Organomodified Silicone Elastomer (OMSE) for Next Generation Personal Care Products

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Abstract: Personal care (PC) products containing commercial silicone elastomer (SE) blends offer superior sensory, due to their silky and non-greasy characteristics. These products contain functional organic actives; namely sunscreens, antibacterial agents and dyes. The functional performance of the PC products is determined by the extent of deposition of the actives on the skin or hair. However, this performance is limited due to incompatibility of organic actives with the silicone elastomer (SE) blend. This review described recent development of organomodified silicone elastomers (OMSE) for enhanced compatibility and superior deposition of actives on the skin or hair. OMSEs contain covalently linked functional actives to the cross-polymeric silicone backbone. OMSE were synthesized by reacting alkenyl functional derivatives of avobenzone, benzylidene malonate, curcumin or hydroxyanthraquinone, suitable crosslinker, solubilizing (e.g. C_nH_{2n} i.e. alkyl) / emulsifying agents (e.g. polyether) with the poly(dimethyl)-co-(methylhydrogen)siloxane copolymer in the presence of platinum catalyst. OMSE showed superior functional performance due to uniform molecular distribution of sunscreen / dye molecules on the substrate surface. Covalently attached sunscreen / dye molecules on the cross-polymeric silicone backbone would show enhanced safety profile due to negligible possibility of penetration through skin.

Keywords: Organomodified polymer, silicone elastomers, skin / hair photodamage, hair color photodegradation, sunscreens, hair colorants, antibacterial polymers, active deposition.

BACKGROUND

Today's personal care (PC) products thrive upon superior sensory and functional performance along with enhanced safety and minimum eco-toxicity. Incorporation of commercial silicone elastomer (SE) blends in such PC products offer silky and non-greasy sensory attributes. This key sensory signature of PC products is attributed to the presence of silicone crosspolymer (i.e. elastomer) swollen in the volatile silicones. Few examples of Dow Corning's commercial SE blends are DC9040, DC9041, DC9045 (INCI: dimethicone crosspolymer); DC 9506, DC 9509 (INCI: dimethicone / vinyl dimethicone crosspolymer). These SE blends are synthesized by reacting linear poly(dimethyl)-co-(methylhydrogen)siloxane copolymer with the divinyl terminated polydimethysiloxane or organic diene as the crosslinker in the presence of platinum catalyst; followed by swelling in volatile silicones. As seen in Figure **1**, SE blend is a 3-dimensional cross-polymer (~ 15%) swollen in volatile silicone (85%).

PC products contain either water-in-oil or oil-in-water compositions which are prepared using SE blend, emulsifiers and topical functional organic actives, namely, sunscreens, dyes and antibacterial agents. The functional performance of these organic actives is determined by their distribution within the composition followed by deposition during application on the skin / hair. However, this performance is limited when organic actives show incompatibility with SE blend (shown in Figure **2**). This incompatibility also results in poor sensory performance.

Recently Dow Corning's commercial organic silicone elastomer (OSE) blends such as EL 8051 (INCI: Isodecyl Neopentanoate and Dimethicone/Bis Isobutyl PPG-20 crosspolymer); EL 8052 (INCI: Isohexadecane and Dimethicone/Bis-Isobutyl PPG 20 crosspolymer) and EL 8050 (INCI: Isododecane and Dimethicone/Bis-Isobutyl PPG- 20 crosspolymer have been introduced to improve compatibility with the organic personal care actives.

In addition to incompatibility issue, these organic actives could pose complex safety issues when they come in contact with skin. Ideally sunscreen molecules are expected to remain on the skin surface as a protective layer against sun radiation and not to penetrate into the underlying viable tissue. Similarly, dye molecules should effectively deposit and distribute evenly on the hair surface. However, literature revealed that the substantial amount of applied sunscreens [1-5] are absorbed through skin [6] and also detected in human urine [2,7-9], gastro intestestinal tract [10] and human milk [8,11]. A significant number of publications revealed case studies showing skin allergy due to commonly used sunscreens [12-15]. Hair dyes also show significant toxicity [16-18] due to their penetration through skin [19,20]. Antimicrobials should be effective against microorganisms and remain safe to

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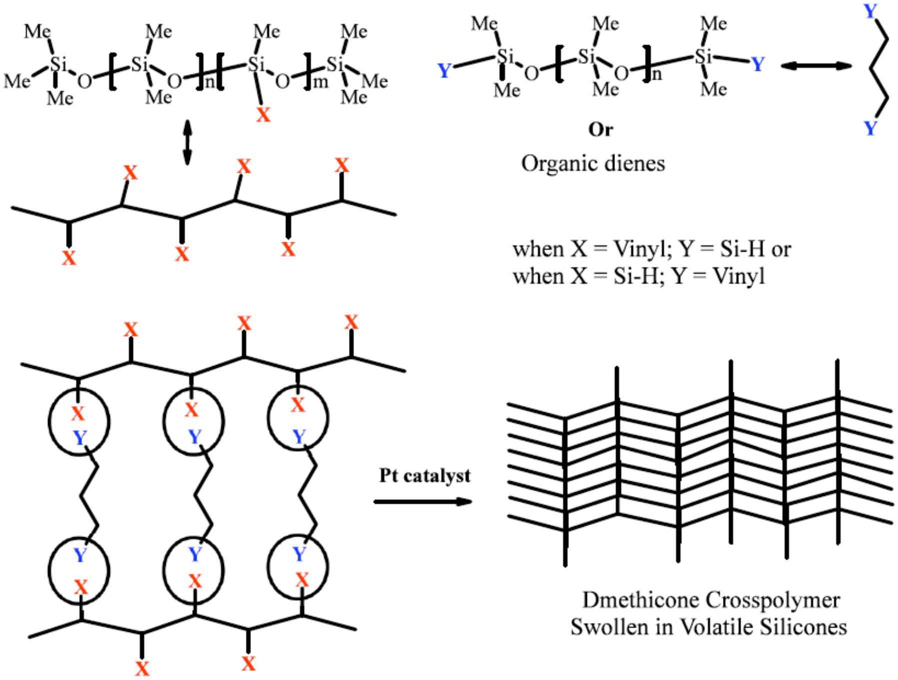


Figure 1: Commercial Silicone Elastomer (SE) blends.

