## Rheological investigation of body cream and body lotion in actual application conditions

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The objective of the present study is to systematically evaluate and compare the rheological behaviors of body cream and body lotion in actual usage situations. Using a strain-controlled rheometer, the steady shear flow properties of commercially available body cream and body lotion were measured over a wide range of shear rates, and the linear viscoelastic properties of these two materials in small amplitude oscillatory shear flow fields were measured over a broad range of angular frequencies. The temperature dependency of the linear viscoelastic behaviors was additionally investigated over a temperature range most relevant to usual human life. The main findings obtained from this study are summarized as follows: (1) Body cream and body lotion exhibit a finite magnitude of yield stress. This feature is directly related to the primary (initial) skin feel that consumers usually experience during actual usage. (2) Body cream and body lotion exhibit a pronounced shear-thinning behavior. This feature is closely connected with the spreadability when cosmetics are applied onto the human skin. (3) The linear viscoelastic behaviors of body cream and body lotion are dominated by an elastic nature. These solid-like properties become a criterion to assess the selfstorage stability of cosmetic products. (4) A modified form of the Cox-Merz rule provides a good ability to predict the relationship between steady shear flow and dynamic viscoelastic properties for body cream and body lotion. (5) The storage modulus and loss modulus of body cream show a qualitatively similar tendency to gradually decrease with an increase in temperature. In the case of body lotion, with an increase in temperature, the storage modulus is progressively decreased while the loss modulus is slightly increased and then decreased. This information gives us a criterion to judge how the characteristics of cosmetic products are changed by the usual human environments.

*Keywords*: body cream, body lotion, cosmetic rheology, primary (initial) skin feel, spreadability, storage stability

### 1. Introduction

Most 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 cosmetics are also greatly dependent on the flow properties of the final products (Colo *et al.*, 2004). Therefore, knowledge of the rheological properties of cosmetic materials becomes an essential key to improve processing efficiency as well as to develop consumer-acceptable final products (Herh *et al.*, 1998).

Consumers have various delicate expectations to cosmetic products in terms of stability, texture, skin-feel, consistency and greasiness, and these parameters exert a crucial impact on their buying preference. Hence, cosmetic manufacturers have to be aware of these facts and should find out the best ways to meet the consumer demands (Forster and Herrington, 1998).

Cosmetic creams and lotions require a sophisticated design of rheological and thermal investigations in order

qualities for the end-user satisfaction. Typically, cosmetic creams and lotions are classified into complex multiplephase emulsions (Eccleston, 1990) which are formulated in the same way with almost similar compositions. However, these two kinds of cosmetics are substantially different in main function as well as in skin-feel that consumers usually experience during application. Cosmetic lotion is basically used to care lightly and maintain the balance of oil and water of the skin. It should be smoothly applied onto the skin and not contain a high portion of oil in order to penetrate into the skin easily. On the other hand, cosmetic cream has slightly different functions from lotion. It is supposed to supply enough moisture and nutrients into the skin, and at the same time, to form a thin protective film onto the skin so as to prevent water loss. Thus, creams are high in oil content allowing the products to have high consistency. Furthermore, creams are very rich and moist in actual skin-feel.

to characterize themselves and to control the functional

When applied to the human skin, they need to spread easily on the skin without feeling greasy or sticky. In addition, during the self storage in local markets, the ingredients of the products should not separate with each other or

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settle down in the container; otherwise, the products would feel lumpy or grainy when applied to the skin. When the product is poured or squeezed from the packaging container, it should not be too hard or too runny. These requirements imply that cosmetic products have to be formulated to meet the consumer satisfaction (Yao and Patel, 2001).

In spite of their practical importance in cosmetic industry, only a few attempts have been made during the past several decades to investigate the rheological properties of body cream and body lotion with respect to their actual application conditions such as spreading and rubbing onto the human skin (Brummer and Godersky, 1999; Yao and Patel, 2001; Moravkova and Stern, 2011). This is a main motivation that we have designed a comprehensive study as to the overall rheological characterization of body cream and body lotion in a wide variety of flow fields most relevant to their actual application situations.

