Rheological Evaluation of Petroleum Jelly as a Base Material in Ointment and Cream Formulations : Linear Viscoelastic Behavior

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(Received May 6, 2011 · Revised May 23, 2011 · Accepted June 3, 2011)

ABSTRACT − The objective of the present study is to systematically characterize a linear viscoelastic behavior of petroleum jelly in small amplitude oscillatory shear flow fields correspondent to the rheological ground state. With this aim, using a strain-controlled rheometer, the dynamic viscoelastic properties of commercially available petroleum jelly have been measured at 37°C (body temperature) over a wide range of angular frequencies at an extremely small strain amplitude of 0.1 %. In this article, the linear viscoelastic behavior was reported in detail and then explained from a structural view-point of petroleum jelly and discussed in depth with respect to the consumer's requirements. Main findings obtained from this study can be summarized as follows : (1) The storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied, meaning that the linear viscoelastic behavior of petroleum jelly is dominated by an elastic nature rather than a viscous nature. (2) Petroleum jelly shows a desirable linear viscoelastic behavior with respect to the consumer's requirements because it is undesirable for the product to flow down from the skin at an initial stage upon contact with the human skin. (3) A fractional derivative model shows an excellent applicability to describe a linear viscoelastic behavior of petroleum jelly. However, this model should be used with a special caution because there exists no physical meaning for the model parameters. (4) A modified form of the Cox-Merz rule gives a good ability to predict the relationship between steady shear flow properties (nonlinear behavior) and dynamic viscoelastic properties (linear behavior) for petroleum jelly.

Key words − Petroleum jelly (petrolatum), Rheology, Linear viscoelastic behavior, Fractional derivative model, Modified form of the Cox-Merz rule

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 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).

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 viewpoint of consumer's demands (Lee et al., 2008; Cha et al., 2009). This is a main motivation that 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.

From our previous study (Park and Song, 2010a) that dealt with a nonlinear rheological behavior in steady shear flow fields correspondent to the spreading condition onto the human body, it was found that : (a) petroleum jelly exhibits a finite magnitude of yield stress which is attributed to its three-dimensional network structure that can show a resistance to flow ; and (b) 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.

These informations are greatly valuable in the sense that the existence of a yield stress plays an important role in determining a storage stability and a sensory feature of the product and that a shear-thinning behavior enhances sensory qualities of pharmaceutical and cosmetic products in which petroleum jelly is used as a base material during their actual usage (i.e., spreading onto the human body) (Park and Song, 2010a).

As a continuation of our serial works, from our second article (Park and Song, 2010b) that dealt with a nonlinear viscoelastic behavior of petroleum jelly in large amplitude oscillatory shear flow fields correspondent to the rubbing condition onto the human body, it was reported that : (a) both the storage modulus and loss modulus show a linear behavior only within an extremely small strain amplitude range and exhibit almost an equivalent strain limit of linear response ; (b) both the storage modulus and loss modulus demonstrate a qualitatively similar strain-dependent nonlinear behavior (i.e., strain-thinning feature), even though the storage modulus shows a stronger dependence on strain amplitude than does the loss modulus ; and (c) as the strain amplitude is increased, the difference between the storage modulus and loss modulus is gradually decreased and subsequently a viscous property becomes superior to an elastic property at sufficiently large strain amplitude range.

These findings are also greatly helpful with respect to actual application situations in the sense that the superiority of a viscous nature in large strain amplitudes enables the product to smoothly flow ahead during the rubbing process onto the human body or skin (Park and Song, 2010b).

However, both the steady shear flow behavior and large amplitude oscillatory shear flow behavior are not able to provide a sufficient information with regard to the relationship between the rheological properties and the microstructure of a material because these flow measurements are in nature a destructive technique and consequently conducted with accompanying a structural breakdown of a material. Moreover, as the

deformation is too fast at high shear rates or at high angular frequencies, a material cannot have enough time to respond to the applied environment of deformation.

In order to reveal the secrets of the microscopic structure of a complex material from its rheological properties, measurement should be made under the rheological ground state where a material is subjected to small deformations. This so-called dynamic test is commonly performed in oscillatory shear flow fields by applying a small amplitude of sinusoidal strain (or stress) to a material and then measuring the resulting stress (or strain) amplitude. The strain (or stress) amplitude adopted in this test should be sufficiently small in order to assure that the response of a material is within the linear viscoelastic region where the stress (or strain) is proportional to the imposed strain (or stress) and the theory of linear viscoelasticity is applicable (Macosko, 1994).

One of the most significant reasons for conducting this small amplitude oscillatory shear (SAOS) test is that it is a non-destructive technique enabling the measurement to be made without incurring structural damage to a material. This allows one to relate the dynamic rheological parameters to the molecular structure of a material. Moreover, all of the other linear viscoelastic functions can be calculated from the dynamic rheological properties using the theory of linear viscoelasticity (Ferry, 1980; Tschoegl, 1989).

Based upon the above-described backgrounds, as a third step of our serial works, the objective of the present study is to systematically characterize a linear viscoelastic behavior of petroleum jelly in small amplitude oscillatory shear flow fields correspondent to the rheological ground state. With this aim, using a strain-controlled rheometer, the dynamic viscoelastic properties of commercially available petroleum jelly have been measured at 37°C (body temperature) over a wide range of angular frequencies at an extremely small strain amplitude of 0.1%.

