Pure paraffin waxes analysis for hybrid rocket solid fuels: rheological, thermal and mechanical characterization

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Abstract

Hybrid rocket engine performance, in terms of regression rate, can be enhanced by the use of liquefying fuels. This paper presents an extends experimental activities on pure paraffins performed at Politecnico di Milano. Different paraffins were tested, both macro-crystalline and micro-crystalline. A quantitative analysis of the properties that mainly influence their applicability in large-scale hybrid engines has been performed by intense experimental activity. Thermal, rheological, mechanical and chemical properties were investigated with the aim to better understand the behaviour of this type of liquefying hybrid fuels.

1. Introduction

Several fundamental studies have proved that by using paraffinic-based materials it can be possible to obtain higher regression rate values compared to those achieved with conventional polymeric fuels like hydroxyl-terminated polybutadiene (HTPB), polyethylene (PE), polymethyl methacrylate (PMMA) or polypropylene (PP) [1]. The melts of a paraffinic material led to obtain a low viscosity liquid layer due the hydrodynamic instability (entrainment effect) [2] [3] from the liquid-phase interface and, basically to high regression rate values. On the other hand good mechanical properties are necessary in order to allow these fuels to be used in real hybrid engines. This paper describes combined experimental activity, with the aim to study the correlations between the properties that influence the applicability of paraffins as fuels in hybrid engines. For thermal properties a Differential Scanner Calorimetry (DSC) was used and tests reveal that one part of the investigated samples are containing, at least, two different fraction characterized by two well-defined melting peaks in the range of 30 – 36 °C and 52 – 54°C. Another sample reveal two melting peaks in the range of 42 - 46 °C and 62 - 64 °C, another in the range of 64 - 67 °C and 83 - 94 °C where the second one occurs at lower heat flow than the other, and for another sample it is identifiable only one dominant melting peak in the range of 65 - 68 °C. Rheological investigations have been performed using a parallel plate rheometer set-up [4] [5] and tests were performed with respect to shear rate and temperature. The storage modulus of all paraffins has been compared with DSC test results, thus revealing a clear correlation between paraffin softening and storage modulus value behaviour. Then, in order to analyze the mechanical behavior of these different pure waxes, tensile tests using a uniaxial elongation test machine were carried out at different load velocities. Some results reveal that, as expected, there is a direct proportionality between the applied tensile velocity and ultimate strength values. A chemical characterization (gas-chromatography) of these paraffins was also carried out for a better comprehension of the thermo-physical behavior of these kind of waxy materials. In almost all macro-crystalline wax samples studied, two main different paraffinic fractions were detected: between C16 – C18 and C30 – C33.

2. Investigated materials

Six different paraffin waxes were characterized, according to the list and the nomenclature of Table 1. The first investigated paraffin was a commercial paraffin (GW), supplied by an Italian Company, with a DSC melting point of 54.9 °C. The second was a Russian product, available in the framework of a cooperation agreement between Politecnico di Milano and the Siberian Branch of the Russian Academy of Sciences, Institute of Petroleum Chemistry located in Tomsk. The third wax (AW) was another commercial product supplied by Sigma Aldrich.

Sasol GmbH was the supplier of two different materials (0907 and 8204). This kind of waxes are characterized by predominantly branched molecules and long chain lengths up to C_{70}, The branching is predominantly located at terminals [3]. Generally they exhibit clear plasticity stickiness in comparison with other paraffin waxes and higher melting temperatures. In contrast, Carlo Erba wax (CEW), supplied by Carlo Erba Reagenti S.p.a. is a macro wax characterized by low molecular mass, low viscosity and low melting and congealing points. From manufacturer information, Sasol 8204 wax is based on an average chain length C29.

Table 1: Composition and density of the investigated pure paraffinic materials.

Fuel	**Manufacturer**	**Given Density, [g/cm^3]**
GW	Gelly Wax	0.88
RW	Russian Wax	0.89
AW	Sigma Aldrich Wax	0.89
0907	Sasol 0907 Wax	0.92
CEW	Carlo Erba Wax	0.89
8204	Sasol 8204 Wax	0.92

3. Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) measurements of the pure waxes were performed with a TA Instruments model 2010 CE thermal analyzer system. All the experiments were performed by using nitrogen gas (33 ml/min) as heating/cooling gas and tested at 10K/min as temperature ramp. The calibration was performed with an Indium standard. All tested samples where weighted by a Mettler Toledo electronic balance (0.1 mg accuracy).
Figure 1 shows the DSC scan of the GW, RW and AW paraffin waxes used throughout this study. Considering GW trace it appear clear that the first endothermic peak is lower than other samples and starts before (at 10°C). RW shows a more noticeable first peak. Table 2 reports the main thermal parameters measured for the tested materials.

