Arch Pharm Res Vol 33, No 1, 141-150, 2010
DOI 10.1007/s12272-010-2236-4

Archives of Pharmacal Research
www.springer.com/12272

Rheological Evaluation of Petroleum Jelly as a Base Material in Ointment and Cream Formulations: Steady Shear Flow Behavior

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(Received August 19, 2009/Revised October 20, 2009/Accepted October 20, 2009)

The objective of the present study is to systematically characterize a nonlinear rheological behavior of petroleum jelly (petrolatum) in steady shear flow fields correspondent to the spreading condition onto the human body. With this aim, using a strain-controlled rheometer, the steady shear flow properties of commercially available petroleum jelly have been measured at 37°C (body temperature) over a wide range of shear rates. In this article, the shear rate dependence of steady shear flow behavior was reported from the experimentally obtained data. In particular, the existence of a yield stress and a non-Newtonian flow behavior were discussed in depth with a special emphasis on their importance in actual application onto the human body. In addition, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative description of the steady shear flow behavior, and then the applicability of these models was examined in detail. Main findings obtained from this study can be summarized as follows : (1) Petroleum jelly exhibits a finite magnitude of yield stress. The appearance of a yield stress is attributed to its three-dimensional network structure that can show a resistance to flow and plays an important role in determining a storage stability and sensory feature of the product. (2) Petroleum jelly demonstrates a pronounced non-Newtonian shear-thinning flow behavior which is well described by a power-law equation and may be interpreted by the disruption of a crystalline network under the influence of mechanical shear deformation. This rheological feature enhances sensory qualities of pharmaceutical and cosmetic products in which petroleum jelly is used as a base material during their actual usage. (3) The Casson, Mizrahi-Berk, Heinz-Casson and Herschel-Bulkley models are all applicable and have almost an equivalent ability to quatitatively describe the steady shear flow behavior of petroleum jelly whereas the Bingham model does not give a good validity. Among these flow models, the Herschel-Bulkley model provides the best applicability.

Key words: Petroleum jelly (petrolatum), Rheology, Steady shear flow behavior, Yield stress, Non-Newtonian shear-thinning viscosity, Viscoplastic flow models

INTRODUCTION

Most pharmaceutical and cosmetic processes such as new ingredient selections, formulation preparations, material packaging and self storage are closely associated with a complex flow of materials. The application and acceptance of pharmaceuticals and cosmetics are also greatly dependent on the flow properties of the final products (Colo et al., 2004). Therefore, a knowledge of the rheological properties of pharmaceutical and cosmetic materials becomes an essential key to improve processing efficiency as well as to develop consumer-acceptable final products.

Pharmaceutical and cosmetic materials range in consistency from fluid to solid state. An important category is comprised of semi-solid products which are the most difficult materials to attempt a rheological characterization because they combine both fluid-like and solid-like properties within the same materials (Herh et al., 1998). Widely-used pharmaceutical and cosmetic products belonging to this category are oint-

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ments, creams, lotions, pastes, gels and major ingredients such as petroleum jelly and anhydrous lanolin; all of which can be classified as a semi-solid material.

In general, rheological measurements on these materials may be made for a number of reasons including (Barry, 1974): (1) to understand the fundamental nature of a system; (2) for quality control of raw materials, final products and manufacturing processes such as mixing, pumping, packaging and filling; (3) to study the effect of different parameters (e.g., formulation, storage time and temperature) on the quality of a final product; and (4) to assess a product with regard to actual usage (e.g., removal from a jar or a tube, spreading and adherence to the skin).

In pharmaceutical industry, petroleum jelly (also called petrolatum or vaseline) is mainly used as a base material in formulating ointments and creams (dermatological preparations). Because of its highly lipophilic character, petroleum jelly is also used as an essential ingredient in the formulations of cosmetic products. It is further used as a masking ointment and as a base for hydrophilic systems containing emulsifiers. Such a widespread usefulness of petroleum jelly is primarily due to its excellent ability in providing lubricity and moisture resistance to various kinds of semi-solid pharmaceutical and cosmetic products such as ointments, creams, lotions and hand cleaners.