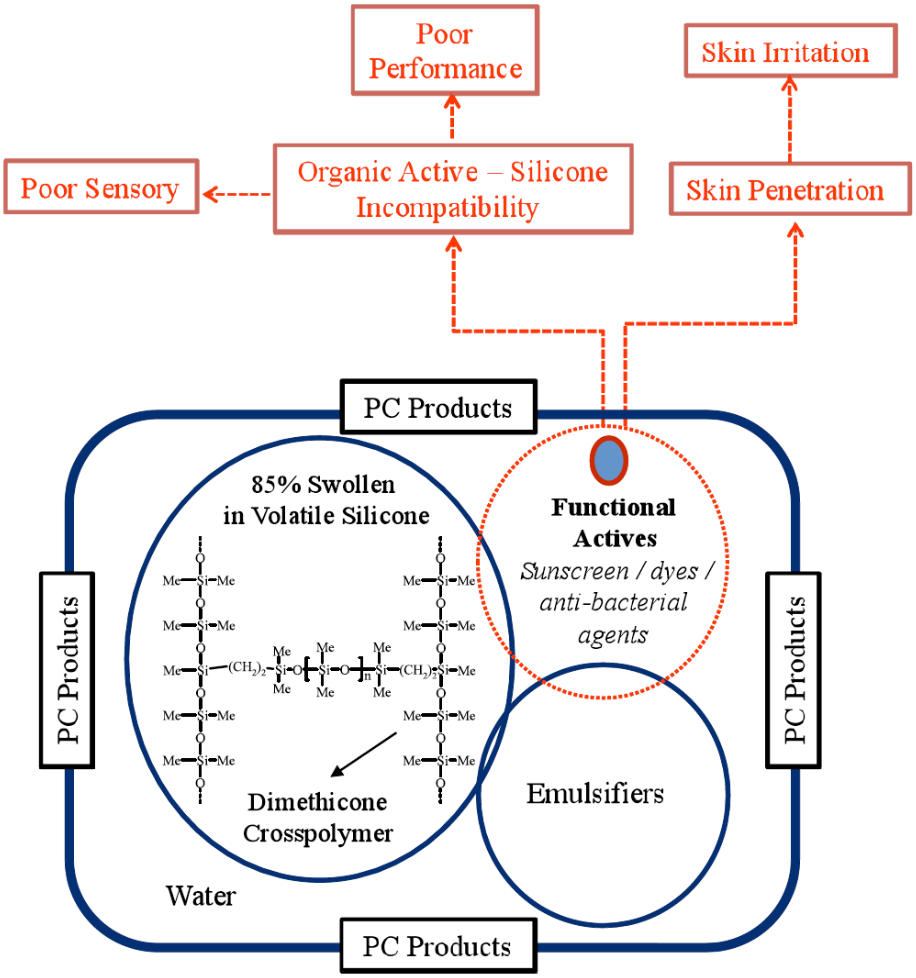
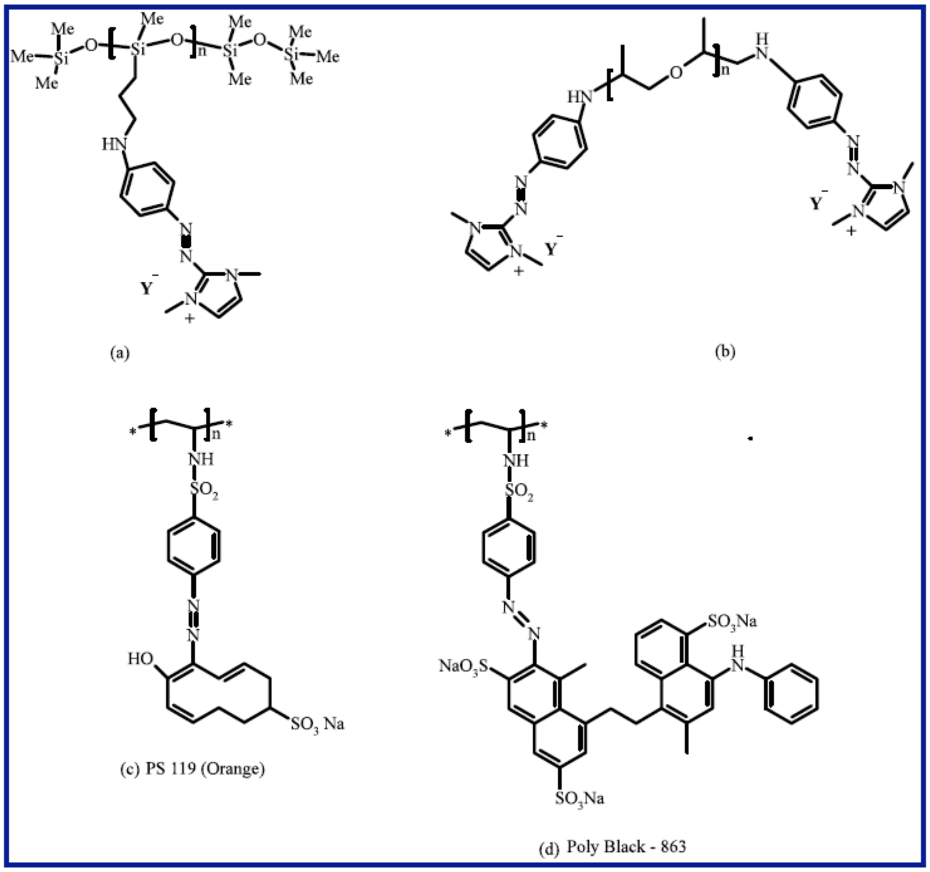


Figure 2: Incompatibility / Insolubility of Organic Functional Actives with Commercial SE Blends.



(a)

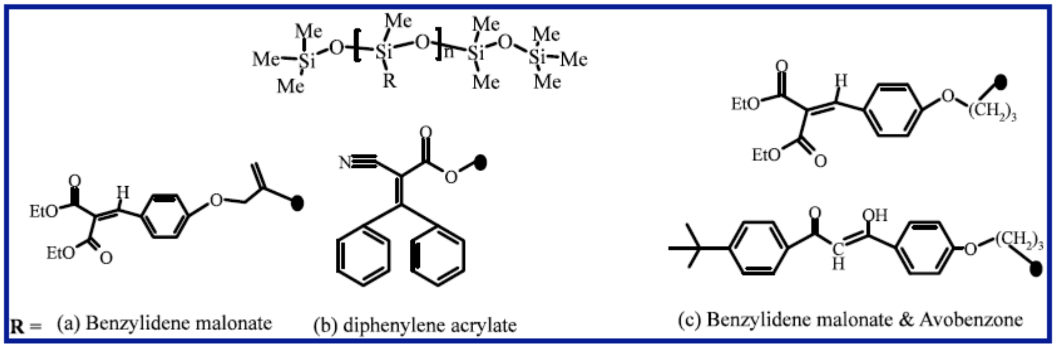
(b)

(c) PS 119 (Orange)

(d) Poly Black - 863

Figure 3: Organomodified Polymeric (OMPs) Colorants (**a**) Polysiloxane and (**b**) Polyetherimine based azo dyes (**c**) PS 119 – Orange (**d**) Poly Black 863.

