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Reducing Facial Wrinkle Size and Increasing Skin Firmness Using Skin Care Polymers

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Synopsis

Many cosmetic polymers shrink on drying, producing a tensile force if coated on a substrate. This tensile force can be used to smoothen wrinkles and pores in facial skin. In this study, we evaluated two polymers, a polyvinylpyrrolidone (PVP) and a polyacrylate, for skin tightening properties. We conducted a double-blinded, placebo-controlled and randomized clinical study with 32 female volunteers aged 35–65 years who perceived themselves to have a loss of skin elasticity. Both polymers were formulated in a model cosmetic emulsion with hydrogenated polyisobutene as the oil phase. We measured skin firmness and tightening parameters at baseline and after each product application. Also, facial images were recorded with a fringe projection instrument. The firming measurements indicated that both polymers instantly tightened facial skin, whereas the placebo product offered no significant tightening benefit. However, in clinical evaluation, only the polyacrylate polymer produced statistically significant improvements in wrinkle size and skin firmness on the face without significant consumer use complaints such as tackiness. We concluded that skin care products using PVP and polyacrylates have the potential to offer immediate and visible benefits to consumers with aged skin.

INTRODUCTION

Erasing the effects of age on the face is one of the most elusive benefits that consumers seek in skin care products. Myriad products are available in commerce today that claim to make consumers appear younger. However, most work by filling in and covering up wrinkles, age spots, and other attributes of aged skin, and others have effects on aged skin that are measured as relatively small improvements over prolonged treatment periods. All must be applied daily for a sustained effect, in contrast to surgical treatments that have a long-term benefit.

Antiaging skin care products generally contain emollient oils and emulsifiers in an aqueous base. Such products moisturize the skin and may improve the tactile properties perceived

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by users. Active ingredients can be included to achieve other benefits, such as skin plumping that smoothes out wrinkles and biological effects on the skin microstructure and mechanical integrity. However, biological product claims in cosmetic products are generally limited by regulatory authorities, because the long-term physiological effects of the active ingredients may not be known. Other antiaging ingredients in skin care products provide an optical effect to hide wrinkles and pores by covering up such imperfections with pigments and film formers. In contrast, products that achieve antiaging effects such as wrinkle and pore size reduction by mechanical means, rather than optical or biological, have not received much attention in the literature.

In addition to active ingredients, skin care products may also contain polymers mainly for their properties as thickeners, rheology modifiers, and film formers. The process of coating, spreading, and drying of cosmetic emulsions containing polymers is not well understood (1). The mechanics of emulsion application, phase behavior of the multicomponent emulsion formulation, polymer deposition and crystallization, skin formation, and surface tension–driven flows (Marangoni flows) all play a role. The drying process of cosmetic emulsions with polymers may not result in homogeneous films (2,3).

In contrast to the drying behavior of aqueous polymer solutions, drying phenomena in polymer dispersions (latexes) have been extensively studied (4–6). The film formation process in those systems is made up of three steps: evaporative drying and ordering of the polymer particles, particle deformation, and polymer diffusion followed by merging of the particles. Significant internal stresses can build up in the polymer film during drying. These can be large enough to cause coating defects or deform the underlying substrate by the shrinking of the film (7). Shrinkage of the film starts at a certain volume fraction of solvent in the film, which is correlated with the glass transition temperature of the polymer T_g, which itself depends on the solvent volume fraction (8). When the glass transition is reached, the polymer chains become less mobile and are unable to flow in response to the drying stress, which causes film shrinkage.

Polymer film shrinkage has been used to obtain a visible reduction in the size of fine lines and wrinkles. Various polymers produce this effect, including bovine serum albumin (9) and synthetic hair styling polymers (10). These materials have a T_g near ambient conditions. Skin covered with a thin film consisting of these polymers experiences tightening when the film shrinks on drying and contracts mechanically. In addition to the tightened skin feel experienced by test subjects, the mechanical properties of the skin are measurably changed (11).

This polymer film shrinkage is a different phenomenon than the stratum corneum shrinkage that is observed when skin is stripped of its surface lipids by surfactant solutions. In that case, consumer-perceivable tightening is caused by dehydration of the underlying skin layers (12,13).