Petroleum jelly is a translucent, yellowish to amber or white, unctuous substance having almost no odor or taste. It is derived from the refinement of crude petroleum oil and is consequently a complex mixture of straight chain, branched chain and cyclic hydrocarbons with varying chain lengths (Pena et al., 1994). Petroleum jelly is chemically related to mineral oil. While mineral oil contains mainly liquid hydrocarbons at room temperature, petroleum jelly is a mixture of solid and liquid hydrocarbons and maintains a solid-like state at room temperature. Petroleum jelly may thus be considered to be a soft-type microcrystalline wax with a high oil content (Pena et al., 1994).

Since petroleum jelly is a major ingredient in a wide variety of topical ointment and cream formulations, the quality and function of these products are greatly controlled by the rheological (or mechanical) properties of petroleum jelly itself. Hence, through a systematic characterization and a complete understanding of the fundamental nature of petroleum jelly, better decisions can be made as to the choice of a specific grade of petroleum jelly for a particular product and for a subsequent manufacture of the final product (Fu and Lidgate, 1985).

As mentioned previously, rheological properties of ointments and creams play a significant role in their manufacturing processes and sensory performances. In addition, they experience a wide range of stresses during removal from a container or a tube and application to the human body or skin. Pharmaceutical and cosmetic industries should therefore have a better knowledge concerning the effects of various parameters that determine the rheological properties of ointments and creams in order to produce desirable final products (Masmoudi et al., 2006). With a complete rheological characterization of petroleum jelly, it may be possible to make necessary adjustments during the manufacturing processes of ointments and creams as well as to achieve optimal product performances.

Due to its paramount importance in pharmaceutical and cosmetic industries, many attempts have been made to investigate the rheological properties of petroleum jelly during the past several decades by means of a continuous shear viscometry, creep/creep recovery tests, and small amplitude oscillatory shear measurements (Boylan, 1966; Davis, 1969; Fu and Lidgate, 1985; Pena et al., 1994; Pandey and Ewing, 2008). However, only a little attention has been given to the rheological characterization in actual usage conditions such as spreading and rubbing onto the human body or skin, even though such a rheological information is much more essential from a view-point of consumer's demands (Lee et al., 2008; Cha et al., 2009).

Based upon the above-described backgrounds, we have designed a comprehensive study as to the overall rheological evaluation of petroleum jelly in a wide variety of flow fields most relevant to its actual application conditions. As a first step of our serial works, the objective of the present study is to systematically characterize a nonlinear rheological behavior of petroleum jelly in steady shear flow fields correspondent to the spreading condition onto the human body. With this aim, using a strain-controlled rheometer, the steady shear flow properties of commercially available petroleum jelly have been measured at 37°C (body temperature) over a wide range of shear rates.

In this article, the shear rate dependence of steady shear flow behavior was reported from the experimentally obtained data. In particular, the existence of a yield stress and a non-Newtonian flow behavior were discussed in depth with a special emphasis on their importance in actual application onto the human body. In addition, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative description of the steady shear flow behavior, and then the applicability of these models was examined in detail.

MATERIALS AND METHODS

Materials

The petroleum jelly sample used in this study was a commercially available product (White Petrolatum USP) supplied from the Vi-Jon® Company. This sample is a translucent and unctuous substance having almost no odor or taste. It is derived from the refinement of crude petroleum oil and is consequently a complex mixture of straight chain, branched chain and cyclic hydrocarbons with varying chain lengths.

It is known that petroleum jelly consists of both solid and liquid hydrocarbons (normal, iso and ring paraffins) in the form of a gel structure, thus maintaining a solid-like state at room temperature (Birdwell and Jessen, 1966; Barry and Grace, 1971). This gel structure is composed of a three-dimensional crystalline network which encloses and immobilizes the liquid hydrocarbons. Disruption of a network structure causes a liquid separation of petroleum jelly, after then imparting a flow ability to this material (Song et al., 2007).

Since petroleum jelly is a major ingredient in a wide variety of topical ointment and cream formulations, the quality and function of these formulations are dominantly dependent on the mechanical and physicochemical properties of petroleum jelly. In addition, because most of topical ointment and cream formulations require a dispersion of an internal phase into petroleum jelly, a great deal of mixing or mechanical shear is needed to achieve a desired homogeneity of the final products.