In this article, the linear viscoelastic behavior was firstly reported in detail from the experimental data obtained from dynamic frequency-sweep tests and then the results were explained from a structural view-point of petroleum jelly. Secondly, the angular frequency dependence of the linear viscoelastic behavior was reported using a well-known power-law type equation. In particular, these results were discussed in depth with respect to the consumer's requirements. Thirdly, a fractional derivative model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behavior of petroleum jelly and then the applicability of this model was examined together with its limitations. Finally, the correlation between visco-

metric functions (steady shear flow properties) and linear viscoelastic functions (dynamic viscoelastic properties) was derived by introducing a modified form of the Cox-Merz rule through a comparison of the steady shear viscosity with the complex viscosity.

Experimental Details

Materials

The petroleum jelly sample used in this study was a commercially available product (White Petrolatum USP) supplied from the Vi-Jon® Company (St. Louis, MO, USA). 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.

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 physico-chemical 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, Piscataway, NJ, USA]. 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, in order to investigate a linear viscoelastic behavior in small amplitude oscillatory shear flow fields, dynamic frequency-sweep measurements were firstly performed for petroleum jelly sample using an ARES equipped with a parallel-plate fixture with a radius of 25 mm and a gap size of 2.5 mm. These frequency-sweep tests were carried out at an isothermal condition of 37°C over an angular frequency range from 0.025 to 100 rad/s with a logarithmically increasing scale at a fixed strain amplitude of 0.1%. From our previous study (Park and Song, 2010b), this extremely small strain value was confirmed to lie within the linear viscoelastic region for petroleum jelly sample.

In addition, steady rate-sweep measurements were conducted using an ARES equipped with a parallel-plate fixture with a radius of 12.5 mm and a gap size of 2.5 mm in order to examine the relationships between linear viscoelastic functions and viscometric functions for petroleum jelly. These rate-sweep tests in steady shear flow fields were carried out at a fixed temperature of 37°C over a shear rate range from 0.025 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 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. All measurements were made at least three times for each test and highly reproducible data were obtained within the coefficients of variation of ±5% in all cases.

Theoretical Background : Fractional Derivative Model

It is a well-known fact that, for Newtonian viscous fluids, the following relationship is applicable :

$$\sigma = \eta\dot{\gamma} = K\frac{d\gamma}{dt} \tag{1}$$

where σ is the shear stress, γ is the shear strain, $\dot{\gamma}$ is the shear strain rate defined as $\dot{\gamma} \equiv d\gamma/dt$, η is the viscosity, and K is a constant (here equal to the Newtonian viscosity, η).

It is also well known that, for Hookean elastic bodies, the following relationship is applied :

$$\sigma = G\gamma = K\frac{d^0\gamma}{dt^0} \tag{2}$$

where σ is the shear stress, γ is the shear strain, G is the elastic modulus defined as $G \equiv \sigma/\gamma$, and K is a constant (here equal to the elastic modulus, G).

For a material that is neither a Hookean solid nor a Newtonian fluid, Bosworth (1946) proposed the following relationship :

$$\sigma = K\frac{d^a\gamma}{dt^a} \quad (0 < a < 1) \tag{3}$$

where σ is the shear stress, γ is the shear strain, and K is a constant.

Based on Eq. (3), a general equation that describes a linear viscoelastic behavior can be developed using the Boltzmann superposition principle. By applying the Boltzmann superposition principle in combination with a fractional derivative concept, Eq. (3) has the following form :

$$\sigma(t) = \sum_{n=1}^{N}\left[K_n\frac{d^{a_n}\gamma}{dt^{a_n}}\right] \tag{4}$$

Eq. (4) can be rewritten in terms of a fractional operator as follows :

$$\sigma(t) = \sum_{n=1}^{N}K_n D^{a_n}[\gamma(t)] \tag{5}$$

Eq. (5) is a general expression for linear viscoelasticity of materials in terms of a fractional derivative. From a practical point of view, however, the material functions need to be derived implicitly from the stress-strain relations. The theory of fractional derivatives and Fourier transform would therefore be employed to manipulate these material functions based on the stress-strain relations.

Mathematically, the definition of a fractional derivative can be expressed as follows (Ross, 1975) :

$$D^{\alpha}[x(t)] \equiv \frac{1}{\Gamma(1-\alpha)}\frac{d}{dt}\int_0^t\frac{x(t-t')}{t'^{\alpha}}dt' \quad (0 < \alpha < 1) \tag{6}$$

where Γ is the gamma function.

The Leibniz rule may be used to differentiate the integral in Eq. (6) and produces the following relationship :

$$D^{\alpha}[x(t)] = \frac{1}{\Gamma(1-\alpha)}\frac{d}{dt}\int_0^t\frac{1}{t'^{\alpha}}\frac{\partial}{\partial t}x(t-t') + \frac{x(0)}{\Gamma(1-\alpha)t^{\alpha}} \tag{7}$$

By applying the Laplace transform to Eq. (7), the following expression is obtained :

$$L\{D^{\alpha}[x(t)]\} = \frac{1}{s^{1-\alpha}}\{sL[x(t)-x(0)]\} + \frac{x(0)}{s^{1-\alpha}} \tag{8}$$

Assuming that $x(0) = 0$ for all $t < 0$, Eq. (8) can then be simplified to :

$$L\{D^{\alpha}[x(t)]\} = s^{\alpha}L\{x(t)\} \tag{9}$$

By applying the Fourier transform to Eq. (9), a useful relationship is produced as follows :

$$F[D^{\alpha}[x(t)]] = (i\omega)^{\alpha}F[x(t)] \tag{10}$$

where $F[x(t)] = \int_{-\infty}^{\infty}x(t)\exp[-i\omega t]dt$ and $x(t) = 0$ for all $t < 0$.

By applying Eq. (10) to Eq. (5), the following expression results :

$$\sigma^*(\omega) = \sum_{n=1}^{N}(i\omega)^{a_n}K_n\gamma^*(\omega) \tag{11}$$

where $\sigma^*(\omega)$ and $\gamma^*(\omega)$ are the transforms of the stress and strain histories (representing the complex stress and complex strain, respectively), a_n and K_n are the constants to be determined from the experimental data, and ω is the angular frequency.

