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# Investigating Film Properties of Polymers Used in Anhydrous Sunscreen Formulations Using Scanning Electron Microscopy (SEM): Polymer/Polymer Interactions and Their Relation to Vapor Transmission

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**Synopsis**

A mechanistic understanding of the role of polymers in waterproofing anhydrous sunscreen formulations has been hypothesized in the past, but has never been clearly established. In this article, we demonstrate the utility of field emission scanning electron microscopy (SEM) to generate images of sunscreen films in the presence and absence of several polymers. VA/butyl maleate/isobornyl acrylate copolymer was studied alone and in combination with hydroxypropyl cellulose and acrylates/dimethicone copolymer. Anhydrous sunscreen formulations were sprayed onto stratum corneum substrates and left to dry. SEM micrographs of treated stratum corneum sections were then collected at various magnifications. Vapor transmission data were collected using an evaporimeter to understand the permeability of these films in the presence and absence of film formers. Examination of the SEM images reveals that after spraying the product onto a layer of corneocytes, the sunscreen filters formed a hydrophobic barrier over the skin, whereas added polymers formed films over the sunscreen layer. The shape of the film formed by various polymers and its porosity were influenced by chemistry and concentration. When more than one polymer was incorporated in the sunscreen formulation, the interactions between the polymers influenced the formation of the film. Cumulative evaporimeter data indicated that the sunscreen phase had the highest reduction in cumulative evaporation rate (39.3%/h) followed by the addition of a film former to the spray, which reached an additional reduction of 17.9%/h in the best case. This method was also used to examine the film properties of a commercial sun protection factor 30 sunscreen product containing VA/butyl maleate/isobornyl acrylate copolymer. SEM micrographs of the commercial product applied to skin showed the same fingerprint as prototype formulations containing VA/butyl maleate/isobornyl acrylate copolymer. Overall, this method can be used by sun care scientists in the development and optimization of anhydrous sunscreen sprays.

## INTRODUCTION

Over the past few years, aerosol sunscreen formulations have been gaining popularity among consumers, as compared to traditional creams and lotions. This is mainly

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because of convenience of application, especially on children. The use of polymers in such formulations has become a standard practice as polymers impart water resistance and contribute to boosting the sun protection factor (SPF) of such preparations. In many instances, polymers affect sensorial properties of the formulations as well. During the past several years, most of the research conducted on the use of polymers in sunscreen formulations has been centered around developing new methodologies for testing *in vitro* SPF and water resistance (1–3). Recently, the effect of polymers on sensorial attributes was also investigated (4). The mechanism by which polymers affect waterproofing of sunscreens was described by Prettypaul and Fares several years ago (5). Although the authors described mechanistic information on the formation of a polymeric film, additional information on the film properties needed to be investigated.

In this study, we developed a direct method by which one can visualize polymer films after they are sprayed onto stratum corneum sheets. The method allows us to study the interaction of various polymer combinations on film surfaces and their ability to form a continuous film on the surface. We used vapor transmission data for such films to understand the breathability of polymer mixtures on the skin and how it is related to *in vitro* water resistance.

## MATERIALS AND METHODS

In this study, we introduce a methodological approach for investigating sunscreen film formation on the skin. Specifically, we probed the interactions of the primary film former, VA/butyl maleate/isobornyl acrylate copolymer, with two commonly used film formers in spray formulations, namely, acrylates/dimethicone and hydroxypropyl cellulose.

All formulations used in this study are displayed in Table I. The chassis developed was quite simple and contains typical ultraviolet A (UVA) and ultraviolet B (UVB) sunscreens, functional polymers, and alcohol (the diluent). The formulations were then aerosolized as described in the following paragraph.