Rheological measurements

The rheological measurements were conducted using an Advanced Rheometric Expansion system (ARES, Rheometric Scientific). ARES is a strain-controlled rheometer that is capable of subjecting a test material to either a dynamic or a steady shear strain and then measuring the resultant torque values expended by the sample in response to the imposed shear strain. When operating this instrument, the dynamic/steady shear strain is applied by the step-motor and the torque value is measured by the force rebalance transducer (FRT).

In this study, the steady shear flow properties of petroleum jelly were measured using an ARES equipped with a parallel-plate fixture with a radius of 12.5 mm and a gap size of 2.5 mm. All measurements were performed at an isothermal condition of 37°C over a wide range of shear rates from 0.05 to 200 1/s with a logarithmically increasing scale.

The reasons why a parallel-plate configuration was chosen as a test geometry are that (Song et al., 2006): (1) cleaning is very easy after each measurement; (2) the plates can be easily covered with sandpaper; and (3) there is a relatively smaller gap error due to a larger gap size between the two plates (2.5 mm in this experiment) compared to a cone-plate fixture where the gap at the center is usually kept at 0.05 mm.

Before the petroleum jelly sample was loaded, the two plates were covered with sandpaper in order to remove a wall slippage between the test material and the plates. Through a preliminary test using a direct visualization technique (Chang et al., 2003) in which a straight line marker was drawn from the upper plate to the lower plate passing through the free surface of the sample, it was confirmed that a wall slip effect could almost be eliminated over a shear rate range tested by covering the plate surfaces with sandpaper.

Special care was taken to minimize the effect of work softening when the petroleum jelly sample was initially loaded on the plate each time. The sample filled up the whole gap by lowering the upper plate down to the pre-designed gap. The extra sample around the edge of the plate was trimmed with a plastic spatula.

In all measurements, a fresh sample was used and rested for 40 min after loading to allow material relaxation and temperature equilibration. It was found from a preliminary test that 40 min of resting time is enough for petroleum jelly sample to be completely relaxed and to be thermally equilibrated. These measurements were made five times and highly reproducible data were obtained within the coefficients of variation of ± 5%.

RESULTS AND DISCUSSION

Yield stress

Fig. 1 shows the flow curve (representation of the shear stress as a function of shear rate) for petroleum jelly at 37°C. As is obvious from Fig. 1, the shear stress tends to level off and approach a limiting constant value as a decrease in shear rate towards zero at low range of shear rates, indicating that petroleum jelly exhibits a finite magnitude of yield stress.

This appearance of a yield stress for petroleum jelly is more dramatically manifested when plotting the steady shear viscosity as a function of shear stress rather than shear rate, as demonstrated in Fig. 2. Two distinctive regions are clearly seen : (1) the existing region of a yield stress reflected by the viscosity that continues to rise at relatively lower range of shear stresses; and (2) the shear-thinning region where the viscosity is substantially decreased with increasing shear stress. These characteristics are