However, Eq. (11) is impractical because it involves too many constants. Hence, the first two terms on the right side of Eq. (11) are chosen for approximation of material functions :

$$\sigma^*(\omega) = [K_1(i\omega)^{a_1} + K_2(i\omega)^{a_2}]\gamma^*(\omega) \tag{12}$$

where K_1, K_2, a_1 and a_2 are the parameters of a simplified model.

According to the theory of linear viscoelasticity, the complex modulus, $G^*(\omega)$, is defined as the ratio of complex stress to complex strain :

$$G^*(\omega) \equiv \sigma^*(\omega)/\gamma^*(\omega) \tag{13}$$

By inserting Eq. (12) into Eq. (13), a frequency-dependent complex modulus is achieved as follows :

$$G^*(\omega) = \sigma^*(\omega)/\gamma^*(\omega) = K_1(i\omega)^{a_1} + K_2(i\omega)^{a_2} \tag{14}$$

It is customary to express the complex modulus in terms of real and imaginary parts :

$$G^*(\omega) = G'(\omega) + iG''(\omega) \tag{15}$$

where $G'(\omega)$ is the storage modulus and $G''(\omega)$ is the loss modulus, respectively.

By decomposing Eq. (14) into real and imaginary parts, the following expression is produced :

$$G^*(\omega) = \left[K_1\omega^{a_1}\cos\left(\frac{\pi}{2}a_1\right) + K_2\omega^{a_2}\cos\left(\frac{\pi}{2}a_2\right) \right]$$
$$+ i\left[K_1\omega^{a_1}\sin\left(\frac{\pi}{2}a_1\right) + K_2\omega^{a_2}\sin\left(\frac{\pi}{2}a_2\right) \right] \tag{16}$$

Therefore, the storage and loss moduli in Eq. (15) can respectively be rewritten with the following explicit functions :

$$G'(\omega) = K_1\omega^{a_1}\cos\left(\frac{\pi}{2}a_1\right) + K_2\omega^{a_2}\cos\left(\frac{\pi}{2}a_2\right) \tag{17}$$

$$G''(\omega) = K_1\omega^{a_1}\sin\left(\frac{\pi}{2}a_1\right) + K_2\omega^{a_2}\sin\left(\frac{\pi}{2}a_2\right) \tag{18}$$

Based on Eq. (17) and Eq. (18), additional frequency-dependent material functions including the dynamic viscosity, $\eta'(\omega)$, and the out-of-phase component of the complex viscosity, $\eta''(\omega)$, can be obtained by the following relationships :

$$\eta'(\omega) = G''(\omega)/\omega = K_1\omega^{a_1-1}\sin\left(\frac{\pi}{2}a_1\right) + K_2\omega^{a_2-1}\sin\left(\frac{\pi}{2}a_2\right) \tag{19}$$

$$\eta''(\omega) = G'(\omega)/\omega = K_1\omega^{a_1-1}\cos\left(\frac{\pi}{2}a_1\right) + K_2\omega^{a_2-1}\cos\left(\frac{\pi}{2}a_2\right) \tag{20}$$

Equations (17) ~ (20) can then be used to simulate a linear viscoelastic behavior of petroleum jelly once the constants in these equations have been determined from the experimental data.

Results and Discussion

Linear viscoelastic behavior

Figure 1 shows the storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, as a function of angular frequency at a fixed strain
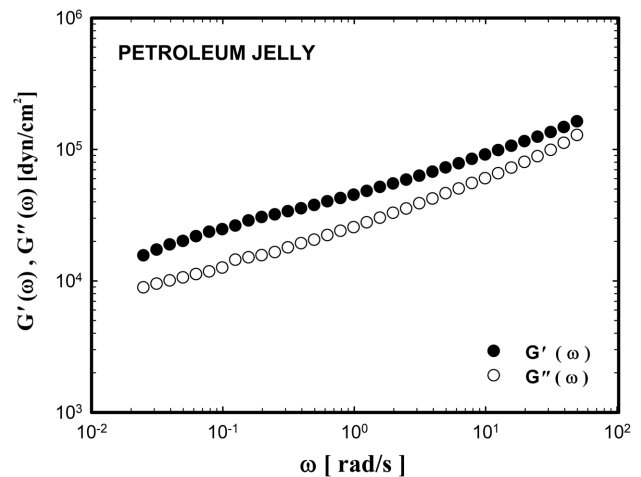

Figure 1. Storage modulus and loss modulus as a function of angular frequency for petroleum Jelly at 37ºC.

amplitude of 0.1% for petroleum jelly at 37ºC. As is obvious from Figure 1, both the storage modulus and loss modulus exhibit a qualitatively similar behavior over a whole range of angular frequencies tested ; these two moduli are gradually increased with an increase in angular frequency.

A more important point to be noted is that the storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied, meaning that the linear viscoelastic behavior of petroleum jelly is dominated by an elastic nature rather than a viscous nature. In addition, both the storage modulus and loss modulus are found to be a weak function of angular frequency, indicating that a gel-like structure is present in petroleum jelly.

From these results, it can be understood that : (1) petroleum jelly forms a gel-like system, as indicated by a dominance of the elastic storage modulus over the viscous loss modulus ; and (2) the angular frequency dependence of the storage modulus infers that a stable (strong) gel is not formed in petroleum jelly.

Such a linear viscoelastic behavior may be attributed to the occurrence of attractive interactions between liquid, microcrystalline and crystalline hydrocarbons formed in petroleum jelly (Barry and Grace, 1971), which can give rise to a weak three-dimensional network and a complex aggregation by means of random physical entanglements and chemical bonding (Birdwell and Jessen, 1966).