### MATERIALS

Butyl methoxydibenzoylmethane (Escalol™ 517), benzophenone-3 (Escalol™ 567), homosalate (Escalol™ HMS), ethylhexyl salicylate (Escalol™ 587), octocrylene (Escalol™ 597), isostearyl neopentanoate (Ceraphyl™ 375), VA/butyl maleate/isobornyl acrylate copolymer (Advantage™ Plus), and hydroxypropyl cellulose (Klucel™ G CS) were supplied by Ashland Specialty Ingredients G.P. (Covington, KY). Acrylates/dimethicone copolymer (KP 545L) was obtained from Shin-Etsu Chemicals (Tokyo, Japan). Alcohol, SD 40-B (200 proof), was provided by Pride Chemical Solutions (Holtsville, NY) and butylene glycol was purchased from Thermo Fisher Scientific (Waltham, MA). In addition, tests were conducted with a commercial SPF 30 aerosol sunscreen formulation containing the following ingredients: avobenzone, octocrylene, oxybenzone, SD alcohol 40-B, isobutane, dimethicone, tocopherol, ascorbyl palmitate, VA/butyl maleate, isobornyl acrylate copolymer, and fragrance.

**Table I**
Formulations Tested

| | Formulations | | | | | |
|---|---|---|---|---|---|---|
| **Ingredients** | A | B | C | D | E | F |
| Phase A | | | | | | |
| Alcohol, SD 40-B (200 proof) | 93.00 | 94.00 | 54.00 | 52.00 | 51.00 | 51.80 |
| Butylene glycol | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Phase B | | | | | | |
| Butyl methoxydibenzoylmethane | | | 3.00 | 3.00 | 3.00 | 3.00 |
| Benzophenone-3 | | | 6.00 | 6.00 | 6.00 | 6.00 |
| Homosalate | | | 15.00 | 15.00 | 15.00 | 15.00 |
| Ethylhexyl salicylate | | | 5.00 | 5.00 | 5.00 | 5.00 |
| Octocrylene | | | 10.00 | 10.00 | 10.00 | 10.00 |
| Isostearyl neopentanoate | 5.00 | | 5.00 | 5.00 | 5.00 | 5.00 |
| Phase C | | | | | | |
| VA/butyl maleate/isobornyl acrylate copolymer (and) alcohol (50% w/w solution in alcohol) | | 4.00 | | 2.00 | 2.00 | 2.00 |
| Hydroxypropyl cellulose | | | | | | 0.20 |
| Acrylates/dimethicone copolymer (and) dimethicone (40/60% w/w) | | | | | 1.00 | |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

### FORMULATION PROCEDURE

In all formulations, phases A and B were weighed separately in different beakers. Phase B was heated to 50°C until all crystals were dissolved and then brought back to room temperature. Phase A was added to phase B and then ingredients of phase C were added to their respective formulations. Formulations were filled into an aluminum can and aerosolized with 30% isobutane (A-31). The actuator was a Moritz twist-to-lock with a Misty 0.025 insert from Aptar (Crystal Lake, IL).

### VAPOR FLUX METHODOLOGY

Evaporimeter measurements were performed using an AquaFlux Model AF200 (Biox Systems, Ltd., London, UK) on pig skin that was placed in a Franz diffusion cell assembly. The evaporimeter was fitted with an adapter to fit directly onto the Franz diffusion cells. Dermatomed pig skin was cut into 400 $mm^2$ sections and placed over the donor chamber. Test samples were applied on the pig skin in quantities of 2 $mg/cm^2$ using an analytical balance and then spread evenly with a finger cot. The receptor fluid was filled with deionized water and the temperature of the skin and the receptor fluid was kept constant at 34°C using a circulating water bath. Skin was equilibrated for 15 min at that temperature before sample application. Data collection (1 point/s) took place over a period of 60 min to monitor the variations in vapor transport as a function of time.

### TAPE STRIPPING PROTOCOL

Products were sprayed onto a stratum corneum layer that was formed on a D-Squame disc. Standard 22 mm D-Squame discs (CuDerm Corporation, Dallas, TX) were used to

collect stratum corneum from the volar forearm of volunteers. Products were sprayed onto the isolated corneocytes from an aerosol placed about 12 inches away from the stratum corneum. The products were left to air-dry for a minimum of 20 min before coating with conductive metals and placing into the scanning electron microscopy (SEM) chamber.

