

# The Effect of Pigments on the Stability of Silicone/Montmorillonite Prosthetic Nanocomposites

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**ABSTRACT:** The purpose of this investigation was to evaluate the protection provided to silicone by pigments, such as dry earth pigments. In addition, the effect of nanostructured and organically modified montmorillonite fillers on the overall behavior of reinforced systems was explored. To obtain relevant data and, furthermore, to reveal possible mechanisms of structural changes that could influence silicone stability, pure and reinforced silicon elastomers were mixed with various colorants and studied for their stability to accelerating aging, during the exposure to UV radiation and humidity. A number of tests were run such as, Attenuated Total Reflectance, Fourier Transform Infrared Spectroscopy (ATR-FTIR), Thermogra-

vimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Tensile measurements. Swelling in toluene and color tests were also carried out. The experimental results showed that the UV aging of silicone elastomers results in chain scission and cross-linking rather than formation of oxygen containing groups. The main conclusion of this work is montmorillonite acts as a significant reinforcement and protects silicone against degradation during exposure to UV irradiation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2659–2667, 2010

**Key words:** polysiloxanes; nanocomposites; clay; aging; thermal properties; mechanical properties

## INTRODUCTION

Silicone elastomers are widely used in many biomedical applications, such as facial prostheses, production of catheters, stents, cardiac leads, respiratory aids, etc.<sup>1</sup> These materials present a wide service temperature range, good optical clarity, weather resistance, low chemical reactivity, and low toxicity. However, their properties may change as a result of aging, eventually to the point where the material is no longer capable for satisfying its function. Therefore, when selecting a particular formulation for engineering applications, it is important to recognize and identify the principle factors involved in degradation for prevention and stabilization efforts in material design issues.

Aging takes place at normal ambient temperatures and increasing the temperature accelerates the rate of underlying degradation process. There are also synergistic effects that must be considered, e.g., materials resistant to UV light alone or to moisture alone, may fail when exposed to the combined action of UV light and moisture, which is most likely to happen under normal conditions of exposure.<sup>2</sup>

Furthermore, silicone biomaterials often operate under conditions where factors such as fatigue, creep, stress relaxation, and chemical attack are significant and, obviously, may interfere with degradation mechanisms.

Normally, silicone rubbers are resistant to irradiations since the energy needed to break the Si—O bond is high. However, the formation of intermolecular cross-links upon irradiation has been reported and stimulated further studies on vulcanization of silicones.<sup>3</sup> Polydimethylsiloxane (PDMS), for instance, is well known to cross-link when exposed to high-energy radiation producing gasses, such as hydrogen and methane, as a result of this radiation damage.<sup>4</sup>

Regarding their physicochemical behavior, it is well known that unfilled elastomers have relatively poor mechanical properties, but silica-reinforced silicone composites present significant improvement of mechanical properties due to hydrogen bonding between the silicone chains and silanol groups present on the surface of the silica filler.<sup>5</sup> However, no clear trends on the role of filler can be found in the literature. In some cases, their use evidenced a stabilizing effect against oxidation, whereas in other cases fillers induced undesirable effects that catalyze degradation.<sup>6</sup>

As far as the mechanism of aging is concerned, it is thought that in conventional silicone micro-composites the observed changes can be attributed to a

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combination of irreversible chemical changes taking place in the bulk polymer network as well as to reversible physical changes that occur at the polymer-filler interface.<sup>7</sup>

Delor-Jestin et al.<sup>8</sup> found that PDMS shows relatively poor stability against photoaging, as well as to thermal and nitric acid aging. Photoaging and thermal aging in oxygen proceed via a radical-based mechanism, and the main steps probably include hydrogen abstraction from the methyl group followed by cross-linking reactions. Nitric acid reacts with the Si—O bond and both, scission and cross-linking reactions possibly occur. Surface treatment of the filler and the addition of phenolic stabilizers were shown to result in an improvement of indoor durability.

A long term study of natural aging for different types of silicone elastomers was carried out by Oldfield and Symes.<sup>9</sup> The best performance was shown by a heat-vulcanized silicone rubber containing iron oxide as pigment, with a less than 10% reduction of tensile strength and 25% decrease of the elongation at break, whereas the hardness presented an increase of no more than 4% after 20 years exposure at Australian sites. More lately, Lewicki et al.<sup>10</sup> studied the aging behavior of montmorillonite reinforced hydroxyl terminated PDMS using degradative thermal analysis. Their results indicated that significant chemical changes take place within the above nanocomposites upon aging, such as acid catalyzed hydrolysis, chain backbiting, and subsequent recombination of chain ends, causing significant restructuring of the polymer-filler network. This leads to the formation of an improved network, that incorporates less free chain ends and is intimately associated with the filler particles, having an overall structure closer to the thermodynamic ideal.