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. Moreover, the crystals consist of fiber-like bundles with colloidal dimensions linked by a large number of

contact points (Pena et al., 1994).

These informations infer that petroleum jelly forms a gel-like structure comprised of both solid and liquid hydrocarbons (normal, iso and cyclic paraffins) attached through random physical entanglements and chemical bonding and that this structure is composed of a three-dimensional crystalline network which encloses and immobilizes the liquid hydrocarbons. The overall rheological behavior of petroleum jelly and its formulations becomes closely dependent on this complex microscopic structure.

At very small strain amplitude ($\gamma_0 = 0.1\%$ in this work), both the entanglement density and bonding strength remain unchanged because no structural breakdown takes place in petroleum jelly. Hence, a viscoelastic response to an externally applied deformation exhibits a linear behavior regardless of the imposed strain amplitude.

The angular frequency dependence of the storage modulus as well as the loss modulus may be quantitatively described by a power-law type relationship expressed as follows :

$$G'(\omega) = K'\omega^{n'} \tag{21}$$

$$G''(\omega) = K''\omega^{n''} \tag{22}$$

where K', K'', n' and n'' are constants ; K' and K'' are the intercepts and n' and n'' are the slopes in the double logarithmic plots of the storage modulus and loss modulus against angular frequency, respectively.

The values of the power-law parameters obtained from a linear regression analysis together with those of the determination coefficients are reported in Table I. As expected, the fits of the experimentally measured data (Figure 1) to the power-law relationships represent quite well the linear viscoelastic behavior of petroleum jelly.

From Table I, it is clear that the value of K' is larger than that of K'', demonstrating that an elastic behavior (storage modulus) is superior to a viscous behavior (loss modulus) for petroleum jelly. This trend is more interestingly evidenced in an another fashion by plotting the phase angle, $\delta(\omega)$, as a function of angular frequency, as illustrated in Figure 2. In spite of being gradually increased with an increase in angular frequency, the phase angle is always lower than 45° over a whole range of angular frequencies tested. These findings indicate that petroleum jelly may be regarded as a solid-like elastic material and characterized by a relatively slower relaxation mechanism.

By the way, it has been well accepted that a linear viscoelastic behavior in small amplitude oscillatory shear flow

Table I. *Calculated power-law parameters of storage modulus and loss modulus for petroleum jelly at 37°C*

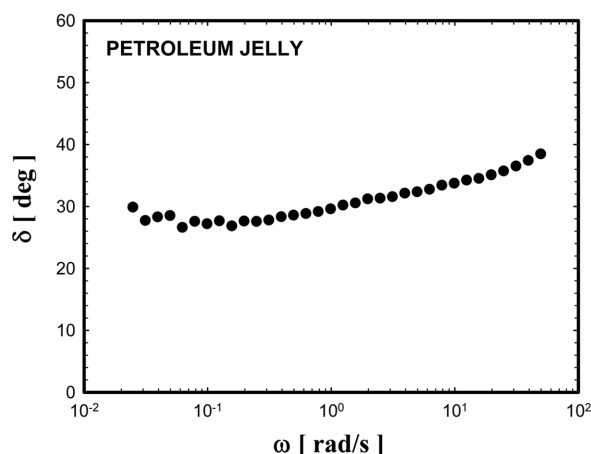|	K' [dyn/cm$^2 \cdot$ (s/rad)$^{n'}$]	n' [-]	R^2
$G'(\omega) = K'\omega^{n'}$			
	4.543×10^4	0.3140	0.9962
	K'' [dyn/cm$^2 \cdot$ (s/rad)$^{n''}$]	n'' [-]	R^2
$G''(\omega) = K''\omega^{n''}$			
	2.524×10^4	0.3972	0.9928

Figure 2. Phase angle as a function of angular frequency for petroleum jelly at 37°C.

fields enables a distinction to be made between strong and weak gels. It has been known that $n' > 0$ for a physical (weak) gel whereas $n' \approx 0$ for a chemical (strong) gel (Ross-Murphy and Shatwell, 1993; Ross-Murphy, 1995; Harrison et al., 1999; Jampala et al., 2005; Kim and Yoo, 2006). The n' value can therefore be used as a quantitative measure of the resemblance of a gel to a chemically cross-linked strong gel system. The n' value of 0.314 was obtained for petroleum jelly sample studied in this work (Table I), indicating that this material does not form a stable (strong) gel but exhibits a weak gel-like behavior.

Now it may be meaningful to discuss the importance of our results from a view-point of consumer's demands. An ease of application of semi-solid pharmaceutical and cosmetic products to the surface of the human skin is a significant factor for consumer's acceptance. This is governed by the texture profile such as extrudability from a container (or a tube), initial sensation upon contact with the skin, spreading and rubbing ability on the skin, adhesiveness and residual greasiness after application (Brummer and Godersky, 1999; Brummer, 2006).

As was deeply discussed in our previous studies (Park and Song, 2010a; 2010b), when considering only the spreading process of an ointment-like material onto the human skin, the magnitude of a yield stress and a shear-thinning flow behavior can be regarded as the most important rheological properties to

fulfill the consumer's requirements. However, during rubbing onto the human skin, informations on the nonlinear viscoelastic behavior obtained from large amplitude oscillatory shear flow measurements become much more helpful in order to better understand the rheological behavior of ointment-like materials in their actual usage situations.