humans/animals and be environmentally friendly. Recent studies revealed that parabens [21-23] showed toxicity and endocrine toxicity due to permeation through skin. Studies showed that parabens retaine in the epidermis and dermis [21,24,25]; followed by UV induced skin damage [26]. However, the extent of active skin penetration depends on their concentrations in the formulations. Hence these actives are used at optimal / safe levels. The sunscreen/dye molecules having Mol. Wt. above 500 Dalton [27] are expected remain non-permeable to skin. Hence organomodified polymers (OMPs) showing UV absorbing [28-30] and colorant [31-34] properties were developed to enhance safety profile of above organic actives. Chemically, OMPs contain inert polymer backbone with covalently anchored antibacterial agents, sunscreens or dye molecules. Chemical structures of select organomodified polymeric (OMPs) colorants and sunscreens are shown in Figures **3**, **4** respectively. Polymeric antimicrobials [35,36] have been designed to be effective against microorganisms and due to their large molecular weight they do not penetrate into the



R = (a) Benzylidene malonate (b) diphenylene acrylate (c) Benzylidene malonate & Avobenzone

Figure 4: Organomodified Polymeric (OMPs) Sunscreens (**a**) Benzylidene malonate polysiloxane [Parsol SLX, by DSM]; (**b**) Undecylcrylene dimethicone [HallBrite PSF, Hallstar] (**c**) Polymeric sunscreens (Unilever).

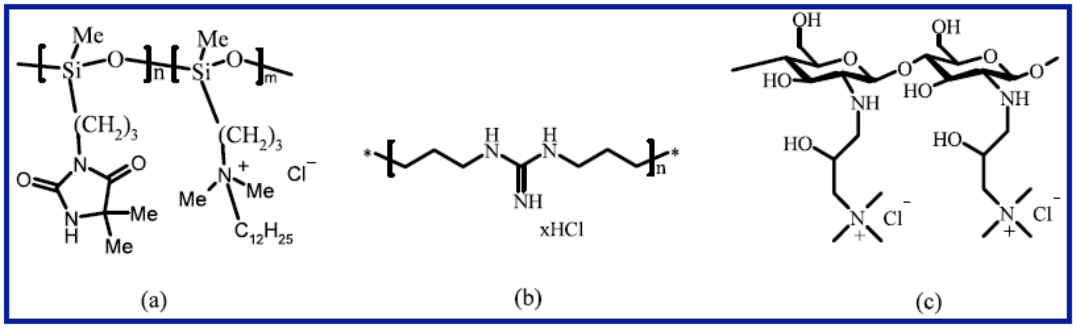


Figure 5: Organomodified Polymeric (OMPs) Antibacterial Agent (**a**) hydantoinyl/quat polysiloxane (**b**) polyhexamethyleneguanidine hydrochloride (**c**) 3-trimethylammonium-2-hydroxypropyl-N-chitosan.

skin. Thus, they could improve the safety profile of broad-spectrum antibacterials. As seen in Figure **5**, poly-(hexamethylen-guanidinium-chloride), poly-[2-(2-ethoxy)-ethoxyethyl)- guanidinium-chloride] [37-40]; 3-trimethylammonium-2-hydroxypropyl-N-chitosan [41,42] have been developed as polymeric antimicrobials or antifungal agents.

As seen in Figure **6**, we developed organomodified silicone elastomers (OMSEs) for enhanced compatibility and superior deposition of actives on the skin [28,29] or hair [31,32]. OMSEs contain covalently linked functional actives on the cross-polymeric dimethicone backbone. As described above, sunscreen / dye – silicone incompatibility leads to poor photoprotection performance. The compositions containing OMSEs showed superior performance when compared with compositions containing free sunscreens and commercial SE blends. Water-in-oil and oil-in-water compositions were prepared using OMSE itself as the formulation base (Figure **6**). Following section describes detail synthesis and performance of organomodified silicone elastomers (OMSE) blends.

BROAD SPECTRUM ORGANOMODIFIED SILICONE ELASTOMER (OMSE-1) BLEND – 1

OMSE-1 was designed by anchoring reactive UV absorbing chromophores onto dimethicone crosspolymer chains [29]. As seen in Figure **7**, 4-

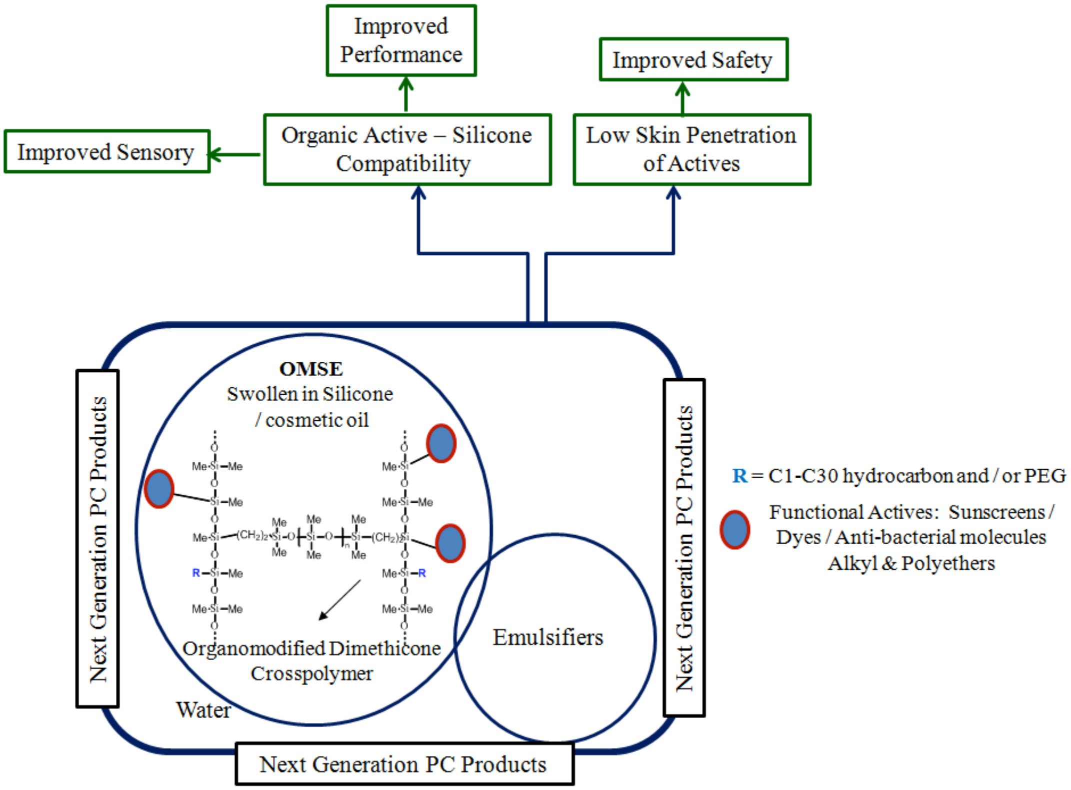


Figure 6: Next Generation OMSEs. Organic actives – Sunscreens / dye molecules.

allyloxy acetophenone was synthesized by reacting 4-hydroxy acetophenone with allyl chloride in the presence of dry potassium carbonate-acetone dispersion. 4-allyloxy, 4-t-butyldibenzoylmethane (reactive UVA chromophore) was synthesized by reacting 4-allyloxy acetophenone with 4-tert-butyl methyl benzoate in the presence of sodium methoxide. Next, allyloxy benzaldehyde was synthesized by reacting 4-hydroxybenzaldehyde with allyl chloride in the presence of dry potassium carbonate-acetone dispersion. 4-allyloxy benzylidene malonate (reactive UVB chromophore) was synthesized by reacting alloxy benzaldehyde with diethyl malonate in the presence of piperidine /acetic acid and benzene.