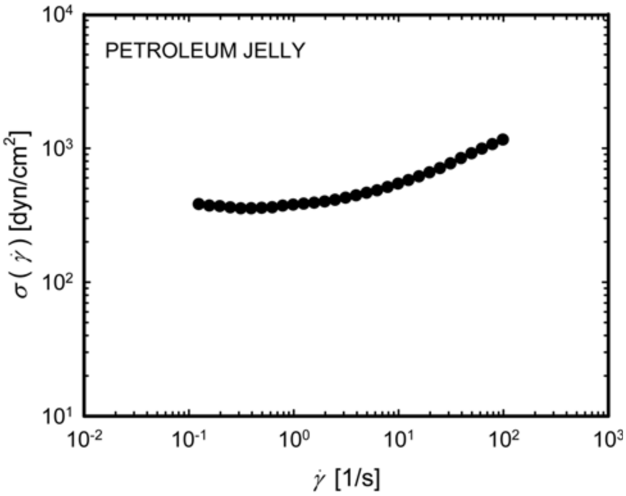

Fig. 1. Flow curve for petroleum jelly at 37°C

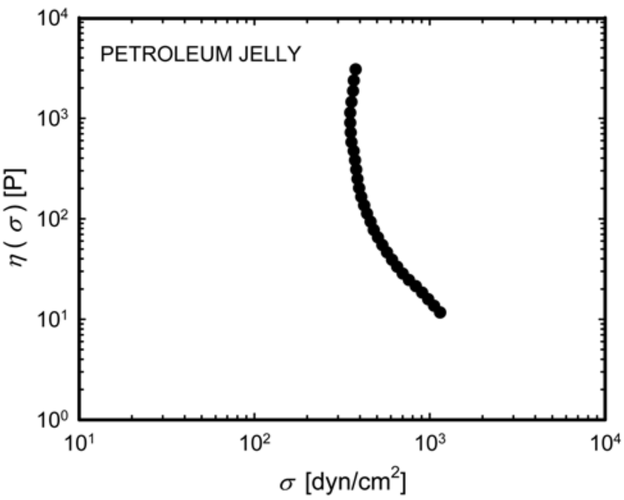

Fig. 2. Steady shear viscosity as a function of shear stress for petroleum jelly at 37°C

quite similar to those frequently observed in other semi-solid food, pharmaceutical, cosmetic and biomedical materials (Song and Chang, 1999; Song et al., 2006; Park and Song, 2008; Kuk and Song, 2009).

The existence of a yield stress for petroleum jelly may be attributed to its three-dimensional network structure that can exhibit a resistance to flow. Petroleum jelly has a two-phase colloidal gel-type structure containing liquid, microcrystalline and crystalline hydrocarbons (Barry and Grace, 1971). During a preparation of petroleum jelly when a molten material is cooled, the stiffening wax phase is developed into an amorphous three-dimensional network or matrix which forms a compact structure with voids of molecular dimensions, while the liquid phase is bound to the network or matrix by a sorption mechanism.

Electron microscope has shown that the crystals consist of fiber-like bundles with colloidal dimensions linked by a large number of contact points (Pena et al., 1994). The overall rheological properties of petroleum jelly and its formulations are closely dependent on this microscopic and submicroscopic wax matrix.

Only when a sufficient magnitude of shear stress (larger than a yield stress) is applied, this three-dimensional network structure becomes broken down. Subsequently, orientation of the molecular chains takes place, leading to a shear-thinning flow behavior at higher shear rates in a similar manner to that encountered in other semi-solid food, pharmaceutical, cosmetic and biomedical products (Song and Chang, 1999; Song et al., 2006; Park and Song, 2008; Kuk and Song, 2009).

Yield stress is an important parameter for topical ointment and cream formulations when considering their self life as well as an ease of application for the consumers to actually use and transfer (Brummer, 2006). The consumer acceptance of pharmaceutical and cosmetic products is strongly governed by their sensory feel from the time when they are taken out from a container or a tube and then applied to the human body or skin. Such a storage stability and sensory feature of these products are determined by their rheological properties, particularly by the magnitude of a yield stress.

Yield stress of pharmaceutical and cosmetic materials should be large enough so that they do not flow out of a container due to their own weight when the container is placed in upside-down position. At the same time, it should not be too large to offer an intensive resistance to flow during an application on the human body. In addition, the smaller the yield stress, the easier the product can be distributed on the human body. This indicates that yield stress plays a crucial role in determining the thickness of the product film layer on the surface of the human body or skin.

Non-Newtonian viscosity

Fig. 3 shows the shear rate dependence of the steady shear viscosity for petroleum jelly at 37°C. As is clear from Fig. 3, while the Newtonian viscosity region is not observed at low shear rates, the steady shear viscosity is sharply decreased as an increase in shear rate, demonstrating that petroleum jelly exhibits a marked non-Newtonian shear-thinning flow behavior.