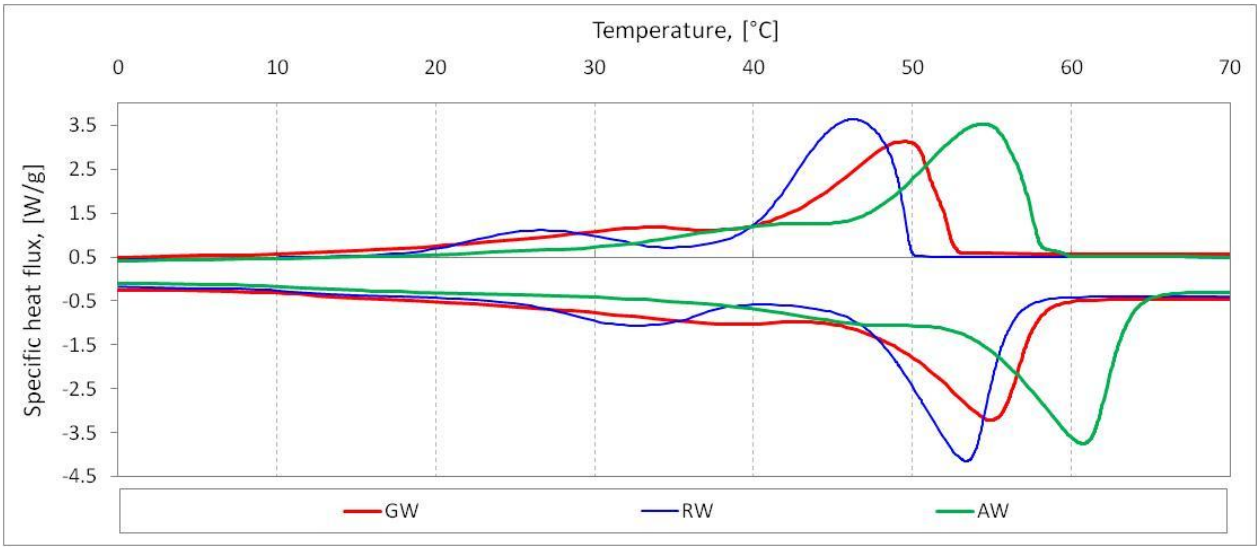

Figure 1: DSC scan of pure GW, RW and AW waxes.

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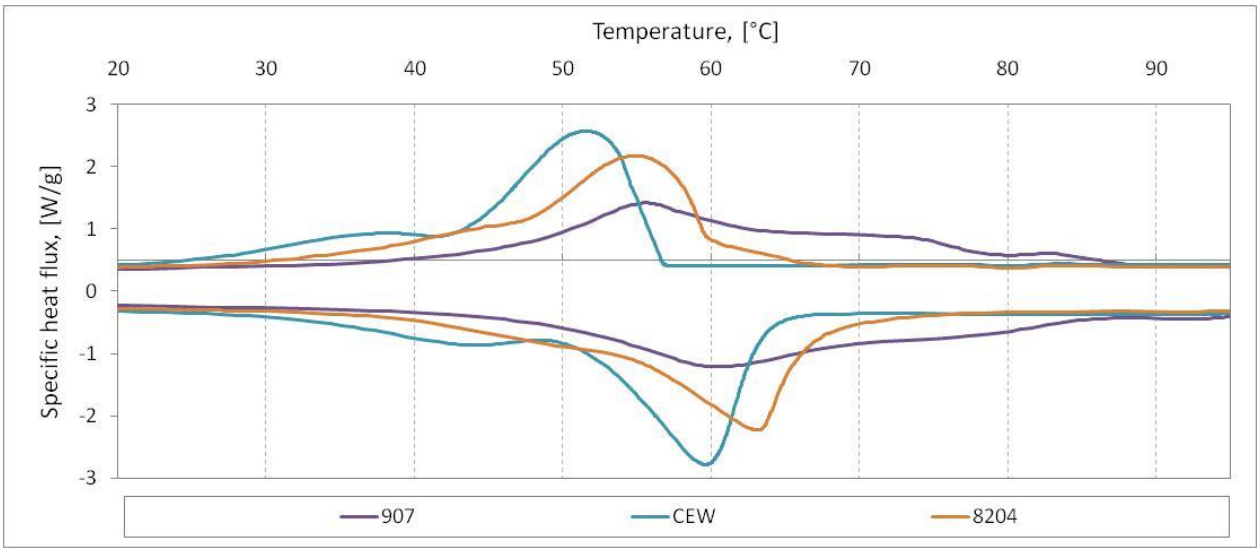

Figure 2: DSC scan of pure 0907, CEW and 8204 waxes.

Carlo Erba wax shows lower melting and congealing main peaks, followed by Sasol 8204 and 0907. This is in agreement with manufacturer datasheets, in which Carlo Erba wax has a nominal congealing temperature range of 58-60 °C, Sasol 8204 a range of 66-70 °C and Sasol 0907 between 83 °C and 94 °C. Sasol 0907 shows a wider melting and solidification range. This is explained by the presence of iso-paraffin (from manufacturer indications, Sasol 0907 is a compound of 36% C34 n-paraffin and 64% C59 iso-paraffin): when its content is high with respect to the n-paraffin, melting and cooling phases occur gradually.

