

# Rheology of Sodium Polyacrylate as an Emulsifier Employed in Cosmetic Emulsions

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**ABSTRACT:** A set of emulsions containing sodium polyacrylate as emulsifier was prepared. The effect of pH, temperature, and polymer concentration on sample stability was studied. Stability of the sample was evaluated through rheology and the morphology techniques. The sample containing 2% (w/w) sodium polyacrylate exhibited more evident changes in storage  $G'$  and loss  $G''$  moduli with respect to 1% and 1.5% (w/w) samples, evidencing a more structured elastic material, even at high temperatures at which a more stable sample is assumed. For most of the systems studied, the storage modulus ( $G'$ ) was always higher than the loss modulus ( $G''$ ) which is attributed to the formation of a strong network arising from the polymer interacting with the oil and aqueous phases; the complexity of this network is related to the action of pH and temperature. These results reveal the conditions at which the polyacrylate offers the best advantages in industrial cosmetic applications, that is, pH levels near 6.5, with a 2% (w/w) polymer concentration and a temperature of 25 °C.

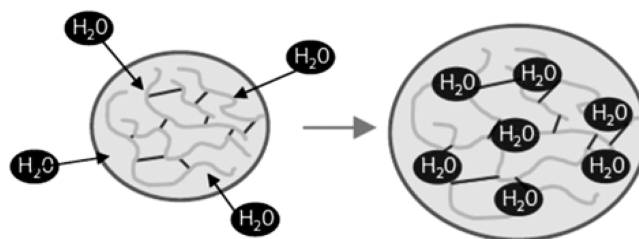
## 1. INTRODUCTION

Emulsions have found a wide range of applications of which the following are certainly worth mentioning: food emulsions, cosmetics, paints, agrochemicals, pharmaceuticals, bitumen emulsions, inks and paper coating, adhesives, and many household products.<sup>1</sup> The rheological properties (viscosity, elastic modulus  $G'$ , and viscous modulus  $G''$ ) of emulsion systems are essential physical attributes of these materials.<sup>2</sup> The creation of an emulsion goes beyond maintaining the oil and aqueous phase together by the action of an emulsifier.<sup>3</sup> This is because the functional properties (viscosity) can be undesirable for the consumer; the product can be too thin (no structure) or too thick (highly structured). Processing problems are also worth considering; viscosity of the product is an essential parameter in mixing, pumping, and packing the finished product.<sup>3,4</sup> Stability issues also affect the shelf life of these products. So, finding the optimum formulation and process conditions becomes critical.

The cosmetic and toiletry industries are areas where more new products and constant innovation are registered. This innovation requires hard work from the research and development laboratories where the new products are generated. An example of this constant change is the transition from traditional emulsions to cream-gel formulations,<sup>1</sup> in which polymeric emulsifiers are used as thickeners or emulsion stabilizers.<sup>3,5</sup>

Polyacrylate is a common emulsifier employed to obtain different emulsion structures. Consequently, a variety of applications are possible including face and hand creams (for normal, dry, or oily skin), body milks and lotions, and sun-

protective products. Polyacrylate has been used as both an emulsifier as well as a rheology modifier; it is supplied as a dustless powder for ease of handling. It thickens rapidly when added to water and will provide yield strength and viscosity to the system, additionally it stabilizes oil in water emulsions regardless of the oil phase (Figure 1), and it is also more stable



**Figure 1.** Thickening mechanism, water molecules enter into the polymer matrix, with subsequent swelling.

in terms of sensitivity to pH (as it was observed here) than other synthetic materials. For decades, rheological measurements have been employed in the characterization of emulsion systems.<sup>6</sup> These emulsions are pseudoplastic materials ( $n < 1$ ) identified by their non-Newtonian flow behavior; the onset of flow is product-specific and differs significantly for lotions and creams. For example, in terms of the critical shear stress at the

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yield point, the emulsion formulation and process varies significantly for creams as compared to lotions.