A shear-thinning flow behavior may be the most common rheological similarity between diverse fluid systems including polymer melts/solutions, suspen-

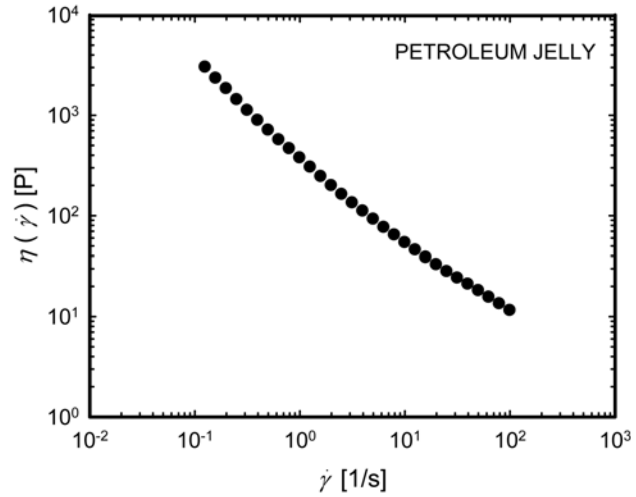

Fig. 3. Shear rate dependence of steady shear viscosity for petroleum jelly at 37°C

sions, emulsions, gels, pastes and liquid foams (Larson, 1999). This behavior is generally explained to arise from chain orientation or alignment of micro-structure with the flow direction, thus leading to a reduction of the local drag. As the shear rate is further increased, the alignment of flow becomes more complete and consequently the shear viscosity is further decreased. The intermolecular interactions may be reduced due to a micro-structural anisotropy resulting from the shear deformation.

A pronounced shear-thinning behavior of petroleum jelly may be interpreted as follows. Petroleum jelly forms a gel-like structure comprised of both solid and liquid hydrocarbons (normal, iso and cyclic paraffins) attached through random entanglement and chemical bonding (Birdwell and Jessen, 1966), resulting in a high shear viscosity at rest or at very low shear rates. This structure is composed of a three-dimensional crystalline network which encloses and immobilizes the liquid hydrocarbons (Song et al., 2007). When subjected to mechanical shear deformation, a crystalline network becomes disrupted, causing a liquid separation of petroleum jelly.

Structural collapse of the iso-paraffins has been reported to be less broken down than that of the normal paraffins under the influence of mechanical shear strain. This is attributed to a finer crystallite gel structure of the iso-paraffins, which is less susceptible to mechanical shear strain than a larger crystallite structure. As the shear rate is progressively increased, the normal paraffins tend to align towards the direction of shear flow, whereas the iso- and cyclic paraffins cannot align as readily and serve to retain the three-dimensional network of the system to some extent. As the shear rate is further increased, all paraffins become aligned concurrent with a rupture of the entangled paraffin chains, resulting in a low shear viscosity at high shear rate region.

This rheological feature enhances sensory qualities of pharmaceutical and cosmetic products in which petroleum jelly is used as a base material and guarantees a high degree of mixability, pumpability and pourability during their processing and actual usage. These are one of the most important reasons why petroleum jelly is widely used as a major ingredient for ointment and cream formulations in pharmaceutical and cosmetic industries.

The shear rate dependence of steady shear viscosity for petroleum jelly seems to be well described by a well-known power-law (or Ostwald-de Waele) equation expressed as follows :

$$\eta(\dot{\gamma}) = K\dot{\gamma}^{n-1} \quad (1)$$

where $\eta(\gamma)$ is the shear rate-dependent viscosity, γ is the shear rate, K is the consistency index, and n is the flow behavior index. As n tends to 1, a shear-thinning nature becomes less pronounced, so that a Newtonian behavior is achieved when n equals to 1.

The values of the power-law parameters (K and n) obtained by a linear regression analysis together with that of the determination coefficient (R^2) are $K = 396.7$ $P \cdot s^{n-1}$, $n = 0.172$, and $R^2 = 0.97$, respectively. As expected, the fits of the experimentally measured data (Fig. 3) to the power-law equation represent quite well the viscous behavior of petroleum jelly.

Now it may be meaningful to discuss the importance of our results with respect to actual usage situations. An ease of application of semi-solid pharmaceutical and cosmetic products to the surface of the human body or skin is a significant factor for consumer acceptance. Each individual person applies ointment-like materials to the skin with a slightly different motion, stroke and shear rate. At this stage, the consumer acceptance of a preparation for topical application (apart from therapeutic and cosmetic effects) is governed by the texture profile such as appearance, odor, extrudability from a container or a tube, initial sensation upon contact with the skin, spreading ability on the skin, adhesiveness and residual greasiness after application (Brummer and Godersky, 1999; Brummer, 2006).