Table 2: Parameters obtained from DSC measurements for paraffinic waxes ('T' temperature, 'ΔH' specific enthalpy, 'm' melting, 'c' cooling)

Material	$T_{m,p}$ 1 [°C]	$T_{m,p}$ 2 [°C]	$T_{m,p}$ 3 [°C]	ΔH_m [J/g]	$T_{c,p}$ 1 [°C]	$T_{c,p}$ 2 [°C]	$T_{c,p}$ 3 [°C]	ΔH_c [J/g]
GW	39.1	54.9	-	219.1	33.6	49.5	-	199.4
RW	32.6	53.4	-	224.9	26.8	46.2	-	200.6
AW	49.5*	60.7	-	256.1	44.0*	58.2	-	228.5
0907	59.7	82.1	98.9	151.4	83.8	70.0	47.1	160.3
CEW	48.6	64.1	-	183.4	37.2	-	-	188.3
8204	48.8	66.8	-	187.7	62.9	50.0	-	186.5

[a] The DSC heating curve shows a double-peak in which the first is sharp. See Fig. 1.
[b] The DSC cooling curve shows a double-peak in which the first peak is sharp. See Fig. 1.

Figure 5 compares the exothermic peaks, measured with TGA technique, for GW and Sasol 0907 waxes. The specific heat curves shows that the combustion process of GW is faster than that observed for 0907. The most important observation is regarding the different amount of ashes observed with the mass loss % trace. As it can be seen, just after the combustion, at 310 °C GW release only the 11% of the initial amount of sample. Sasol 0907 shows an amount of ashes of about 16%, probably linked with a different higher concentration of high-molecular mass fraction (See Figure 8 for the chemical composition of these kind of paraffins). The curves which show the mass loss (%) point out that the sample gasification occurs approximately in the range between 200 and 300 °C for GW and 240°C and 400°C for 0907. The residual mass, at higher temperature, is due to ashes, hard to be oxidized; for this reason the oxidation process takes much more time than the main combustion process.

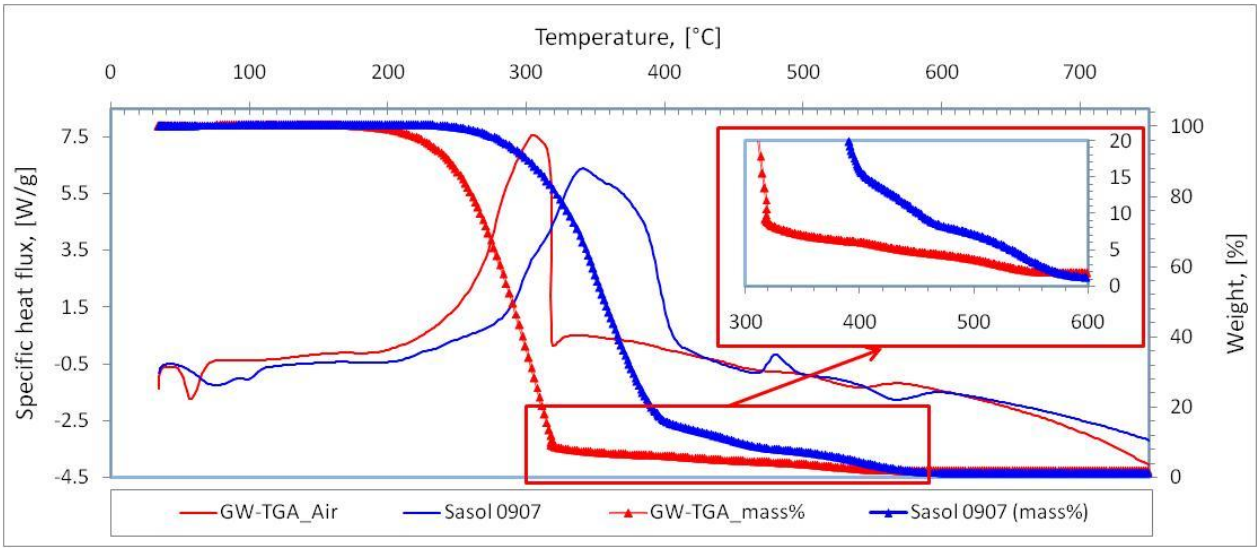

Figure 3: Comparison of the TGA and percentage mass loss trends for pure GW and 0907 waxes .

4. Rheology

In order to obtain the viscoelastic behaviour of the investigated formulations a rotational rheometer was used. In particular all the experiments were carried out by a *Rheometrics Dynamic Analyzer RDA II* using a parallel plate apparatus to study the elastic and storage moduli (G', G'').