Additionally, flow parameters obtained by continual and/or oscillatory rheological measurements provide information regarding the system colloidal structure and physical stability, that is, internal structure response to flow.<sup>7</sup> With emulsions being thermodynamically unstable systems (emulsion systems evolve as time passes and phase separation occurs eventually), the most important factor to be considered in emulsion technology is undoubtedly the evolution of their properties. Therefore, the rheology of emulsions is constantly focusing on its relationship with emulsion stability regarded as the response of the fluid structure to flow and time.<sup>8</sup> For all of the aforementioned reasons, rheological properties of emulsions are known to be of great importance. In the case of cosmetic emulsions, these properties are closely related to consumers' acceptance and as such, represent an important factor for their sales potential. In fact, fulfilling consumer expectations has become imperative in the food and personal care industry. Proper assessment of features related to human perception merits great attention for both scientific and practical reasons.<sup>9</sup>

The rheological properties of emulsions are influenced by their colloidal structure and therefore can be related to physical properties, and it is a challenging prospect to relate these measurements to consumer perception.<sup>7-9</sup> It is well-known that application and acceptance of semisolid products are greatly dependent on the flow properties of the final product.<sup>10</sup> When applied on the skin, the material is subjected to deformation so that rheology describes, explains, and measures the material response to that deformation. Rheological measurements are usually performed in order to predict behavior of the product in real conditions during formulation, processing, and application.<sup>11-13</sup>

This work focuses on the characterization of a cosmetic emulsion using polyacrylate as a synthetic emulsifier through rheological measurements (continuous steady state and oscillatory flow) to evaluate the effect of pH, temperature, and polymer concentration. The rheological properties of the emulsions were investigated in terms of the continuous shear steady state viscosity and the linear viscoelastic response, that is, the evolution of the elastic  $G'$  and viscous  $G''$  moduli. Finally, the dynamic mechanical properties were matched with the emulsion morphology.

## 2. EXPERIMENTAL SECTION

**2.1. Emulsions Preparation.** Emulsions were prepared by dispersing sodium polyacrylate (PAM) (Evonik Goldschmidt GmbH, Germany) as an emulsifier in deionized water; contents and concentration of this emulsion are presented in Table 1.

The preparation of the samples was according to the so-called hot-cold procedure as follows: (a) The ingredients of phase A (aqueous phase, see Table 1) are blended at 70 °C with constant stirring for 1 h,<sup>14</sup> then while the mixture was stirred, the polyacrylate was slowly added to phase A (30 min). (b) Separately, phase B ingredients (see Table 1) are blended at 70 °C while stirring at 700 rpm. (c) Finally both dispersions from steps "a" and "b" are mixed together slowly with stirring for 1 h at 70 °C. After preparation, the rheological behavior of the emulsions was evaluated.

The modulation of pH for the prepared emulsions was performed with an HCl solution for acidification and a sodium hydroxide solution for basification.

**Table 1. Cosmetic Emulsion Composition (% w/w)**

| phase | ingredients   | %               |
|-------|---|-----------------|
| A     | deionized water   | $C_{bp}$ to 100 |
| A     | disodium EDTA   | 0.10            |
| A     | sodium polyacrylate, hydrogenated polydecene, trideceth-6 <sup>a</sup>        | 1-2             |
| B     | mineral oil   | 3.00            |
| B     | castoryl maleate <sup>a</sup>   | 0.50            |
| B     | cyclotetrasiloxane <sup>a</sup>   | 0.50            |
| B     | disodium lauriminodipropionate tocopheryl phosphates <sup>a</sup>             | 0.30            |
| B     | propylene glycol, diazolidinyl urea, iodopropynyl butylcarbamate <sup>a</sup> | 0.50            |
| total |   | 100.00          |

<sup>a</sup>Commercial products, pharmaceutical grade.

**2.2. Rheological Measurements.** All the rheological measurements were performed with an AG2 (model TA) controlled stress rheometer. Concentric cylinders (25 mm diameter) and parallel plates (25 mm diameter) were used; the gap between the two plates was 0.5 mm in parallel plate. The geometries were selected depending on the viscosity of the emulsion.

The emulsions were characterized in steady-shear viscosity function  $\eta$  ( $\dot{\gamma}$ ) and under oscillatory flow. The former was carried out by using a unidirectional steady-shear flow ranging from 1 to 300 1/s, and the latter was accomplished in the linear viscoelastic regime that was previously determined for each of the studied conditions (<10%).<sup>14,15</sup> The angular frequencies of the tests ranged from 1 to 300 rad/s at different temperatures (10, 25, and 45 °C);<sup>14-17</sup> both  $G'$  (elastic) and  $G''$  (viscous) moduli were recorded and used to analyze the rheological behavior of the samples. All tests were carried out in triplicate to ensure the reproducibility.

**2.3. Microscopy.** Micrographs were obtained with an OLYMPUS BX45TF Olympus Optical Co. Ltd., Tokyo, Japan, microscope equipped with a 30 W lamp (390-420 nm wavelengths reflected light), a 100× objective was used. The images from microscopy were analyzed to obtain information regarding the morphology of the emulsions.