The topical application procedure may be subdivided into four steps : (a) removal of a product from a container, (b) initial (or primary) sensation on the skin, (c) secondary sensation during spreading on the skin, and (d) final impression due to a residue on the skin. Among these steps, the textural properties corresponding to the steps (b) and (c) are consistency and spreadability, respectively. Consistency can be assessed at low shear rates and thus correlated with a yield stress. On the other hand, spreadability can be subjectively assessed at high shear rates and hence associated with a shear-thinning flow behavior.

From these facts, it is understood that two important parameters that should be evaluated when considering a consistency and a spreadability problem of a product are the initial resistance to flow and the shear-dependent viscosity over a wide range of shear rates. This process is exactly analogous to the generation of steady shear flow in a rotational rheometer. The magnitude of a yield stress and the values of the power-law parameters obtained using this equipment are then to become a direct quantitative indication of the consistency and spreadability of a product, respectively. The present work has been designed based upon these backgrounds and therefore obtained results are believed to provide an important information as to an actual application of petroleum jelly and petroleum jelly-based formulations to the human body or skin.

Applicability of viscoplastic flow models

The yield stress of a material is defined as the minimum shear stress that must be applied to a material to induce flow. The physical meaning and the real existence of a true yield has long been a subject of serious debate among rheological scientists (Hartnett and Hu, 1989; Barnes, 1999; Hadjistamov, 2003; Stokes and Telford, 2004; Zhu et al., 2005) on the grounds that any material will flow provided that a sufficiently long time is given. Barnes and Walters (1985) initiated this debate in their article titled "The yield stress myth?" in which they stated that "if a material flows at high shear stresses, it will also flow, however slowly, at low stresses". This statement means that there exists no real yield stress since, even at an infinitesimally small stress, any material will flow if the time scale of the observation is sufficiently long. Nevertheless, the engineering reality of a yield stress, which depends on the time scale of the measurement, is a useful as well as a desirable concept because there are many industrial and practical problems that can smoothly be solved with considering a yield stress of a raw material or a final product.

It is true that, given a sufficient amount of time within which to initiate flow, most materials would not exhibit a yield stress from a purely theoretical point of view. Because of the dependence of all material processes on strict time limitations, however, the concept of a yield stress is helpful for process design/control and modeling. In fact, many material processes generally involve a residence time which is significantly shorter than that required to support the theoretical view-point.

The determination of a yield stress in any material system is difficult. When dealing with a yield stress as a true material parameter, two key-points should be kept in mind; the obtained yield stress value is usually dependent not only on the accuracy of the instrument/equipment but also on the time scale of the observation. Therefore, there exists no generally accepted standard procedure to determine a yield stress value. Many techniques have been devised for the measurement of a yield stress during the past several decades (Cheng, 1986; Nguyen and Boger, 1992; Liddell and Boger, 1996; Rao and Steffe, 1997; Barnes and Nguyen, 2001; Brunn and Asoud, 2002; Genovese and Rao, 2005; Canet et al., 2005). One of the most common techniques is an indirect measurement which involves an extrapolation of the shear stress-shear rate data obtained from conventional rheometers to zero shear rate. This can be done either without or with the use of a rheological model. The extrapolated yield stress relies on the accurate experimental data at low shear rate range.

In this study, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative description of the steady shear flow behavior of petroleum jelly, and then the applicability of these models was also examined in detail.

A general viscoplastic flow model having a yield stress term may be expressed by the following form :

$$\sigma^{n_1} = \sigma_y^{n_1} + k\dot{\gamma}^{n_2} \tag{2}$$

where σ is the shear stress, σ_y is the yield stress, $\dot{\gamma}$ is the shear rate; n_1 and n_2 are material parameters related to the material's flow behavior, and consequently, each flow model is determined according to the conditions of n_1 and n_2.

Table I summarizes the viscoplastic flow models (Bingham, 1922; Casson, 1959; Herschel and Bulkley, 1926; Mizrahi and Berk, 1972; Heinz, 1959) adopted in this study and their flow characteristics. Here σ_y is the yield stress of each model and k is the consistency index related to a high-shear limiting viscosity, η_∞, as the shear rate is increased towards infinity. n is the flow behavior index; a material parameter that determines the shear-thinning nature of a material. In order that the models summarized in Table I could predict a shear-thinning behavior, both n_1 and n_2 must be a positive value and n_1 should be larger than n_2 or equivalent to n_2.