Figures 4 and 5 shows the trend of G' and G'' for pure GW and RW respectively. A strain sweep test was performed in order to determine the linearity behavior of the GW. A set of 1% strain tests was decided to be the best drawback with the desired linearity of the G'/strain behavior and the sensitivity of the instrument. All the paraffinic materials considered in this work were tested at 1% strain and results were shown in figure 4, 5, 6 and 7. Figure 5 shows two G' and G'' trends measured with strain 0.05% (green circles) and 1% (purple circles) in both cases is easy to see the strong influence on elastic and storage moduli both of the crystalline phase transition and the first endothermic peak responsible of the paraffin softening. The shift occurring between the endothermic peak pointed out by DSC test and the beginning of G' sharp decrease (and symmetrically the sharp increase of G'') has to be linked to the different mass of the samples (2mg vs. 2 g). Different masses are characterized by different thermal inertia.

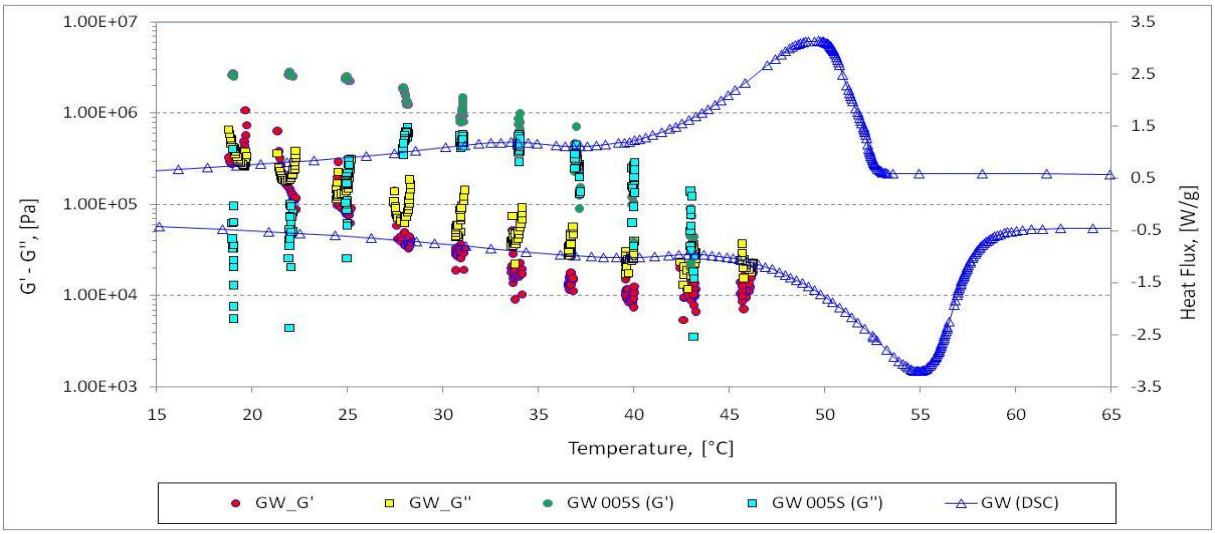

Figure 4: Trend of G' and G'' vs. T for pure wax GW, comparison with DSC trace.

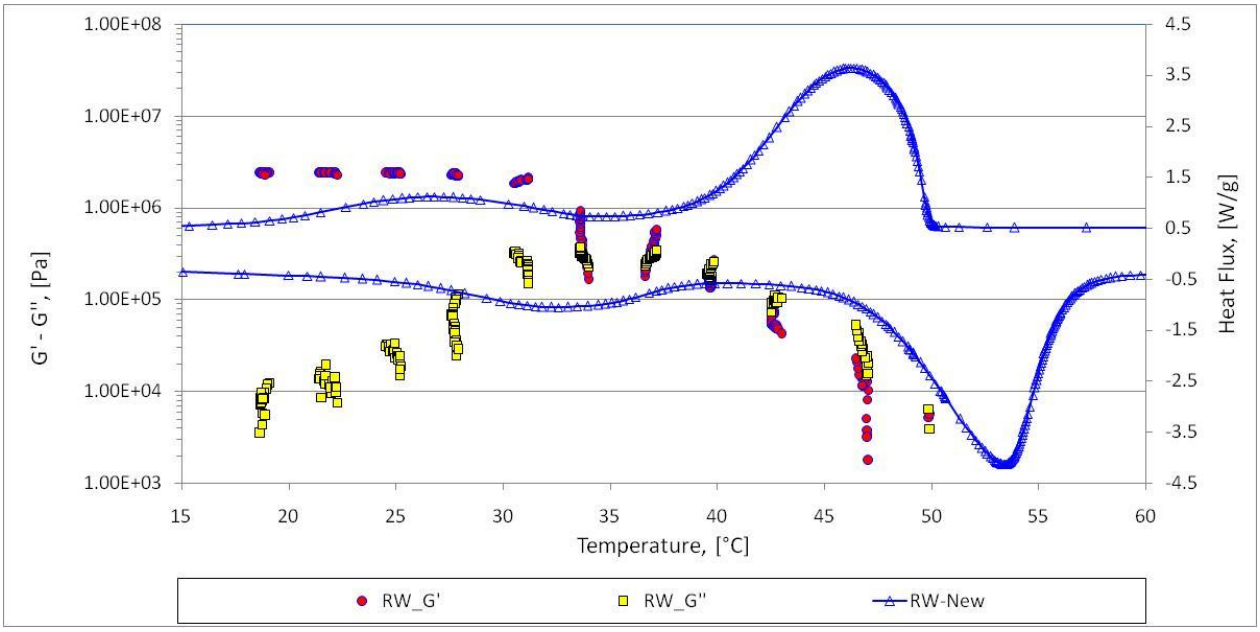

Figure 5: Trend of G' and G'' vs. T for pure wax RW, comparison with DSC trace.

