Short communication

The effect of molecular composition of naphthenic mineral oil on the glass transition temperature

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ABSTRACT

Differential scanning calorimetry (DSC) has been applied to analyze the glass transition temperature of refined hydrogenated naphthenic mineral oils. The impact of the aromatic content and the degree of hydrogenation have been studied. A change in aromatic content for refined hydrogenated mineral oils was found to give only a limited impact on the glass transition temperature of the oil.

A silica gel separation was conducted and by using the hereby obtained fractions as components in the Fox equation, the glass transition temperature was calculated. The calculated values for the oils are in agreement with the values obtained in the DSC measurement.

The aromatic content and the viscosity of mineral oils influence T_g. However, for the oils in this study, the change in T_g was small for relatively large changes in aromatic content.

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1. Introduction

Naphthenic mineral oils are extensively used in the polymer and lubrication industries. The composition of the oil influences the properties of the final product, e.g. the glass transition temperature (T_g) [1–5]. The glass transition phenomenon [6] can be observed in any liquid material that forms, or can be forced to form, an amorphous solid and is often said to be a function of the degree of molecule mobility in the material [3,7–10]. Any factor that enhances motion ought to decrease T_g. Consequently, the molecular structure has a large influence on T_g.

Differential scanning calorimetry (DSC) has been used to study properties of petroleum products, mainly focusing on wax content, since the late 1960s [11–17]. The present work discusses carbon type distribution and the influence of aromatic hydrocarbons on T_g of refined naphthenic mineral oils.

2. Experimental

2.1. Materials

The oils used in this study were wax free, refined naphthenic oils of different hydrogenation degrees. The oils are denoted A–D in descending order of degree of hydrogenation. The degree of hydrogenation is inversely related to the aromatic content of the oil, C_A. Some characteristics of the oils are given in Table 1.

2.2. Analysis, separation and fractionation techniques

A liquid nitrogen cooled DSC unit (2920 MDSC) from TA instruments was used. The samples were placed in uncovered standard Al sample pans and the sample masses were between 5 and 20 mg (commonly 13–17 mg). Nitrogen gas (>99.999%) was used as cell purge gas (50 mL/min).

The DSC analysis cycle began with heating of the samples to 70 °C where they were kept isothermal for 5 min and then cooled down to −120 °C with a programmed cooling rate of −10 °C/min. At −120 °C, the samples were kept isothermal for 5 min before they were re-heated to 70 °C with a programmed heating speed of 10 °C/min. The T_g value on heating has been used.

A selection of the oils was separated into fractions by silica gel separation. A glass column (500 mm × 40 mm) was charged with a slurry of 250 g silica gel 40 (70–230 mesh ASTM) in n-pentane. The oil sample (10 g) mixed with n-pentane (10 mL) was then added to the column. As eluents, n-pentane (500 mL, ≥99%), toluene (500 mL, ≥99%) and ethyl acetate (500 mL, ≥99%) were used. Fractions from the same oil with no or minor variations in refractive index were pooled together. To obtain sufficient amounts of the different fractions of each oil the separation was repeated.

The separation follows the ASTM 2007-03 standard with some minor deviations: ethyl acetate was used instead of acetone as it has a lower vapour pressure and the clay gel process was excluded as the oils in this study did not contain any asphaltenes. Hence, the fractions was noted as; saturated, aromatic and polar in accordance with the ASTM 2007-3 nomenclature [22].

The presence of aromatic compound in the obtained fractions was analyzed by using TLC plates (ALUGRAM® SIL G/UV) which,

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Table 1
Some characteristics of the test oils.