In this work, we studied two film-forming polymers with relatively high T_g values, a poly (vinylpyrrolidone) (PVP) polymer and an acrylate/methacrylamide copolymer (AMC) (14). For PVP, the T_g decreases as the weight fraction of water in the polymer solution increases, reaching room temperature at 75–90 weight percent PVP, depending on the molecular weight of the polymer (15). Following the model described previously, film shrinkage and skin tightening is expected when the film has lost enough water through absorption and drying to reach such high polymer levels. The AMC polymer was chosen because its T_g value is the highest in a portfolio of commercial hair styling polymers.

Here, we will show that the two polymers studied cause shrinkage in cosmetic films, leading to a consumer-perceivable reduction in size of features such as pores and wrinkles on the underlying skin substrate.

MATERIALS AND METHODS

PRODUCT FORMULATIONS

We used model emulsion formulations with 5 w% hydrogenated polyisobutene (Luvitol Lite; BASF Corporation, Florham Park, NJ) as the oil phase and 1 w% of a phenoxyethanol/ethylhexylglycerin preservative (Euxyl PE 9010; Schülke & Mayr GmbH, Fairfield, NJ) (Table I). The pH was adjusted with sodium hydroxide (AMRESCO LLC, Solon, OH). The polymers used were an acrylate/methacrylamide copolymer ("AMC", Luviset One; BASF Corporation), PVP (Luviskol K90; BASF Corporation) and carbomer (Rheocare C Plus; BASF Corporation).

For the PVP and placebo formulations, carbomer was predispersed in water and neutralized before all other ingredients were added, after which the product was homogenized using a Silverson homogenizer. For the other formulations, all ingredients were combined and homogenized until uniform.

GLASS TRANSITION TEMPERATURE MEASUREMENTS

To obtain solid polymer samples, 5% neutralized polymer solutions were prepared and 10 g of the solution dried in an aluminum pan with a diameter of approximately 3 cm. The conditioning of the resulting polymer films at different humidities (50%, 75%, and 90% relative humidity (RH)) was carried out with the open aluminum differential scanning calorimeter (DSC) pans in three different desiccators. The desired RH in the desiccators was adjusted using different salt solutions: calcium nitrate for 50% RH, sodium chloride for 75% RH, and barium chloride for 90% RH.

The samples were conditioned until a constant weight of the aluminum pans was reached. The difference in weight (start vs. equilibrium state) was analyzed to obtain the water uptake of the polymer films. In the next step, the pans were closed and the glass transition was investigated using a TA Instruments Q2000 differential scanning calorimeter (TA Instruments, New Castle, DL). T_g was determined as the midpoint temperature, where half of the specific heat increment occurred.

Table I
Model Emulsion Formulations

Product #	4% AMC	2% AMC	PVP	Placebo
Deionized water	89.7 w%	91.7	91.9	93.4
Hydrogenated polyisobutene	5.0	5.0	5.0	5.0
Phenoxyethanol/ethylhexylglycerin mixture	1.0	1.0	1.0	1.0
Acrylate/methacrylamide copolymer (AMC)	4.0	2.0		
PVP			1.5	
Carbomer			0.5	0.5
Sodium hydroxide	0.3	0.3	0.1	0.1

CLINICAL STUDY PROTOCOL

Thirty two healthy female subjects were recruited for this study. They were 35–65 years old, were graded with a score of 2–4 on the Skin Aging Atlas (16) for crow's feet wrinkles, and considered themselves to have a loss of elasticity in the skin. The study started on July 20, 2015 and concluded on July 24, 2015. All subjects executed an Informed Consent Form before the study started.

The principles of Good Clinical Practice, as defined by the International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use, were followed except for the requirement that investigational products should be manufactured, handled, and stored in accordance with applicable Good Manufacturing Practice, which is not a requirement for cosmetic products. The study protocol was reviewed and approved by our Institutional Review Board on June 18, 2015. There were no adverse events encountered and no protocol amendments or deviations took place.

About 0.4 g of each test product was applied evenly to the left or right side of the face in a randomized manner. The test was double blind and subjects served as their own reference. Four test products were applied over the 2 day duration of the study. For 3 days before the study, subjects cleansed the face twice a day with PURPOSE® Gentle Cleansing Wash (Valeant Consumer Products, Montreal, Canada). On study days, subjects acclimated for 20 min, after which facial images were recorded and skin mechanical measurements were taken. Two test products were applied in a split-face fashion after the baseline measurements, after which additional images and mechanical measurements were taken.