On the other hand, at an initial stage upon contact with the human skin, it is undesirable for the product to flow down from the skin. This means that the rheological behavior at rest or at very small strain amplitudes must be dominated by an elastic nature rather than a viscous nature. As can be clearly observed from Figure 1 and Figure 2, the storage modulus is always greater than the loss modulus over a whole range of angular frequencies tested, indicating that petroleum jelly exhibits a desirable linear viscoelastic behavior with respect to the consumer's requirements.

Applicability of a fractional derivative model

Rheological studies become particularly helpful when predictable relationships for the rheological properties of complex materials could be developed from a molecular or a microstructural architecture of the constituent species. However, the actual molecule is an extremely complicated mechanical system with a large number of contact points and with enormous number of degree of freedom. A mechanistic basis for the interpretation of the experimentally measured data must be introduced in order to accurately understand and properly use the obtained rheological information. Such an interpretation in terms of the theoretical mechanisms can provide a guideline needed to relate the rheological behavior with structure or composition and to predict the textural properties of complex systems.

During the last several decades, a group of scientists has made use of the rheological constitutive equations employing the fractional derivatives to describe a viscoelastic behavior of polymeric materials. Various relaxation equations have been a central focus for their research interest. In general, these equations can be derived from the well-known mechanical models (e.g., the Maxwell or the Kelvin-Voight models) by means of substituting the time ordinary derivatives of stress and strain by derivatives of fractional order. These new models have a great advantage for quantitatively describing a linear viscoelastic behavior in the sense that fewer terms with a small number of empirical parameters may be required to develop successful fractional derivative relationships.

In this work, a fractional derivative model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behav-

ior of petroleum jelly and then the applicability of this model was examined together with its limitations.

Figure 3 and Figure 4 represent the simulation results of a fractional derivative model to the storage modulus/loss modulus and the dynamic viscosity/out-of-phase viscosity, respectively, for petroleum jelly at 37°C. As is clear from the two figures, over a whole range of angular frequencies tested, a fractional derivative model shows a very good applicability to describe quantitatively a linear viscoelastic behavior of petroleum jelly in the sense that : (a) almost no discrepancies are observed between the experimentally obtained linear viscoelastic functions and the theoretically obtained curves ; (b) with an increase in angular frequency, both the storage and loss moduli are increased while both the dynamic and out-of-phase viscosities are decreased ; and (c) the storage modulus is always larger than the loss modulus and the out-of-phase viscosity is consistently greater than the dynamic viscosity.
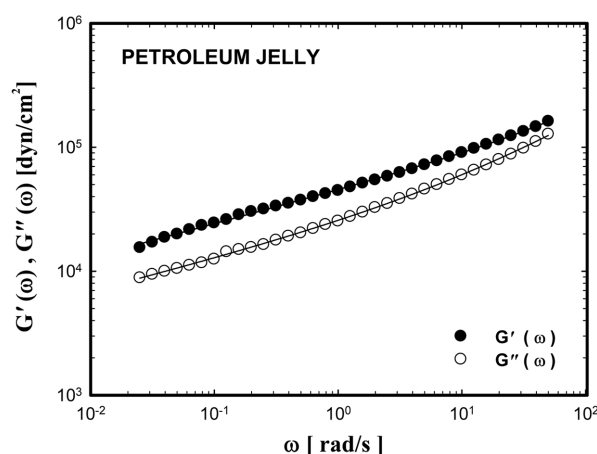

Figure 3. Applicability of a fractional derivative model to storage modulus and loss modulus for petroleum jelly at 37°C.
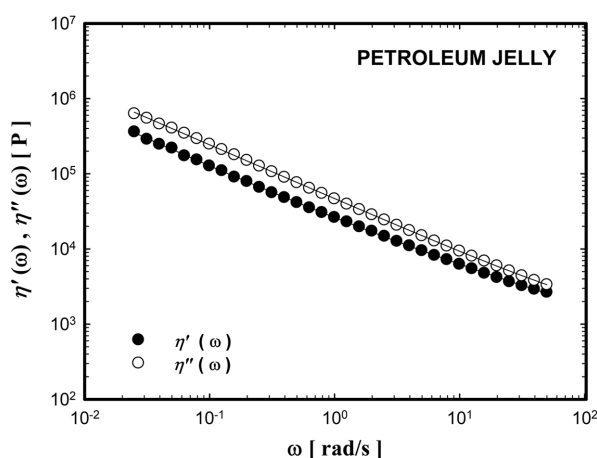

Figure 4. Applicability of a fractional derivative model to dynamic viscosity and out-of-phase viscosity for petroleum jelly at 37°C.

Table II. *Parameters of a fractional derivative model for petroleum jelly at 37°C*

$G'(\omega)$, $G''(\omega)$ / $\eta'(\omega)$, $\eta''(\omega)$	K_1	K_2	a_1	a_2	R^2
$G'(\omega)$	17137	49317	0.9733	0.2700	0.9986
$G''(\omega)$	55523	5123	0.2496	0.6931	0.9994
$\eta'(\omega)$	-17080	-15722	0.2071	0.5648	0.9997
$\eta''(\omega)$	365	108553	1.111	0.2815	0.9997

A least-squares fitting method was used in this study in order to determine the parameters (K_1, K_2 a_1, a_2) of a fractional derivative model from the experimentally measured linear viscoelastic properties. The values of the model parameters for petroleum jelly along with those of the determination coefficients are given in Table II.

Judging from the values of the determination coefficients ($R^2 > 0.99$ for all linear viscoelastic functions), it can be confirmed that the simulation results are in good agreement with the experimentally measured data and consequently a fractional derivative model has an excellent ability to predict a linear viscoelastic behavior of petroleum jelly.

