Drug Development and Industrial Pharmacy, 34:157–163, 2008

ISSN: 0363-9045 print / 1520-5762 online
DOI: 10.1080/03639040701484569

informa
healthcare

Rheological Characterization of Petrolatum Using a Controlled Stress Rheometer

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The current study focuses on characterizing the rheological characteristics of different petrolatum grades using a controlled stress rheometer. Both steady-state flow and dynamic oscillatory tests were conducted on the petrolatums. The thermorheological scans were found to be the most informative and reproducible for this study. Significant differences in the structure were observed between the petrolatum grades. The structural differences were found to be most significant in the temperature range 25–35°C. The findings from this study will help in identifying the critical parameters (for e.g., temperature, mixing) during the processing and handling of such materials, which can have a direct impact on the product rheology and performance.

Keywords rheology; petrolatum; thermorheological scans; structure; dynamic oscillatory testing

INTRODUCTION

White petrolatum is the major ingredient in most ointments, along with waxes and oils added to stiffen and reduce tack (Pena, Lee, & Stearns, 1994). These materials are widely used in the pharmaceutical, cosmetic, food, textile, and other industries. Rheological properties of ointments have a significant role to play in terms of processing (e.g., pumping through pipes or tubes, and storage) and aesthetics (e.g., spreadability on the skin surface). In addition, they undergo a wide range of stresses during removal from the container or tube, and application. Since the rheology of such materials is dependent on the field of application, industries need a better understanding of factors that determine the rheological properties in order to obtain the desired physical characteristics (Fu & Lidgate, 1985, Masmoundi, Piccerelle, LeDreau, & Kister, 2006). With a complete understanding of the rheological characteristics, necessary adjustments could be made during the manufacturing process in order to achieve optimal product performance.

Since petrolatum is the major ingredient in most ointments, this study focuses on characterization of petrolatum rheology. Petrolatums consist of mixtures of *n*-, *iso*-, and cyclic paraffins, with different proportions defining the characteristics of the different petrolatum grades. A detailed discussion on the structure of petrolatum has been provided by Barry and Grace (1971). They indicate that petrolatum is a two-phase colloidal system, which contains liquid, microcrystalline, and crystalline paraffins. They attribute the differences in constituents of petrolatums to differences in the sources of crude material, differences in types and extents of refining, and differences in blending processes after refining. They conclude that petrolatum is an extremely variable material.

Several attempts have been made in the past to characterize petrolatum. Barry and Grace (1970, 1971) have shown that small strain testing is necessary for all rheological procedures, which is not possible using conventional viscometers. This type of testing is typically done so that the sample structure is not destroyed during measurements. In order to get meaningful data from this technique a stress or a strain sweep was needed to be performed on the sample to determine its linear viscoelastic region. Radebaugh and Simonelli (1983) used a rotational rheometer to study the viscoelastic properties of anhydrous lanolin. They conducted strain sweep tests ramping the strain from 3.5%–50%. They could not establish the linear viscoelastic region for their sample, as they were limited in the lowest obtainable strain of the instrument at the time. More recently, advances have been made in rheology instrumentation, for example, TA instruments AR-1000 and 2000 series, which can be operated at very low percent strains (~10^{-3}). Tamburic, Craig, Vuleta, and Milic (1996) studied the rheology of a semi-solid emulsion cream system containing white soft paraffin and a silicone emulsifier. They concluded that it was possible to formulate creams using low concentrations of emulsifier and high concentrations of water, and that thermorheology along with flow and dynamic testing was an effective way of characterizing the rheology of such systems. Rudraraju and Wyandt

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(I and II, 2005) conducted both flow and dynamic oscillatory tests on different Avicel® grades and at different concentrations. They showed how the dynamic oscillatory tests are superior to the flow tests in that the sample structure is retained during oscillatory measurements, and valuable information regarding the structure of the sample can be obtained.

In the current work, both flow and oscillatory testing is conducted on different grades of petrolatum to investigate any differences in the rheology between them. Since the rheology of petrolatum is extremely sensitive to temperature (Tamburic et al., 1996), temperature ramp-up and ramp-down studies were also conducted.

