Fig. 6. Shear stress as a function of shear rate

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РЕОЛОГІЧНІ ВЛАСТИВОСТІ РОЗЧИНІВ НАФТОПОЛІМЕРНИХ СМОЛ С9

Р.О. Субтельний, І.Г. Балітський, Б.О. Дзіняк

В даній роботі досліджено реологічні властивості розчинів нафтополімерних смол С9, синтезованих різними методами олігомеризації. Розглянуто поведінку розчинів смол з точки зору динамічної в'язкості, напруження зсуву та швидкості зсуву як функції температури, зокрема в діапазоні 293–343 К. Встановлено, що в'язкість цих розчинів зменшується з підвищенням температури, що є типовим для псевдопластичних, неньютонівських рідин. Температурний коефіцієнт для смол знаходиться в межах від –0,009 до –0,021 мПа·с/К, що вказує на те, що підвищення температури приводить до вираженого зменшення в'язкості. Розглянуто зв'язок між температурою і густиною на одиницю в'язкості, яка зростає в досліджуваному температурному діапазоні. Густина на одиницю в'язкості при 293 К коливається від 507,0 до 1012,1 кг/м^3, а при 343 К – від 1083,7 до 2085,5 кг/м^3. Ці варіації вказують на відмінності в молекулярних структурах та їх вплив на поведінку потоку за різних температурних умов. Індекс течії (n) змінюється від –0,187 до –0,078, і вказує на псевдопластичну поведінку розчинів смол. Константа консистенції, яка є мірою опору матеріалу течії, знаходиться в діапазоні від 2,1 до 5,55 Па·с^n. Ці результати демонструють, що в'язкість розчинів зменшується зі збільшенням швидкості зсуву, що додатково підтверджує псевдопластичну природу смол. Ці реологічні характеристики вказують на те, що смоли С9 придатні для використання у високотемпературних середовищах і в композиціях, що вимагають стабільної текучості, таких як лакофарбові покриття.

Ключові слова: реологія, в'язкість, швидкість зсуву, напруження зсуву, смола С9, розчин, олігомер.

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