Rheological tests have been performed from 21 °C up to the temperature at which a rheological response is given. As shown in Figure 6, micro paraffin Sasol 0907 shows a fall down in storage modulus value at 48 °C. This is in agreement with DSC test results, because this temperature value corresponds, in DSC graph, at the initial (in melting phase) and final (in cooling phase) heat absorption and release. This means that the capability of Sasol 0907 to preserve its elastic energy is associated to the paraffin softening phase. Considering all shear rate tested values, from 0.5 up to 50 Hz, in the range between 21 °C and 48 °C the storage modulus values vary between 1.81E06 Pa and 2.38E06 Pa . Instead loss modulus has higher variability in function of shear rate test conditions and values increase starting from 39 °C.

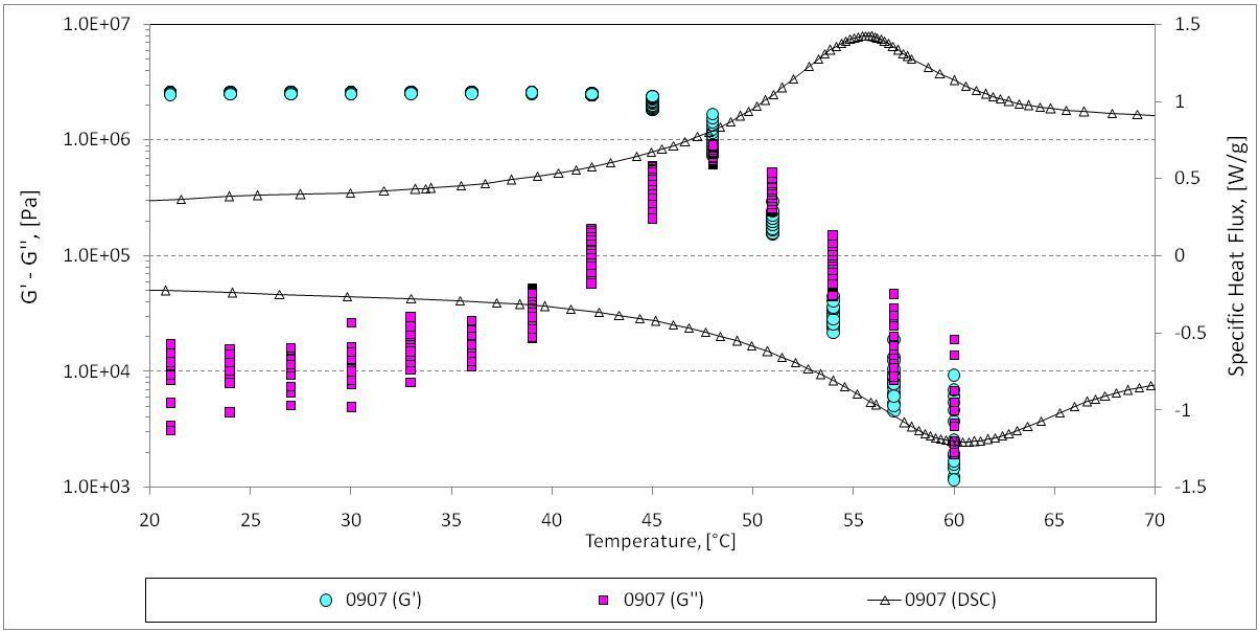

Figure 6: Trend of G' and G'' for pure Sasol 0907compared with its DSC trace.

Sasol 8204 behaves in the same way as Sasol 0907. Results are shown in figure 7. The storage modulus starts to fall down between 48 and 51 °C and main congealing peak is visible at 62.9 °C. Storage modulus values up to 48 °C vary from 1.56E06 and 2.54E06 Pa, that maintains the same order of magnitude of Sasol 0907.