MATERIALS AND METHODS

There were three different grades (Grades A, B, and C) of petrolatum studied in this work (Table 1). A fourth grade, Grade D, was prepared by melting and mixing Grades B and C at 70°C in the ratio 1.0:1.5, followed by cooling to room temperature. A TA instruments AR-2000 controlled stress rheometer was used for this study. This unit has a drag cup motor drive system, an air bearing mounting for the measurement system, a sensitive optical encoder for measuring displacement, and a rapid response peltier heater (–15 to 100°C). The samples were analyzed on the rheometer using 40 mm stainless steel plate geometry, with a plate gap of 1000 μm. The operating parameters were established based on discussions with TA instruments' personnel and some initial testing results on the petrolatum used in this work. The sample of petrolatum was loaded onto the rheometer with care to minimize shear during loading. The peltier plate was maintained at 25°C during the loading of the sample. A fresh sample was loaded for each test to ensure that the shear "history" associated with each sample was as similar as possible. Repeat runs were conducted on most experiments in order to establish repeatability.

There were several types of tests conducted on each sample in order to characterize completely the rheology of petrolatum.

TABLE 1
Description of Different Petrolatum Grades Evaluated in the Current Work

Petrolatum Grade	Petrolatum Source
A	Sonneborn® Protopet 1S White petrolatum USP
B	Sonneborn® Low-bleed White petrolatum
C	Sonneborn® Snow White petrolatum
D	Mixture of Grades B and C in the ratio 1.0:1.5

Continuous Flow Experiments

In a controlled stress rheometer, a torque or stress is applied to one plate and the displacement or rotational speed (strain rate) of the same plate is measured. The controlled stress rheometer offers more careful control over the variables of primary interest in comparison to other rotational rheometers where, for example, the strain rate may be the controlled variable. This means that in the controlled stress approach it is possible to gradually increase the stress applied to the material and detect the point at which the material yields. Additionally, the rapid response peltier plate makes the system well suited for conducting temperature ramping studies.

In order to characterize the petrolatum, the steady-state flow mode was used initially. Each sample was subjected to a range of shear stress; shear rates, and temperature ramping experiments.

1. *Shear Stress*: Shear stress was varied increasingly between 0.1–1000 Pa (depending on the operating temperatures) to study its effect on the viscosity of the petrolatum at three temperatures (25, 30, 35°C). The data obtained were plotted on a log-log scale (viscosity vs. shear stress) which made the spotting of yield stress easier (Masmoudi et al., 2006).
2. *Temperature Ramp-Down*: The temperature was ramped down from 70 to 23°C and from 40 to 23°C, at a fixed angular velocity of the plate geometry. The sample was equilibrated at the starting temperature for 10 min before each run after loading the sample. In order to study the effect of angular velocity on viscosity, the angular velocity was varied at four levels (0.01, 0.1, 0.5, 1 rad/s). The temperature was ramped at three different rates: 0.2, 1, and 2°C/min. The data thus generated are referred to as "thermorheological scans."
3. *Temperature Ramp-Up*: The temperature was ramped up from 23 to 70°C, at a plate angular velocity of 0.1 rad/s, in order to understand the rheological changes that the different petrolatum grades undergo as the temperature is increased.

Oscillatory Dynamic Experiments

Although continuous flow experiments provide a lot of useful information on the flow properties (for e.g., yield stress, viscosity, thixotropy, effect of temperature on viscosity) of the material, they are only a part of the complete rheological characterization of viscoelastic materials. Dynamic oscillation testing is critical in understanding the structural (micro or macro) changes that the sample undergoes with changes in stress, time, or temperature. By subjecting a specimen to an oscillatory stress and determining the response, both the elastic and viscous or damping characteristics could be obtained. The oscillatory mode also avoids the breakdown of the sample structure within a determined frequency range. Above a certain strain value, the material starts to flow, and is no longer in the linear viscoelastic region. A small sinusoidal shear stress or strain (within the linear viscoelastic region) was applied on the sample, and the amplitude of the resulting strain or stress and

the phase angle between the input and the output is recorded. The parameters measured during these tests include G′ (elastic or storage modulus), G′ (viscous or loss modulus), loss tangent, and complex viscosity, and are discussed in more detail later.