### SEM PROTOCOL

Treated D-Squame discs were placed on 25 mm OD Pelco Tabs (Ted Pella, Inc., Redding, CA). The pin stubs were placed in a sputter coater (Leica EM ACE600; Leica Microsystems, Wetzler, Germany) and coated for 60 s with gold/palladium, resulting in a 10-nm thick layer. The stubs were attached to a multisample mount and placed into the SEM (Hitachi SU-5000, Tokyo, Japan), which has variable pressure and field emission scanning capabilities. For the analysis of the coated stratum corneum layers, we used high vacuum mode ($<1 \times 10^{-3}$ Pa) and collected photomicrographs starting at ×300 and extending to higher magnifications to elucidate details associated with the sunscreen application. Most images were collected using a secondary electron detector, but a backscatter detector was also used for samples that exhibited poor contrast properties. 3D images were also captured by SEM.

## RESULTS

In this study, we sought to determine key properties of sunscreen preparations applied to skin. Using evaporimetry in conjunction with a Franz diffusion cell apparatus and *ex vivo* skin, vapor flux data were generated for the sunscreens, allowing for the determination of the water permeability of the sunscreen films. Employing SEM, we developed a novel methodology for determining the morphological film properties when sunscreens are applied to skin. The utility of the technique, aimed at discerning the microscopic film properties, lies in the use of layers of corneocyte cells collected by tape stripping. In this manner, the substrate has the same surface properties as *in vivo* skin.

### EVAPORIMETER STUDIES

Four formulations were tested in this study, namely, Formulations C, D, E, and F. Because Formulations A and B consist mostly of alcohol, their water permeability was not tested. Instead, water and sunflower seed oil were used as negative and positive controls and yielded a cumulative evaporation of $88.0 \times 10^3$ and $12.6 \times 10^3$ g $m^{-2}$ $h^{-1}$, respectively. Both the positive and negative controls were significantly different from all treatments and from each other. The data generated for the four formulations studied are displayed in Figure 1. Formulations C, D, E, and F yielded cumulative evaporations of 53.4, 37.7, 46.0, and $36.6 \times 10^3$ g $m^{-2}$ $h^{-1}$, respectively. Only Formulation C was significantly different (when comparing Formulations C, D, E, and F), in which case there was a greater rate of evaporation.

Formulations D, E, and F, which contained VA/butyl maleate/isobornyl acrylate copolymer and its combination with acrylates/dimethicone copolymer or hydroxypropyl cellulose,