In addition to an ability to describe accurately a linear viscoelastic behavior of petroleum jelly as demonstrated in this work and shown by more extensive results presented elsewhere (Ma and Barbosa-Canovas, 1996; Song and Jiang, 1998), a fractional derivative model has been reported to produce elliptical stress-strain hysteresis loops (Lissajous curves) for a sinusoidal motion of a viscoelastic material (Bagley and Torvik, 1983). For these reasons, it can be concluded that a fractional derivative model may be an attractive means for predicting the frequency-dependent stress-strain relationships of a class of viscoelastic materials.

However, a fractional derivative model may be at present regarded as a semi-empirical relationship because there exists no real physical meaning for the model parameters which are obtained from a least-squares fitting method. Therefore, this model must be used with a special caution and then applied to the situations where only a linear viscoelastic behavior is dealt with. In this respect, further research should be needed to reveal the physical meaning of the model parameters.

Relationships between viscometric functions and linear viscoelastic functions

Rheological properties of viscoelastic materials can be characterized by well-defined classical rheometrical techniques performed in steady shear and/or oscillatory shear flow fields. It may be greatly desirable to interrelate material properties
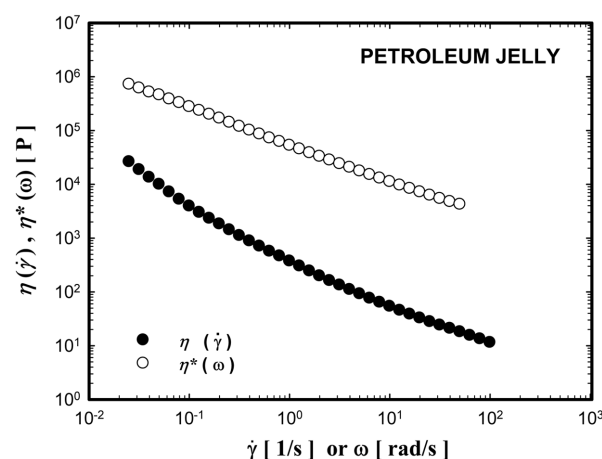
Figure 5. Comparison of steady shear viscosity with complex viscosity for petroleum jelly at 37°C.

obtained from different types of experiments because some inevitable limitations in steady shear rheometry (for instance, wall slippage and sample migration) can be overcome by using a different type of experiment and then relating the obtained material properties back to the framework of interest.

Previous studies as to the rheology of polymeric systems have suggested that there exist some relationships between material functions describing the steady shear flow properties and those describing the dynamic viscoelastic properties (Dealy and Wissbrun, 1990; Carreau et al., 1997). An important feature of these findings is that a nonlinear behavior in steady shear flow fields in which the deformations are large could be mathematically correlated with a linear behavior in small amplitude oscillatory shear flow fields in which the deformations are small (Barnes et al., 1989).

Some of the most difficult material properties of complex materials to experimentally determine are viscometric functions (i.e., steady shear rheological properties). On the other hand, linear viscoelastic functions in small amplitude oscillatory shear flow fields can be measured relatively with ease and with a good reproducibility over a reasonably wide range of angular frequencies.

In this work, the correlations between steady shear flow (nonlinear behavior) and dynamic viscoelastic (linear behavior) properties for petroleum jelly were examined by introducing a modified form of the Cox-Merz rule (1958) through a comparison of the steady shear viscosity with the complex viscosity.

Figure 5 shows a comparison between the steady shear viscosity, $\eta(\dot{\gamma})$, as a function of shear rate and the complex viscosity, $|\eta^*(\omega)|$, as a function of angular frequency for petroleum jelly at 37°C. As is clear from Figure 5, the complex

viscosity is much larger than the steady shear viscosity over a whole range of shear rates and angular frequencies tested. This indicates that the Cox-Merz rule is not applicable to describe the relationship between steady shear flow and dynamic viscoelastic properties for petroleum jelly.

A departure from the Cox-Merz rule for petroleum jelly is attributed to a structural decay due to the extent of strain magnitudes applied to the material ; petroleum jelly undergoes a severe structural breakdown beyond a certain critical strain magnitude in steady shear rheometry.

The applied strain magnitudes in steady shear rheometry are large enough to destroy the structured inter- and intra- molecular associations of petroleum jelly. In this case, when the steady state viscosity is reached, the structure becomes an equilibrium configuration that is very different from that of the undeformed state. On the other hand, during dynamic viscoelastic measurements, the imposed strain amplitude is so small ($\gamma_0 = 0.1\%$ in the present work) that it does not cause any significant change in the structural configuration of the material.

As a consequence, the overall resistance to deformation in dynamic viscoelastic measurements is bound to be stronger than the resistance portrayed in steady shear rheometry at large strain magnitudes where the steady shear viscosity is measured under such a structurally destroyed state. This results in the greater complex viscosity than the steady shear viscosity for petroleum jelly.

From a closer examination of Figure 5, it is easily recognized that the double logarithmic plots of the steady shear viscosity as well as the complex viscosity demonstrate a linear decrease with an increase in shear rate and angular frequency. This implies that these two viscosities may be described by a well-known power-law flow equation as follows.

Steady shear viscosity : $\eta(\dot{\gamma}) = k\dot{\gamma}^{m-1}$ (23)

Complex viscosity : $\left|\eta^*(\omega)\right| = k^*\dot{\gamma}^{m^*-1}$ (24)

where k and k^* are the consistency indices, m and m^* are the flow behavior indices, repectively, which are to be determined from the experimental data. In the case of the steady shear viscosity, as m tends to 1, a shear-thinning nature becomes less pronounced, so that a Newtonian flow behavior is achieved when m equals to 1.