The principal objective of the present study has been to systematically evaluate and compare the rheological behaviors of body cream and body lotion with regard to primary (or initial) skin feel, spreadability, self-storage stability and environmental sensitivity. To this end, using a strain-controlled rheometer, the steady shear flow properties of commercially available body cream and body lotion were measured over a wide range of shear rates, and the linear viscoelastic properties of these two materials in small amplitude oscillatory shear flow fields were measured over a broad range of angular frequencies. In addition, the temperature dependency of the linear viscoelastic behavior was investigated over a temperature range most relevant to usual human life.

In this article, the appearance of a yield stress and a

marked shear-thinning flow behavior was firstly reported in detail on the basis of the experimental data obtained from steady rate-sweep measurements and then discussed in terms of primary (or initial) skin feel upon contact with the human skin and spreadability on the human skin, respectively. The linear viscoelasticity was secondly presented from the experimental data obtained from dynamic frequency-sweep tests and then explained with respect to self-storage stability of the products. Thirdly, the correlations between viscometric functions (steady shear flow properties) and linear viscoelastic functions (dynamic viscoelastic properties) were examined by introducing a modified form of the Cox-Merz rule through a comparison of the steady shear viscosity with the complex viscosity. Finally, the temperature-dependent viscoelastic behavior was presented and then interpreted with regard to environmental sensitivity of the products.

## 2. Experimental Details

#### 2.1. Materials

The body cream and body lotion samples used in this study were commercially available NIVEA<sup>®</sup> Refreshingly Soft Moisturizing Body Cream and NIVEA<sup>®</sup> Moisturizing Body Lotion supplied from the Beiersdorf AG Co. (Germany). These two materials are widely-used world-famous body care products applicable to face, hands and normal skin.

Table 1 summarizes the functional classification of ingredients contained in body cream and body lotion used in this work. As can be seen from Table 1, substantial portion of whole ingredients is acted as an emollient which perform a significant role in the rheological properties of

Table 1. Functional classification of ingredients contained in body cream and body lotion used in this study.

| Function            | Body Cream  | Body Lotion   |  |
|---------------------|---|---|--|
| Solvent             | Water   | Water   |  |
| Humectant           | Glycerin, Butylene Glycol   | Glycerin, Sea Salt  |  |
| Emollient           | Mineral Oil, Butylene Glycol, Myristyl Myristate, Glyceryl<br>Stearate, Hydrogenated Coco-Glycerides, Jojoba Seed Oil,<br>Tocopheryl Acetate, Polyglyceryl-2 Caprate, Dimethicone | Dicaprylyl Carbonate, Dimethicone, Mineral Oil,<br>Glyceryl Stearate, Myristyl Myristate, (Grape) Seed<br>Oil, Sea Salt, Tocopheryl Acetate |  |
| Emulsion stabilizer | Myristyl Alcohol, Lanolin Alcohol, Sodium Carbomer  | Cetyl Alcohol, Sodium Carbomer  |  |
| Thickening agent    | Myristyl Alcohol, Microcrystalline Wax, Lanolin Alcohol, Sodium Carbomer  | Cetyl Alcohol, Sodium Carbomer  |  |
| Binder              | Microcrystalline Wax, Lanolin Alcohol   |   |  |
| Surfactant          | Stearic Acid, Glyceryl Stearate, Polyglyceryl-2 Caprate   | Glyceryl Stearate, Cetyl Alcohol, PEG-40 Stearate   |  |
| Perfume             | Phenoxyethanol, Linalool, Citronellol, Alpha-Isomethyl Ionone,<br>Butylphenyl Methylpropional, Limonene, Benzyl Alcohol,<br>Benzyl Salicylate                                     | Taurine, Methylparaben, Propylparaben,<br>Phenoxyethanol  |  |
| Preservative        | Phenoxyethanol, Benzyl Alcohol  | Methylparaben, Propylparaben, Phenoxyethanol  |  |

the products (Lukic *et al.*, 2012). Emollients (also commonly referred to as moisturizers) are products that help to soften the external layers of the skin (epidermis) or to treat the dried skin. Most emollients are forms of oil or grease such as mineral oil, squalene, and lanolin. They work by increasing the ability of the skin to hold water, providing the skin with a layer of oil to prevent water loss, and lubricating the skin. With these characteristics, emollients make a considerable contribution to give end-products softness and moisturizing so as to meet the customer expectations (Lukic *et al.*, 2012).