1. *Oscillatory Stress Sweep*: Oscillatory stress sweep was performed to establish the linear viscoelastic region (LVR) of all samples before running temperature ramp-down oscillatory tests. The frequency was kept constant at 1 Hz.
2. *Temperature Ramp-Down*: A stress or strain value was chosen in the LVR that was previously established for the sample. Since this will be a function of the temperature, the temperature ramp was performed over a relatively shorter range (in comparison to the flow tests) of 40–23°C. This was done to ensure that the sample remains in the LVR even with the change in temperature during the run. This test was conducted at varying cooling rates (0.2–2°C/min) to examine its effect on the structure of the petrolatum. The frequency was kept constant at 1 Hz.

RESULTS AND DISCUSSION

Shear stress was varied to study its effect on viscosity at three temperatures (25, 30, 35°C) for all grades (Grades A, B, and C) of petrolatum. Figure 1 shows the results for Grade A petrolatum at three different temperatures. As expected, the viscosity as well as the yield stress decreases with an increase in temperature. Similar trends were obtained for Grades B and C. The yield stress values were evaluated using Ellis' model and are shown in Table 2. Figure 2 shows a comparison in viscosity between the three grades (Grades A, B, and C) of petrolatum at 30°C. The viscosity of Grade B petrolatum was observed to be higher than Grades A and C at 30°C.

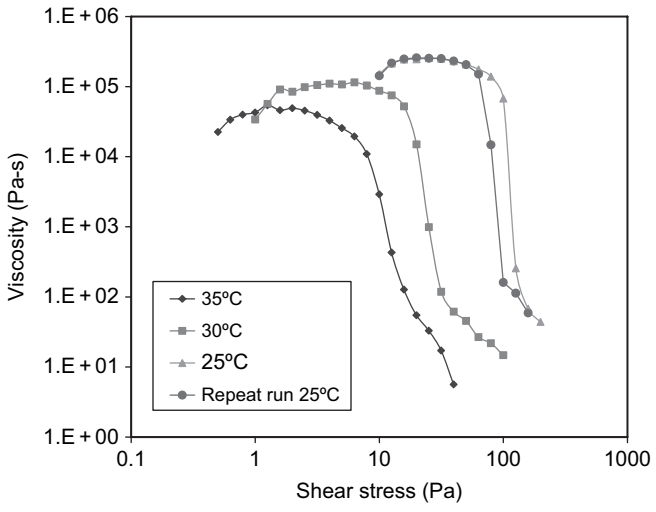

FIGURE 1. Grade A petrolatum viscosity as a function of shear stress and temperature.

TABLE 2
Yield Stress of Different Petrolatum Grades at Three Temperatures as Obtained from Stress Sweep Curves Using Ellis' Model

Temperature (ºC)	Petrolatum Grade	Yield Stress (Pa) Obtained from Ellis' Model
35	A	5.53
30	A	16.67
25	A	97.28
35	B	10.00
30	B	20.00
25	B	73.31
35	C	9.29
30	C	11.36
25	C	95.88

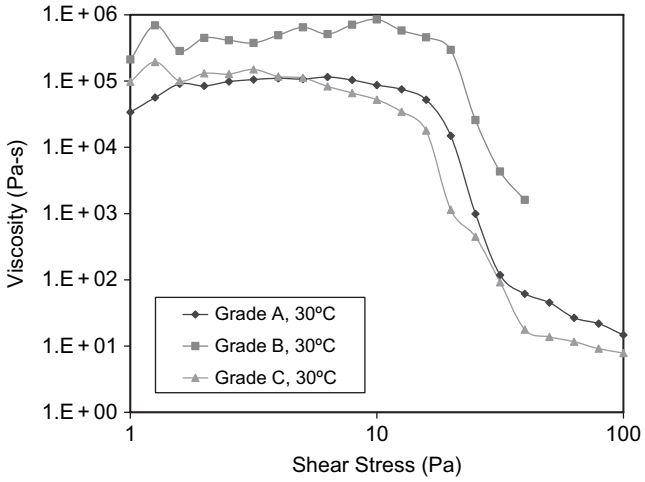

FIGURE 2. Viscosity as a function of shear stress at 30ºC for three petrolatum grades.