As seen in Figure **8**, broad spectrum UVA and UVB absorbing organomodified silicone elastomer [29] (OMSE) blend -1 was synthesized by reacting 4-allyloxy, 4’-t-butyl dibenzoylmethane (reactive UVA chromophore), 4-allyloxy benzylidine malonate class (reactive UVB chromophore); divinyl terminated polydimethylsiloxane (VTP); octadecene, polyethylene glycol monoallyl ether (Clariant) with poly(methylhydrogen)-co-(dimethyl)siloxane copolymer in the presence of Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution and dry toluene at 110°C for ~5 hours. The product was obtained in a gel form (covalently attached with UV chromophores). The toluene was distilled off under vacuum and replaced with decamethyl cyclopentasiloxane (D_5). The extent of viscosity was tuned by changing crosslinking density and amount of poly(ethylene glycol) and stearyl (C18) segments.

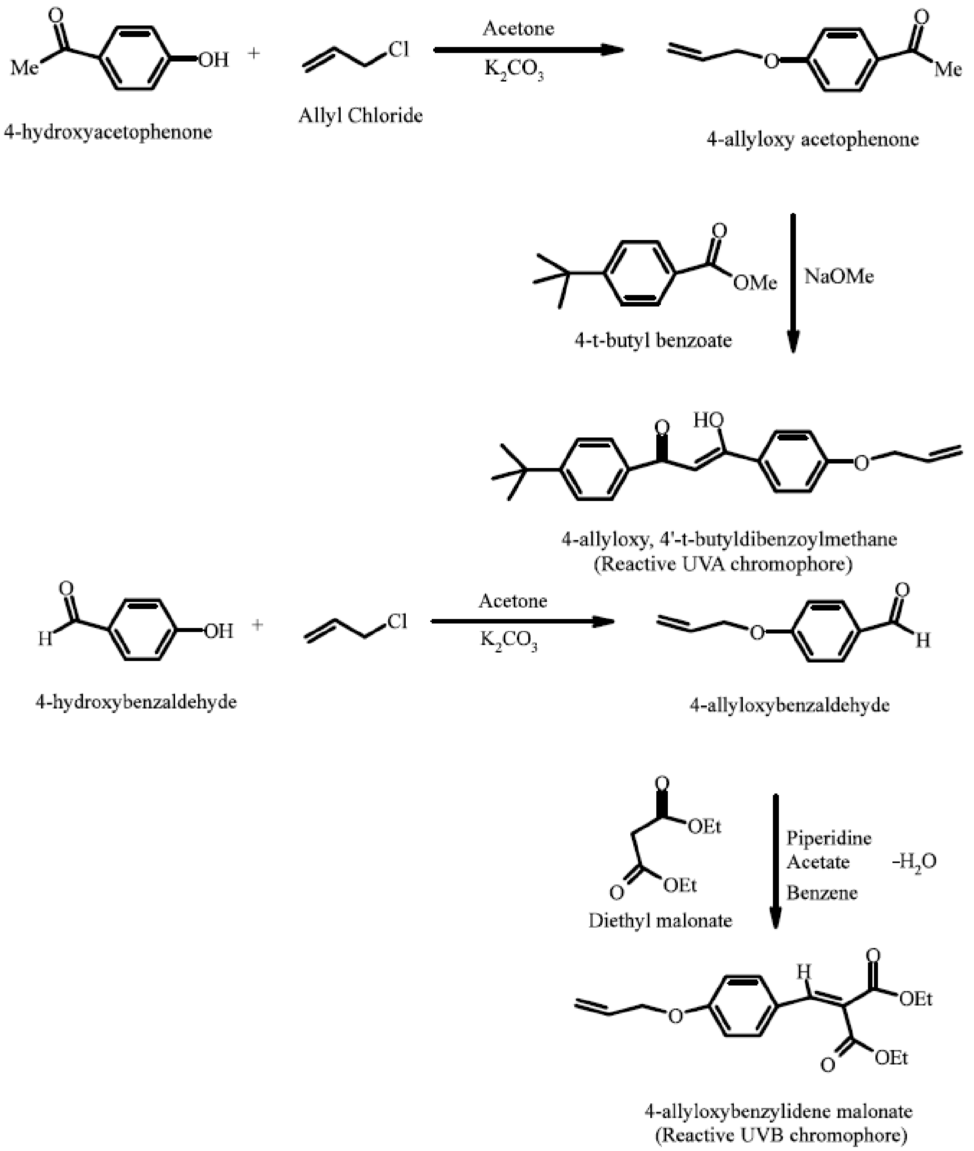


Figure 7: Synthesis of reactive UVA & UVB derivatives chromophores.

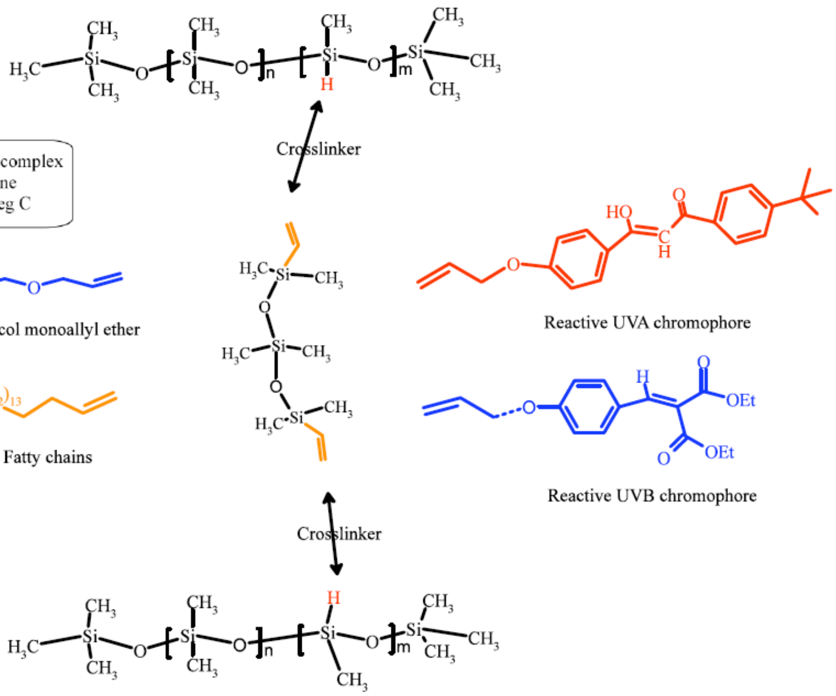


Figure 8: Synthesis of Broad Spectrum Organomodified Silicone Elastomer Blend - 1 for skin.