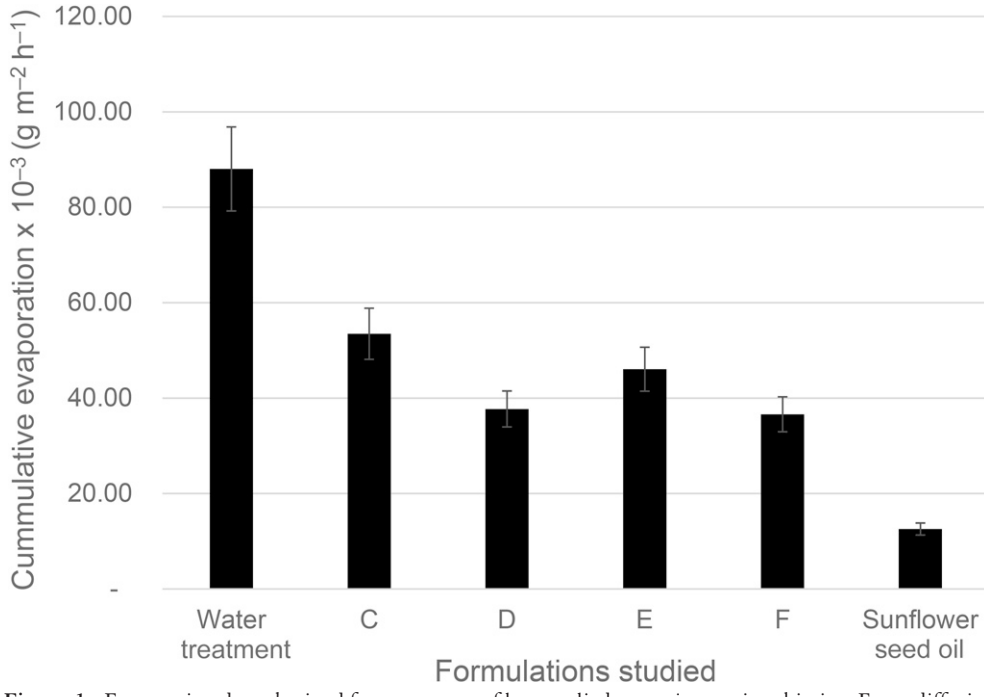


**Figure 1.** Evaporation data obtained from sunscreen films applied to *ex vivo* porcine skin in a Franz diffusion cell apparatus.

formed significantly less permeable films than Formulation C, which did not contain any polymer. Cumulative evaporimeter data indicated that the sunscreen phase had the highest reduction in cumulative evaporation rate, specifically 39.3%/h, followed by the addition of a film former to the spray which reached an additional reduction of 17.9%/h in the best case. These findings are quite reasonable, as sunscreen filter concentrations are typically much higher (typically 20–30% w/w) than polymer concentrations (typically 1–3% w/w) in the final formulation.

The data from the evaporimeter studies confirmed that the sunscreen filters play a more important role in water vapor transmission than the polymers added to the formulation. This finding seems to correlate with previously presented data (6). It is also important to note that the addition of polymers to the sunscreen formulations increased its *in vitro* water resistance.

## MICROSCOPIC EVALUATION OF FILMS ON SKIN

To better understand the deposition characteristics of the sunscreen systems on skin, we used SEM to carefully monitor the deposition behavior of sunscreen films and to elucidate the architectural role played by several polymeric systems in the sunscreens. Figures 2 and 3 contain micrographs of corneocytes treated with all of the studied formulations at ×300 (Figure 2) and ×500 or ×1,000 (Figure 3) magnifications, respectively.