The thermorheological scans were conducted at four angular velocities of the plate thereby covering a wide range (0.01–1 rad/s) of angular velocities of the plate or geometry. This setup would resemble the mixing operation inside a tank during the manufacturing process and will therefore provide insights into the rheology of the petrolatum during that stage. Figure 3 shows the results from the thermorheological scans conducted on Grade A petrolatum in the form of viscosity versus temperature graph on a semi-logarithmic scale. The temperature ramp down rate was kept constant at 2°C/min while varying plate angular velocities. A repeat run at 0.1 rad/s is also shown to demonstrate the repeatability of the results. It is clear from the figure that for all conditions the viscosity was essentially the same for all samples at temperatures greater than 50°C. The angular velocity is seen to have a significant effect on the thermorheological profile; lower viscosities observed at a higher

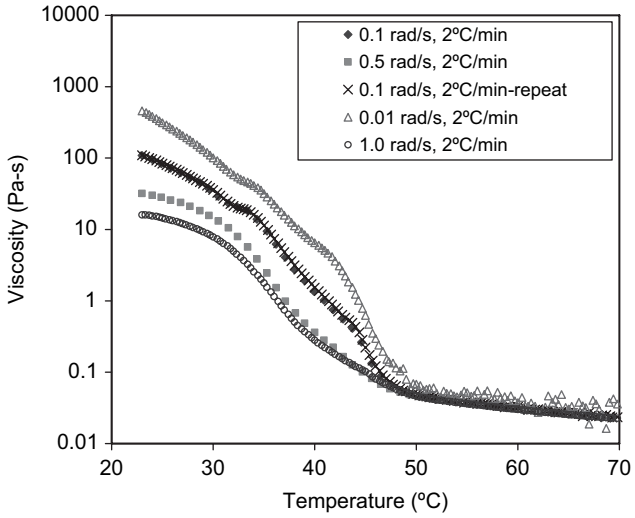

FIGURE 3. Thermorheological scans (cooling) on Grade A petrolatum as a function of plate angular velocity (0.01–1 rad/s) @ 2ºC/min.

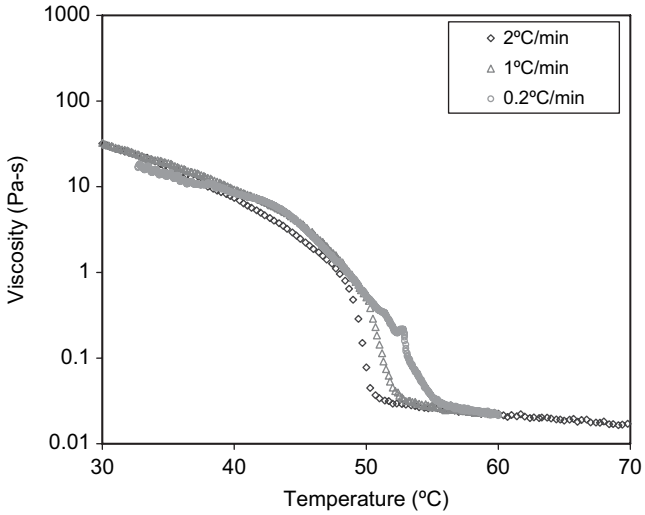

FIGURE 5. Thermorheological scans (cooling) on Grade D petrolatum as a function of cooling rate at a plate angular velocity of 0.1 rad/s.

angular velocity. The superimposing curves resulting from the repeat runs demonstrate the good repeatability of the thermorheological scans.

In order to study the effect of cooling rate on the ultimate viscosity, three cooling rates (0.2, 1, and 2°C/min) were used. Figure 4 shows the thermorheological scans on Grade A petrolatum as a function of cooling rate and plate angular velocity of plate or "mixing." Figure 5 shows the thermorheological scans (cooling) on Grade D petrolatum as a function of cooling rate at a plate angular velocity of 0.1 rad/s. The thermorheological profile is slightly altered with a change in cooling rate, but the angular velocity is seen to have a more significant impact on the final viscosity. It can be seen in Figure 5 (in the temperature range ~ 48–55°C), that the viscosity is highest for the slowest cooling rate. This could be due to the fact that at a slower cooling rate the sample gets more time to build its structure, and hence has higher viscosity.

