

## Research Article

# Gel Based Sunscreen Containing Surface Modified TiO<sub>2</sub> Obtained by Sol-Gel Process: Proposal for a Transparent UV Inorganic Filter

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Inorganic UV filters, as titanium dioxide (TiO<sub>2</sub>), have become attractive because of their role in protecting the skin against the damage caused by the continuous exposure to the sun. However, their high refractive index, responsible for a white residue when applied on the skin, has led to the development of alternative inorganic materials, such as TiO<sub>2</sub> nanoparticles. Thus, the aim of this study was the development of transparent and stable gel formulations containing surface modified TiO<sub>2</sub> nanoparticles for application in sunscreens. Also, the physical and chemical properties of formulations containing TiO<sub>2</sub> nanoparticles were evaluated. The UV absorption spectroscopy analyses indicated that the formulations containing TiO<sub>2</sub> nanoparticles had a broad protection spectrum. The diffuse reflectance spectroscopy revealed that the use of PTSH surface modified TiO<sub>2</sub> nanoparticles improved the transparency of the sunscreen formulations compared to that containing commercial ones. The rheology analyses showed that the amount of nanoparticles incorporated in the formulations influences the gel-like or liquid-like behavior. The results showed that the surface modified TiO<sub>2</sub> nanoparticles are a promising innovative UV filter and the formulations containing these nanoparticles are interesting candidates for being used as sunscreen.

## 1. Introduction

The exposure to ultraviolet (UV) radiations can cause extensive damage to the skin, varying from sunburn and precocious aging to serious lesions such as skin cancers [1]. A manner to prevent skin cancers is the use of sunscreens that absorb, scatter, and/or reflect UVA and UVB radiations.

Substances that act as filters are classified into two groups: organic filters (chemical absorbers) and inorganic filters (physical blockers) depending on their mechanism of action. Among the inorganic filters, zinc oxide (ZnO) and titanium dioxide (TiO<sub>2</sub>) are the mostly used. They interact with the incident solar radiation by reflecting, absorbing, or scattering it [2].

Inorganic filters are currently being used because they are stable when exposed to UV radiation, they are not able to

penetrate the skin, they do not cause damage to the epidermal cells, and they present low allergenicity. Furthermore, they offer a wide spectrum of protection and provide efficacy against UV-induced skin damage [3–5].

However, even considering all of their advantages, the formulations containing opaque inorganic oxides show low cosmetic acceptability. The high refractive index may produce on the skin a particularly white appearance because of the light reflection mechanism, which makes the product with a visual considered unpleasant by the consumers [3, 5, 6].

The solution to solve this problem may be the development of smaller particles of titanium dioxide. It could be reached by modifying the obtainment process and minimizing the interactions with the visible light (becoming transparent when applied on the skin). Lot of studies, including

of industries, are seeking for alternatives to micronize or sub-micronized these inorganic filters, making them in nanoscale. The nanoscale inorganic filters present advantages, such as the facility in their incorporation on cosmetic formulations and, also, the pleasant sensorial aspect of the final formulation [7–11].

To obtain TiO<sub>2</sub> nanoparticles modified and with desirable size, different synthesis routes have been assessed. One of these routes is the sol-gel process that occurs by hydrolysis followed by condensation reactions and the precursors are generally alkoxides dissolved in organic solvents [12]. In this route, the structural features of nanoparticles achieved are strictly related to the control of the parameters involved in the sol-gel reactions [13], such as temperature and time. Moreover, the use of surface modifier agents, such as complexing compounds, is an emerging strategy. In this way p-toluene sulfonic acid (PTSH) has been demonstrated to be a good candidate to the modification of TiO<sub>2</sub> nanoparticles surface, allowing the control of size, shape, and aggregation of TiO<sub>2</sub> nanoparticles obtained by the sol-gel process [13, 14]. Structural analysis of samples prepared with different hydrolysis ratio and acidity ratio demonstrated that PTSH involves TiO<sub>2</sub> surfaces preventing the nanoparticles aggregation and allowing the achievement of transparent and high concentrated suspensions [14, 15].

The commercial formulations of sunscreens are usually presented in the form of gel, cream, spray, or other topical products [16]. The gels are advantageous over other excipients because they are less greasy and are constituted by a transparent base, being preferred by people of oily skin. The gels are obtained through natural or synthetic hydrophilic thickeners, such as polymers and copolymers [17, 18].