Even though the composition of body cream and body lotion used in this study is highly analogous, body cream contains greater amounts of waxes, solid oil-based ingredients, polymers and thickening agents in order to differentiate the degree of greasiness and viscosity from those of body lotion. These materials play a more important role in determining the rheological properties of cosmetics than do the aqueous constituents (Pal, 1996; Miller *et al.*, 1999; Penzes *et al.*, 2004; Medina-Torres *et al.*, 2014). Based on this point, it is plausible that certain ingredients used as an emollient, a surfactant, an emulsion stabilizer, a thickening agent and a binder in these samples have resulted in rheologically common and different properties between body cream and body lotion.

### 2.2. Rheological measurements

All rheological measurements have been conducted using an Advanced Rheometric Expansion System (ARES) [Rheometric Scientific, Piscataway, NJ, USA]. ARES is a well-known 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 the steady shear flow behaviors of body cream and body lotion, steady rate-sweep measurements were firstly performed using an ARES equipped with a parallel-plate fixture with a radius of 12.5 mm and a gap size of 2.0 mm. These rate-sweep tests in steady shear flow fields were carried out at a fixed temperature of 35°C, which can be assumed to be actual skin temperature, over a wide range of shear rates from 0.01 to 625 1/s with a logarithmically increasing scale.

Next, dynamic frequency-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 2.0 mm in order to evaluate the linear viscoelastic behaviors in small amplitude oscillatory shear flow fields. These frequency-sweep experiments were carried out at an isothermal condition of 35°C over a broad range of angular frequencies from 0.025 to 100 rad/s with a logarithmically

increasing scale at constant strain amplitudes of 1% and 0.2% for body cream and body lotion, respectively. From preliminary strain-sweep tests, these two strain values were confirmed to lie within the linear viscoelastic region for body cream and body lotion, respectively.

Finally, the temperature-dependent viscoelastic behaviors of body cream and body lotion were investigated from temperature-ramp tests using an ARES equipped with a parallel-plate fixture with a radius of 12.5 mm and a gap size of 2.0 mm. These temperature-ramp tests were conducted at a fixed angular frequency of 1 rad/s and a constant strain amplitude of 0.1% over a temperature range of  $10 \sim 50^{\circ}$ C (most relevant to usual human life) with temperature rise being increased by  $0.5^{\circ}$ C/min.

Before the cream and lotion samples were 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 in which a straight line marker was drawn from the upper plate to the lower plate passing through the free surface of the sample (Chang *et al.*, 2003), 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 cream and lotion samples were 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 plates was trimmed with a plastic spatula. All measurements were made for a fresh sample to obtain precise experimental results and conducted at least three times for each test. Through these careful considerations, highly reproducible data were obtained within the coefficients of variation of  $\pm 5\%$  in all cases.

### 3. Results and Discussion

## 3.1. Yield stress as a measure of primary (initial) skin feel

Fig. 1a shows the flow curves (representation of the shear stress as a function of shear rate) for body cream and body lotion at 35°C. For both of body cream and body lotion, the shear stress tends to approach a limiting constant value as a decrease in shear rate towards zero at low range of shear rates, indicating that these two products exhibit a finite magnitude of yield stress. It is also clearly observed that the shear stress of body cream is approximately 10 times larger than that of body lotion over a whole range of shear rates tested.

These results are more dramatically manifested when plotting the steady shear viscosity as a function of shear stress rather than shear rate, as demonstrated in Fig. 1b which was directly obtained from the data of Fig. 1a. Two distinctive regions are clearly seen: (1) the existing region



**Fig. 1.** (a) Shear stress as a function of shear rate and (b) steady shear viscosity as a function of shear stress for body cream and body lotion at  $35^{\circ}$ C, where (b) was directly obtained from the data of (a).

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 shear viscosity is substantially decreased with increasing shear stress. It is also shown that the flow curve for body cream exists on the right side of that for body lotion, implying that the yield stress of body cream is larger than that of body lotion.

The appearance of a yield stress for body cream and body lotion may be attributed to the existence of sodium carbomer which was used in both products as an emulsion stabilizer and a thickening agent. Sodium carbomer is a type of carbomer that is also called carbopol. Sodium carbomer is a synthetic polymer frequently used to thicken, suspend and stabilize cosmetic formulations and to modify rheological properties. It has been widely used in cosmetic and pharmaceutical preparations with the advantages of an excellent function as a thickening agent and an exhibition of a wide range of flow properties even at very low concentrations (Ketz *et al.*, 1988; Islam *et al.*, 2004; Lee and Song, 2011).