General chemical structure of organomodified silicone elastomer (OMSE) blend – 1 is shown in Figure **9**.

As seen in Figure **10**, various solutions of (OMSE) blend – 1 in toluene (500 – 1500 ppm) showed broad spectrum absorption in both UVA and UVB region; indicating presence of covalently attached chromophores. This broad spectrum UV efficacy was compared with the UV efficacy of 10 ppm free 4-allyloxy, 4’-t-butyl dibenzoylmethane (reactive UVA chromophore), 4-allyloxy benzylidene malonate (reactive UVB chromophore) respectively.

Broad Spectrum Organomodified Silicone Elastomer (OMSE-1) Blend – 2

Hair undergoes photodamage [43,44] when exposed to harmful sun radiations [45-47]. Hair colorants also undergo photo fading or photodegradation during the sun exposure. These colorants also produce significant amount of reactive oxygen species (ROS), which trigger various oxidative damaging chemistries in hair. Hence sun-exposed hair or colorants initiate photo-oxidation of amino acids / disulfide linkage inside cuticle [44] example; R-S-S-R → R-S-S-OH + R-OH → R-S-SO_2H → R-S-SO_3H → RSO_3H + H_2SO_4. UV mediated disruption of the

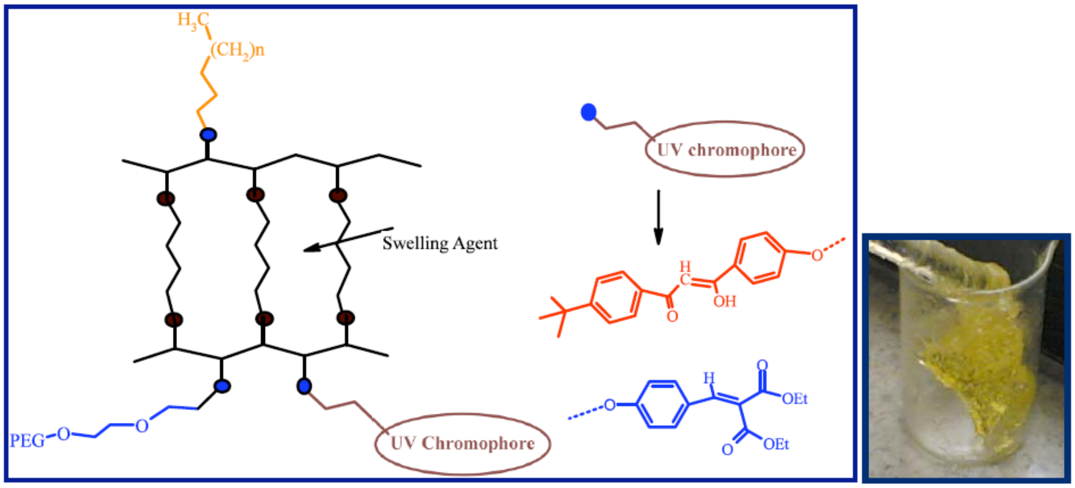


Figure 9: Chemical Structure of OMSE Blend – 1.

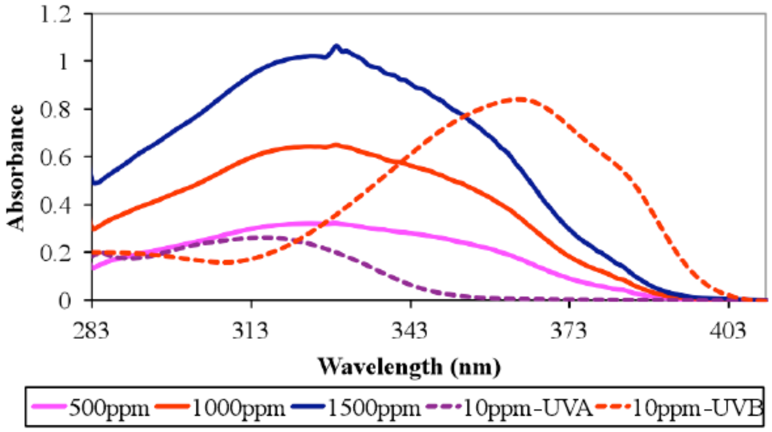


Figure 10: UV absorption efficacy of OMSE Blend - 1.

disulfide linkages triggers mechanical damage, which make hair dull, rough-textured, dry and brittle [43, 44]. It is therefore important to protect both hair and its dye/colorant using organic sunscreens, along with minimal production of ROS. However, hair care products would thrive upon selective deposition of sunscreen and/or photostable colorants through conditioner or shampoo based products. Polysiloxane copolymer grafted with methoxycinnamic acid ester & cationic alkoylamidopropyl dimethyl ammonium groups [30], benzylidene malonate polysiloxane (Parsol SLX from DSM) [48,49], cinnamidopropyltrimonium chloride (IncroquatUV283 from Croda) & Polyamide-2 (Solamer GR8 from Nalco) are known to deposit on hair effectively through water based rinse compositions.

We designed new broad spectrum organomodified silicone elastomer blends – 2/3/4, suitable for depositing sunscreen / colorants, through conditioner / shampoo based system. The quaternary ammonium groups present on the OMSE blend – 2; facilitated deposition of sunscreens or colorant molecules on the hair surface. As seen in Figure **11**, the *OMSE Blend – 2* was synthesized [29] by reacting 4-allyloxy, 4'-t-butyl dibenzoylmethane (reactive UVA chromophore), 4-allyloxy benzylidene malonate class (reactive UVB