Despite the several gel favorable characteristics, the incorporation of inorganic filters, even though microparticulated, is a challenge because the inorganic filters tend to easily aggregate, resulting in an undesirable opaque aspect [18]. Accordingly, the present research studied how the surface modified titanium dioxide nanoparticles may facilitate the incorporation of them into a gel excipient.

During the development of formulations containing inorganic UV filters, the stability and physical characteristics of them must be considered to ensure their efficacy and safety. Also, the characteristics of the excipient, the result of combination between filters, and the stability of the formulation must also be considered [19]. The physical stability of a formulation can be evaluated by rheology. The prediction of instability processes is possible due to alterations in some parameters such as viscosity, solubility, creaming facilitation, and hydration of polymers [20]. Therefore, it is important to understand the rheological behavior during handling, mixing, processing, transporting, storage, and application of such formulations [20].

The purpose of this study was the development of transparent and stable gel formulations containing surface modified TiO<sub>2</sub> nanoparticles and the study of their physical-chemical properties, such as diffuse reflectance, absorbance, and rheological aspects related to the photoprotection activity of the sunscreens.

## 2. Materials and Methods

**2.1. Materials.** p-Toluene sulfonic acid, PTSH (Vetec Química Fina), titanium tetraisopropoxide, Ti(O<sup>i</sup>Pr)<sub>4</sub> (Sigma Aldrich), isopropanol (Merck), Carbopol 940 (Labor), and triethanolamine (Oxiten) were used as received, without further purification. Commercial TiO<sub>2</sub> microparticles (Sachtleben, Krefeld, Germany) were used to compare with TiO<sub>2</sub> nanoparticles synthesized via sol-gel process.

**2.2. TiO<sub>2</sub> Nanoparticles Synthesis.** The TiO<sub>2</sub> nanoparticles with surface modified were prepared by the sol-gel method earlier described [15]. Previously an aqueous solution of PTSH was prepared and subsequently a solution of Ti(O<sup>i</sup>Pr)<sub>4</sub> in isopropanol in a dry chamber. The PTSH solution was added into the solution of titanium isopropoxide under continuous stirring at room temperature. The amounts of water and PTSH used during the synthesis were calculated from the molar ratio relative to Ti ( $H = [H_2O]/[Ti]$ ) and  $P = [PTSH]/[Ti]$ ), being the nominal hydrolysis ratio (H) equal to 1 and the nominal acidity ratio (P) equal to 0.05.

To obtain the xerogel (powder), the earlier prepared sol was dried at 100°C until complete evaporation of the solvent. Subsequently, the powder was macerated.

**2.3. Preparation of Sunscreen.** The sunscreen formulations were prepared using Carbopol 940 (2% dispersion) as polymer of the gel cosmetic excipient and the TiO<sub>2</sub> xerogel was used as inorganic filters. Firstly, the polymer was homogenized in water and then the TiO<sub>2</sub> xerogel was added under stirring. Hereafter, the pH was adjusted with the addition of triethanolamine 50% (w/w) until reaching pH between 5 and 7.

### 2.4. Physical-Chemical Characterization

**2.4.1. UV Absorption Spectroscopy.** The measurement of the spectral absorption of UV radiation (290–400 nm) through a substrate before and after application of the sunscreen was performed. The formulation containing 10 and 15% of TiO<sub>2</sub> xerogel P0.05H1 and the formulation containing 15% of the commercial TiO<sub>2</sub> were measured. The gel formulation without TiO<sub>2</sub> particles was, also, measured.

The substrate used was a 3M® Transpore tape applied on clean 2 mm thick quartz slides. Approximately 2 mg/cm<sup>2</sup> of the formulation was uniformly spread using a finger glove. The samples were allowed to air dry and the plates were placed inside the UV-2000S Ultraviolet Transmittance Analyzer. Before running the sample, the blank slide was loaded into the sample holder for the blank scan. Irradiation took place at nine different areas of the substrate. The experiment was performed in triplicate and the spectral data were processed by the Labsphere software where the critical wavelength was calculated.

**2.4.2. Diffuse Reflectance Spectroscopy.** The diffuse reflectance spectra of the formulations were carried out in the Cary spectrophotometer equipped with a HARRICK attachment

TABLE 1: Sunscreen formulations developed varying components and concentrations (%).