**2.4. Statistical Analysis.** Whenever applicable, obtained results were expressed as mean  $\pm$  SD. Statistical analysis was carried out using Sigma-Stat (version 3.1, Virginia, USA). Differences in the computed parameters were considered significant when the computed probabilities were less than 0.05.

## 3. RESULTS AND DISCUSSION

**3.1. Steady-Shear Flow Measurements.** The steady-state rheology experimental results were adjusted to the power law model described by eq 1:<sup>15-17</sup>

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

where  $k$  is the flow consistency index (Pa·s<sup>n</sup>) and  $n$  is the flow behavior index. The parameters  $n$  and  $k$  are obtained by a linear regression analysis (Table 2). It is important to note that the viscosity of the spreadable pharmaceutical products lies in the range of 50000 to 150000 cps, and there are also dosage forms for infants with a viscosity of 40000 cps.

**3.1.1. Concentration Effect.** The viscosity profiles [ $\eta$  vs  $\dot{\gamma}$ ] of the emulsions at different polyacrylate contents with constant pH (6.5) and 25 °C are shown in Figure 2. As expected, viscosity increases consistently with polyacrylate content in all the shear rate range studied, the viscosity curves also showed

Table 2. Rheological Parameters of Power Law Model

| [x] % (w/w)           | $k$              |        | $T$ (°C)           |  | $k$              |        | pH                    |  | $k$              |        |
|-----------------------|------------------|--------|--------------------|--|------------------|--------|-----------------------|--|------------------|--------|
| pH = 6.5, $T = 25$ °C | Pas <sup>n</sup> | n      | pH = 6.5, 2% (w/w) |  | Pas <sup>n</sup> | n      | $T = 25$ °C, 2% (w/w) |  | Pas <sup>n</sup> | n      |
| 1.0                   | 36.83            | 0.3358 | 10                 |  | 86.05            | 0.3136 | 4.0                   |  | 0.3586           | 0.7050 |
| 1.5                   | 0.7024           | 0.3358 | 25                 |  | 80.11            | 0.3071 | 6.5                   |  | 80.11            | 0.3071 |
| 2.0                   | 0.8011           | 0.3071 | 45                 |  | 72.12            | 0.3082 | 9.0                   |  | 88.78            | 0.2917 |

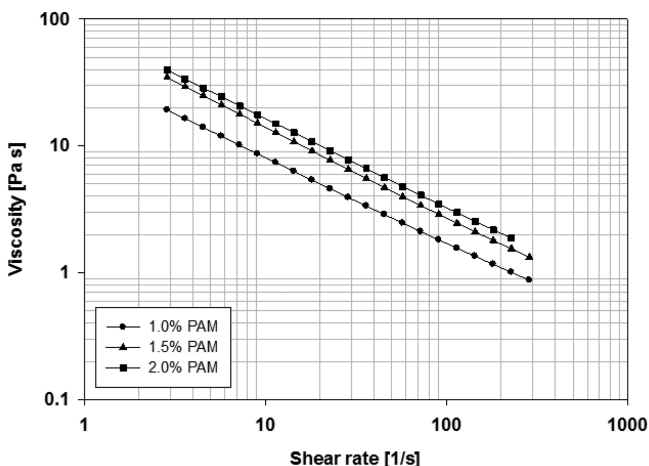


Figure 2. Effect of polymer concentration on the steady-shear viscosity of emulsion maintaining pH = 6.5 and temperature at 25 °C.

shear thinning characteristics which evidence the structure response to flow. As the shear rate increases, the fluid structures become disrupted and the polymer molecules align toward the flow direction, this reduces the viscosity, a more stable structure becomes shear thinning at higher shear rates (stronger interactions are produced by a higher interphase area and more dispersed particles). Then, all samples have essentially the same shear-thinning slope. In Figure 2, a significant increase of viscosity is evident at concentrations from 1 to 1.5% (w/w), whereas at concentrations above 1.5% (w/w) the viscosity of the emulsion tends to stabilize. We think that the polyacrylate is reaching optimum swelling conditions at concentrations near 1.5–2% (w/w)<sup>6,18</sup> and that is why the viscosity does not increase so much as in the lower concentration regime, that is, a concentration < 1.5% (w/w). Viscosity is built by the swelling of the dispersed polymer, and this is known to provide an elegant skin feel and sun care in the final emulsion.