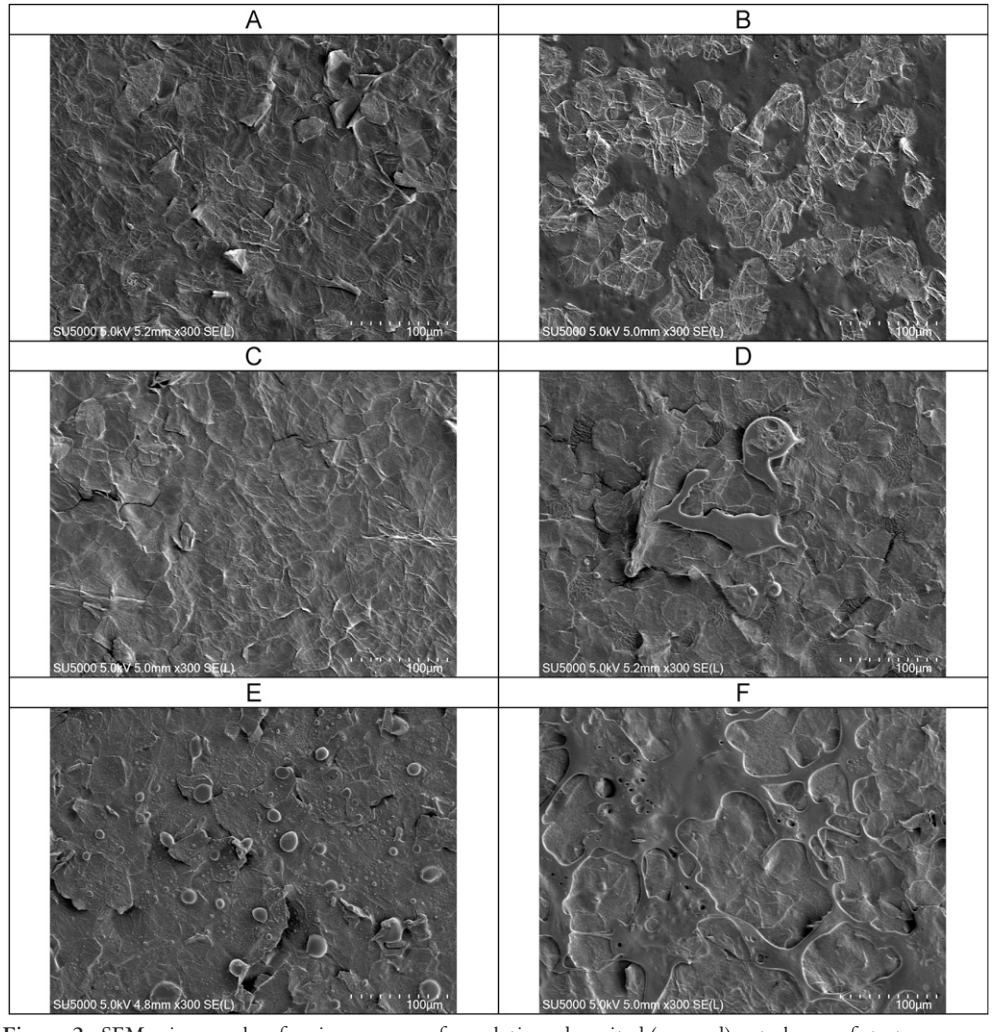


**Figure 2.** SEM micrographs of various sun care formulations deposited (sprayed) onto layers of stratum corneum cells (magnification = ×300). (A) Formulation A, (B) Formulation B, (C) Formulation C, (D) Formulation D, (E) Formulation E, and (F) Formulation F.

Observation of the behavior of Formulation A demonstrated that this system did not leave any noticeable residue on the stratum corneum. The corneocytes appear very distinct and no apparent film was deposited on its surface. Such results are expected as Formulation A contains about 93% (w/w) alcohol, which most likely evaporated before obtaining the micrographs.

On the other hand, for Formulation B, which contained the polymeric film former VA/butyl maleate/isobornyl acrylate copolymer at a level of 1% (w/w), we observed that the polymer formed a network over the stratum corneum. The network appeared a bit darker in the image than the corneocyte background. One interesting aspect of this film former is its ability to form a clear, interconnected network over the stratum corneum as opposed to a distinct spray particle deposited on the surface.