Formulations	% TiO <sub>2</sub> P0.05H1	% commercial TiO <sub>2</sub>	% Carbopol 940 (2% dispersion)	% H <sub>2</sub> O
Formulation 1	2.5	—	10	87.5
Formulation 2	5	—	20	75
Formulation 3	10	—	25	65
Formulation 4	15	—	40	45
Formulation 5	20	—	45	35
Formulation 6	25	—	50	25
Base formulation	—	—	50	50
Commercial TiO <sub>2</sub> formulation	—	15	50	35

diffuse accessory. The same amount of each sample was placed in the sample holder and the surface of the samples was homogenized using a glass slide. The reflectance measurements of the formulations containing commercial TiO<sub>2</sub> and xerogel TiO<sub>2</sub> were referenced to the MgO optical standard in the visible spectrum (400–700 nm). The results were obtained in percentage of reflectance ( $R\%$ ).

**2.4.3. Rheology.** Rheological tests were performed using a stress controlled rheometer AR2000ex (TA Instruments, Surrey, England) in flow mode with a cone-plate geometry (40 mm) and gap of 200  $\mu\text{m}$ . Steady shear rate sweep tests (upward and downward) were conducted over a range of shear rates from 0 to 200  $\text{s}^{-1}$ . Rheological measurements in the oscillatory shear mode were performed using the same geometry. In dynamic frequency sweep tests, firstly, the linear viscoelastic region (LVR) was identified through an oscillatory stress sweep at a fixed frequency (1 Hz). Secondly, samples were subjected to frequency sweep tests at 25°C over the frequency range of 0.6 to 100 rad/s, at a constant stress (1 Pa). The elastic modulus ( $G'$ ) and loss modulus ( $G''$ ) were determined using the program Rheology Modifier Advantage Control AR.

### 3. Results and Discussions

**3.1. Synthesis of Nanoparticles and Development of the Sunscreen Gel Formulation.** Table 1 presents several sunscreen formulations developed with various concentrations of TiO<sub>2</sub> xerogel, obtained by sol-gel process and commercial TiO<sub>2</sub>.

The polymer used in the formulations was Carbopol 940, a strongly coiled polymer when dried. After its dispersion in water its chains are hydrated and tightly knotted by hydrogen bonding, exhibiting a pH in solution around 3.0. Thus, an alkali, that is, triethanolamine, is applied for obtaining the maximum thickening effect (pH between 6 and 10). A uniform gel structure is obtained when the chain of the polymer is kept uncoiled due to the repulsive forces between two adjacent negatively charged groups along the polymer chain [21]. In this way, the gel structure stability was strongly influenced by the presence of charges in solution. The TiO<sub>2</sub> nanoparticles were modified by PTSH and present negative charges in their surface as showed in our previous study [22].

Table 1 shows the maximum concentration of TiO<sub>2</sub> that was incorporated in the gel based formulations.

Figure 1 shows the visual aspect of (a) commercial TiO<sub>2</sub> powder, (b) TiO<sub>2</sub> xerogel nanoparticles powder, (c) sunscreen formulation with commercial TiO<sub>2</sub>, (d) sunscreen formulation with TiO<sub>2</sub> xerogel nanoparticles, and (e) and (f) these last two formulations, respectively, applied in a surface. It can be observed that nanoparticles obtained by sol-gel process (b) presented finer powder when compared to the commercial TiO<sub>2</sub> used (a), improving its dispersion into the formulations and, probably, also, the stability of the sunscreens. Figure 1 also shows that the formulation containing TiO<sub>2</sub> xerogel nanoparticles (f) appears more homogeneous and transparent when applied to a surface, differing from the formulation containing commercial TiO<sub>2</sub> (e), which produces a more whitish residue. This difference could be attributed to the transparency promoted by the PTSH surface modifier that can prevent the particles aggregation in the formulation.

Figure 2 presents the scheme of the Carbopol 940 chain coiled before neutralization and the behavior of the inorganic filters nanoparticles with and without charges into the gel chain after neutralization. The inorganic nanoparticles are surrounded by negative charges, which prevent their aggregation, forming a uniform system. By the other side, the unmodified nanoparticles are tightly aggregated due to the insufficient charges on their surface. In addition, unmodified nanoparticles can be synthesized using methodologies that do not ensure homogeneous size and shape, leading to the formation of heterogeneous system, which affects the photoprotection activity of the sunscreen formulation.