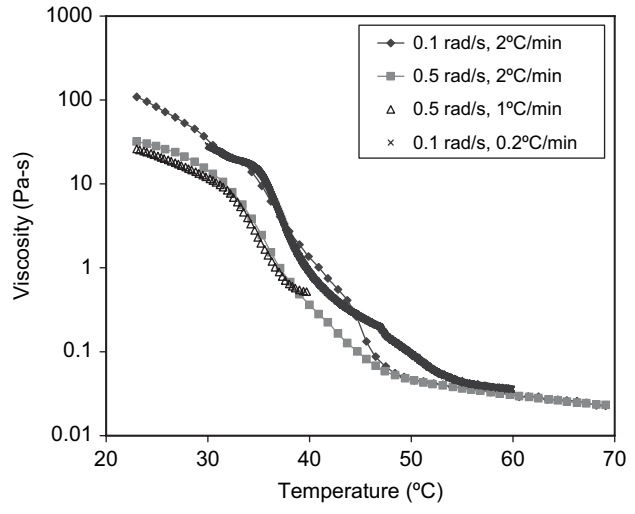

FIGURE 4. Thermorheological scans (cooling) on Grade A petrolatum as a function of cooling rate and plate angular velocity of plate or "mixing."

Figures 6 (A) and (B) compare the thermorheological scans for the four grades of petrolatum at 0.1 rad/s and 0.5 rad/s angular velocity of the plate. Interestingly, all the petrolatum grades appear to have similar viscosities at temperatures close to room temperature (25°–30ºC) as well as at very high temperatures (> 55°C), but have dissimilar profiles between these two temperature ranges. The melting ranges given in the BP (42°–60°C) and USP (38°–60°C) (Tamburic et al., 1996) could explain the similar viscosity values seen at elevated temperatures. The steep fall in viscosity is seen close to 50°C for Grade C petrolatum compared to 45°C for Grade B. Grade A petrolatum shows a much more gradual change in the viscosity with changes in temperature. Significant differences in the behavior of the petrolatum grades are seen in the temperature range 35°–50°C. Comparing Figures 6 (A) and (B), it can be seen that the final viscosity (close to room temperature) is higher for the lower "mixing" rate case (0.1 rad/s). The data on Grade D were found to lie between its two constituting petrolatums (Grades B and C). Similar observations were made for the heating thermorheological profiles. Figure 7 shows the profiles for the four petrolatum grades while heating from 23° to 70°C at 2°C/min at an angular velocity of 0.1 rad/s. Again, the different petrolatum grades have similar viscosities close to room temperature but significant differences in viscosities are noted in the range 35°–60°C.

The flow experiments are a good way to characterize the viscosity of the samples, but as discussed before, they do not provide any structure information. There is a constant shift towards using dynamic oscillatory data to characterize rheology.

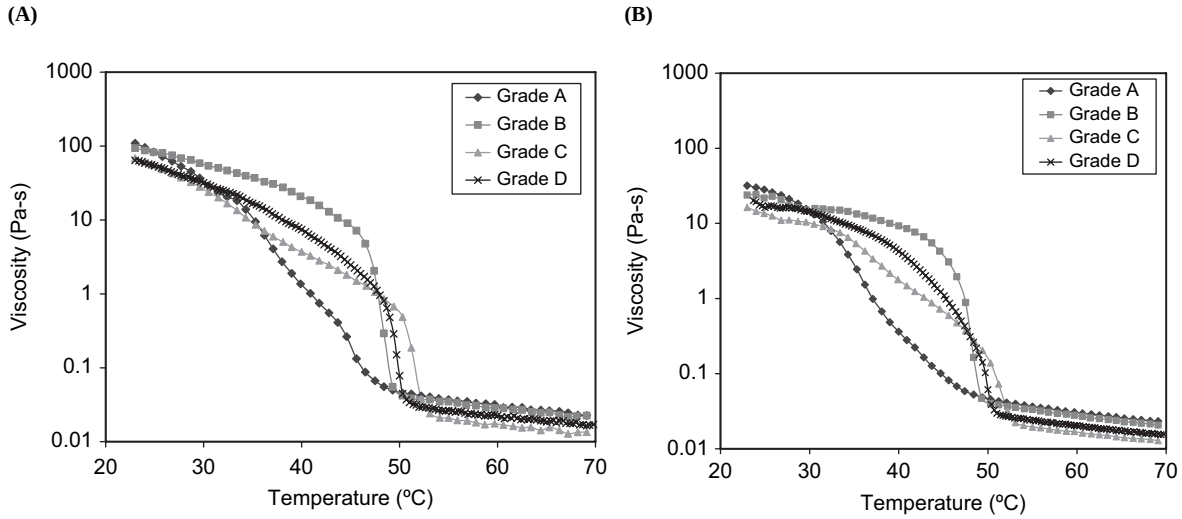

FIGURE 6. Thermorheological scans (cooling ≅ 2°C/min) of the 4 grades of petrolatum at a plate angular velocity of (A) 0.1 rad/s and (B) 0.5 rad/s.