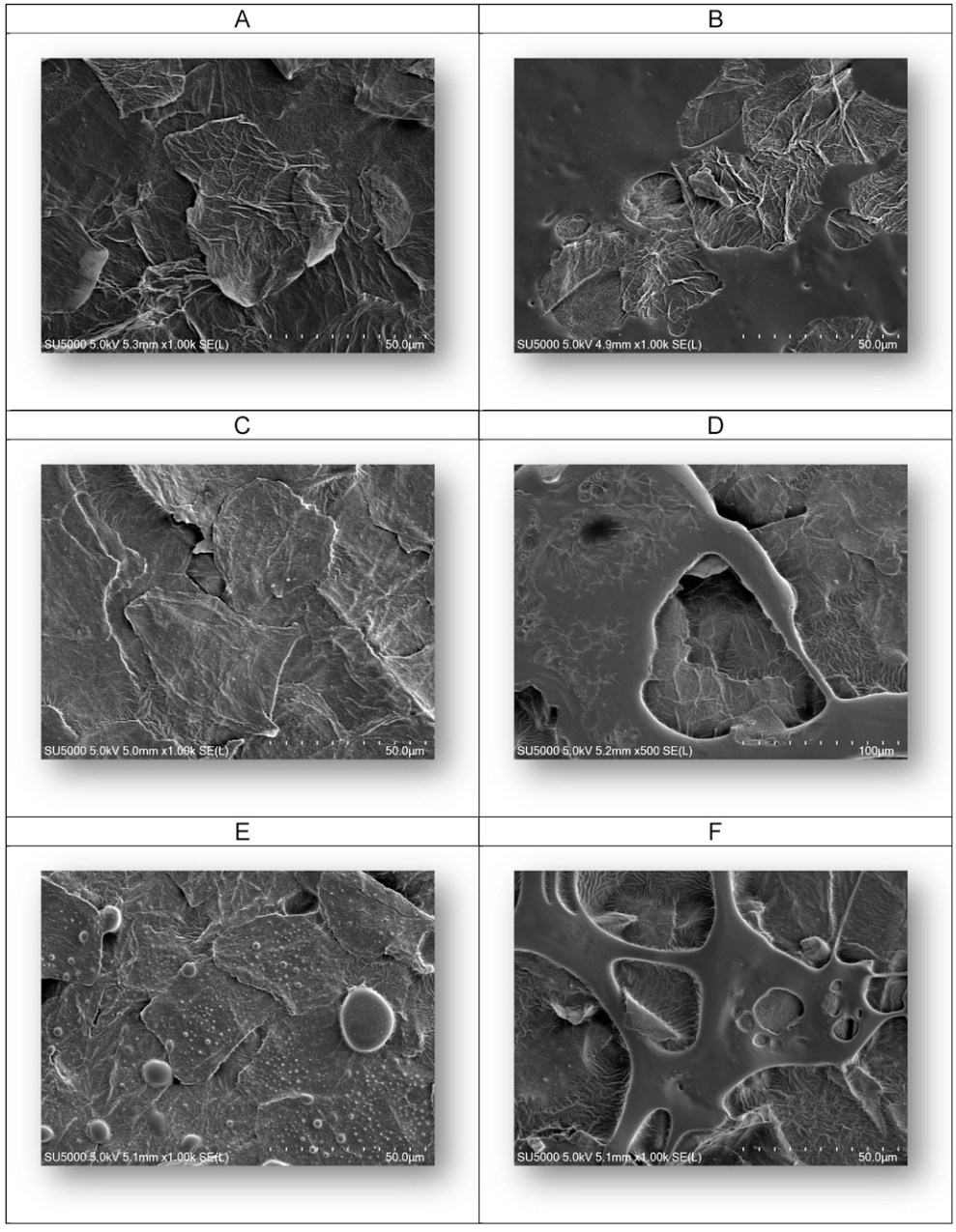


**Figure 3.** SEM micrographs of various sun care formulations deposited (sprayed) onto layers of stratum corneum cells (magnification = 500–×1,000). (A) Formulation A, (B) Formulation B, (C) Formulation C, (D) Formulation D, (E) Formulation E, and (F) Formulation F.

Formulation C, which contained a sunscreen phase, but no polymer, appears to have covered the entire surface of the corneocytes with a sunscreen film. The film entirely covered the surface, as evident in the SEM micrographs. The individual corneocytes were less apparent as the film entirely covered the surface. There are many similarities between

Figures 2A and C and 3A and C due to the absence of the film former which typically appears on the surface of the corneocytes and is not present in these formulations. This confirms the fact that the sunscreen phase blends well with the corneocytes.

Formulation D represents a typical sun care spray formulation, which contained a sunscreen phase and a relatively low level (1% w/w) of film former. As expected, the sunscreen phase formed a continuous film over the corneocytes. The film former did not form the same type of network that we observed when the polymer was used alone (Figure 3B) but rather formed discrete blotches on the surface of the sunscreen film. This behavior confirms that there is an interaction between the sunscreen phase and the film former, which indicates that portions of the film former intercalate the sunscreen film, whereas the remaining portion of the film former creates a film over the sunscreen layer.