**3.2. UV Absorption Spectroscopy.** Figure 3 shows the absorbance spectra of the sunscreen formulations with 10 and 15% of P0.05H1 TiO<sub>2</sub> nanoparticles, 15% of commercial TiO<sub>2</sub> particles, and also the gel based formulation without TiO<sub>2</sub> nanoparticles in order to compare the absorption activity of the samples. It is noteworthy that the PTSH modified TiO<sub>2</sub> nanoparticles and commercial TiO<sub>2</sub> particles are solely responsible for the UV protection in the formulations analyzed in this study. The gel based cosmetic formulation prepared with Carbopol 940 without TiO<sub>2</sub> does not affect the absorption of UVB and UVA radiation, presenting absorbance about 0 in this spectral range. Two important pieces of information can be extracted from the absorbance



FIGURE 1: Photographs of (a) commercial  $\text{TiO}_2$  powder, (b)  $\text{TiO}_2$  xerogel nanoparticles powder, (c) sunscreen formulation with commercial  $\text{TiO}_2$ , (d) sunscreen formulation with  $\text{TiO}_2$  xerogel nanoparticles, and (e) and (f) these last two formulations, respectively, applied to a surface.

spectra: the shape of the absorbance spectra, which points out the protection capability in different spectral regions, and the amplitude of the spectra, which indicates the protection degree [23]. It can be observed that the higher the concentration of  $\text{TiO}_2$  nanoparticles is, the higher the

absorbance intensity throughout UVA and UVB range is, and thus the higher the protection of the sunscreen formulation against UVA and UVB radiations is. The absorbance intensity of the formulation containing commercial  $\text{TiO}_2$  particles is higher than the other containing PTSH modified  $\text{TiO}_2$