MECHANICAL MEASUREMENTS

The mechanical properties of skin were assessed using a Ballistometer (Dia-stron, Broomall, PA) and a Cutometer® SEM 575 (Courage & Khazaka, Cologne, Germany). The Ballistometer determines skin elasticity by monitoring the bouncing of a stylus on the skin surface. The Cutometer measures the deformation of skin produced by suction for a brief time period (17). Although the elasticity measurement principle is different, the two instruments often show the same trends.

The Cutometer generates a range of mechanical properties that relate to skin elasticity, deformation under stress, and recovery. We have focused on the R0 and R3 parameters, which relate to the maximum amplitude of deformation of the skin initially and after three cycles of deformation and recovery, respectively, indicating skin firmness after repeated deformation (18). In both cases, lower values of the parameters indicate less viscous deformation and therefore firmer, more elastic skin.

The Ballistometer measures the coefficient of restitution (CoR), which is based on the stylus bounce height relative to the starting height, a measure of the skin elasticity. Higher values indicate the skin is more elastic and firmer (19). Hence, if skin becomes firmer over the course of the study, we expect R0 and R3 to decline and the CoR to increase.

Cutometer measurements were taken on the left and right cheekbones with four curves recorded on each area for each subject and an average calculated. Ballistometer data were obtained on the left and right temples, with three measurements taken at each location and an average calculated.

SKIN IMAGING METHODS

Facial images of the subjects were obtained with a VISIA-CR 2D facial imaging system (Canfield Scientific, Fairfield, NJ) and with an AEVA-HE 3D Imaging System (Eotech SA, Marcoussis, France). The VISIA records and automatically analyzes left, right, and frontal facial views, but does not capture depth information on facial features such as pores and wrinkles. VISIA-CR 2D images were taken as full face images with front, left, and right views.

The AEVA-HE 3D system uses fringe projection and cameras to analyze the topography of the skin surface, including wrinkles and other surface features. The skin roughness is calculated as two parameters, the arithmetic mean of the surface roughness, Sa, and the root mean square of the surface roughness, Sq. Additional parameters used by the AEVA system are the curvature area and density, defined as the area of all features that have a certain set curvature and the ratio of that area to the total area, respectively. We used a curvature set point of 0.5–1.0 mm, which corresponds to fine lines in the skin. The higher values of curvature area or density suggest more visibility of the fine lines. Finally, AEVA also reports total detected wrinkle area and volume, which are determined by the instrument software.

AEVA images were recorded as full face images with 160 mm focal length lenses. The zones for analysis were the cheek and crow's feet areas.

CONSUMER PERCEPTION

Subjects' perception of product performance and acceptance was evaluated through self-administered questionnaires, using an internet-based survey administrator (SurveyMonkey). The subjects completed the questionnaires individually without any extrinsic influences such as other volunteers or the results of technical measurements. The consumer perception questionnaires instructed subjects to consider the entire half face to which they had applied product when completing the questionnaire.

STATISTICAL ANALYSIS

For the clinical instrument data, we computed the descriptive statistics (means, standard deviation, and standard errors of the mean (SEM) of each parameter and the change of each parameter before and after product application. The percentage change from baseline was calculated by subtracting each subject's baseline parameter value from the value after product application. Statistical analysis of the change in the parameters was conducted with Minitab® software (Minitab, Inc., State College, PA). The normality of the data distribution was confirmed with the Kolmogorov–Smirnov test and the equality of variances was confirmed with a Levene's test. Once normality and equal variance were confirmed, a paired t-test was conducted to compare the parameters before and after product application. In addition, a one-way analysis of variance (ANOVA) followed by Tukey's test was conducted to compare the before and after application change of each parameter for the four different treatment products at 95% confidence level (p-value < 0.05).