In general, carbomer consists of poly(acrylic acid) crosslinked with allyl ether pentaerythritol, allyl ether of sucrose or allyl ether of propylene (Ketz *et al.*, 1988). Its polymer chains form a three-dimensional network structure by cross-linking with one another. The cross-linked microgel structure where individual particles are closely packed with their neighbors has a resistance to flow (Islam *et al.*, 2004). Only when a sufficient magnitude of shear stress (larger than a yield stress) is applied, this network structure becomes broken down. Subsequently, the alignment of polymer chains takes place, resulting in a shear-thinning flow behavior (Calderas *et al.*, 2013).

Approximately 10 times difference in yield stress values between body cream and body lotion may be explained by the following two reasons. Firstly, carbomer shows different rheological properties dependent on concentration (Oppong et al., 2006). Typically, since quantitative values of viscoelastic properties become larger as an increase in concentration of applied carbomer (Edsman et al., 1996), it is expected that the concentration of sodium carbomer used in the two products would not be the same even though the exact amount of the ingredients is not displayed. Secondly, unlike body lotion, body cream contains extra ingredients that work as a thickening agent and a binder; microcrystalline wax and lanolin alcohol. In particular, microcrystalline waxes are mostly comprised of iso-paraffinic (branched) saturated hydrocarbons forming a small, thin, and translucent solid crystalline structure, making them more elastic and flexible than paraffin wax which consists of straight-chain saturated hydrocarbons. From these features of ingredients contained in the two products, the difference in rheological behaviors between body cream and body lotion can be deduced.

Such a yield-stress characteristic, which may be the minimum required force to extrude or pour contents from the product's containers, is directly related to the primary (or initial) sensory feel that consumers experience during actual usage (Moravkova and Stern, 2011; Bekker *et al.*, 2013). In this respect, yield stress is an essential rheological property for cosmetics. When body cream or body lotion is taken from the containers and placed onto the human skin, the content should keep the shape maintained for a while without flowing down from the skin.

From the experimental results (Figs. 1a and 1b), it is obvious that the magnitude of yield stress of body cream is approximately 10 times greater than that of body lotion. This feature would exert an influence on the selection of containers during the process of manufacturing. That is, a wide-opened jar is usually selected as a cream's container, whereas a narrow-opened bottle is often used for lotion. In addition, consumers could easily feel the different magnitudes in yield stress between body cream and body lotion when they are taken from the containers. At the time when the human fingers are initially in contact with the surface of cosmetics, the force required to the fingers becomes much larger for body cream than for body lotion. In general, yield stress of cosmetic products should be large enough so that the contents do not flow out of the container due to their own weight when the container is placed in upside-down position. At the same time, yield stress should not be too large to offer an intensive resistance to flow during application on the human skin. In addition, the smaller the yield stress, the easier the product can be distributed on the skin. This indicates that yield stress plays a crucial role in determining the thickness of the product film layer on the surface of the human skin (Park and Song, 2010a).

## 3.2. Shear-thinning viscosity as a measure of spreadability

Fig. 2 shows the shear rate dependence of the steady shear viscosity for body cream and body lotion at 35°C. While the Newtonian flow region is not observed at low shear rates, the steady shear viscosity of body cream and body lotion is sharply decreased as an increase in shear rate over a whole range of shear rates tested, demonstrating that these two products exhibit a pronounced non-Newtonian shear-thinning behavior. It is also clearly observed that the steady shear viscosity of body cream is almost 10 times greater than that of body lotion.

A shear-thinning behavior observed in body cream and body lotion may be interpreted by the changes of microstructure and alignment of polymer chain segments in sodium carbomer which was aforementioned as a primary factor of yield stress property. At low shear rates, body cream and body lotion have high viscosity derived from the cross-linked gel network structure of carbomer. With a progressive increment in shear rate, however, the number of entanglements between polymer chain segments and side chains is decreased, and the microgel structure becomes deformed and destroyed (Islam *et al.*, 2004). These make the polymer chain segments aligned in the direction of flow, and consequently the steady shear viscosity is decreased.

Structural factors inducing quantitatively different shearthinning behaviors between body cream and body lotion are analogous to those concretely explained in the former section. As compared with body cream, body lotion includes less sorts and contents of oily ingredients and thickening agents, leading to relatively weak entanglements and chemical bonding that can form the microstructure of a material. Because of this fact, the shear viscosity values exhibit almost 10 times difference between body cream and body lotion, as displayed in Fig. 2.