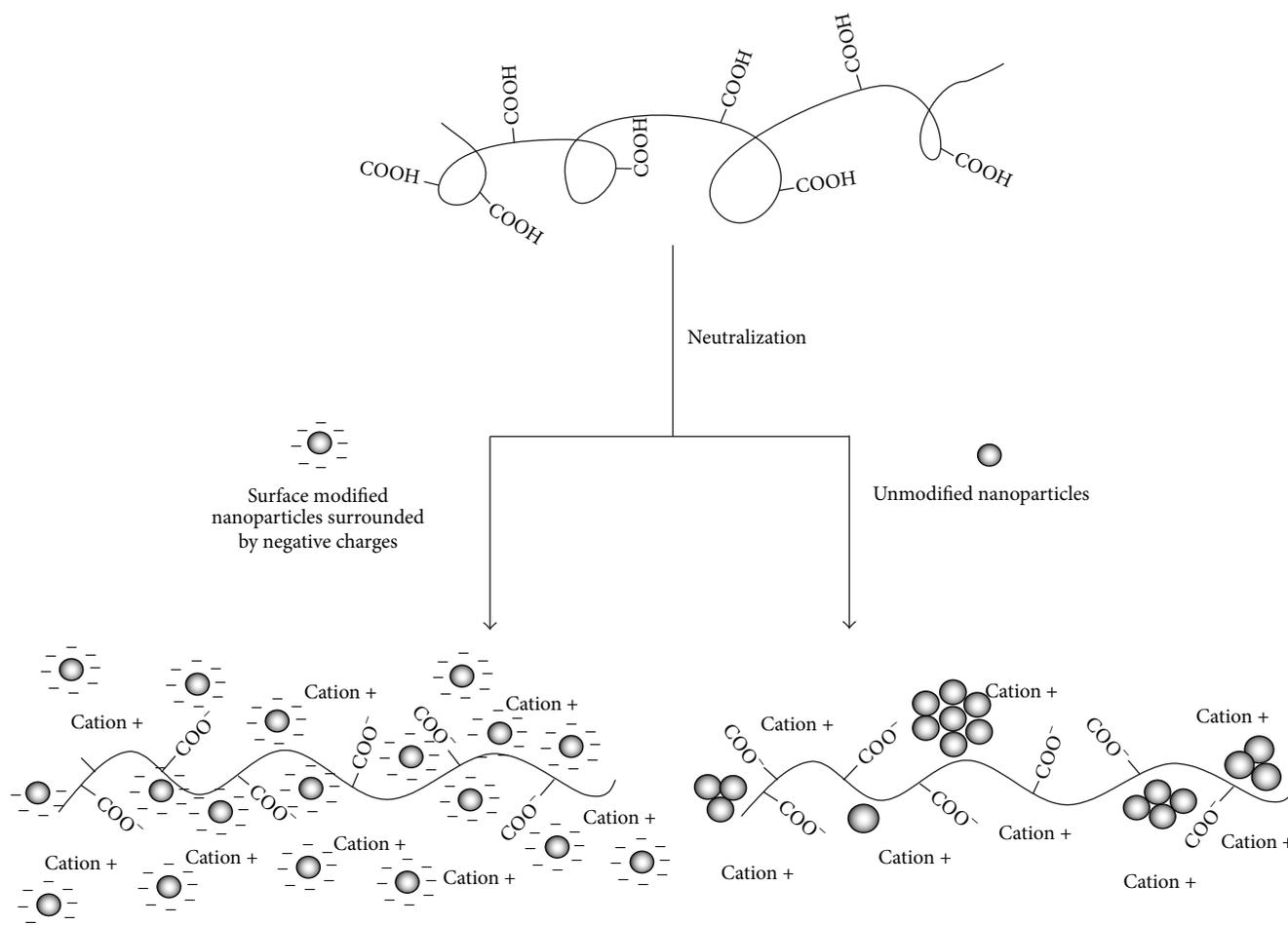


FIGURE 2: Scheme of the Carbopol® 940 chain coiled before neutralization and the behavior of the inorganic filter nanoparticles with and without charges into the gel chain after neutralization.

nanoparticles. According to Yang et al. this behavior was not expected once nanosized particles usually absorb more UV radiation than submicrometer-size particles [24].

Among the *in vitro* methodologies used to evaluate the efficiency of sunscreen protection, Diffey proposed the critical wavelength ( $\lambda_c$ ) method which studies the absorbance spectrum reduced to a single index by means of UV substrate spectrophotometry [25].  $\lambda_c$  is determined when the area under the spectrum from 290 nm (the approximate lower wavelength limit of terrestrial sunlight) to  $\lambda_c$  is 90% of the integral of the absorbance spectrum from 290 to 400 nm [26]. Figure 3 appoints also the  $\lambda_c$  at 384 nm of the sunscreen formulations containing 15% and 10% of P0.05H1 TiO<sub>2</sub> nanoparticles.  $\lambda_c$  of both formulations were higher than 370 nm; thus, the formulations are classified as broad-spectrum protection [26]. In this case, there are no significant differences between the UVA (320 to 400 nm) and UVB (290 to 320 nm) intensity absorption. This behavior was not expected once TiO<sub>2</sub> is absorbed mainly in the UVB range; thus, the PTSH surface modified TiO<sub>2</sub> nanoparticles present broad-spectrum protection. It is important to highlight that

TiO<sub>2</sub> acts as inorganic filter blocking UV radiation physically by scattering and reflecting the incoming radiation and chemically by absorbing it [27]. Therefore, the UV absorbance measurements evaluate only the physical activity of TiO<sub>2</sub>.

Mie law gives a general relation on the diffusion of radiation, while Rayleigh relates the radius dispersion to the intensity at a given wavelength, for very small particles. According to Rayleigh, the radiation scattered can be inversely proportional to the fourth power of the wavelength. It is possible to conclude that when the particles are smaller, the scattering of UV radiation is better, in a wavelength below 400 nm [28, 29].

**3.3. Diffuse Reflectance Spectroscopy.** Diffuse reflectance spectroscopy has been used to evaluate the transparency of several materials in the visible spectrum [30]. Figure 4 presents the visible diffuse reflectance spectra of sunscreen formulations containing commercial TiO<sub>2</sub> and PTSH surface modified TiO<sub>2</sub> nanoparticles. Formulations containing TiO<sub>2</sub> nanoparticles displayed lower reflectance (about 45%) in the