Table III tabulates the values of the power-law parameters obtained from a linear regression analysis together with those of the determination coefficients. As expected, the fits of the experimentally measured data (Figure 5) to the power-law

Table III. *Calculated power-law parameters of steady shear viscosity and complex viscosity for petroleum jelly at 37°C*

$\eta(\dot{\gamma}) = k\dot{\gamma}^{m-1}$		$\left|\eta^*(\omega)\right| = k^*\dot{\gamma}^{m^*-1}$	
k (P·s^{n-1})	396	k^* (P·s^{n-1})	54633
m (-)	0.1720	m^* (-)	0.3233
R^2	0.9718	R^2	0.9976

Table IV. *Empirical correlation constants between steady shear viscosity and complex viscosity for petroleum jelly at 37°C*

$\left|\eta^*(\omega)\right| = C[\eta(\dot{\gamma})]^{\alpha}$	
C (P$^{1-\alpha}$)	733
α (-)	0.7233
R^2	0.9993

relations represent quite well the steady shear viscosity as well as the complex viscosity for petroleum jelly. In addition, it is also confirmed that the consistency index is much larger for complex viscosity as a consequence of the stronger resistance to deformation in dynamic viscoelastic measurements.

From these results (Table III), it may be suggested that the correlation between steady shear viscosity and complex viscosity can be derived from a nonlinear modification of the Cox-Merz rule as follows :

$$\left|\eta^*(\omega)\right| = C \cdot [\eta(\dot{\gamma})]^{\alpha} \quad \text{at} \ \dot{\gamma} = \omega \qquad (25)$$

where C and α are the material constants to be determined from the experimental data.

In Eq. (25), the value of a material constant C becomes an indication of the difference in magnitude between steady shear viscosity and complex viscosity. The larger the C value, the greater the difference in magnitude between the two viscosities. A material with a α value closer to 1 exhibits a linear relationship between steady shear viscosity and complex viscosity. Hence, when $\alpha \approx 1$, the C value becomes equivalent to a shift factor between the two viscosities.

The values of the material constants calculated from Eq. (25) are reported in Table IV. Judging from the value of the determination coefficient ($R^2 > 0.99$), it can be concluded that a modified form of the Cox-Merz rule gives a good ability to predict the relationship between steady shear flow properties and dynamic viscoelastic properties for petroleum jelly.

Besides our results reported in this article, Eq. (25) has previously been proved to be applicable for semi-solid food products such as mayonnaise, tomato ketchup, wasabi and yogurt (Song and Chang, 1998; Yu and Gunasekaran, 2001). This finding stimulates us that further study is needed to verify the

usefulness of Eq. (25) for other semi-solid pharmaceutical systems which show similar rheological properties to petroleum jelly. In fact, such an attempt has been being made by our research group for anhydrous lanolin (Park, 2008), pharmaceutical ointments (Cha, 2011) and commercial toothpastes (Kwon, 2011) and the results will be reported in the near future.

Conclusions

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 linear viscoelastic behavior of petroleum jelly in small amplitude oscillatory shear flow fields correspondent to the rheological ground state. With this aim, using a strain-controlled rheometer, the dynamic viscoelastic properties of commercially available petroleum jelly have been measured at 37ºC (body temperature) over a wide range of angular frequencies at an extremely small strain amplitude of 0.1%.

In this article, the linear viscoelastic behavior was firstly reported in detail from the experimental data obtained from dynamic frequency-sweep tests and then the results were explained from a structural view-point of petroleum jelly. Secondly, the angular frequency dependence of the linear viscoelastic behavior was reported using a well-known power-law type equation. In particular, these results were discussed in depth with respect to the consumer's requirements. Thirdly, a fractional derivative model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behavior of petroleum jelly and then the applicability of this model was examined together with its limitations. Finally, the correlation between viscometric functions (steady shear flow properties) and linear viscoelastic functions (dynamic viscoelastic properties) was derived by introducing a modified form of the Cox-Merz rule through a comparison of the steady shear viscosity with the complex viscosity. Main findings obtained from this study can be summarized as follows :

(1) The storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied. This means that the linear viscoelastic behavior of petroleum jelly is dominated by an elastic nature rather than a viscous nature.

(2) Both the storage modulus and loss modulus are a weak function of angular frequency, indicating that a gel-like structure is present in petroleum jelly.

(3) Such a linear viscoelastic behavior is attributed to the occurrence of attractive interactions between liquid, microcrystalline and crystalline hydrocarbons formed in petroleum jelly, which can give rise to a weak three-dimensional network and a complex aggregation by means of random physical entanglements and chemical bonding.

(4) The angular frequency dependence of the storage modulus as well as the loss modulus for petroleum jelly can be quantitatively well described by a power-law type relationship.

(5) The phase angle is always lower than 45º over a whole range of angular frequencies tested. This implies that petroleum jelly may be regarded as a solid-like elastic material and characterized by a relatively slower relaxation mechanism.

(6) Petroleum jelly shows a desirable linear viscoelastic behavior with respect to the consumer's requirements because it is undesirable for the product to flow down from the skin at an initial stage upon contact with the human skin.

(7) A fractional derivative model shows an excellent applicability to describe a linear viscoelastic behavior of petroleum jelly. However, this model should be used with a special caution because there exists no physical meaning for the model parameters.

(8) A modified form of the Cox-Merz rule gives a good ability to predict the relationship between steady shear flow properties (nonlinear behavior) and dynamic viscoelastic properties (linear behavior) for petroleum jelly.

Acknowledgements

References

Bagley, R.L., Torvik, P.J., 1983. A theoretical base for the application of fractional calculus to viscoelasticity. J. Rheol. 27, 201-210.

Barnes, H.A., Hutton, J.F., Walters, K., 1989. An Introdution to Rheology. Elsevier, Amsterdam, Netherlands.

Barry, B.W., Grace, A. J., 1971. Structural, rheological and textural properties of soft paraffins. J. Texture Studies 2, 259-279.