This rheological feature is closely connected with the spreadability which is regarded as one of the most important properties when cosmetics are applied onto the human skin at actual usage conditions (Garg *et al.*, 2002; Park and Song, 2010a; Moravkova and Stern, 2011; Bekker *et al.*, 2013). At the moment of spreading in one direction,



**Fig. 2.** Shear rate dependence of steady shear viscosity for body cream and body lotion at 35°C.

cosmetics should be smoothly spreaded onto the skin with forming a thin and even layer. Therefore, a shear-thinning behavior becomes bound to be essential, leading to a decrease in shear viscosity as the shear rate is increased.

Likewise a yield-stress feature, the shear viscosity of body cream is almost 10 times higher than that of body lotion. Body cream and body lotion have a similar role to supply moisture and/or nutrients to the skin. However, body cream has additional functions which are to protect the skin from externally imposed stimulus and to prevent the skin from losing moisture and nutrients by forming a protective film. In order to meet these requirements, large amounts of oily ingredients and other functional agents such as an emulsion stabilizer, a thickening agent and a binder are added to body cream, resulting that a thick and highly viscous body cream is formulated. Ultimately, it is desirable for body cream to show a much higher shear viscosity than body lotion.

An ease of application of semi-solid cosmetic products to the surface of the human skin is a significant factor for consumer acceptance. Each individual person applies cosmetic 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 is governed by the texture profile such as appearance, odor, extrudability from a container, initial sensation upon contact with the skin, spreading ability on the skin, adhesiveness and residual greasiness after application (Brummer and Godersky, 1999; Brummer, 2006; Moravkova and Stern, 2011).

The topical application procedure may be subdivided into four steps: (a) removal of a product from a container, (b) primary (or initial) sensation on the skin, (c) secondary sensation during spreading on the skin, and (d) final impression due to a residue on the skin (Park and Song, 2010a). 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 whereas spreadability can be subjectively assessed at high shear rates and hence associated with a shear-thinning viscosity (Bekker *et al.*, 2013). For these reasons, the magnitude of a yield stress and the values of the power-law parameters of a shear-thinning viscosity are then able to become a direct quantitative indication of the consistency and spreadability of a cosmetic product, respectively (Park and Song, 2010a).

# 3.3. Linear viscoelasticity as a measure of storage stability

Figs. 3a and 3b show the storage modulus,  $G'(\omega)$ , and loss modulus,  $G''(\omega)$ , as a function of angular frequency for body cream and body lotion, respectively, at 35°C. As is obvious from Fig. 3a, both the storage modulus and loss modulus of body cream exhibit a qualitatively similar behavior over a whole range of angular frequencies tested; these two moduli are almost constant or slightly increased with an increase in angular frequency. Meanwhile, the storage modulus and loss modulus of body lotion are increased as an increase in angular frequency, with the loss modulus showing a slight decrease at an angular fre-



**Fig. 3.** Storage modulus and loss modulus as a function of angular frequency for (a) body cream and (b) body lotion at 35°C.

quency range higher than 10 rad/s, as demonstrated in Fig 3b.

A more important point to be noted is that, for both of body cream and body lotion, the storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied, meaning that the linear viscoelastic behaviors of body cream and body lotion are dominated by an elastic nature rather than a viscous nature.

A supplementary evidence can be found by plotting the loss tangent  $[\tan \delta = G''(\omega)/G'(\omega)]$  as a function of angular frequency, as displayed in Fig. 4. The values of tan $\delta$  for these two materials are placed lower than unity, exhibiting a solid-like elastic behavior. In addition, both the storage modulus and loss modulus are found to be a weak function of angular frequency, indicating that gel-like structures are present in body cream and body lotion.

A common primary factor to elucidate the linear viscoelastic behaviors observed in body cream and body lotion may originate from the attractive interactions within poly-(acrylic acid) forming sodium carbomer. First of all, the linear viscoelastic properties characterized in body cream may be attributed to the interactions (cross-linking, entanglement, and aggregation) of polymer chains consisted in sodium carbomer and crystalline structures made up with iso-paraffins of microcrystalline wax. Entanglements of poly(acrylic acid) and small crystalline structures of microcrystalline wax develop strong gel network structure, engendering no change in entanglement density and network structure cross-linked between polymer chains at very small strain amplitude ( $\gamma_0 = 1\%$  in this work). Therefore, the angular frequency dependence on storage modulus and loss modulus is not substantial for body cream, and an elastic nature is superior to a viscous nature over an entire range of angular frequencies measured.