In Formulations E and F, two distinct polymers were added at low concentrations to study the interaction of composite film formers on the surface characteristics of the films created. Specifically, acrylates/dimethicone copolymer and hydroxypropyl cellulose, respectively, were added to Formulations E and F. By examination of the surface topography of the films created, we observed that the surface properties of the two films were completely different. In the case of acrylates/dimethicone copolymer, there was no interaction of this polymer with the existing VA/butyl maleate/isobornyl acrylate copolymer. In fact, it appeared that acrylates/dimethicone copolymer formed discrete particles on the surface of the film. On the other hand, the addition of hydroxypropyl cellulose to the existing polymer (VA/butyl maleate/isoburnyl acrylate copolymer) created a very defined network of the two polymers on the surface of the sunscreen film.

In an effort to study the applicability of this methodology to other formulations, we examined the film morphology of an SPF 30 commercial sunscreen containing VA/butyl maleate/isobornyl acrylate copolymer as a polymeric film former. The micrographs of the commercial sunscreen and Formulation D are displayed in Figure 4. Examination of the two micrographs indicates a number of similarities between the two films created. In both instances, the polymer formed a film over the sunscreen film, and the polymeric film is made up of discrete particles rather than a network. The behavior of the film former was

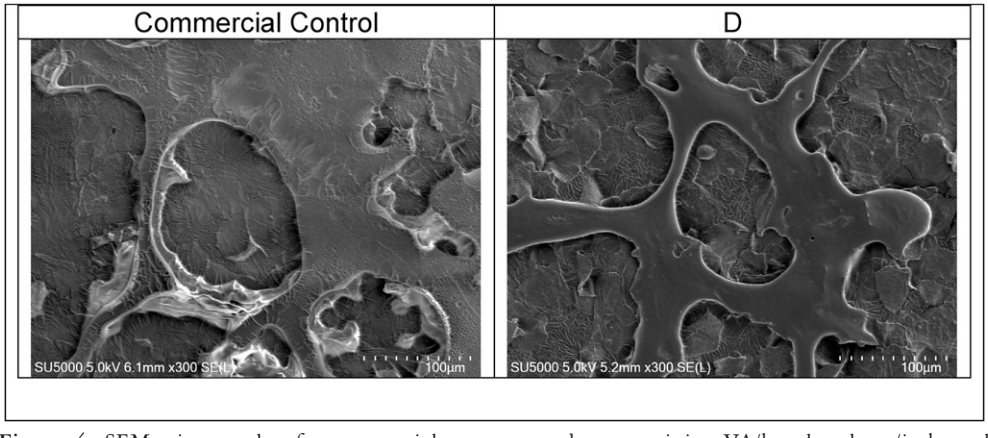


**Figure 4.** SEM micrographs of a commercial sun care product containing VA/butyl maleate/isobornyl acrylate copolymer deposited (sprayed) onto layers of stratum corneum cells (magnification = ×300).

similar to the results already presented in this report, as well as additional unpublished data, and was independent of the composition of sunscreen phase.

The effect of polymer concentration on the film characteristics was also studied. We increased the concentration of polymer in Formulation D from 1%–3% (w/w). An SEM micrograph taken of this composition is displayed in Figure 5, which clearly demonstrates that the polymer formed a very defined film over the corneocyte surface. The film characteristics were quite similar, but because of the increased concentration of the film former to 3% (w/w), there was better surface coverage. Figure 5 also displays a 3D micrograph of the film formed over the surface of the skin and sunscreen phase.

In summary, this method confirms earlier findings that a polymeric film typically forms over/above the sunscreen film when an anhydrous sunscreen is sprayed on the skin (5). Because the polymeric film is present as the uppermost layer on the skin, it will not only influence water resistance but will also affect the aesthetics of formulations. This makes selection of the correct polymer or polymer combination, as well as their levels in the formulation, of paramount importance.