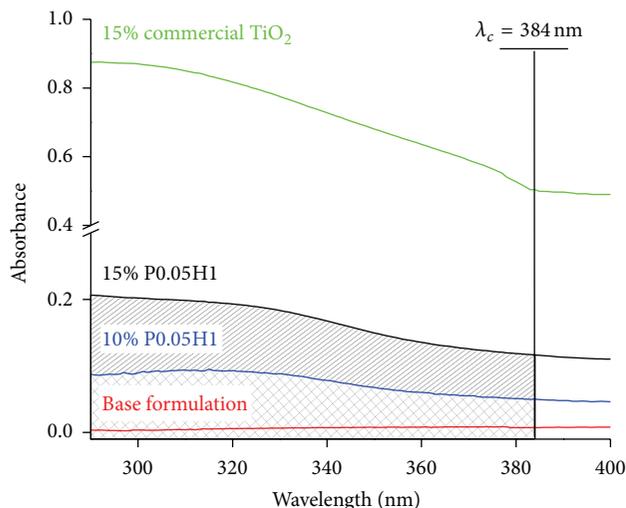


FIGURE 3: Absorbance spectra of sunscreen formulations with 10% and 15% of P.0.05H1  $\text{TiO}_2$  nanoparticles, 15% of commercial  $\text{TiO}_2$  particles, and without  $\text{TiO}_2$  nanoparticles (base formulation).

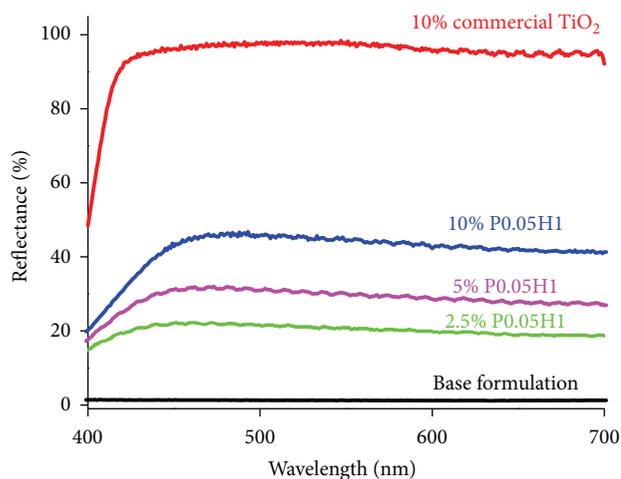


FIGURE 4: Diffuse reflectance spectra in the UV-Visible region of formulations containing 2.5%, 5%, and 10% of P.0.05H1  $\text{TiO}_2$  nanoparticles and 10% commercial  $\text{TiO}_2$  formulation.

visible region compared with the formulation containing the same concentration of commercial  $\text{TiO}_2$  (about 100%).

The lower the percentage of reflectance is, the greater the transparency of the formulation is. A difference in the transparency among the samples can be observed, which decreases with the increase of  $\text{TiO}_2$  nanoparticles concentration. The formulation with 10%  $\text{TiO}_2$  nanoparticles has almost half of the reflectance of the formulation with the same concentration of commercial  $\text{TiO}_2$ . Thus, the use of PTSH surface modified  $\text{TiO}_2$  nanoparticles improved the transparency of the sunscreen formulations compared to that containing commercial ones. This is mainly due to the repulsion of negative charges which surrounds the PTSH modified  $\text{TiO}_2$  nanoparticles, as shown in Figure 2, that prevents the nanoparticle aggregation. In this way, it is

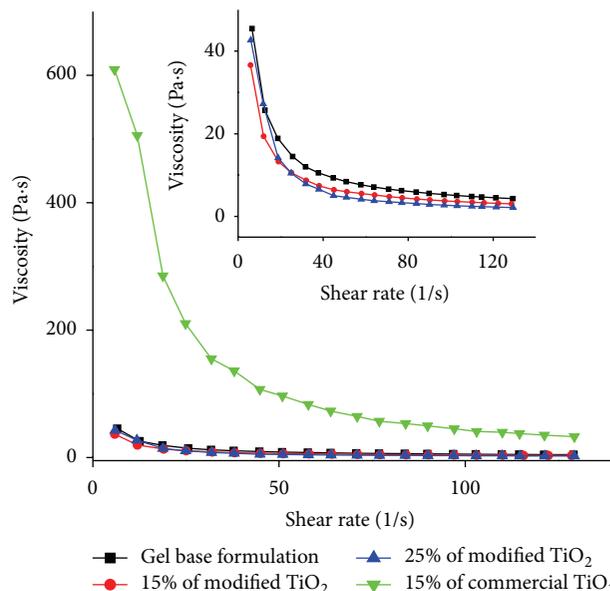


FIGURE 5: Shear viscosity as a function of shear rate of gel based formulation and, also, formulations containing 15% of commercial  $\text{TiO}_2$  and 15% and 25% of P.0.05H1  $\text{TiO}_2$  nanoparticles. The insert displays a zoom in the formulations without commercial  $\text{TiO}_2$  nanoparticles.

possible to incorporate the same amount of nanoparticles obtaining a more transparent and desirable system than the commercial ones.