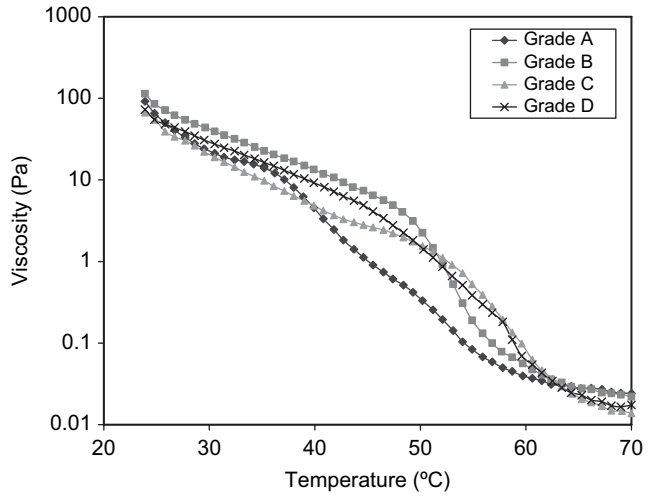

FIGURE 7. Thermorheological scans (heating ≅ 2ºC/min) of the four grades of petrolatum at a plate angular velocity of 0.1 rad/s.

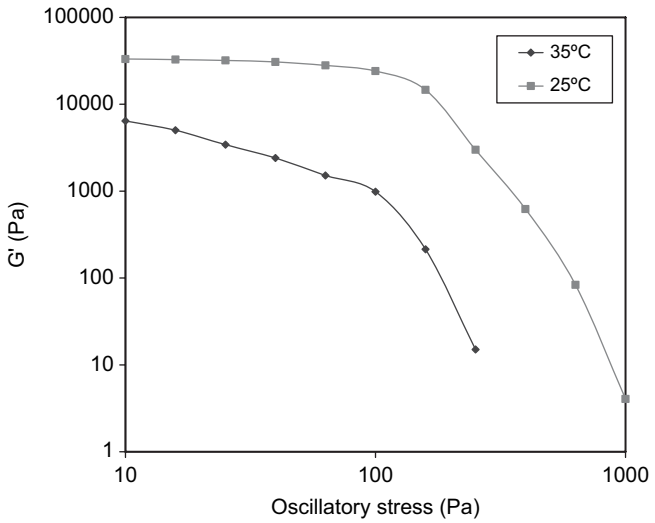

FIGURE 8. Typical data set used to establish the linear viscoelastic range of a sample over a temperature range, Grade B petrolatum, in this case.

If the sample is operated in the LVR during the oscillatory testing, the sample is not destroyed while taking measurements, unlike the flow experiments. An oscillatory shear stress ramp is performed at different temperatures in order to establish the linear viscoelastic range of the sample over a range of temperature, which is then used during an oscillatory temperature ramping study. A typical example is shown in Figure 8 for Grade B petrolatum at 25° and 35°C. At stresses below the critical stress, the sample behaves like a viscoelastic solid. When this critical stress is exceeded, the sample starts to flow (identified by a sudden reduction in the value of G′). Figure 8 also shows that the sample has more structure (higher G′) and a longer viscoelastic region at 25°C in comparison to 35°C.

Figure 9 (A) shows the oscillatory temperature ramp-down data from 40 to 23°C at a rate of 1°C/min for the four grades of petrolatum. G′ is a measure of dynamic elastic behavior, and G″ is a measure of the dynamic viscous behavior. The trends of G′ (elastic or storage modulus) and G″ (viscous or loss modulus) were found to be similar, although G′ was greater than G″ for all petrolatum grades. Grade A petrolatum shows the biggest increase in the G′ and G″ with a decrease in temperature, followed by Grade C and then Grade B. The data for Grade D were found to lie between the data for Grades B and C. It should be pointed out that the G′ and G″ for all grades are significantly different from each other at temperatures greater than 30°C.