On the other hand, body lotion does not have extra ingredients that have a role as a binder. In addition, weakly bonded and cross-linked gel structure formed in body



**Fig. 4.** Loss tangent as a function of angular frequency for body cream and body lotion at 35°C.

lotion causes the occurrence of partially structural breakage as the angular frequency is progressively increased. This leads to a result that both the storage modulus and loss modulus are increasingly augmented. Since a complete breakdown in structure does not happen at such a small strain amplitude applied to body lotion ( $\gamma_0 = 0.2\%$  in this work) which lies within a linear viscoelastic region, cross-linked network structure keeps maintained during dynamic frequency sweep tests. Consequently, a similar viscoelastic behavior to that of body cream is observed in body lotion; the dominance of an elastic nature rather than a viscous nature over an entire range of angular frequencies measured.

These linear viscoelastic features could become criteria to assess the storage stability of cosmetic products at rest or at very small external deformation (Miller *et al.*, 1999; Tadros, 2004; Masmoudi *et al.*, 2006; Park and Song, 2010b). When cosmetics are displayed on the store's shelf or stored in warehouse or room where only a small stimulus or deformation is applied to the products, it is advisable for cosmetic products to have a solid-like elastic nature than a liquid-like viscous nature in order to keep the shape and structure of the products preserved, leading to stay in a stable condition for a long time.

As can be seen from Fig. 3 and Fig. 4, the linear rheology of body cream and body lotion is dominated by an elastic behavior over a wide range of angular frequencies, indicating that both materials present outstanding storage stability. In addition, according to a weak dependency of the linear viscoelasticity on angular frequency, it is also expected that body cream is easier to be stored due to its gel-like firmness based on the cross-linked network structure and strong chemical bonding.

# 3.4. Relationships between viscometric functions and linear viscoelastic functions

Some of the most difficult properties of complex materials to experimentally determine are viscometric functions (*i.e.*, steady shear rheological properties). On the contrary, 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 body cream and body lotion were examined by introducing a modified form of the Cox-Merz rule (Song and Chang, 1999; Yu and Gunasekaran, 2001; Park and Song, 2011) through a comparison of the steady shear viscosity with the complex viscosity.

Figs. 5a and 5b show 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 body cream and body lotion, respectively, at



**Fig. 5.** Comparison of steady shear viscosity with complex viscosity for (a) body cream and (b) body lotion at 35°C.

35°C. As is clear from these figures, the complex viscosity is 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 body cream and body lotion. A departure from the Cox-Merz rule for body cream and body lotion is attributed to a structural decay due to the extent of strain magnitudes applied to the materials; body cream and body lotion undergo 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 intramolecular associations of body cream and body lotion. In this case, when the steady state viscosity is reached, the structure becomes an equilibrium configuration which is very different from that of the undeformed state. On the other hand, during dynamic viscoelastic measurements (i.e., frequency-sweep tests), the imposed strain amplitudes are so small ( $\gamma_0 = 1\%$  for body cream and  $\gamma_0 = 0.2\%$ for body lotion in the present work) that they do not cause any significant change in the structural configuration of the materials.

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 body cream and body lotion.

From a closer examination of Figs. 5a and 5b, 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:  $\eta(\dot{\gamma}) = k\dot{\gamma}^{m-1}$ , (1)

Complex viscosity: 
$$\left|\eta^{*}(\omega)\right| = k^{*}\dot{\gamma}^{m-1}$$
 (2)

where k and  $k^*$  are the consistency indices, m and  $m^*$  are the flow behavior indices, respectively, 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 2 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 (Fig. 5) to the power-law relations represent quite well the steady shear viscosity as well as the complex viscosity for body cream and body lotion. 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 2), 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 (Song and Chang, 1999; Yu and Gunasekaran, 2001; Park and Song, 2011):

$$\left|\eta^{*}(\omega)\right| = C \cdot \left[\eta(\dot{\gamma})\right]^{\alpha} \text{ at } \dot{\gamma} = \omega$$
(3)

where *C* and  $\alpha$  are the material constants to be determined from the experimental data.