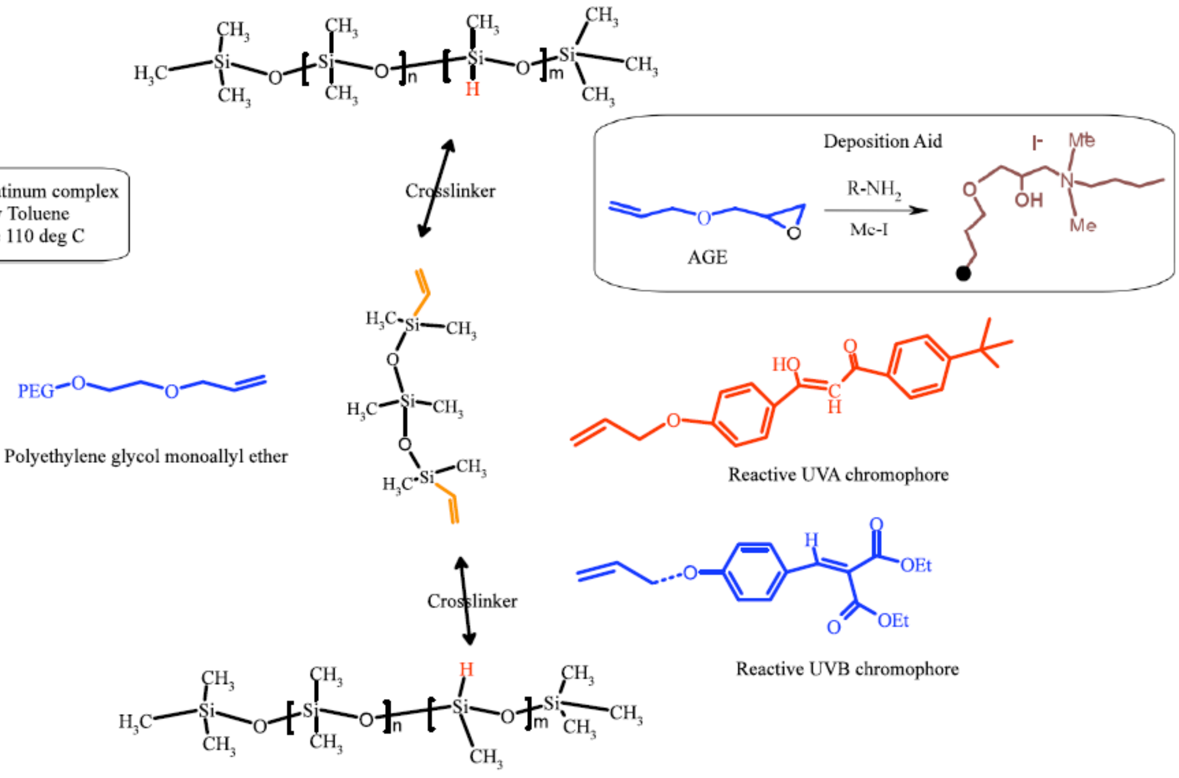


Figure 11: Synthesis of Broad Spectrum OMSE Blend – 2 for hair.

chromophore); divinyl terminated polydimethylsiloxane (VTP); polyethylene glycol monoallyl ether (Clariant); with poly(methylhydrogen)-co-(dimethyl)siloxane copolymer in the presence of platinum catalyst and dry toluene at 110°C, for ~5 hours.

The chromophore level present on the silicone elastomer was tuned to maintain about 20% un-reacted Si-H. The gel was further homogenized and analysed using FTIR to determine free Si-H groups. The remaining Si-H groups were further reacted with allyl glycidyl ether (AGE). After complete removal of AGE, the epoxy modified gel was reacted with butyl amine ($C_4H_9NH_2$) followed by quaternization using methyl iodide (Me-I). General chemical structure of organomodified silicone elastomer (OMSE) blend – 2 is shown in Figure **12**.

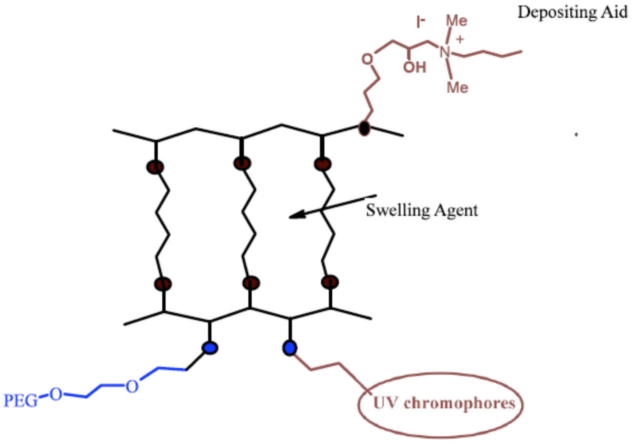


Figure 12: Chemical Structure of Organomodified Silicone Elastomer -2 blend for deposition through conditioner/shampoo.

As seen in Figure **13**, 250 and 500 ppm solution of (OMSE) blend – 2 showed broad spectrum absorption in both UVA and UVB region indicating presence of covalently attached UVA and UVB absorbing chromophores.

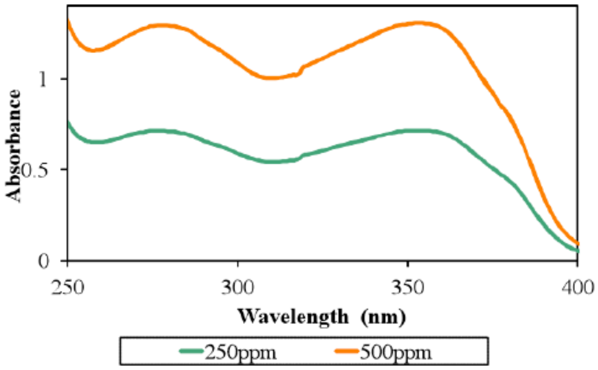


Figure 13: UV absorption efficacy of OMSE Blend – 2.

Next, OMSE Blend - 2 were deposited on the hair surface *via* water based rinse method. 10 g of hair swatches were washed with hot water for 30 minutes. It was further washed with conventional shampoo (without conditioners) and rinsed with distilled water. 2 g of hair sample was placed in 2 gpl solution of OMSE blend – 2. The mixture was stirred for 10 minutes. The hair sample was rinsed in water twice and air dried. As seen in Figure **14**, the deposited OMSE - 2 was extracted in methanol (50 mL) and detected using UV spectrophotometer.

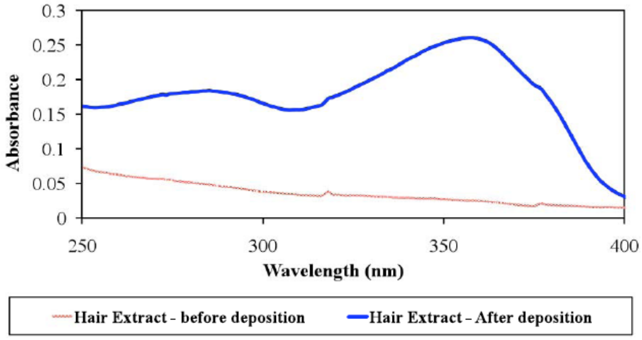


Figure 14: UV absorption spectra of methanolic extract of hair (**a**) before and (**b**) after OMSE-2 deposition.

Based on the calibration data; about 2.6 mg of OMSE blend – 2 was found to be deposited on hair surface [29]. (*Note: This amount was quantified based on calibration plot of polymer in methanol at different concentration).* Control rinse solution containing free UVA and UVB chromophores did not show any deposition.