## DISCUSSION

The work presented in this article is the result of several years of investigation. The methodology presented appears quite simple and straightforward but the authors investigated many other methods and substrates that did not provide the same clarity and visuals. Among substrates investigated, we conducted studies with Vitro Skin™, silicone elastomers, and pig skin. None of these substrates had similar surface energy or topology like human corneocytes. In addition, standardization of the methodology was quite important to achieve reproducible results. All formulations (except the commercial control) were sprayed from the same size and type can/nozzle and contained the same propellant and were pressurized similarly. Spray rate and velocity were standardized as well. From an imaging stand point, multiple images were captured from each sample to ensure reproducibility of the methodology.

The work presented in this article elucidated mechanistic information about polymer behavior in sunscreen formulation. One striking myth that this article uncovered is that

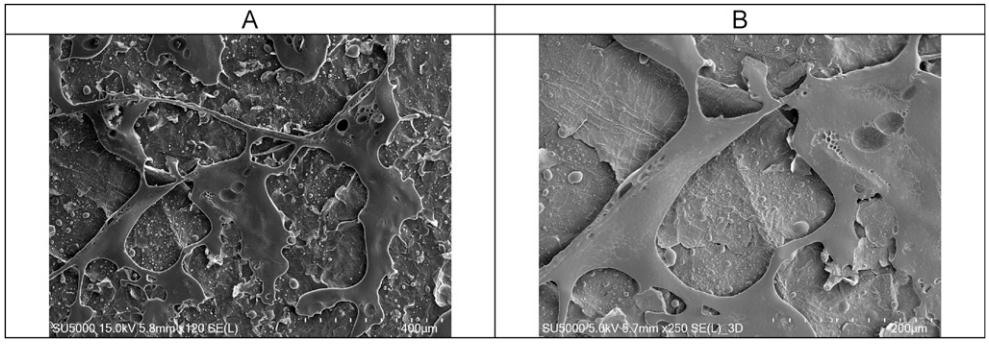


**Figure 5.** SEM micrographs of Formulation D with an adjusted concentration of 3% (w/w) VA/butyl maleate/isobornyl acrylate copolymer. (A) Conventional backscatter and (B) 3D images are shown at ×120 and ×250, respectively. The 3D image can be viewed with red and cyan 3D glasses.

polymers do not form continuous films on the surface of the skin. Polymers really form networks that contain mesh-like structures rather than continuous films. This is of course intuitive since the level of polymers in the sunscreen formulation is only 1–2% (w/w). However, because the network is quite hydrophobic, it is difficult for water to penetrate due to the sunscreen system's high surface tension. One other interesting finding is that immiscible polymers will not be miscible on the skin after the alcohol evaporates, and will not form continuous films, as in the case with VA/butyl maleate/isobornyl acrylate copolymer and acrylates/dimethicone copolymer. On the other hand, miscible polymers will form continuous films on the skin such as in the case of VA/butyl maleate/isobornyl acrylate copolymer and hydroxypropyl cellulose. A chemist can run simple miscibility tests before adding such polymers to the formulation to avoid any future incompatibilities.

## CONCLUSIONS

In this article, we present an innovative technique that enables scientists to visualize sunscreen films created on a stratum corneum substrate. Furthermore, it allows for the morphological investigation of polymeric film formers in sun care formulations and helps to elucidate their interactions with films formed by sunscreen actives. We used SEM to visualize the deposition of films from sun care formulations on layers of stratum corneum, obtained from tape stripping studies. Overall, we found that sunscreen films formed by sunscreen actives resulted in a continuous film on the surface, as evidenced by SEM studies and evaporimetry. Introduction of polymeric additives to the formulation allowed for the formation of separate films that contained a network architecture—dependent on the physicochemical properties of the polymer—resulting in unique interactions between films comprising the sunscreen filters and the polymer.

## ACKNOWLEDGMENTS

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