**3.1.2. Temperature Effect.** Figure 3 shows the effect of temperature on the 2% (w/w) polyacrylate sample at pH 6.5. It can be observed that the change in viscosity is not a factor that generates macrostructural changes in the flow behavior of the emulsion since the change of viscosity from 10 to 45 °C, which corresponds to skin surface temperature,<sup>19</sup> is not as intense as with the polyacrylate content, similar results were found at the other concentrations studied (not shown). The values of the flow consistency index at different temperatures remain constant (all curves are parallel) which means that this material is stable to temperature at the conditions studied (degradation is ruled out as results showed reversibility). Therefore, the spreading of the product is independent of the temperature at application.

**3.1.3. pH Effect.** Figure 4 shows the viscosity profile of emulsions with 2.0% (w/w) sodium polyacrylate (PAM) at 25 °C. When the pH of the formulation is 4.0, the viscosity is greatly reduced as well as the flow consistency index ( $n = 0.7$ ) indicating a less structured material with almost Newtonian

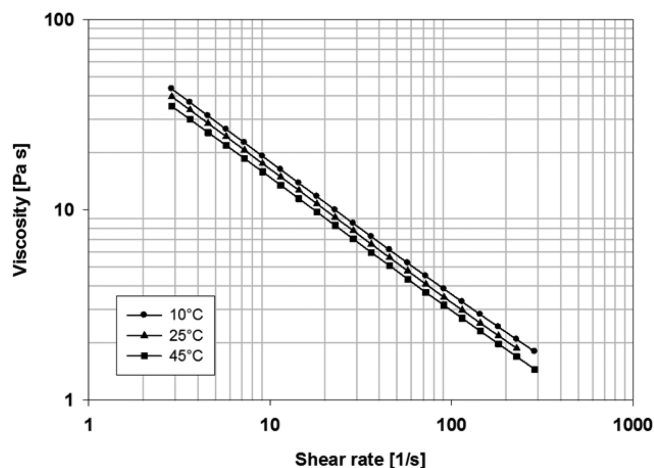


Figure 3. Effect of temperature on the steady-shear viscosity of 2.0% (w/w) polymer emulsions maintaining pH = 6.5.

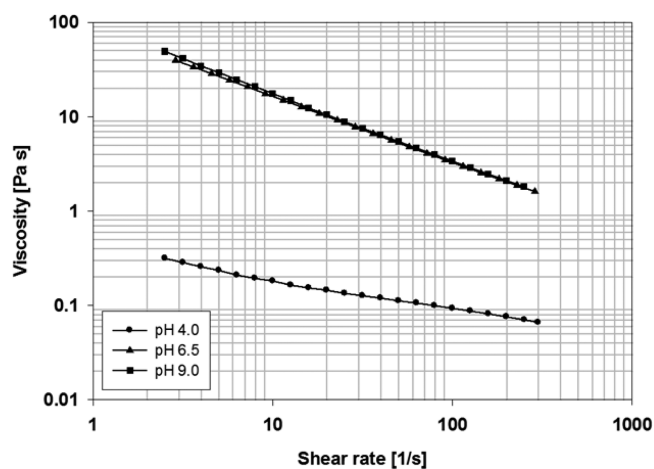


Figure 4. Effect of pH on the steady-shear viscosity of 2.0% (w/w) polymer emulsion maintaining temperature at 25 °C.

behavior. The decrease in pH causes a loss of structure in the emulsion, this effect is related to reduced cation–anion interactions resulting in polymer chains with higher mobility and reduced particle–particle interactions. This result indicates that there is a critical pH value for structure build up between 4 and 6 pH. Above this critical pH value, the formation of a more stable network is evident and consistent with previous reports.<sup>6</sup>

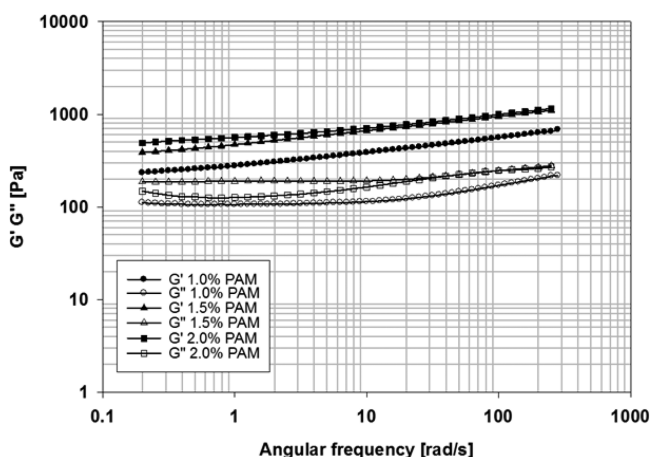
The pH will start to thicken the emulsion at around pH 6 and is then stable up to pH 9. This makes it ideal for the majority of personal care applications. The important fact that no neutralization before application is necessary simplifies the preparation of cosmetic products and increases the potential application of polyacrylate.