**3.4. Rheology.** Figure 5 shows the shear viscosity as a function of shear rate of the gel based formulation and, also, of the formulations containing 15% of commercial  $\text{TiO}_2$  and 15% and 25% of P.0.05H1  $\text{TiO}_2$  nanoparticles. The rheograms showed that the addition of modified inorganic UV filters to the base formulation did not change the properties of it; however, 15% of commercial  $\text{TiO}_2$  caused a meaningful increase in viscosity.

A reduction in the viscosity of the formulations was verified as a function of shear rate. These results suggest that the addition of these inorganic UV filters led to changes in the viscosity of the formulation compared to the concentration of nanoparticles incorporated. This is a common behavior [31] of sunscreens containing a higher percentage of inorganic UV filters powders added directly to the vehicle, resulting in flocculation in the formulation.

Figure 6 presents the storage ( $G'$ ) and loss moduli ( $G''$ ) as a function of frequency of (a) gel based formulation and, also, the formulations containing (b) 15% of commercial  $\text{TiO}_2$  and (c) 15% and (d) 25% of P.0.05H1  $\text{TiO}_2$  nanoparticles. In the gel based formulation (Figure 6(a)) it is possible to observe  $G'$  higher than  $G''$  and frequency independent, indicating the predominance of the consolidated elastic structure. This behavior is due to cross-linking between the gel polymer chains, as expected for gels. In the formulations containing 15% of commercial  $\text{TiO}_2$  (Figure 6(b)) and 25% of P.0.05H1