The consumer perception data were analyzed with Minitab® software as well. Performance parameters were evaluated through the use of a 6-point scale (1 = not at all; 2 = slightly; 3 = somewhat; 4 = moderately; 5 = very; and 6 = extremely). A 5-point scale

(1 = slightly; 2 = somewhat; 3 = moderately; 4 = very; and 5 = extremely) was employed to evaluate the perception of reduction in wrinkle visibility. To determine differences in the perception ratings among the test products, a one-way ANOVA at a 95% confidence level (p-value < 0.05) was performed for each parameter followed by a Tukey comparisons test. Again, the normal distribution and equality of variances were confirmed for each parameter through a Kolmogorov–Smirnov test and a Levene's test, respectively, before the ANOVA.

RESULTS

POLYMER GLASS TRANSITION MEASUREMENTS

The polymers investigated differ markedly in their response to environmental humidity (Figure 1). The PVP absorbs over 50% water at 90% relative humidity, leading to a decline in glass transition temperature to below freezing. The dependence of T_g on polymer content confirms the pattern measured by Buera et al. (14). On the other hand, the AMC absorbs much less water even at 90% relative humidity and its decline in T_g is much less steep. Significantly, the T_g is near room temperature at high water levels. This indicates that at room temperature the glass transition of AMC solutions is reached after evaporation of a relatively small amount of water compared with PVP.

MECHANICAL PROPERTIES OF THE SKIN

Treatment of the facial skin with the polymer formulations made skin firmer in both Cutometer and Ballistometer measurements. All polymers increased firmness significantly over baseline as measured by Cutometer parameters R0 and R3 (Figure 2). Moreover, the 4% AMC formulation increased skin firmness significantly more than the placebo. There was no significant difference in skin tightening between the 4% AMC, 2% AMC, and PVP formulations, nor was there a significant difference between the 2% AMC, PVP, and placebo formulations.

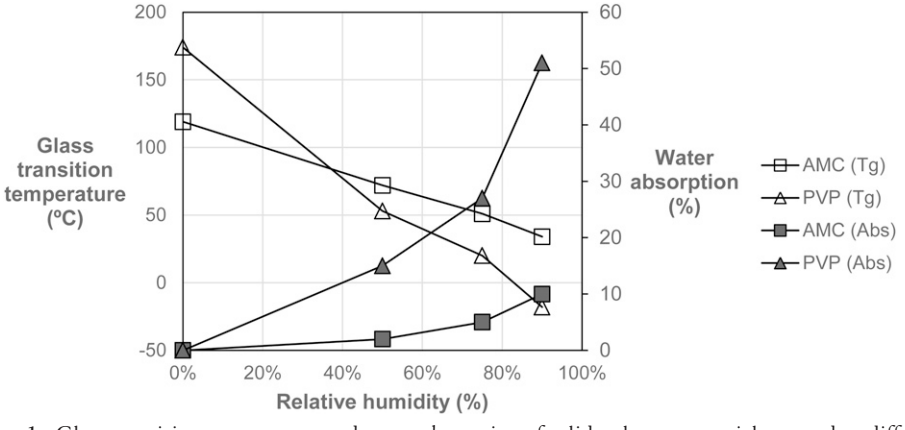

Figure 1. Glass transition temperature and water absorption of solid polymer material exposed to different levels of relative humidity.

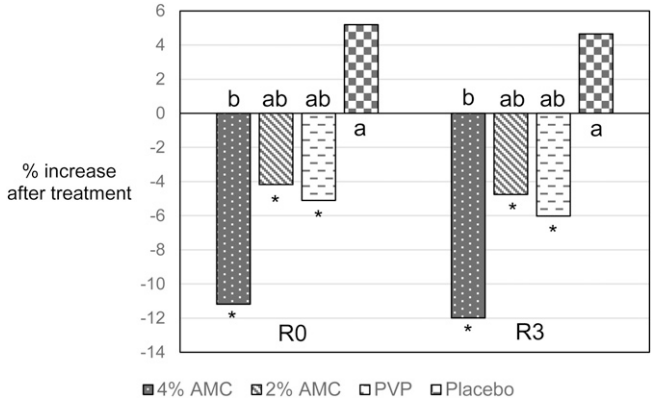

Figure 2. Change in Cutometer parameters R0 and R3 after treatment with polymer formulations. Lower values indicate firmer, more elastic skin. Treatments denoted with different letters are significantly different from each other ($p \leq 0.05$). Those denoted with * are significantly different from baseline (no treatment) ($p \leq 0.05$).