The rheological properties (steady state viscosity and oscillatory flow moduli) are influenced by several factors, such as pH, temperature, and polymer concentrations as it has

been demonstrated; this is consistent with previous reports.<sup>6,18,19</sup> Finding the optimum conditions for end-use application requires a further study of the structure in essentially a nondestructive test such as oscillatory linear rheological flow.

**3.2. Oscillatory Flow Measurements.** To perform measurements in the linear viscoelastic region, the linear region must be determined first (amplitude sweep test). The linear viscoelastic response characterization is given in terms of storage ( $G'$ ) and loss ( $G''$ ) modules as frequency functions. Linear oscillatory shear flow measurements (SAOS) are in essence nondestructive tests since only a very small deformation is applied to the fluid at a certain frequency.<sup>16–20</sup>

**3.2.1. Concentration Effect.** Figure 5 shows the oscillatory flow curves as a function of polymer concentration maintaining

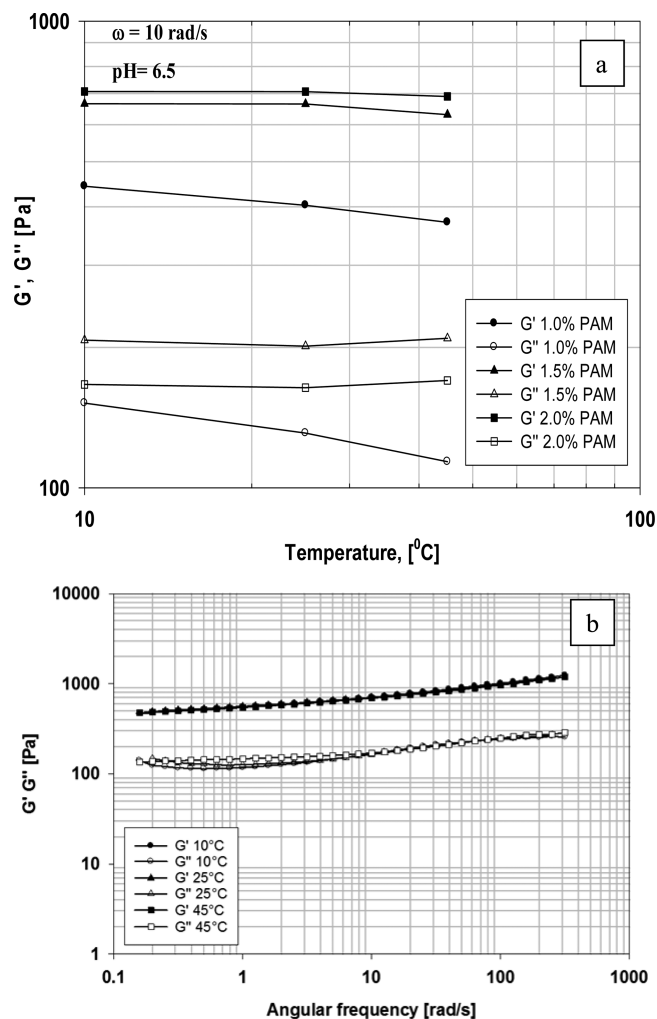


**Figure 5.** Frequency dependence of the storage module  $G'$  and loss module  $G''$  for different concentrations of polymer maintaining pH = 6.5 and temperature of 25 °C.

a pH of 6.5 and a temperature of 25 °C. As it can be observed, similar viscoelastic behavior was found for emulsions with 1.5% and 2.0% (w/w) sodium polyacrylate (curves for  $G'$  overlap at high frequencies), which differs for the emulsion at 1.0% (w/w) polymer content, this system also shows a more evident change of slope in the  $G'$  curve which is evidence of a structural change.<sup>6,18,20,21</sup> As it was observed for the viscosity in Figure 2, the values of the loss modulus ( $G''$ ) tend to stabilize at concentrations above 1.5% (w/w), which was associated with the gel reaching optimum swelling conditions.<sup>6</sup>