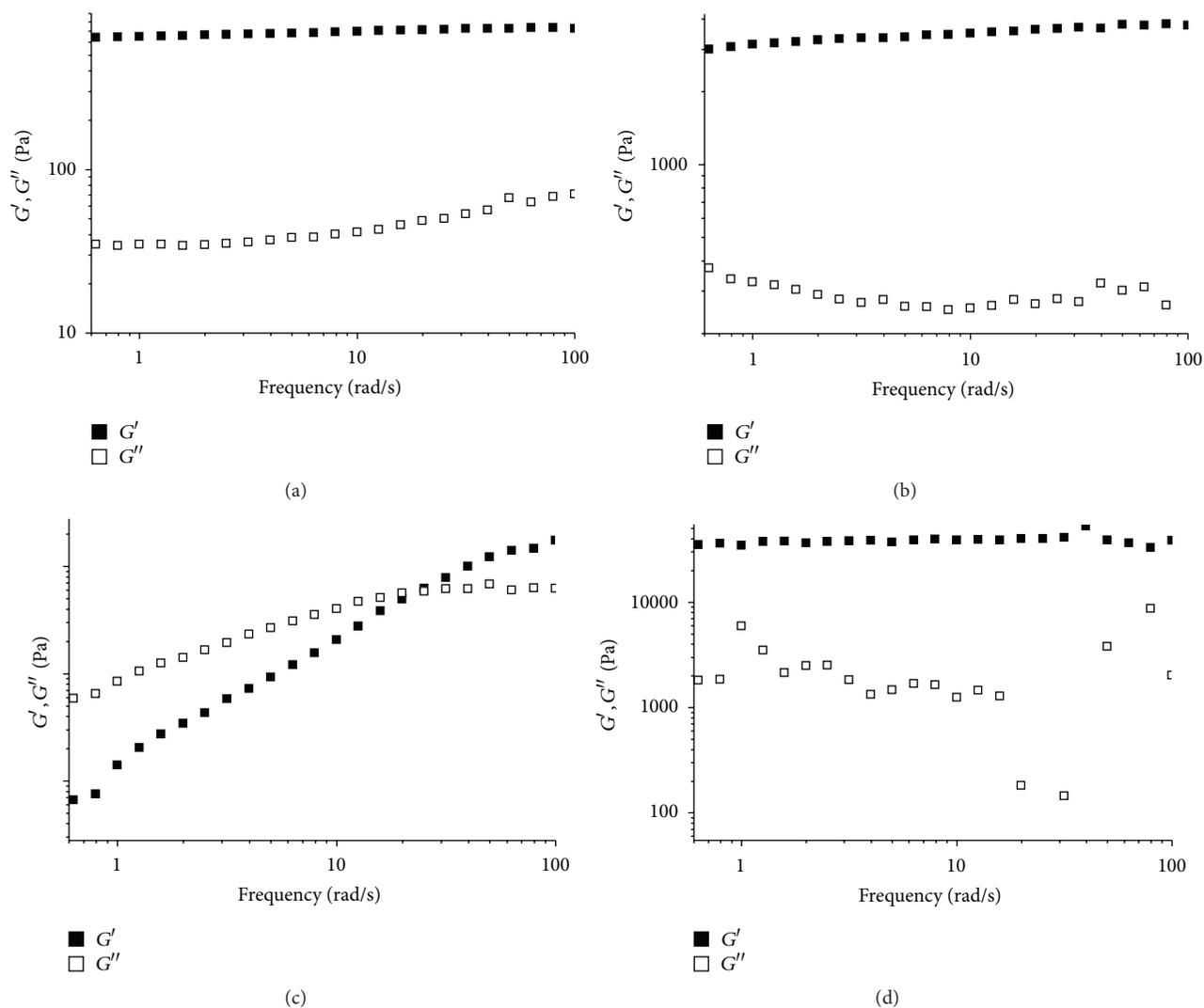


FIGURE 6: Storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of frequency of the (a) gel based formulation and, also, formulations containing (b) 15% of commercial  $\text{TiO}_2$  and (c) 15% and (d) 25% of P0.05H1  $\text{TiO}_2$  nanoparticles.

$\text{TiO}_2$  nanoparticles (Figure 6(d)), both moduli remain constant with the increase of the frequency and  $G'$  is higher than  $G''$ . This frequency independence was also observed in Carbopol 940 gel without nanoparticles, demonstrating that the nanoparticles do not affect the cross-linking of the polymer chains. Different behavior was observed for the formulation containing 15% of P0.05H1  $\text{TiO}_2$  nanoparticles (Figure 6(c)). A crossover between  $G''$  and  $G'$  occurs above 25 rad/s, showing more gel-like behavior with increasing frequency. This result indicates that 15% of P0.05H1  $\text{TiO}_2$  nanoparticles were a disadvantage for the cross-linking of the polymer chains. The same behavior could be expected with increasing nanoparticles concentration, because the surface charges also increase. However, the concentration increase to 25% xerogel was accompanied by a slight increase of  $G'$ , which shows favoring of the cross-linked system. This is also confirmed by the great dispersion of  $G''$  values. In the commercial  $\text{TiO}_2$  formulation case,  $G'$  and  $G''$  are

frequency independent, indicating that it does not affect the links between the polymer chains. Although the commercial  $\text{TiO}_2$  was added in the same concentration of the xerogel (15%), which prevented cross-linking of the gel, this sample is independent of frequency and possibly does not have sufficient surface charge to disfavor cross-linking of the polymer chains.

#### 4. Conclusions

We developed broad-spectrum photoprotection gel based formulations containing surface modified  $\text{TiO}_2$  nanoparticles. The purpose of obtaining more transparent formulations compared to commercial ones was achieved as showed by diffuse reflectance spectra. As expected, commercial  $\text{TiO}_2$  without surface modification seems to flocculate showing accentuated viscosity compared to PTSH surface modified  $\text{TiO}_2$  nanoparticles. The gel based formulation and the

formulations containing 15% and 25% of TiO<sub>2</sub> nanoparticles presented storage module higher than loss module as function of frequency underling the predominance of the consolidated elastic structure, which is characteristic from the cross-linking between the gel polymer chains. However, the formulation containing 15% of PTSH TiO<sub>2</sub> nanoparticles presented a crossover between loss module and storage module as function of frequency indicating a disadvantage for the cross-linking of the polymer chains. The surface modified TiO<sub>2</sub> nanoparticles obtained by sol-gel process presented promising properties for transparent sunscreen with broad-spectrum photoprotection.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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