In Ballistometer testing, the differences were more pronounced (Figure 3). The 4% AMC formulation made skin significantly more elastic than all other formulations. Two percent AMC made skin significantly less elastic than the placebo formulation and significantly less elastic than before treatment. However, 2% AMC did not differ significantly from PVP or placebo or from baseline before treatment.

SKIN TOPOLOGY BY FRINGE PROJECTION

The topology of the skin—roughness, fine lines, and wrinkles—was measured by image analysis of 3D photographs recorded with the AEVA system. The formulations applied to the skin did not differ significantly in this analysis, but there were some that were significantly different from the baseline before treatment. One of these was present in the surface roughness measurements, which did not show significant differences between the

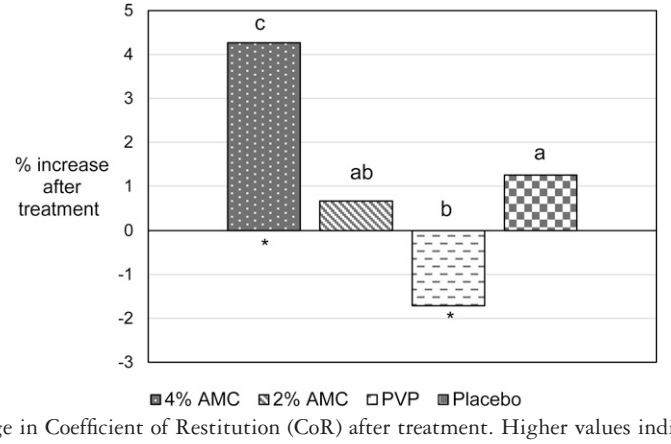

Figure 3. Change in Coefficient of Restitution (CoR) after treatment. Higher values indicate firmer, more elastic skin. Treatments denoted with different letters are significantly different from each other ($p \leq 0.05$). Those denoted with * are significantly different from baseline (no treatment) ($p \leq 0.05$).

polymer formulations. However, for the 4% AMC formulation the skin roughness on the cheek was significantly reduced compared with baseline, for both parameters Sa and Sq (Figure 4).

The skin curvature area and density, which indicate the visibility of fine lines and wrinkles, showed a similar pattern (Figure 5). A significant decrease in curvature area compared with baseline occurred after treatment with 4% AMC, whereas a significant decrease in curvature density was seen with both 2% AMC and PVP. The PVP and placebo formulations did not show any significant changes in the curvature parameters.

Figure 6 shows the total wrinkle volume and area reported by AEVA. Wrinkle volume, but not area, decreased significantly for 2% AMC. There was a relatively large decrease for 4% AMC as well, but this was not statistically significant.

In summary, the fringe projection data obtained with the AEVA system showed that the 4% AMC and 2% AMC formulations were effective in reducing the skin roughness and the visibility and volume of fine lines and wrinkles. However, the formulations did not differ significantly from each other.

CONSUMER PERCEPTION OF PRODUCT EFFECTS

To test consumer acceptance of the prototype formulations, we surveyed the study subjects on their perception of the products' effects. Specifically, we intended to learn if the subjects experienced a tightened skin feel and if they judged their appearance to be improved after product application (Figure 7). The subjects were also asked how tacky the products felt during all phases in the application process and whether the tacky feel was acceptable to them (Figure 8).

As shown in Figure 7, the subjects on average found the 4% AMC formulation to yield a significantly higher rating for tightened skin feel and tightened skin appearance than both 2% AMC and the placebo. The 2% AMC formulation was also rated significantly higher than the placebo for tightened skin feel. None of the other differences were statistically significant. Notably, there were no significant differences between the formulations on smooth skin appearance.

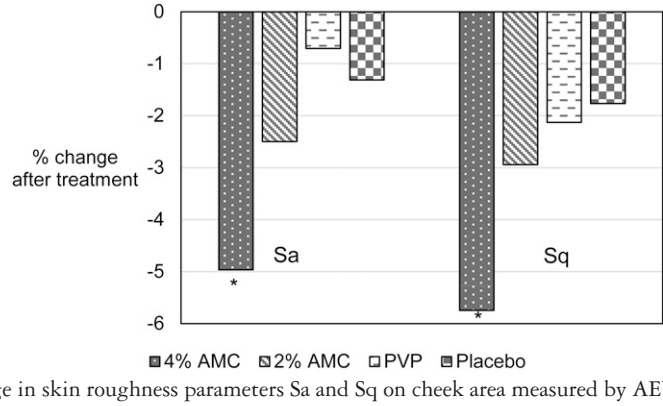

Figure 4. Change in skin roughness parameters Sa and Sq on cheek area measured by AEVA analysis. There are no significant differences between treatments ($p > 0.05$). Treatments denoted with * are significantly different from baseline (no treatment) ($p \leq 0.05$).