Birdwell, B.F., Jessen, F.W., 1966. Crystallization of petroleum

waxes. Nature 209, 366-368.

Bosworth, R.C.L., 1946. A definition of plasticity. Nature 137, 447.

Boylan, J.C., 1966. Rheological study of selected pharmaceutical semisolids. J. Pharm. Sci. 55, 710-715.

Brummer, R., 2006. Rheology Essentials of Cosmetic and Food Emulsions. Springer-Verlag, Berlin/Heidelberg, Germany.

Brummer, R., Godersky, S., 1999. Rheological studies to objectify sensations occurring when cosmetic emulsions are applied to the skin. Colloids and Surfaces A : Physicochem. Eng. Aspects 152, 89-94.

Carreau, P.J., De Kee, D.C.R., Chhabra, R.P., 1997. Rheology of Polymeric Systems : Principles and Applications. Hanser Publishers, New York, USA.

Cha, M.J., 2011. Rheological characterization of pharmaceutical ointments. M. E. Thesis, Pusan National University, Korea.

Cha, M.J., Park, E.K., Song, K.W., 2009. Rheological evaluation of pharmaceutical ointments in spreading and rubbing conditions. Theor. Appl. Rheol. 13, 193-197.

Chang, G.S., Koo, J.S., Song, K.W., 2003. Wall slip of vaseline in steady shear rheometry. Korea-Australia Rheol. J. 15, 55-61.

Cox, W.P., Merz, E.H., 1958. Correlation of dynamic and steady flow viscosities. J. Polym. Sci. 28, 619-622.

Davis, S.S., 1969. Viscoelastic properties of pharmaceutical semi-solids (1) : Ointment bases. J. Pharm. Sci. 58, 412-418.

Dealy, J.M., Wissbrun, K.F., 1990. Melt Rheology and Its Role in Plastics Processing : Theory and Applications. Van Nostrand Reinhold, New York, USA.

Ferry, J.D., 1980. Viscoelastic Properties of Polymers. 3rd Ed. John Wiley & Sons, New York, USA.

Fu, R.C.C., Lidgate, D.M., 1985. Characterization of the shear sensitivity property of petrolatum. J. Pharm. Sci. 74, 290-294.

Harrison, G., Franks, G.V., Tirtaatmadja, V., Boger, D.V., 1999. Suspensions and polymers : Common links in rheology. Korea-Australia Rheol. J. 11, 197-218.

Jampala, S.N., Manolache, S., Gunasekaran, S., Denes, F.S., 2005. Plasma-enhanced modification of xanthan gum and its effect on rheological properties. J. Agric. Food Chem. 53, 3618-3625.

Kim, C., Yoo, B., 2006. Rheological properties of rice starch-xanthan gum mixtures. J. Food Eng. 75, 120-128.

Kwon, M.J., 2011. Nonlinear viscoelastic properties of toothpastes. M.E. Thesis, Pusan National University, Korea.

Lee, K.W., Park, E.K., Song, K.W., 2008. Rheological assessment of hand lotions with respect to stability and application. Theor.

Appl. Rheol. 12, 151-154.

Ma, L., Barbosa-Canovas, G.V., 1996. Simulating viscoelastic properties of selected food gums and gum mixtures using a fractional derivative model. J. Texture Studies 27, 307-325.

Macosko, C.W., 1994. Rheology : Principles, Measurements and Applications. VCH Publishers, New York, USA.

Pandey, P., Ewing, G.D., 2008. Rheological characterization of petrolatum using a controlled stress rheometer. Drug Devel. Ind. Pharm. 34, 157-163.

Park, E.K., 2008. Rheological evaluation of semi-solid pharmaceutical ingredients. M. E. Thesis, Pusan National University, Korea.

Park, E.K., Song, K.W., 2010a. Rheological evaluation of petroleum jelly as a base material in ointment and cream formulations : Steady shear flow behavior. Arch. Pharm. Res. 33, 141-150.

Park, E.K., Song, K.W., 2010b. Rheological evaluation of petroleum jelly as a base material in ointment and cream formulations with respect to rubbing onto the human body. Korea-Australia Rheol. J. 22, 279-289.

Pena, L.E., Lee, B.L., Stearns, J.F., 1994. Structural rheology of a model ointment. Pharm. Res. 11, 875-881.

Ross, B., 1975. A brief history and exposition of the fundamental theory of fractional calculus. In : Fractional Calculus and Its Applications. (A. Dold and B. Eckmann Eds.). Springer-Verlag, Berlin, Germany, 1-36.

Ross-Murphy, S. B., 1995. Structure-property relationships in food biopolymer gels and solutions. J. Rheol. 39, 1451-1463.

Ross-Murphy, S. B., Shatwell, K. P., 1993. Polysaccharide strong and weak gels. Biorheology 30, 217-227.

Song, K.W., Chang, G.S., 1998. Steady shear flow and dynamic viscoelastic properties of semi-solid food materials. Kor. J. Rheol. 11, 143-152.

Song, D.Y., Jiang, T.Q., 1998. Study on the constitutive equation with fractional derivative for the viscoelastic fluids : Modified Jeffreys model and its application. Rheol. Acta 37, 512-517.

Song, K.W., Kuk, H.Y., Chang, G.S., 2006. Rheology of concentrated xanthan gum solutions : Oscillatory shear flow behavior. Korea-Australia Rheol. J. 18, 67-81.

Tschoegl, N.W., 1989. The Phenomenological Theory of Linear Viscoelastic Behavior. Springer-Verlag, Berlin, Germany.

Yu, C., Gunasekaran, S., 2001. Correlation of dynamic and steady flow viscosities of food materials. Appl. Rheol. 11, 134-140.