Broad Spectrum Organomodified Silicone Elastomer (OMSE) Blend – 3 / 4

Superior solubilization photostable colorant / pigments were achieved *via* covalent attachment to silicone crosspolymer [31,32]. As seen in Figure **15**, mono and diallyloxy curcumin [31] was synthesized by reacting curcumin with allyl bromide in the presence of dry sodium methoxide / acetone dispersion. Next, 2-allyloxy,1-hydroxyanthraquinone [32] was synthesized by reacting 1,2-dihydroxyanthraquinones with allyl bromide in the presence of dry potassium carbonate / acetone dispersion.

Organomodified elastomer (OMSE) blend – 3 or 4 were synthesized by reacting mono and diallyloxy curcumin [31] or 2-allyloxy 1-hydroxyanthraquinone [32] respectively, divinyl terminated polydimethylsiloxane (VTP); octadecene, polyethylene glycol monoallyl ether (Clariant) with poly(methylhydrogen)-co(dimethyl) siloxane copolymer in the presence of platinum catalyst

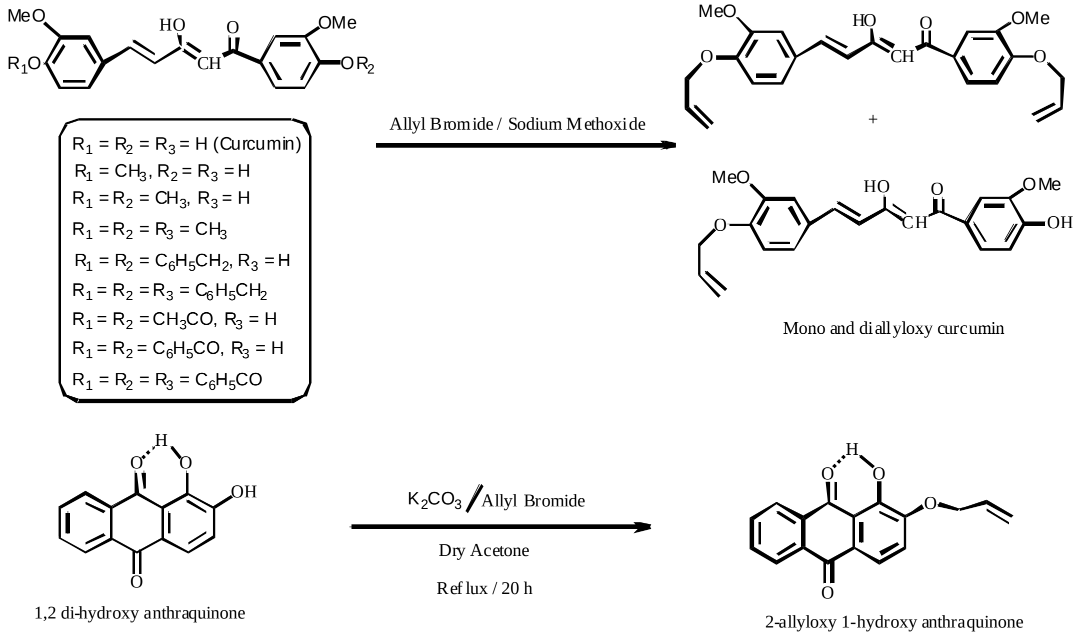


Figure 15: Synthesis of reactive colorant chromophores.

(Sigma-Aldrich) and dry toluene at about 110°C for ~5 hours.

Photoprotection efficacy of OMSE blend - 3 and 4 (shown in Figure **16**) were tested using standard transmittance method. The apparatus design is shown in Figure **17**. Control mix containing free curcumin (10%, control-1) / hydroxyanthraquinone (6%, control-2) and commercial silicone elastomer gel (DC 9040) were prepared. Control mix or *OMSE blend – 3 or 4* (~ 2 mg/cm^2) was applied on a transpore tape (3M) using standard procedure [50]. The intensity of simulated solar atlas sun lamp was adjusted to 500 W/m^2. The transpore tape/sample was dried for 15 minutes prior to UV exposure. The transmitted energy / spectrum were recorded through the OMSE blend - 3 or 4 or control mix films present on the transpore tape; using spectroradiometer (International Lights Model: RPS 900-R). The transmitted energy / spectrum obtained through the transpore tape were used as the background data.

As seen Figure **18**, OMSE blend – 3/4 blends i.e. curcumin / hydroxyanthraquinone modified silicone elastomer gel showed superior broad spectrum protection indicating uniform distribution on the surface. In comparison control sample containing free curcumin / hydroxyanthraquinone and commercial silicone elastomer (DC 9040, Dow Corning) showed poor protection due to incompatibility of curcumin / hydroxyanthraquinone with silicone elastomer blend.

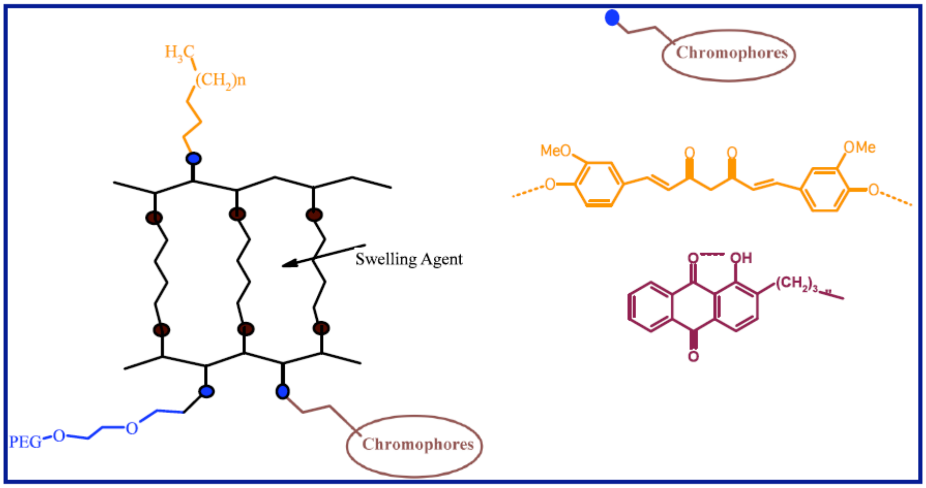


Figure 16: Chemical Structure of OMSE blend - 3 / 4.