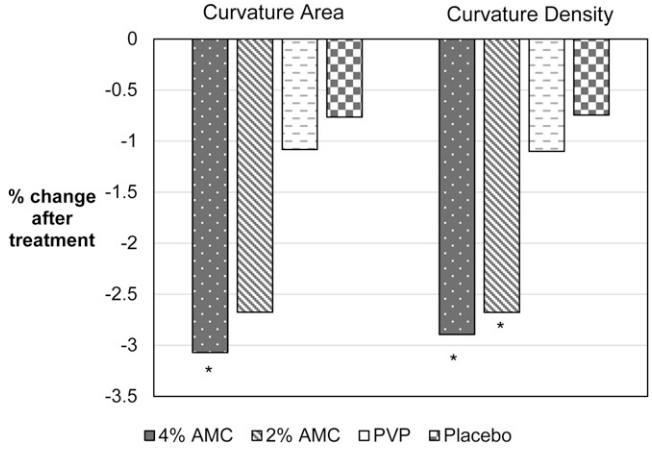

Figure 5. Change in skin curvature area and curvature density on the cheek area measured by AEVA analysis. A decline in curvature indicates lower visibility of fine lines. There are no significant differences between treatments ($p > 0.05$). Treatments denoted with * are significantly different from baseline (no treatment) ($p \leq 0.05$).

The data in Figure 8 shows that the formulations which produced a tightening sensation were also the most tacky. Four percent AMC was rated significantly higher than the benchmark and the placebo for tacky feel during application, tacky feel during drying time, and tacky feel after drying. The 2% AMC formulation was also rated significantly higher than the benchmark and placebo for tacky feel during drying time.

However, although these formulations were rated higher for tackiness, consumer acceptance was still high. With the exception of 4% AMC during application, a significant majority ($p \leq 0.05$, 75% or more of respondents) found the tacky feel of the products to be acceptable.

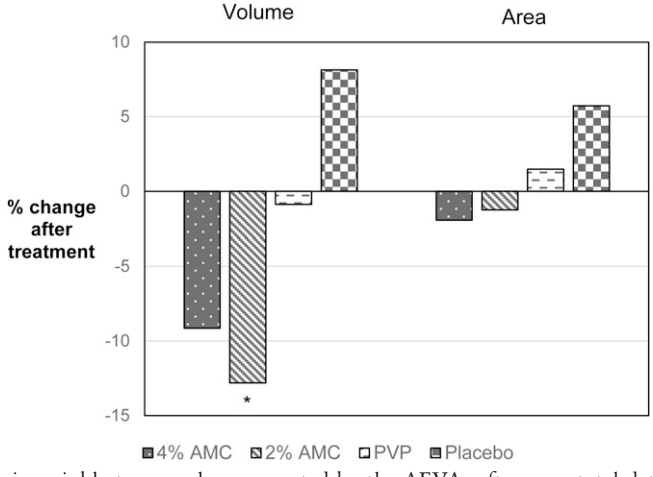

Figure 6. Change in wrinkle topography as reported by the AEVA software as total detected wrinkle area and volume. Treatments denoted with * are significantly different from baseline (no treatment) ($p \leq 0.05$). The data show that total wrinkle volume decreased significantly for skin treated with the 2% AMC formulation. There are no significant differences between treatments ($p > 0.05$).