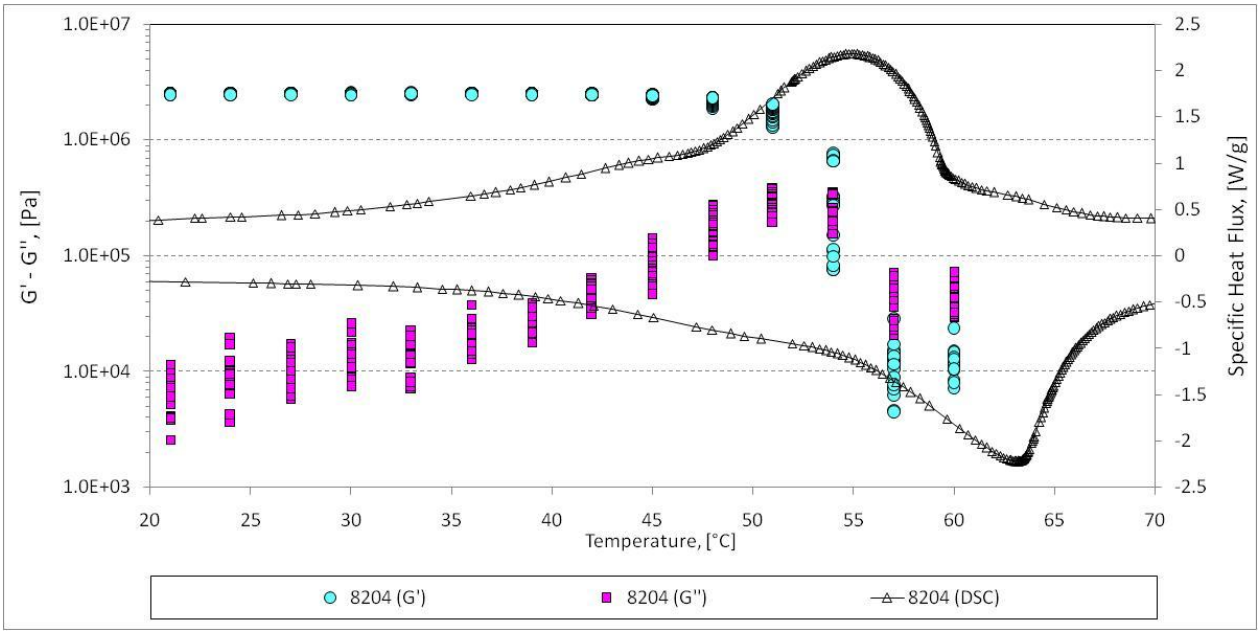

Figure 7: Trend of G' and G'' for pure Sasol 8204compared with its DSC trace

5. Mechanical properties

Tensile tests have been performed with MTS 858 instrument. Load has been applied at two different velocities, 0.5 and 5 mm/s. The elongation has been measured using an extensimeter carefully inserted in the central zone of the restricted samples area. Test sample dimensions and post processing have been done according to UNI-EN-ISO 527 norm for plastic materials. Elastic modulus has been calculated in both methods described in the reference norm and no significant differences have been pointed out.

At increasing velocities of applied load, both elastic modulus and maximum stress show higher values for all tested waxes.

As it can be seen considering data listed in Table 3 GW shows the lowest mechanical properties when compared with the other paraffinic materials. Tensile tests carried on GW, RW and AW were performed only at 0.5 mm/min because of the noticeable frailty of these materials.

At both velocities of the applied load, Carlo Erba wax shows fragile rupture, after a sensible slope decreasing of the stress-strain curve, more evident in tests performed at 0.5 mm/s. Sasol 8204 shows a clear elasto-plastic deformation phase, in which residual deformations are present and associated to the plastic deformation contribution. Then a localized deformation characterized by a rapid area section decrease in a small part of the sample is visible (striction phase, descending part of the stress-strain curve) and, after this phase, rupture is reached. Micro-crystalline wax Sasol 0907 shows elastic behaviour and reach rupture in the elastic field (fragile rupture).

15 tests have been executed for each wax and test condition. Mean values comparison in terms of elastic moduli and maximum stress is presented in the following histograms. As expected, due to the high stickiness of micro-waxes, Sasol 0907 shows higher elastic modulus both at 0.5 and 5 mm/s tested velocities. Sasol 8204 tested at 5 mm/s velocity reaches higher maximum stress, 3.09 MPa mean value, following Sasol 0907 with a value of 2.25 MPa and Carlo Erba with a value of 1.67 MPa.

Table 3: Parameters obtained from tensile measurements for paraffinic waxes
('$E_{d,av}$' average elastic modulus, differences ratio,
'$E_{r,av}$' average elastic modulus, regression,
'SD' standard deviation, 'σ_{max}' maximum load)

Material	Speed [mm/min]	$E_{d,av}$ [MPa]	SD [MPa]	$E_{r,av}$ [MPa]	SD [MPa]	σ_{max} [MPa]	SD [MPa]
GW	0.5	42.4	9.0	41.7	9.3	0.28	0.08
RW	0.5	124.1	17.4	122.2	17.3	0.59	0.04
AW	0.5	182.6	11.6	181.7	11.2	1.48	0.06
CEW	0.5	231.3	18.0	231.6	16.8	1.07	0.05
CEW	5.0	365.7	46.7	362.2	44.4	1.67	0.10
8204	0.5	520.6	68.8	520.1	72.5	2.27	0.22
8204	5.0	717.6	49.2	720.7	55.4	3.09	0.22
0907	0.5	672.9	66.9	671.4	66.0	1.74	0.19
0907	5.0	827.7	53.7	826.4	54.2	2.25	0.23