In the present work, in order to determine the material parameters of each model, a linear regression analysis was used for both the Bingham and Casson models, while a nonlinear regression analysis adopt-

Table I. Viscoplastic flow models used in this study and their characteristics

Flow model	Equation	n_1	n_2	η_∞	Shearthinning condition
Bingham	$\sigma = \sigma_y + k\dot{\gamma}$	1	1	k	-
Casson	$\sigma^{1/2} = \sigma_y^{1/2} + k\dot{\gamma}^{1/2}$	0.5	0.5	k^2	-
Herschel-Bulkley	$\sigma = \sigma_y + k\dot{\gamma}^n$	1	n	0 k, if n=1	$0 < n \leq 1$
Mizrahi-Berk	$\sigma^{1/2} = \sigma_y^{1/2} + k\dot{\gamma}^n$	0.5	n	0 k^2, if $n = 0.5$	$0 < n \leq 0.5$
Heinz-Casson	$\sigma^n = \sigma_y^n + k\dot{\gamma}^n$	n	n	$k^{1/n}$	$0 < n$

ing the Levenberg-Marquardt method was used for the Herschel-Bulkley, Mizrahi-Berk, and Casson models.

The values of the material parameters calculated from the viscoplastic flow models along with those of the determination coefficients are reported in Table II. The value of a flow behavior index provides a reference for the assessment of a shear-thinning nature; as this value becomes closer to zero, a more pronounced shear-thinning behavior is observed.

First of all, the Bingham model does not give a good ability for predicting the flow behavior of petroleum jelly because this model follows a Newtonian behavior once the yield stress is exceeded. As reported in the previous section, petroleum jelly was found to exhibit a marked non-Newtonian shear-thinning flow behavior.

Secondly, judging from the values of the determination coefficients, the Casson model shows a relatively good applicability. This is somewhat unexpected in considering an unreality of the assumptions introduced when this model was theoretically developed. One of the important assumptions of the Casson model was that solid particles form a one-dimensional chain-like structure in a two-phase suspension when dispersed in Newtonian media, disregarding other configurations or interactions. However, petroleum jelly is believed to form a three-dimensional network structure comprised of both solid and liquid hydrocarbons attached through random entanglement and chemical bonding. In spite of such an incompleteness, our result is in agreement with the previous study reported by Remizov et al. (2000) who stated that the Casson model describes well the rheological behavior of paraffin-containing dispersions.

Table II. Calculated flow model parameters for petroleum jelly at 37°C

Flow model	σ_y (dyn/cm^2)	k (P · s^{n-1})	n (-)	R^2
Bingham	380	10.080	-	0.927
Casson	321	1.675	-	0.988
Herschel-Bulkley	338	44.510	0.646	0.998
Mizrahi-Berk	328	1.491	0.526	0.989
Heinz-Casson	330	1.977	0.542	0.989

Nextly, both the Mizrahi-Berk and Heinz-Casson models also give a good ability to describe the flow behavior of petroleum jelly. These two models have the values of determination coefficients greater than 0.98 and show a clear tendency that the yield stress values exhibit almost no differences.

Finally, a closer examination of Table II indicates that, among the five flow models considered in this work, the Herschel-Bulkley model provides the most excellent ability for predicting the flow behavior of petroleum jelly ($R^2 = 0.998$). This model is an extended version of a simple power-law flow equation to include a yield stress term and has been reported to be very useful to quantitatively describe the steady shear flow behavior of various kinds of soft materials such as semi-solid foodstuffs, pharmaceutical and cosmetic products (Holdsworth, 1993; Kim et al., 1995; Kim et al., 1997; Song and Chang, 1999; Park and Song, 2008; Kuk and Song, 2009).

By the way, it should be considered here that, even though similar values of the determination coefficients are obtained for different flow models, there exists a possibility for each model to provide a dissimilar ability to predict the flow behavior of a material. In order to confirm this matter, all models used in this study were directly applied to the experimentally measured shear stress-shear rate data for petroleum jelly. The obtained results are displayed in Fig. 4.