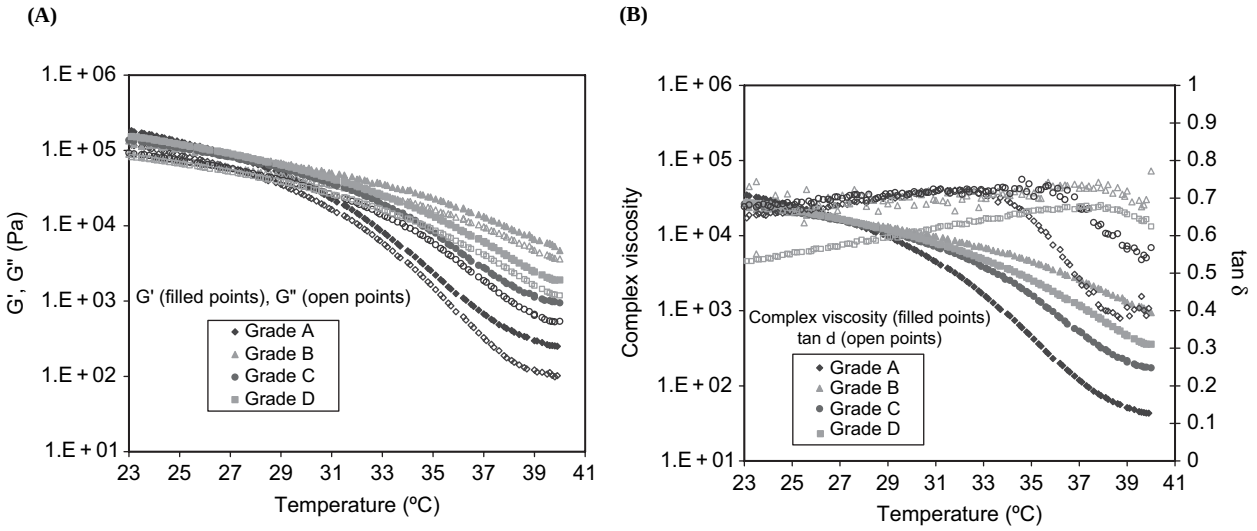

FIGURE 9. (A) Oscillatory temperature ramp-down from 40 to 23ºC ≅ 1ºC/min for the four grades of petrolatum (G″: Filled data points, G′: Open data points), (B) Complex viscosity modulus and tan δ as a function of temperature during an oscillatory temperature ramp-down ≅ 1 ºC/min ($|\eta^*|$: Filled data points, tan δ: Open data points). The value of tan δ is shown on the secondary *y*-axis.

The loss tangent (tan δ) is defined as the ratio of loss modulus to storage modulus and is dimensionless (Eq. 1). It provides a comparative parameter that combines both elastic and viscous contributions of the system (Adeyeye, Jain, Ghorab, & Reilli Jr., 2002).

$$\tan\delta = \frac{G''}{G'} \tag{1}$$

The modulus of complex viscosity ($|\eta^*|$) of the sample along with tan δ is plotted in Figure 9 (B) for all grades of petrolatum. The value of tan δ is shown on the secondary y-axis. A value of tan δ greater than 0.5 indicates that the material is predominantly viscous. The complex viscosity can be defined by Eqs. 2 and 3 (Barnes, 2000), where is the oscillation frequency. The complex viscosity modulus is observed to follow similar trends as seen during the flow experiments. Temperature is seen to have the maximum effect on Grade A petrolatum (complex viscosity and tan δ) in the range 40°–23°C, followed by Grades C, Grade D, and Grade B, respectively (Figure 9(B)).

$$\left|\eta^*\right| = \left[(\eta') + \left(\frac{G'}{\omega^2}\right)\right]^{1/2} \tag{2}$$

$$\eta' = \frac{G''}{\omega} \tag{3}$$

Figure 10 shows the effect of the rate of cooling on the structure of Grade A petrolatum. Both G′ and G″ individually start at the same viscosity at 40°C and end at almost the same viscosity at 23°C for both the cooling rates. However, it is interesting to note that there are significant differences in the structure (G′ and G″ values) in between these two temperatures, with higher values observed for the 0.2°C/min case.