6. Chemical analysis

A chemical analysis of all considered paraffinic materials was performed by using a GC-MS method (Perkin Elmer Clarus 66-MS).
A mixture of different solvent (ciclohexane, eptane and dichloromethane) was used to obtain a clear solution of the selected material (6 mg of every paraffin). A set of parameters (oven: T_{in} = 150°C for 1 min, ramp = 10 K/min, T_{fin} = 280°C; carrier gas: helium, solvent delay: 6 min) was selected to find the distribution of aliphatic chains.
Two different methods were used to correctly identify the chemical composition of the selected material: by comparison with an electronic library (Nist2004) and by determining the retention time of a linear C_{20} standard hydrocarbon solvent.
Figure 8 shows a comparison of GC graphs reporting the percentage area distribution versus retention time. As it can be seen the first peak of each GC graph was collected after several minutes depending of the molecular mass of the eluited fraction. Higher is the molecular mass of the aliphatic fraction, longer is the retention time with a non linear distribution.

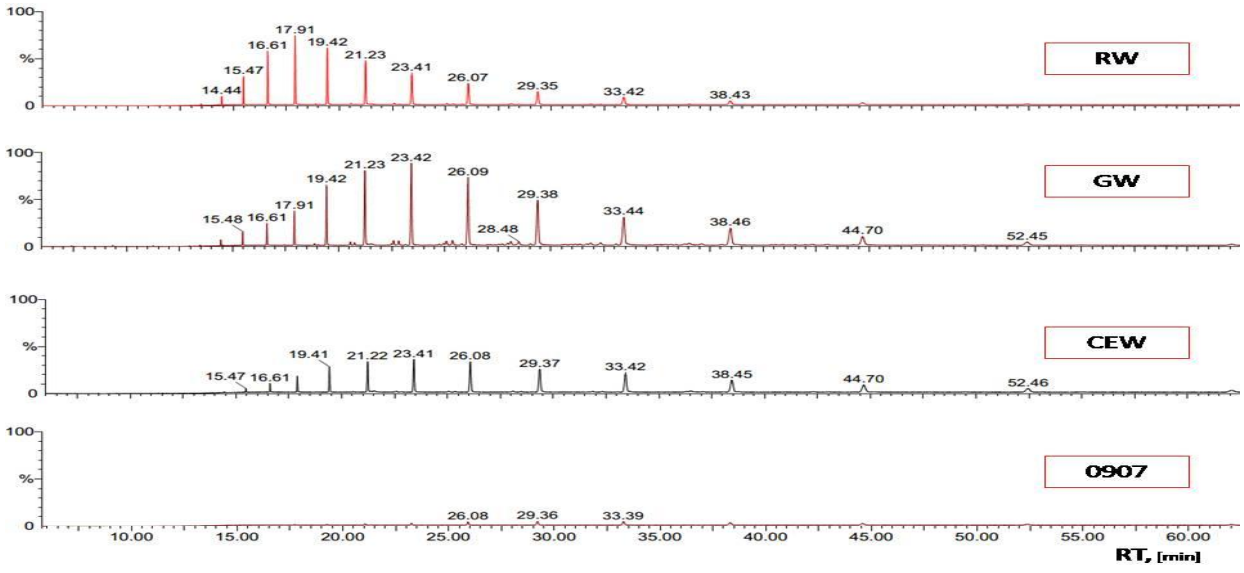

Figure 8: Chemical composition of several paraffin waxes: GW, RW, CEW and Sasol .

Considering Sasol 0907 (Sasol 8204 was very similar) shown in figure 8, it is clearly visible the difference with other specimens in terms of intensity of signal. A very low concentration of aliphatic hydrocarbons was detected in this sample probably because of a scarce or negligible eluition process inside the gaschromatographic column. In presence of high polar substances or high molecular mass (higher than C_{50}), the GC-MS method falls, so other analytical techniques should be taken in account.
Figure 9 shows a comparison of elastic modulus (G') of GW, RW and AW with the chemical analysis of each sample. The mass fraction distribution of aliphatic chains in each sample, was plotted versus the corresponding melting temperature (Nist data) of each fraction between C_{20} and C_{32}.
As it can be seen, considering RW and AW, a coherent link between elastic modulus and the chemical composition. A C_{20}, C_{21} mass fraction higher in RW sample than in AW sample was observed (10.2% and 14.6% Vs. 1.6% and 3.6% respectively) and could explain why the elastic modulus for RW falls before than AW. The temperature shift between the falls of G' (34°C for RW and 40°C for AW) values and the melting temperature typical of C_{20} (39°C) and C_{21} (43°C) can be easily explained considering that RW at 34°C is soft, not completely melted.
The elastic modulus falls for GW was less rapid than the other two paraffins. A possible explanation could be linked with the presence of lighter than C_{20} aliphatic chains, characterized to have a less softening temperature than that typical of C_{20}. If the initial temperature of the oven (in which the gas-chromatographic column is placed) for the selected GC-MS method is 150°C, it could be possible that the lighter fractions flow out of the column before the start of the data acquisition. To support this explanation a qualitative observation was done by placing on a paper sheet a small amount of all the paraffinic materials investigated. After few hour an oily mark was only observed below the GW sample. Other GC-MS tests will be carried out to clarify this point.