**3.2.2. Temperature Effect.** Regarding the influence of temperature on the viscoelastic properties, Figure 6a shows that the emulsions are temperature independent within the temperature range studied because the moduli values are the same; this confirms again the thermal stability of the emulsions. Figure 6b shows the mechanical spectrum in oscillatory flow for the sample at 2% (w/w) and 6.5 pH, the system shows a weak gel behavior, with the storage modulus ( $G'$ ) dominating over the loss modulus ( $G''$ ). For all samples,  $G'$  values were 1 order of magnitude higher than  $G''$  values at all investigated temperatures, which indicates a structured material easily deformable upon application of shear (i.e., spreadability).

Furthermore, among the tested emulsions, differences between  $G'$  values are greater than those between  $G''$ . Temperature caused the decrease of all parameters with  $G''$  being more temperature sensitive than  $G'$ . Overall rheological assessment at different temperatures indicates that the

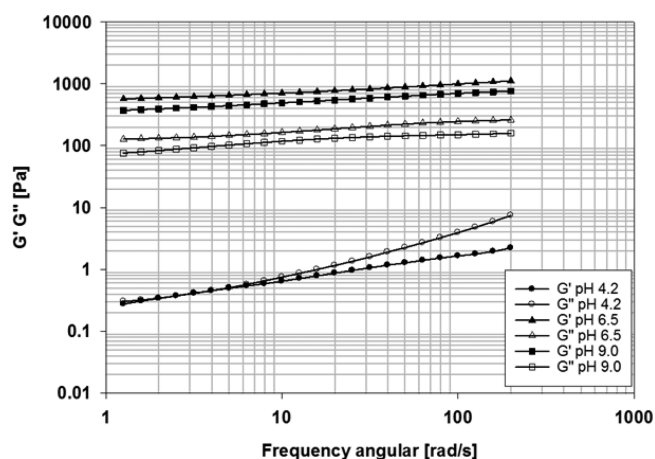


**Figure 6.** (a) Dependence of the storage module  $G'$  and loss module  $G''$  for different temperatures at 1%, 1.5%, and 2% (w/w) PAM on the emulsion. (b) Frequency dependence of the storage module  $G'$  and loss module  $G''$  for different temperatures, maintaining 2.0% (w/w) polymer concentration and pH = 6.5.

emulsions are stable to temperature especially in the range from room to skin surface temperature.

**3.2.3. pH Effect.** The effect of pH on the polymer is shown in Figure 7 where it can be observed that for pH 6.5 and 9.0 the storage module ( $G'$ ) and the loss module ( $G''$ ) are very similar, having a bigger influence of the elastic component over the viscous component ( $G' > G''$ ). This behavior does not hold for the emulsions of pH 4.0, which not only have lower values in their mechanic response ( $G'$  and  $G''$ ), but they also show that the viscous modulus dominates over the elastic modulus ( $G'' > G'$ ). This is an indication that there is a critical pH value below which a network structure is not well formed; this is consistent with the steady-shear viscosity results.<sup>20–22</sup> The pH value of the emulsion has a great impact on the swelling behavior of the gels.<sup>18</sup> Two different behaviors were observed in relation to the pH effect: A significant increment in the viscosity and oscillatory shear moduli of the gel at pH 4–6 which is evidenced by a sol–gel transition (below pH 6,  $G'' > G'$  and above pH 6,  $G' > G''$ ) and stabilization of the viscosity at pH 6–7 with a weak gel behavior.

A polymer network is formed when an electrical interaction between atoms is present (van der Waals forces, hydrogen



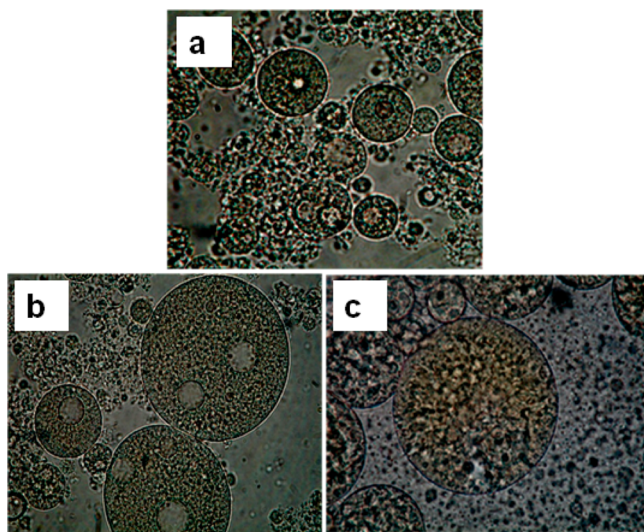
**Figure 7.** Frequency dependence of the storage module  $G'$  and loss module  $G''$  for different pH values, maintaining 2.0% (w/w) polymer concentration and and temperature at 25 °C.