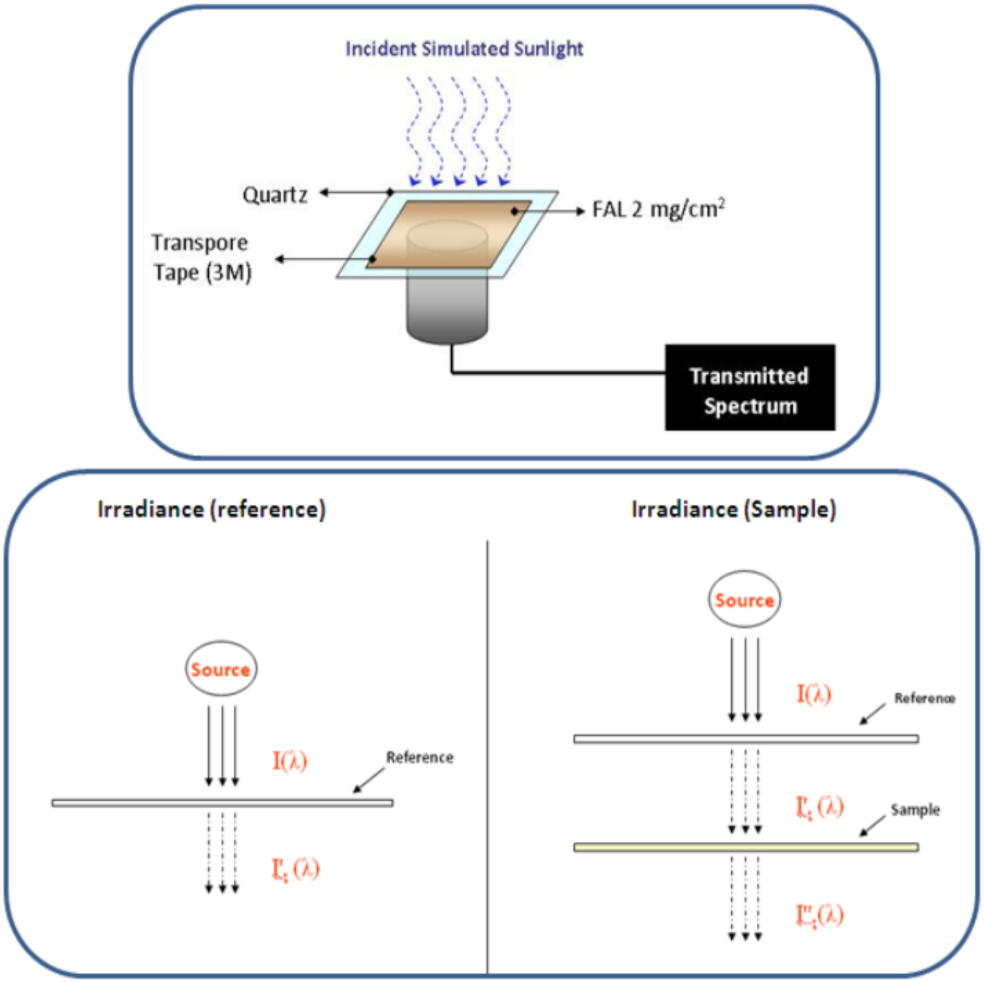
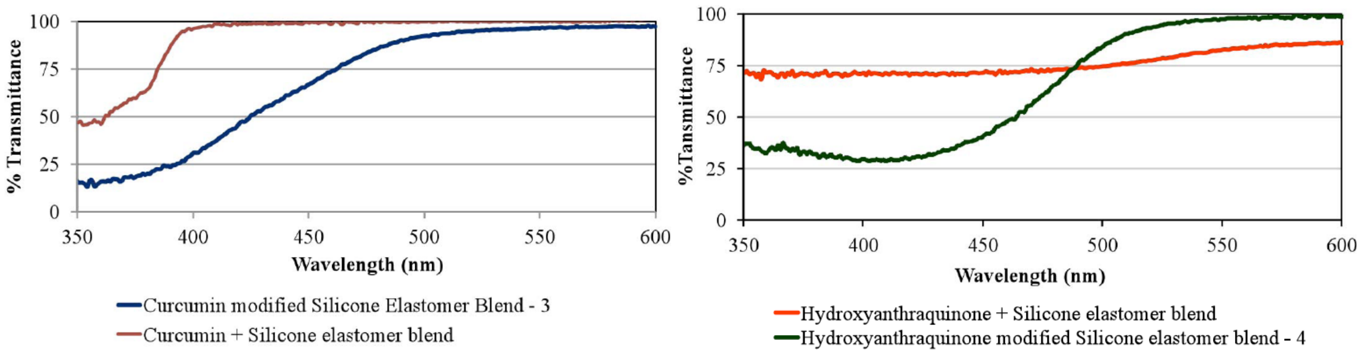


Figure 17: Quantification of transmitted energy through silicone elastomer blend 3 & 4.



(**a**) (**b**)

Figure 18: UV absorption efficacy of (**a**) OMSE Blend – 3 (Blue line) & Control-1 (Brown-line) (**b**) OMSE Blend – 4 (Green line) & Control-2 (Red-line).

We also used this method to evaluate photostability. OMSE blend – 4 film on a transpore tape was exposed to solar simulated sun light for 30, 60, 90 and 120 minutes and respective transmitted energy / spectrum were recorded. Figure **19** shows UV-Visible transmittance spectra of OMSE blend – 4 after exposure to 30, 60, 90 and 120 minutes of solar simulated sunlight. These transmittance spectra were compared with the spectrum obtained before exposure. The result indicated marginal change in UV-Visible transmittance efficacy of OMSE blend – 4 after exposure to 60 minutes of solar simulated radiation. We obtained superior photostability of OMSE blend – 4 for 120 minutes of solar simulated sun exposure.

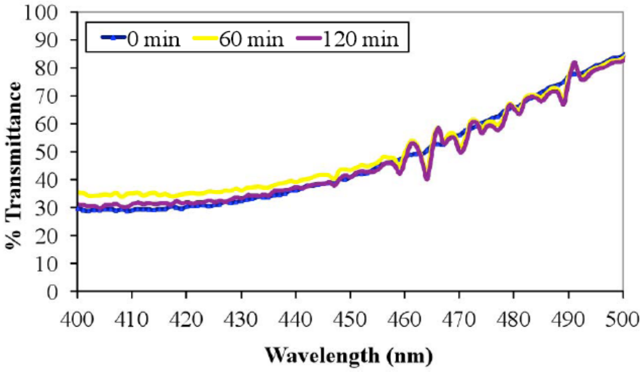


Figure 19: *In vitro* visible light protection efficacy of OMSE blend – 4 before (0) and after the 30, 60, 90 and 120 minutes of exposure to solar simulated sunlight.

SUMMARY

UV absorbing Organomodified silicone elastomer (OMSE) blends were synthesized by reacting alkenyl functional (a) sunscreen derivatives of avobenzone, benzelidine malonate, curcumin or hydroxyanthraquinone, a suitable crosslinker solubilizing (e.g. C_nH_{2n} i.e. alkyl) / emulsifying agents (e.g. polyether) with the poly(dimethyl)-co-(methylhydrogen)siloxane copolymer in the presence of platinum catalyst. OMSE showed superior performance over mixture of commercial dye/sunscreens and silicone elastomer blends due to uniform distribution of chromophores on the substrate surface. Covalently attached sunscreen / dye molecules on the cross-polymeric silicone backbone would show enhanced safety profile due to negligible possibility of penetration through skin.

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