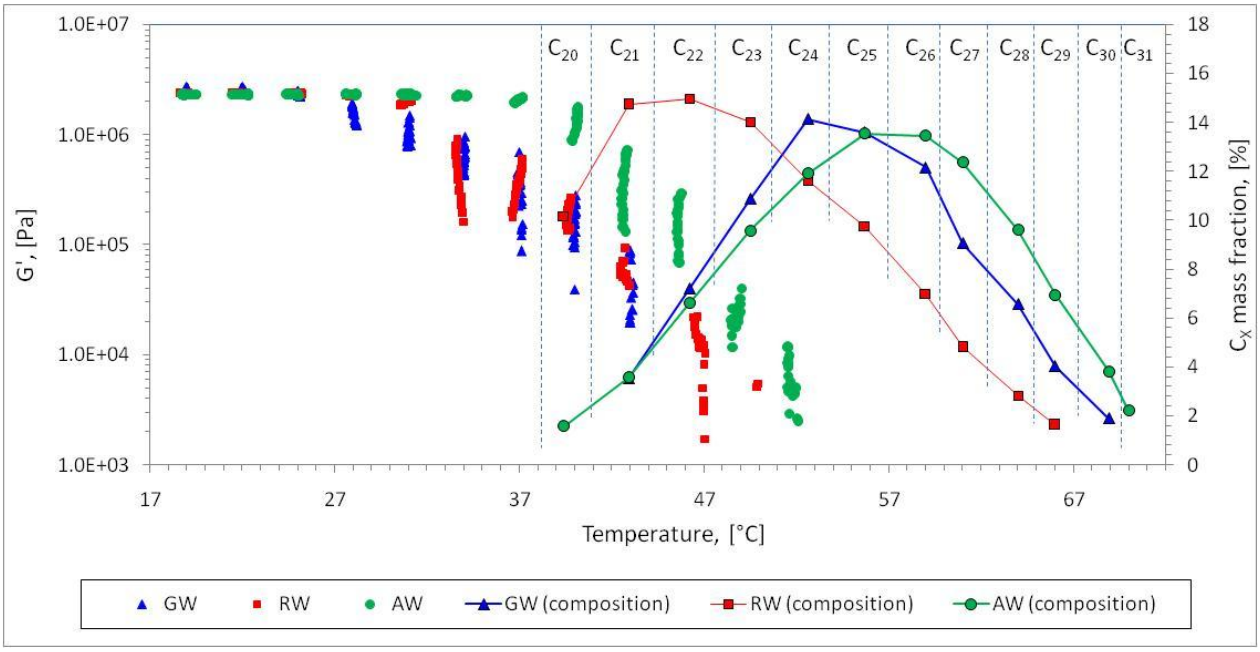

Figure 9: Trend of G' and G'' for pure GW, RW and AW compared with its chemical composition

7. Conclusions

To achieve a better comprehension of the behaviour of the selected paraffinic waxes, a thermal, rheological mechanical and chemical characterization were performed. Considering the sum of observation linked with the heavy (probably long chain fraction) carbon fraction responsible for the high ash content (TGA and mass loss experiments) of 0907 compared with GW and the rheological behaviour, a coherent trend with the chemical composition could be pointed out. The strong influence of the temperature (if it is between the first endothermic peak and second exothermic/cooling peak) on G' behaviour of all the materials tested was clearly shown. As the temperature of the paraffine is approaching to this range (the material, usually brittle, is going to become soft), the elastic modulus falls very rapidly. Gas-chromatographic analysis shows that a possible explanation of this behaviour could be linked with the presence of light carbon fraction responsible of the anticipated softening of the whole mixture.

Differential Scanner Calorimetry results pointed out the different behaviour of Carlo Erba wax and Sasol 8204 if compared to micro crystalline Sasol 0907, which shows a gradual melting and congealing curves. Congealing peaks are in agreement with manufacturer indications, thus revealing that the micro paraffin presents the highest melting temperature range. Rheological tests reveal that micro crystalline wax gives a valid rheological response at higher temperatures, 48°C, and, up to this temperature, presents a higher storage modulus value for all shear rate test conditions. Tensile tests reveal that, as expected Sasol 0907 shows higher elastic modulus both at 0.5 and 5 mm/s tested velocities, which trend was expected due to the high stickiness of micro-waxes. Sasol 8204 reaches the highest maximum stress, 3.09 MPa mean value, followed by Sasol 0907 with a value of 2.25 MPa and Carlo Erba with a value of 1.67 MPa.

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