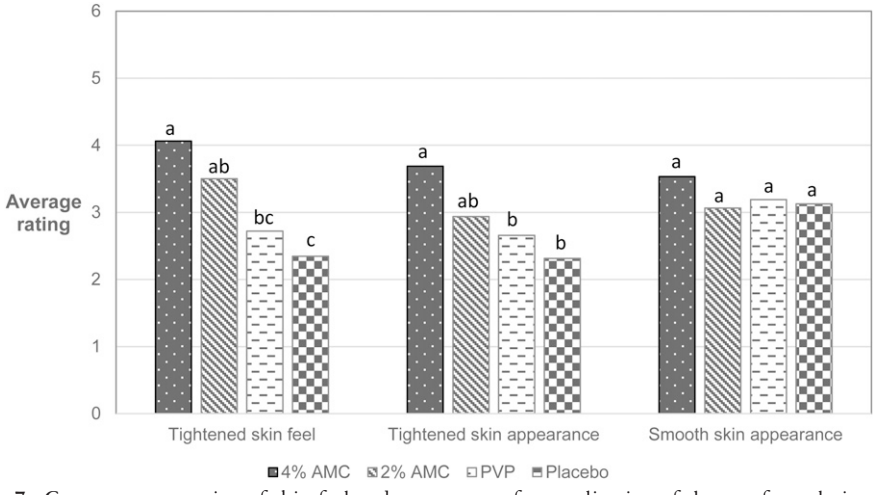

Figure 7. Consumer perception of skin feel and appearance after application of the test formulations. Subjects were asked to rate their responses on a scale from 1 (not at tightened/smooth) to 6 (extremely tightened/smooth) for the first three questions. Treatments denoted with different letters are significantly different from each other within the same question ($p \leq 0.05$).

DISCUSSION

PRODUCT IMPACT ON SKIN DURING APPLICATION

In this study, we analyzed the impact of product formulations containing skin care polymers on the skin surface. For the polymers studied, the formulation was somewhat tacky on initial application, but became less tacky as it dried and the tackiness of the skin was

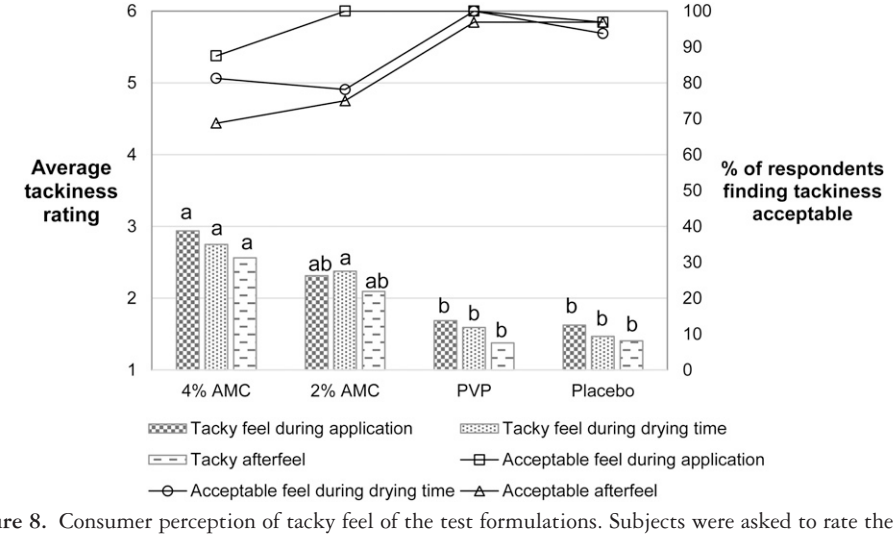

Figure 8. Consumer perception of tacky feel of the test formulations. Subjects were asked to rate the tacky feel during three stages of the application process on a scale from 1 (not at all tacky) to 6 (extremely tacky). They were also asked if the tacky feel was acceptable (yes or no response). Treatments denoted with different letters are significantly different from each other within the same question ($p \leq 0.05$).

never unacceptable to most study participants. After application, the skin felt and appeared tightened for the polymer formulations, but not smoother than with the formulations without polymer. The tighter feel and appearance was confirmed by the measurements of the mechanical properties of the skin surface using two independent instrumental methods. Moreover, the surface roughness and visibility of fine lines and wrinkles were reduced with the 4% AMC formulation. Total wrinkle volume decreased for 2% AMC, but total wrinkle area was unchanged, indicating that wrinkle depth decreased.