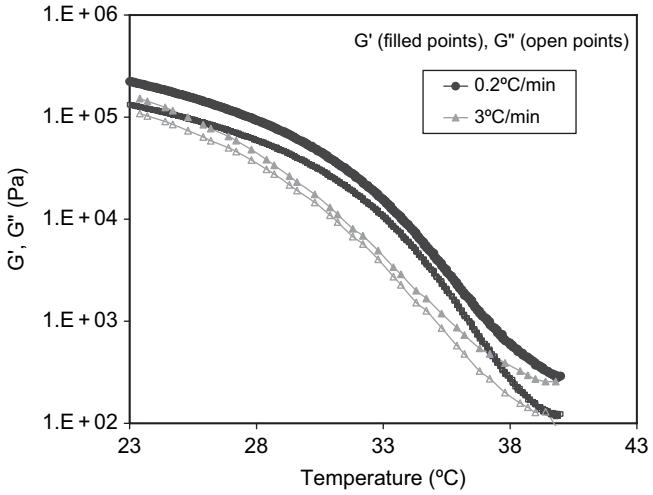

FIGURE 10. Effect of cooling rate on the structure of Grade A petrolatum.

SUMMARY AND CONCLUSIONS

There were significant differences noted in the rheological behavior amongst the grades of petrolatum studied. An AR-2000 rheometer was able to characterize effectively the rheology of petrolatum and detect differences between different grades of petrolatum. Such rheological measurements can

serve as good preformulation tool in predicting product performance.

Both steady-state flow and dynamic oscillatory tests were conducted on the petrolatums. The thermorheological scans were found to be the most informative and reproducible for this study. This test was particularly useful in capturing rheological differences between different petrolatum grades as a function of temperature. This is somewhat expected as petrolatum is a temperature sensitive material. The thermorheological scans were conducted with continuous "mixing" during the experiment. This, in part, mimics the process conditions that petrolatum based products experience during manufacturing, filling, and storage. It was shown that the rate of mixing had a significant effect on the final viscosity of the petrolatum. The cooling rate was not found to have a significant effect on the final viscosity of the different petrolatum grades. The Grade D data were found to lie between the data of Grades B and C for all experiments, including the dynamic oscillatory tests.

Information on the structure of the petrolatum, as it cools down (40°–23°C), was obtained using dynamic oscillatory tests. Significant differences in the structure (G′ and G″ values) were observed between the petrolatum grades. The structural differences were found to be more significant in the temperature range 25°–35°C, with A grade having the least structure (lowest G′) to it. This is of interest since the typical filling temperatures for an ointment generally range from 25°–35°C. The relationship between rheology and temperature could explain some of the problems encountered during the filling stages, and can provide guidance to avoid them; e.g., a slight increase in temperature during the filling stage can help the flow of product and eliminate plug flow (Pena et al., 1994).

While monitoring the structure of the petrolatum at different cooling rates, it was found that the cooling rate had a significant effect on the final structure of the petrolatum while operating in the temperature range 25°–35°C. This is interesting considering that the viscosity was not significantly affected by the rate of cooling during the flow testing, which is the conventional testing method. As the temperature of petrolatum is outside this temperature range, the differences in the structure at different cooling rates become insignificant. This means that if a particular petrolatum grade is cooled to, for example, 30°C at a particular cooling rate, and is cooled to 30°C at a different cooling rate, then the structure of the two resultant petrolatums can be different. This will directly affect the performance of the petrolatum in the later stages of manufacturing (e.g., storage, filling), and could potentially lead to problems such as "bleeding" of the petrolatum if the next manufacturing stage was optimized and designed with certain petrolatum characteristics in mind. It is therefore very clear that it is essential to have a precise control on the temperature during the process to obtain reproducible and desirable rheological characteristics.

The results obtained from this study provide a better understanding of the differences that can arise due to petrolatum grade variation and will be useful during the manufacturing and filling process of an ointment or cream that utilizes these grades of petrolatum. It would be feasible to have a better control of the manufacturing and filling process since mechanical and thermal effects on the petrolatum can be obtained, as demonstrated in the current study.

ACKNOWLEDGMENT

The authors are thankful to Terri Chen, Ph.D., from TA Instruments (New Castle, DE) for her help with the operation of AR-2000 rheometer used in this work.

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