Taking into account the above presented literature survey, some formulations of condensation type silicon elastomer were prepared and studied in this work. The purpose of this investigation was to evaluate the effect of colorants on the stability of silicone elastomer, in combination with nanoparticles of montmorillonite used as reinforcement. To collect the necessary data and explore possible mechanisms of structural changes that probably could influence silicone stability, various tests and measurements were run and the obtained results were discussed.

## EXPERIMENTAL

### Materials

Silanol terminated PDMS, grade DMS-S31 (Gelest, Karlsruhe, Germany) was the silicon base elastomers used in this work and the reaction system also a tetrapropoxysilane (TPOS, Aldrich, Steinheim, Germany) crosslinker as well as dibutyl tin dilaurate (Aldrich, Steinheim, Germany) as catalyst.

**TABLE I**  
Main Characteristics of the Nanoclay Used in This Work

Cloisite® 30B	
Organic modifier: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\   \\ \text{CH}_3 - \text{N}^+ - \text{T} \\   \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$
	Where: T is tallow (~ 65% C18, ~ 30% C16, ~ 5% C14)
Modifier concentration	90 meq/100 g clay
Weight loss in ignition	30%

Yellow (P215) and green (P227) dry pigments supplied from Principality Medical (Newport, UK) were used as colorants at concentrations of 0.2% w/w. According to the supplier's specifications, the chemical composition of these pigments is ferric oxide powders. Commercial montmorillonite clay under the trade name Cloisite® 30B supplied by Southern Clay Products (Rockwood Clay Additives GmbH, Moosburg, Germany) was also used as reinforcing nanofiller. The main characteristics of the above clay are presented in Table I.

### Preparation of nanocomposites

Silicone elastomer (10 g) was weighed in a glass beaker, and then 1 g of crosslinker and 0.1 g of accelerator were added, followed by the appropriate amount of montmorillonite filler. After stirring with a glass rod to homogenize the mixture, efficient dispersion of nanoparticles was achieved by sonicating with an ultrasound probe, the PDMS, and the appropriate amount of clay for 8 min, at room temperature. The cross-linking system was then added and dispersed into the mixture, and the samples were cast into molds and cured at room temperature for 12 h, to produce sheets of 3.5 mm thickness.

### Accelerated aging process

Samples from the above sheets were exposed to accelerated aging conditions, using the appropriate weatherometer chamber, type QUV-Weathering Testers (Q-Panel, Lab Products, Cleveland, OH).

The aging tests were run according to ASTM D 4587-01 and ASTM D 4329-99. Specimens were exposed to repeated cycles consisting of combined exposure to UV-radiation and damp heating. UV-radiation was produced using a lamp type UVB-313. Water in the bottom of the test chamber was heated, to fill the chamber with hot vapor and create 100% humidity at 50°C.

The specific set-up of the accelerated aging procedure performed in this work was:

- i. 8 h UV-radiation with a power of 0.76 W/(m<sup>2</sup> nm) at 60 ± 2.5°C.
- ii. 4 h water-condensate at 50 ± 2.5°C.

### Attenuated total reflectance Fourier transform infrared spectroscopy

For the determination of changes in the chemical structure of the OMMT/PDMS composites, Attenuated total reflectance (ATR) measurements were performed, using a Nicolet (Madison, WI) Fourier transform infrared spectroscopy (FTIR) spectrometer (model Magna IR 750; DTGS detector; Nichrome source; beamsplitter; KBr). A total of 100 scans were applied with a resolution up to 4 cm<sup>-1</sup>. Spectra were obtained at the ATR mode using a standard ZnSe 45° flat plate Contact Sampler (12 reflections; Spectra-Tech, Stamford, CT) on which samples of PDMS were placed. The obtained spectroscopic data were treated by employing the standard software (OMNIC 3.1, Nicolet).

All spectra were smoothed using the “automatic smooth” function of the above software, which uses the Savitsky-Golay algorithm (5-point moving second-degree polynomial). After the as described procedure, the baseline was corrected using the “automatic baseline correct” function.

### Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were run in a DSC 1 model Mettler Toledo (Schwerzenbach, Switzerland) differential scanning calorimeter. Samples of ~ 10 mg were accurately weighed in an analytical balance and encapsulated in aluminum pans. All runs were conducted under nitrogen flow of 20 cm<sup>3</sup>/min to limit thermo-oxidative degradation. The samples were cooled from 30°C to -150°C at a rate of -10°C/min and remained at this temperature for 5 min to erase previous thermal history. After this treatment, the samples were heated from -150°C to 30°C at 5°C/min. The temperatures of glass transition ( $T_g$ ), crystallization ( $T_c$ ), and melting ( $T_m$ ) as well as the heat of fusion ( $\Delta H_m$ ), were calculated from the thermographs corresponding to the heating cycle.

### Thermogravimetric analyses

Thermogravimetric analyses (TGA) of OMMT/PDMS nanocomposites were performed with Mettler Toledo (Schwerzenbach, Switzerland) thermogravimetric analyzer (model TGA-DTA). The tests were run with samples of 10 mg at a heating rate of 10°C/min from 25°C to 700°C, in a nitrogen atmosphere.

### Tensile properties

Tensile tests were carried out according to ASTM D 412 specification in an Instron (model 4466, Bucks,

UK) tensometer, equipped with a load cell of maximum capacity of 10 kN, operating at grip separation speed of 100 mm/min. All measurements were run at 25°C.

### Swelling experiments

The solvent uptake of immersed PDMS nanocomposite samples was also measured at 25°C. Prewighed samples were immersed in toluene and at different time intervals, the swollen samples were rapidly blotted and reweighed to minimize evaporation of the absorbed toluene. Reweighing continued for a few days and the final weight of the swollen sample was recorded at the equilibrium state.

### Color tests

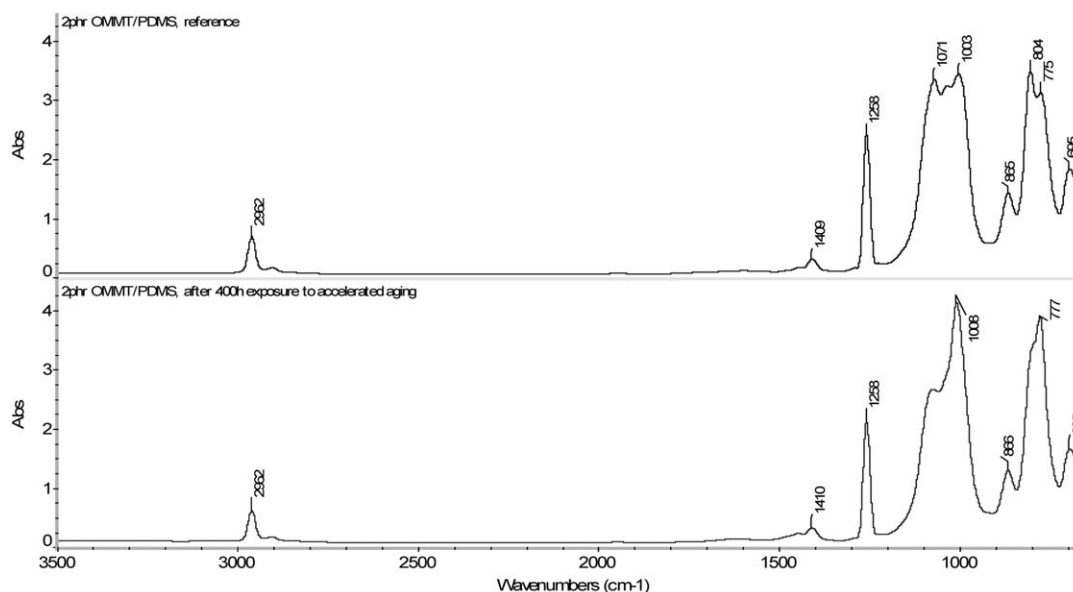
Color changes ( $\Delta E$ ) were examined with a micro-color tristimulus colorimeter (Micromatch plus, Sheen Instruments, Surrey, UK). This instrument is designated to measure color characteristics in the CIE LAB color system according to ASTM D 2244-68. The system is an approximately uniform color space using three parameters ( $L$ ,  $a$ ,  $b$ ) to define color, where ( $L$ ) measures the light-dark character, ( $a$ ) the red-green character, and ( $b$ ) the yellow-blue character. Color change can be calculated from the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a_L)^2 + (\Delta b_L)^2} \quad (1)$$

## RESULTS AND DISCUSSION

### Attenuated total reflectance fourier transform infrared spectroscopy

As already mentioned, the scope of FTIR-ATR measurements (Fig. 1) was to provide evidence about possible chemical interactions taking place during the accelerated aging procedure. Spectra of the irradiated specimens were obtained and compared with those of the same specimens before exposure. The peaks recorded for OMMT/PDMS nanocomposites are presented in Table II. No obvious differences were recorded in the spectroscopic patterns of the samples exposed to accelerated aging conditions as compared with those used as reference specimens, which suggests that the role of oxygen attack is negligible under the experimental conditions of this work. The weak absorption band appeared at 1610 cm<sup>-1</sup> may be associated with carbonyl groups present in the chemical structure of catalyst<sup>11</sup> and, therefore, this band cannot be further detected after extraction of samples in hot toluene that obviously results in leaching of the catalyst residue.