Method:/Oil:	Viscosity at 40 °C, [mm²/s] ASTM D 445[a]	Density at 15 °C, [kg/m³] ASTM D4052[a]	Refractive index at 20 °C ASTM D1747[a]	Hydrocarbon type analysis, C_A [%] ASTM D2140[a]
1. (A100)	85	0.891	1.483	0
2. (B8)	9	0.872	1.475	1
3. (B23)	35	0.880	1.480	1
4. (B100)	100	0.893	1.487	1
5. (C8)	8	0.879	1.478	4
6. (C100)	104	0.906	1.494	5
7. (D8)	9	0.886	1.485	9
8. (D23)	22	0.901	1.493	10
9. (D100)	110	0.916	1.502	11
10. (D200)	220	0.921	1.505	12
11. (D400)	370	0.924	1.508	15

[a] The oil characteristics are measured in accordance with the ASTM standards [18–21].

due to fluorescence from conjugated double-bonds, visualizes aromatic compounds as spots under a UV-light (254 nm). N-pentane was used as eluent in the TLC analysis.

3. Results and discussion

Mineral oils are conventionally divided into paraffinic and naphthenic oils. This classification is based on physical properties such as density, viscosity index and the Watson characterization factor [16]. The classification is related to the character of the crude oil. Readers unfamiliar with oil chemistry are referred to Speight [23].

The majority of the hydrocarbons in refined naphthenic mineral oil are of paraffinic and naphthenic type, only a small part of the hydrocarbons is aromatic.

The result obtained in this study indicates that a change in aromaticity for refined hydrogenated mineral oils has a limited impact on T_g of the oil. It is the overall molecular composition of the oil which determines T_g and not only the aromatic content.

If oils of similar viscosity but of different degrees of hydrogenation are compared, small shifts in T_g can be seen as the aromatic content (C_A) increases up to one order of magnitude (Table 2). Based on our results it is likely that the large increase in T_g of nearly 30 °C reported by Masson as the aromatic content increases by 4% may be due to a viscosity increase rather than solely an effect of an increase in the aromatic content [24].

One other trend that can be seen is that T_g increases as the viscosity of the oil increases when the aromatic content is held constant. This is illustrated in Table 2 as sample nos. 2–4 all have an aromatic content of 1% but the increase in viscosity from 8, 25 and 100 cSt respectively lead to T_g values of −90, −77 and −64 °C. This result is in line with the theory that a higher viscosity will give a lower degree of molecular mobility and thereby increase T_g [25]. The relationship between viscosity and T_g has been discussed by Ferry in detail [26].

As density and viscosity index are important physical properties when classifying mineral oils, the correlation between these properties and T_g was investigated. T_g was found to increase linearly

with both density and refractive index for oils having the same degree of hydrogenation (Appendix A).

In order to study the effect on T_g of saturated, aromatic and of polar heterorganic compounds present in oils, a silica gel separation was performed on a selection of the oils. In the TLC analysis, all fractions obtained from the silica gel separation showed fluorescence which indicates presence of conjugated carbon–carbon double-bonds even in the earliest eluated oil containing fractions. In refined, hydrogenated mineral oils, conjugated carbon–carbon double-bonds are only present in aromatic structures and presence of fluorescence in the early fractions indicates that molecules which mainly classify as saturated and act as saturated molecules in the interaction with silica gel may still contain a small aromatic content. This is not addressed in the ASTM D 2007 method.

The effect of aromatics on T_g is visualized when comparing the saturated fraction containing nearly no aromatics to the aromatic fraction containing virtually only aromatic hydrocarbons (Fig. 1). T_g increases from the first eluated (saturated) fraction to the aromatic, through to the last eluated (polar) fraction (Table 3). This increase in T_g is probably due to increased dipole-dipole interactions in combination with a decreased rotational freedom arising from hydrogen bonding.

The T_g values for the oils before separation were found to be located between the T_g values of the saturated and the aromatic fractions (Table 3). This led us to conclude that the apparent T_g of oil is the combined T_g of the molecular structures present.