These results are consistent with the effects on skin produced by a drying and contracting polymer film. The mechanical measurements, optical observations and consumer feedback prove that the reduced wrinkle visibility is not due to an optical blurring effect. The polymer films have an evident mechanical impact on the skin surface and skin microstructure. During drying of the aqueous polymer solution, a continuous thin polymer film is formed covering all or most of the skin surface. This film contracts and smoothens out the skin, reducing wrinkle depth and producing a perceivable tightening sensation to test subjects.

MECHANISM OF SHRINKING STRESS GENERATION

The film contraction is analogous to film shrinkage as observed in polymer latexes. The mechanism may be very similar as well, although the particle coalescence step would not occur. For our study we selected skin care polymers, AMC and PVP, with a relatively high T_g at high moisture levels. As the polymer film dries, the moisture level in the film decreases until the glass transition is reached and drying stresses are generated (Figure 9). However, the film at that level needs to be strong enough to sustain these stresses without cracking or breaking. If the water content of the film is too low when T_g is reached, the film could be too thin to sustain mechanical stresses without cracking. Hence, for a shrinking polymer film, the water content of the film should be above a certain percentage when the T_g approximates the skin temperature. The mechanical stresses observed in the AMC and PVP films confirm this model.

In future work, studying the drying phenomena in films of polymers with lower T_g would be interesting as the drying stresses would potentially occur when the film is relatively

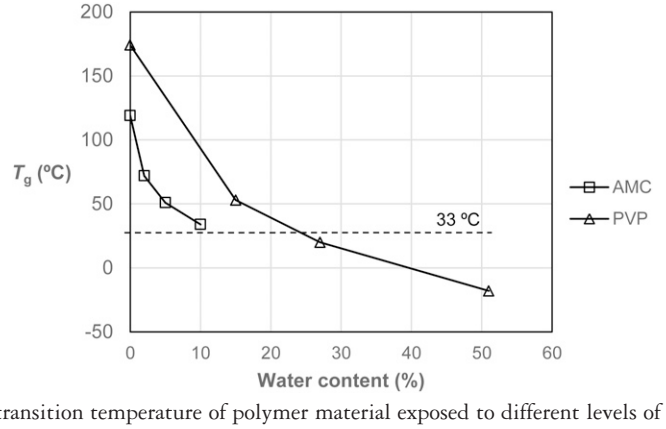

Figure 9. Glass transition temperature of polymer material exposed to different levels of relative humidity versus water content (same data as in Figure 1). As the water content decreases during drying, T_g reaches skin temperature (33°C) and drying stresses start.

thin, leading to cracks that could limit the area of mechanical impact. The dependence of T_g on the polymer weight fraction in the emulsion system also remains to be elucidated, as does the influence of other emulsion components such as the oil phase.

DIFFERENCES BETWEEN POLYMER FORMULATIONS

Among the three polymer formulations studies, the formulation with 4% polyacrylate showed the highest efficacy in skin tightening. It was significantly better than the placebo in the change in the R0 and R3 parameters and significantly better than all other formulations in the change in CoR. Against baseline, it outperformed significantly in the change in skin roughness in terms of parameters Sq and Sa, in the change in curvature density and area, and outperformed directionally in the change in total wrinkle volume. In consumer perception, it was significantly better than the placebo formulation and the benchmark formulation with PVP. It was perceived as significantly tackier on application than the PVP and placebo formulations, but this tackiness was acceptable.

The formulation with 2% polyacrylate showed skin tightening as well, but not as strong and in most experiments not strong enough for statistical significance. Also, the formulation with 1.5% PVP showed significant tightening against baseline in the Cutometer measurements only, but not in any of the other experimental studies. Moreover, the test subjects were unable to perceive any tightening effect with this formulation.

In summary, the polyacrylate polymer was superior to PVP in skin tightening efficacy, particularly at the higher concentration of 4% in our model emulsion formulation.

CONCLUSION

We have shown that the skin care polymers studied reduce facial wrinkle size and make skin firmer. Skin firming measures indicated that both polymers instantly tightened facial skin, whereas the placebo product offered no significant tightening benefit. However, in clinical evaluation only the polyacrylate polymer produced clinically significant improvements in wrinkle size and skin firmness on the face without significant consumer use negatives such as tackiness. Skin care products with materials such as this have the potential to offer immediate and visible benefits to consumers with aged skin. The tightened skin feel that users perceived is a direct and welcome signal of product efficacy.

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