bonds) and when the polymer content is sufficient for polymer–polymer interactions. These interactions are modified by the concentration of anions or cations such as  $H^+$  or  $OH^-$ . Additionally, as is well known, the temperature increases the movement and vibration of the atoms and as a consequence viscosity and both moduli  $G''$  and  $G'$  are decreased.

The different rheological behaviors observed are possibly the results of diverse structural arrangements that are induced by the well-versed conditions, which are finally translated in different mechanical properties ( $G'$  and  $G''$ ).<sup>16–21</sup> Experimental results and modeling are used to explain the rheological behavior of the investigated samples.

Results of rheological measurements alone are not sufficient enough to make final conclusions regarding overall emulsion characteristics; yet certain differentiations between different conditions could be made and used as guidelines at various stages of product formulation/reformulation process.

**3.3. Microscopy.** Finally, images from optic microscopy analysis of the batches of polyacrylate at different pH values investigated are shown in Figure 8. Figure 8a shows a



**Figure 8.** Microphotographs of the emulsions at different pH values: (a) pH 4.2, (b) pH 6.5, and (c) pH 9, maintaining 2.0% (w/w) polymer concentration and temperature at 25 °C.

heterogeneous system (many particle aggregates domains) corresponding to a pH of 4 which we believe is associated with the decrease in viscosity shown for this system, while at pH 6.5 and 9 (Figure 8b,c), a more homogeneous well-dispersed system is found (few particle aggregates domains and more dispersed particles). This is an indication that there is a critical pH value below which a network structure is not well formed which is consistent with the rheological results.

From the micrographs it was evident that the emulsion at pH 4 was the more unstable one and that the emulsions at pH 6.5 and 9 formed a stable particle–particle interaction network. The rheological behavior and morphology results can be attributed to a combination of two factors: The first one is that the lower droplet size results in a reduction of the free energy associated with the strength of the interaction. The second one is that the creation of a larger specific surface area in the fine emulsion will simultaneously be accompanied by a reduction in the amount of unabsorbed polymer. These two factors imply a considerably reduction of flocculation for the emulsions containing the smaller droplets.<sup>21</sup>

In summary, the viscoelastic behavior linearly increases with the polymer content. The results showed that at low frequency with high-polymer the elastic modulus dominates the viscoelasticity ( $G' > G''$ )<sup>21–23</sup> and these results help to identify the conditions in which the polymer offers the best advantages in industrial applications: pH 6.5, polymer concentration of 2% (w/w), and a temperature of 25 °C.

#### 4. CONCLUSIONS

All samples showed shear-thinning behavior. For a polymer concentration of 2.0% (w/w) the mechanic changes are more evident (highest steady-shear viscosity and moduli,  $G'$  and  $G''$ ) as compared with the other concentrations evaluated. This is due to the formation of a polymer network more stable to the flow; the nature of this network is pH- and temperature-dependent.

The viscoelastic response of the studied mixtures increases as the polymer concentration rises, becoming more resistant to deformation even at high temperatures. The pH is a determining factor in the rheological behavior of the emulsions that contain sodium polyacrylate; this is because the rheological properties suffered evident changes related to the stability of the network formed by the polymer.

A critical pH value has been encountered to attain a stable network; below this critical pH, network formation is incomplete. These results help to identify the conditions in which the polymer offers the best advantages in industrial applications: pH 6.5, polymer concentration of 2% (w/w), and a temperature of 25 °C.

The results confirmed that rheology can be used to differentiate emulsions regarding mechanical properties and the best process conditions can be selected according to the end-use application to obtain tailor-made cosmetics. Skin feel is an important sensory area for cosmetic products.

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##### Notes

The authors declare no competing financial interest.