**Figure 1** ATR spectra of 2 phr OMMT/PDMS nanocomposites after 400 h exposure to accelerated aging in comparison with unexposed (reference) specimens.

Similarly, no significant concentration of oxygenated products was detected in the IR spectra obtained by Virlogeux et al.,<sup>12</sup> who tested high temperature vulcanized PDMS after 5000 h of accelerated photo-aging. However, an unexpected tendency to cross-linking upon aging was reported for these materials, even in the absence of a peroxide cross-linker. The above authors interpreted this phenomenon by assuming chromophoric impurities or double bonds present in the initial elastomer, as it was an industrial formulation.

The effect of environmental aging on medical grade silicones was also studied by Leslie et al.<sup>13</sup> The differences in absorbance found by FTIR analysis between the reference and aged samples were attributed to some competing processes, such as continued cross-linking alongside oxidation.

Chaudhry and Billingham<sup>11</sup> studied the effect of long term storage of a typical room-temperature vulcanized, foamed, and silica filled siloxane rubber both, in air and inert conditions up to 200°C. No significant chemical changes were found in these systems by IR spectroscopy, except the loss of peaks associated with the catalyst and its solvent.

### Differential scanning calorimetry

The thermal transitions were determined using the appropriate calorimeter (DSC) apparatus, capable of being cooled with liquid nitrogen and working in an atmosphere of flowing nitrogen. The obtained results are presented in Table III and show that pure PDMS and Cloisite 30B nanocomposites display melting point near  $-44^{\circ}\text{C}$ . During cooling, the PDMS crystallizes at  $-70^{\circ}\text{C}$ . From Table III and Figure 2, it is

observed that the accelerated aging does not have any obvious effect on the thermal response of pure PDMS. On the other hand, the incorporation of nanofiller seems to rise the glass transition temperature ( $T_g$ ), probably because of further restriction of chain mobility due to cross-linking or to decrease of free volume.<sup>14</sup> Interestingly, aging of the reinforced silicone results in a decrease of  $T_g$  that can be attributed to changes of the silicone elastomer structure, such as chain scission.

Table III shows that the melting enthalpy of reinforced silicone is lower than that of the pure elastomer and further drops upon aging. This effect might also be due to chain scission and cross-linking, since these changes are likely to reduce crystallinity. In fact, DSC is often used to investigate the crystallinity of polymers and since that cross-linking is well known to influence the ability of polymers to crystallize, the DSC curves after aging can be an indirect method for monitoring cross-linking. Delor-Jestin et al.<sup>8</sup> monitored the change in crystallinity of PDMS

**TABLE II**  
Assignment of IR Spectra of OMMT/PDMS Nanocomposites

IR region ( $\text{cm}^{-1}$ )	Description
775	$-\text{CH}_3$ rocking and $\equiv\text{Si}-\text{C}\equiv$ stretching in $\equiv\text{Si}-\text{CH}_3$
865	$\equiv\text{Si}-\text{O}$ stretching in $\equiv\text{Si}-\text{OH}$ , $\text{Si}-\text{CH}_3$ wagging and $\text{Si}-\text{C}$ symmetric stretching
1003–1071	$\text{Si}-\text{O}-\text{Si}$ asymmetric stretching
1258	$\text{CH}_3$ symmetric deformation in $\equiv\text{Si}-\text{CH}_3$
1409	$\text{CH}_3$ asymmetric deformation in $\equiv\text{Si}-\text{CH}_3$
2962	$\text{CH}$ stretching of $\text{CH}_3$