In Eq. (3), 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 value of  $\alpha$ 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. (3) are reported in Table 3. 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 provides a good ability to predict the relationship between steady shear flow properties and dynamic viscoelastic properties for body cream and body lotion.

## 3.5. Temperature-dependent viscoelastic behavior as a measure of environmental sensitivity

Figs. 6a and 6b demonstrate the temperature dependence of the storage modulus, G'(T), loss modulus, G''(T), and loss tangent,  $\tan \delta(T)$ , over a temperature range from 10 to 50°C for body cream and body lotion, respectively. As illustrated in Fig. 6a, the storage modulus and loss modulus of body cream show a qualitatively similar tendency to gradually decrease with an increase in temperature, being a commonly expected temperature-dependent behavior. Besides, the storage modulus is always larger than the loss modulus over a whole range of temperatures tested. This is well manifested by the loss tangent which is much smaller than unity, meaning that an elastic nature is dominant to a viscous nature over a whole range of temperatures tested.

On the other hand, as is obvious from Fig. 6b, body

**Table 3.** Empirical correlation constants between steady shear viscosity and complex viscosity for body cream and body lotion at  $35^{\circ}$ C.

| $\left \eta^{*}(\omega)\right  = C[\eta(\dot{\gamma})]^{\alpha}$ |            |             |  |  |  |  |
|--|------------|-------------|--|--|--|--|
|  | Body Cream | Body Lotion |  |  |  |  |
| $C\left(\mathbb{P}^{1-\alpha}\right)$                            | 8.2267     | 21.6940     |  |  |  |  |
| α(-)   | 0.9056     | 0.7301      |  |  |  |  |
| $\mathbb{R}^2$   | 0.9999     | 0.9960      |  |  |  |  |

Table 2. Calculated power-law parameters of steady shear viscosity and complex viscosity for body cream and body lotion at 35°C.

| $\eta(\dot{\gamma}) = k\dot{\gamma}^{m-1}$ |            |             | $\left \eta^{*}(\omega)\right  = k^{*}\omega^{m^{*}-1}$ |            |             |
|--|------------|-------------|---|------------|-------------|
|  | Body Cream | Body Lotion |   | Body Cream | Body Lotion |
| $k (\mathbf{P} \cdot \mathbf{s}^{n-1})$    | 1404       | 231         | $k^*$ (P·s <sup>n-1</sup> )                             | 10926      | 1711        |
| m (-)                                      | 0.0148     | 0.0824      | <i>m</i> <sup>*</sup> (-)                               | 0.1033     | 0.3062      |
| $\mathbf{R}^2$                             | 0.9972     | 0.9979      | $\mathbb{R}^2$  | 0.9992     | 0.9986      |



Fig. 6. Temperature dependence of storage modulus, loss modulus and loss tangent for (a) body cream and (b) body lotion.

lotion shows that, while the storage modulus is progressively decreased with an increase in temperature, the loss modulus is slightly increased until approximately 33°C and then decreased with increasing temperature. In addition, the difference between the storage modulus and loss modulus is continuously decreased and subsequently the value of loss tangent approaches unity at higher temperatures around 50°C. This result implies that a viscous nature becomes strongly revealed as much as an elastic nature with an increase in temperatures.

These different temperature-dependent behaviors observed in body cream and body lotion may come from the two factors: (a) diverse melting points of the ingredients used as a thickening agent, an emulsion stabilizer and a binder in body cream and body lotion, and (b) the internal structure formed by the ingredients.

First of all, various melting temperatures of many components contained in body cream and body lotion differentiate the points where the pre-formed structure starts to be destroyed. As the temperature is increased, therefore, the internal structure does not maintain its original configuration, and the deformed and destroyed proportion becomes expanded, leading to the results that the storage modulus and loss modulus are decreased as an increase in temperature. However, the loss modulus of body lotion exhibits a quite unexpected behavior that shows a slight increase and decrease over a whole range of temperatures tested. It is estimated that, body lotion consists of the ingredients that are not largely dependent on temperature particularly in the viscous region, while body cream is formed by the ingredients that have a strong temperature dependency.

Next, it is an interesting result that the temperaturedependent behaviors of loss tangents for body cream and body lotion are clearly different from each other. As compared to body lotion, body cream contains additional ingredient (microcrystalline wax and lanolin alcohol) as a binder, and also consists of various emulsion stabilizers and thickening agents. These ingredients make the structure firmly cross-linked, engendering an elastic nature to be always superior to a viscous nature over a wide range of temperatures. Subsequently, the value of loss tangent for body cream approaches 0.1, even though the two moduli are progressively decreased as an increase in temperature.