There are a number of equations to correlate T_g of a mixture to T_g of the components. For miscible polymer mixtures the Fox equation applies [27]:
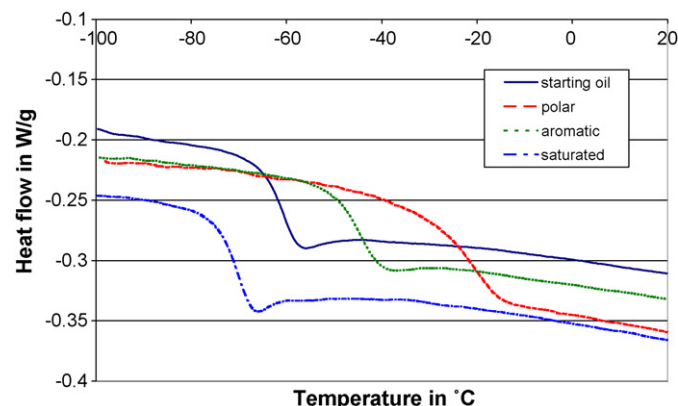
$$\frac{1}{T_g} = \sum_{i=1}^{n} \frac{x_i}{T_{gi}} \tag{1}$$

Table 2
.

Sample	Viscosity [mm²/s] ASTM D445	C_A [%] ASTM D2140	T_g [°C]
2. (B8)	9	1	−90
5. (C8)	8	4	−89
7. (D8)	9	9	−87
3. (B23)	25	1	−77
8. (D23)	22	10	−74
1. (A100)	85	0	−63
4. (B100)	100	1	−64
6. (C100)	104	5	−62
9. (D100)	110	11	−60

Fig. 1. Heat flows curves from heating of the oil no 9 (D100) and fractions thereof.

Table 3
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Sample	Fraction	Composition w%, according to ASTM D2007-03	T_g DSC, °C
4. (B100)	–	–	−64
	Saturated	91.4	−67
	Aromatic	8.6	−53
	Polar	0.1	–[a]
6. (C100)	–	–	−62
	Saturated	75.6	−71
	Aromatic	23.8	−46
	Polar	0.6	−24
9. (D100)	–	–	−60
	Saturated	73.5	−70
	Aromatic	25.7	−44
	Polar	0.8	−20
10. (D200)	–	–	−55
	Saturated	55.5	−66
	Aromatic	42.7	−43
	Polar	1.8	−20
11. (D400)	–	–	−52
	Saturated	65	−64
	Aromatic	32	−43
	Polar	3	−9[b]

[a] The obtained amount was not sufficient for DSC analysis.

[b] The somewhat low value is probably due solvent residue as ethyl acetate was used to facilitate sample preparation since the fraction was hard and stiff.

Table 4
Calculated T_g values by using the Fox equation.

Sample	Calculated T_g Fox eq. (°C)	Measured T_g DSC (°C)
4. (B100)	−65	−64
6. (C100)	−62	−62
9. (D100)	−60	−60
10. (D200)	−52	−55
11. (D400)	−47	−52

where x_i is the weight fraction of component i and n is the number of components.

By using the different fractions obtained by the silica separation as components in the Fox equation (Eq. (1)), T_g of the oils has been calculated (Table 4).

These calculated values are in good concurrence with the values obtained through the DSC measurements.

The fact that only a single T_g value was obtained, despite the oil being a mixture, differentiates naphthenic oil from polymer blends, for which more than one T_g value is often seen [28]. The single T_g value in combination with the correlation with the Fox equation indicates that the molecular groups present in naphthenic oil are fully miscible in each other.

The heat capacity (Cp) can be expressed as the heat flow (q/t) divided by the heating rate (T/t). A glass transition appears as a step in the baseline of the recorded DSC curve. In the curves obtained through the DSC measurements clear changes in the heat capacity of the oils but no changes in latent heat associated with crystallisation and melting were detected. Based on this,

and on general literature regarding glass–liquid transitions in non-polymers [11,13,14,24], we believe that the phenomenon studied here is indeed a continuous thermal transition.

4. Conclusions

The aromatic content and the viscosity of mineral oils influence T_g. However, for well-refined hydrogenated oils the change in T_g is small for relatively large changes in aromatic content and the viscosity effect prevails.

The single T_g obtained for all tested oils in combination with the Fox equation correlation indicates that the molecular groups present in naphthenic mineral oils are fully miscible in each other.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.11.002.

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