The Bingham model shows a relatively large discrepancy between the obtained results and the experimentally measured data over an entire range of shear rates tested, and moreover, represents a larger yield

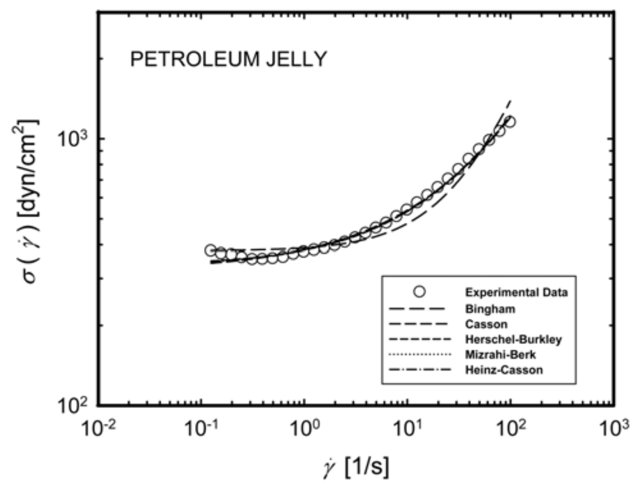

Fig. 4. Applicability of viscoplastic flow models to petroleum jelly at 37°C

stress than the experimentally measured.

On the other hand, the Casson, Mizrahi-Berk, Heinz-Casson and Herschel-Bulkley models are all in good agreement with the experimentally measured data over a whole range of shear rates tested. Furthermore, no discrepancies are observed between these four models, indicating that they have almost an equivalent ability to predict the flow behavior of petroleum jelly.

From these results, it may be concluded that these four (Casson, Mizrahi-Berk, Heinz-Casson and Herschel-Bulkley) models are regarded as useful relationships to quantitatively evaluate the steady shear flow behavior of petroleum jelly and that the Herschel-Bulkley model has the best applicability among these flow models.

CONCLUSION

Petroleum jelly (petrolatum) is used as a major ingredient in a wide variety of topical ointment and cream formulations. The quality and function of these formulations are therefore greatly dependent on the rheological (or mechanical) properties of petroleum jelly itself. However, only a little attention has been given to the rheological investigation of petroleum jelly in actual usage conditions such as spreading and rubbing onto the human body or skin.

The objective of the present study is to systematically characterize a nonlinear rheological behavior of petroleum jelly in steady shear flow fields correspondent to the spreading condition onto the human body. With this aim, using a strain-controlled rheometer, the steady shear flow properties of commercially available petroleum jelly have been measured at 37°C (body temperature) over a wide range of shear rates.

In this article, the shear rate dependence of steady shear flow behavior was reported from the experimentally obtained data. In particular, the existence of a yield stress and a non-Newtonian flow behavior were discussed in depth with a special emphasis on their importance in actual application onto the human body. In addition, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative description of the steady shear flow behavior, and then the applicability of these models was examined in detail. Main findings obtained from this study can be summarized as follows :

(1) Petroleum jelly exhibits a finite magnitude of yield stress. The appearance of a yield stress is attributed to its three-dimensional network structure that can show a resistance to flow and plays an important role in determining a storage stability and sensory feature of the product.

(2) Petroleum jelly demonstrates a pronounced non-Newtonian shear-thinning flow behavior which is well described by a power-law equation and may be interpreted by the disruption of a crystalline network under the influence of mechanical shear deformation. This rheological feature enhances sensory qualities of pharmaceutical and cosmetic products in which petroleum jelly is used as a base material during their actual usage.

(3) The Casson, Mizrahi-Berk, Heinz-Casson and Herschel-Bulkley models are all applicable and have almost an equivalent ability to quantitatively describe the steady shear flow behavior of petroleum jelly whereas the Bingham model does not give a good validity. Among these flow models, the Herschel-Bulkley model provides the best applicability.

ACKNOWLEDGEMENTS

One of the authors (E.K. Park) would like to express her gratitude to the Korea Science and Engineering Foundation (KOSEF) for the financial support provided within her master course of Graduate School from September 2007 to August 2008 during which she had been able to continue her study as a Research Scholarship Student of the KOSEF (Scholarship No. : S2-2007-000-00441-1).

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