On the other hand, body lotion includes less sorts and amounts of emulsion stabilizers and thickening agents, and does not contain binders. These may cause a relatively weak cross-linked network structure and chemical bonding in body lotion. For these reasons, it is expected that, as an increase in temperature, each ingredient starts to be melted and a network structure becomes rapidly destroyed, which is followed by weakening an elastic nature. Ultimately, the value of loss tangent for body lotion approaches unity, presenting an equal balance between elastic and viscous features.

This unique rheological information helps to figure out how the characteristics of body cream and body lotion are changed by the human environments (Yao and Patel, 2001). As displayed in Fig. 6a, the linear viscoelastic properties of body cream are dominated by an elastic nature at storage temperature (20°C) as well as at skin temperature (35°C), even though there exists a quantitatively progressive decrease in storage modulus and loss modulus as the environmental temperature is increased. From this fact, it is expected that body cream can keep the intrinsic characteristics of thickness and richness around actual usage temperatures.

In the case of body lotion, however, as an increase in temperature, an elastic nature is getting weakened, and eventually the value of loss tangent approaches unity. Based on this result, it is thought that body lotion would be more smoothly spreaded with a thin layer onto the human skin at actual usage temperature  $(35^{\circ}C)$  than at storage temperature  $(20^{\circ}C)$ .

## 4. Conclusions

The principal objective of the present study has been to

systematically evaluate and compare the rheological behaviors of body cream and body lotion in actual usage situations with regard to primary (or initial) skin feel, spreadability, self-storage stability and environmental sensitivity. To this end, using a strain-controlled rheometer, the steady shear flow properties of commercially available body cream and body lotion were measured over a wide range of shear rates, and the linear viscoelastic properties of these two materials in small amplitude oscillatory shear flow fields were measured over a broad range of angular frequencies. In addition, the temperature dependency of the linear viscoelastic behaviors was investigated over a temperature range most relevant to usual human life.

Body cream and body lotion are regarded as a viscoplastic material having a finite magnitude of yield stress. The appearance of a yield stress for these two products is attributed to the cross-linked network microgel structure formed by sodium carbomer that shows a resistance to flow. This yield stress feature is directly related to the primary (initial) skin feel that consumers usually experience during actual usage. The yield stress of body cream is approximately 10 times larger than that of body lotion. This difference exerts an influence on the selection of the product's containers during the process of manufacturing.

Body cream and body lotion exhibit a pronounced non-Newtonian shear-thinning flow behavior. The appearance of a shear-thinning behavior for these two products is interpreted by the changes of microstructure and alignment of polymer chain segments in sodium carbomer. This rheological feature is closely connected with the spreadability which is one of the most necessary rheological properties when cosmetics are applied onto the human skin. The steady shear viscosity of body cream is almost 10 times higher than that of body lotion. This difference allows body cream to have additional functions to protect the skin from externally imposed stimulus and to prevent the skin from losing moisture and nutrients by forming a protective film.

The linear viscoelastic behaviors of body cream and body lotion are dominated by an elastic nature rather than a viscous nature. A primary factor to explain the linear viscoelastic behaviors of these two products originates from the attractive interactions within poly(acrylic acid) forming sodium carbomer. These linear viscoelastic properties (solid-like behavior) become a criterion to assess the self-storage stability of cosmetic products when they are displayed on the store's shelf or stored in the warehouse or placed in the room where only an extremely small stimulus or deformation is applied to the products. A modified form of the Cox-Merz rule provides a good ability to predict the relationship between steady shear flow properties (nonlinear behavior) for body cream and body lotion.

The storage modulus and loss modulus of body cream

show a qualitatively similar tendency to gradually decrease with an increase in temperature. The storage modulus is always larger than the loss modulus over a wide range of temperatures. In the case of body lotion, with an increase in temperature, the storage modulus is progressively decreased while the loss modulus is slightly increased and then decreased. These different temperature-dependent behaviors between the two products come from the diverse melting points of the ingredients and the firmness of the internal structure formed by the ingredients. This rheological information gives us a criterion to judge how the characteristics of cosmetic products are changed by the usual human environments.

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