## ■ REFERENCES

- (1) Swarbrick, J.; Boylan, J. C. *Encyclopedia of Pharmaceutical Technology*, 2nd ed.; Marcel Dekker, Inc.: New York, 2001; Vol. 20.
- (2) Barnes, H. A. Rheology of emulsions—A review. *Colloids Surf, A* **1994**, *91*, 89–95.
- (3) Laba, D., (Ed.), *Rheological Properties of Cosmetics and Toiletries*; Marcel Dekker, Inc.: New York, 1993; Vol. 13.
- (4) Bird, R. B. Ed. *Dynamics of Polymeric Liquids Fluid Mechanics*; John Wiley & Sons: New York, 1972; Vol. 1, Chapter 4.
- (5) Medina Torres, L. *Estudio reológico del mucilago de nopal y su efecto sinérgico con otros hidrocoloides de uso alimenticio*. Ph.D. Thesis, UNAM, Facultad de Química: México, 2005.
- (6) Oguz, O.; Sarişik, S. B. Swelling behavior of poly\_acrylamide-co-sodium acrylate\_ hydrogels in aqueous salt solutions: Theory versus experiments. *Eur. Polym. J.* **2000**, *36*, 393–399.
- (7) Tadros, T. Application of rheology for assessment and prediction of the long-term physical stability of emulsions. *Adv. Colloid Interface Sci.* **2004**, *108–109*, 227–258.
- (8) Gallegos, C.; Franco, J. M. Rheology of food, cosmetics and pharmaceuticals. *Curr. Opin. Colloid Interface Sci.* **1999**, *4* (4), 288–293.
- (9) Rossi, G. B.; Berglund, B. Measurement involving human perception and interpretation. *Measurement* **2011**, *44* (5), 815–822.
- (10) Trapp, M. Is there room for improvement in the emollients for adjuvant therapy. *J. Eur. Acad. Derm. Venereol.* **2007**, *21* (s2), 14–18.
- (11) Kim, K. H.; Gohtani, S.; Yamano, Y. Effects of oil droplets on physical and sensory properties of o/w emulsion agar gel. *J. Texture Stud.* **1996**, *27* (6), 655–670.
- (12) Brummer, R.; Godersky, S. Rheological studies to objectify sensations occurring when cosmetic emulsions are applied to the skin. *Colloids Surf, A* **1999**, *152* (1), 89–94.
- (13) Park, E. K.; Song, K. W. Rheological evaluation of petroleum jelly as a base material in ointment and cream formulations: Steady shear flow behavior. *Arch. Pharm. Res.* **2010**, *33* (1), 141–150.
- (14) Usui, F.; Maeda, K.; Kusai, A.; Nishimura, K.; Yamamoto, K. Inhibitory effects of water-soluble polymers on precipitation of RS-8359. *Int. J. Pharm.* **1997**, *154* (1), 59–66.
- (15) Mezger, T. G. Ed. *The Rheology Handbook: For Users of Rotational and Oscillatory Rheometers*; Vincentz Network GmbH & Co. KG: Hannover, Germany, 2006.
- (16) Bird, R. B.; Armstrong, R. C.; Hassager, O. Eds. *Dynamics of Polymeric Liquids, Fluid Mechanics*, 1st ed.; John Wiley & Sons: New York, 1977, Vol. 1.
- (17) Macosko, C. W. Ed. *Rheology: Principles, Measurements and Applications*; VCH: New York, 1994.
- (18) Tanaka, T. Phase transition in gels and a single polymer. *Polymer* **1979**, *20* (11), 1404–1412.
- (19) Siewert, M.; Dressman, J.; Brown, C. K.; Shah, V. P.; Aiache, J. M.; Aoyagi, N.; Williams, R. FIP/AAPS guidelines to dissolution/in vitro release testing of novel/special dosage forms. *AAPS Pharm. Sci. Tech* **2003**, *4* (1), 43–52.
- (20) Lee, C. H.; Moturi, V.; Lee, Y. Thixotropic property in pharmaceutical formulations. *J. Controlled Release* **2009**, *136* (2), 88–98.
- (21) Medina-Torres, L.; Calderas, F.; Gallegos-Infante, J. A.; González-Laredo, R. F.; Rocha-Guzmán, N. Stability of alcoholic emulsions containing different caseinates as a function of temperature and storage time. *Colloids Surf, A* **2009**, *352* (1–3), 38–46.
- (22) Lyoo, W. S.; Kim, B. C.; Ha, W. S. Rheological and rheo-optical properties of high molecular weight syndiotactic and atactic polyvinylalcohol solutions. *Polym. Eng. Sci.* **1997**, *37* (7), 1259–1265.
- (23) Ferry, J. D. (Ed.), *Viscoelastic Properties of Polymers*; John Wiley & Sons Inc.: New York, 1980.