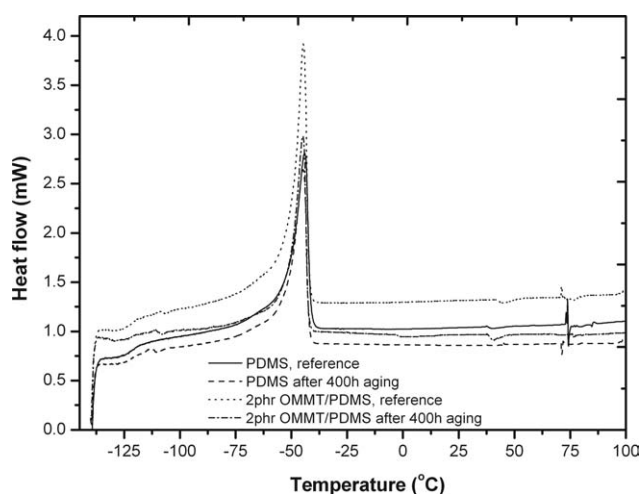
**TABLE III**  
DSC Analysis Data of OMMT/PDMS Nanocomposites After 400 h Exposure to Accelerated Aging in Comparison with Unexposed (Reference) Specimens

Samples	$T_m$ (°C)	$T_c$ (°C)	$T_g$ (°C)	$\Delta H_m$ (J/g)
PDMS, reference	$-44.46 \pm 0.47$	$-70.91 \pm 0.10$	$-121.41 \pm 0.81$	$27.56 \pm 0.28$
PDMS after 400 h of exposure	$-45.10 \pm 0.69$	$-70.90 \pm 0.09$	$-119.64 \pm 3.08$	$25.03 \pm 1.23$
2 phr OMMT/PDMS, reference	$-44.51 \pm 0.30$	$-70.14 \pm 0.24$	$-119.74 \pm 0.70$	$26.18 \pm 0.42$
2 phr OMMT/PDMS after 400 h of exposure	$-44.88 \pm 0.25$	$-71.97 \pm 0.34$	$-121.32 \pm 0.94$	$25.10 \pm 2.85$

during the time of irradiation, using a DSC device which allows to perform *in situ* photo-aging in DSC capsules. In PDMS samples with significant crystallinity (50%) photo DSC shows a fast decrease in crystallinity, suggesting cross-linking reactions. However, an opposite effect was observed for low crystallinity samples (15–20%) probably because of a stronger effect of scission reactions that may facilitate crystallization. According to Stevenson et al.,<sup>3</sup> electron irradiation in air increases the apparent crosslink density of silicon rubber and this effect is much stronger in the presence of silica filler, since links at the polymer-silica interfaces have been created. The observed decrease in crystallinity upon irradiation was related to the increase of apparent cross-link density that can limit segmental diffusion and crystallization. The above authors also reported an increase in the amplitude of relaxation process, associated with the glass transition near  $-125^\circ\text{C}$ , since a larger amount of amorphous phase is present due to the hindrance of crystallization behavior. The observed decrease in  $T_m$  with irradiation was attributed to the decrease of crystallite thickness as a result of the cross-linking reactions induced by irradiation.<sup>3</sup>

### Thermogravimetric analysis

The thermal stability of PDMS and 2 phr OMMT/PDMS nanocomposites was assessed by means of TGA. As it can be seen in Table IV, OMMT/PDMS



**Figure 2** DSC curves of OMMT/PDMS nanocomposites after 400 h exposure to accelerated aging in comparison with unexposed (reference) specimens.

systems present higher onset ( $T_{\text{onset}}$ ) and maximum rate ( $T_{\text{peak}}$ ) temperatures of thermal degradation, in comparison with unfilled PDMS. A decrease of about 9 and  $29^\circ\text{C}$ , for  $T_{\text{onset}}$  and  $T_{\text{peak}}$ , respectively, was recorded in the case of pure PDMS specimens, whereas a decrease of  $9^\circ\text{C}$  in both temperatures was observed for PDMS nanocomposites. Further to the above, pure and reinforced PDMS specimens exposed to accelerating aging for 400 h, present lower remaining weight in comparison with samples before aging. The above behavior can be again interpreted as a result of structural changes promoted by aging, that could include oxidation and chain scission. Since the FTIR analysis did not reveal any new oxygen containing groups in the obtained spectra, we can conclude that chain scission is the reaction taking place to some extent during UV aging of PDMS.

Improvement of the thermal stability of OMMT/hydroxyl terminated PDMS hybrids, being very close to those of aerosilica-filled silicone rubber, was reported by Wang et al.,<sup>15</sup> whereas an increase in char residue and promising flame retardant properties were determined when methyl vinyl silicone rubber nanocomposites containing 1 wt % montmorillonite were tested by thermogravimetric analysis.<sup>16</sup>

Ding and Liu<sup>17</sup> studied the effect of accelerated weathering upon the exposure of silicone sealants to heat ( $80^\circ\text{C}$ ) and ultraviolet radiation (UVA). They observed that TGA curves of the specimens exposed to weathering show a tendency to move to the high temperature region in comparison with the original material. This suggests that the post-cross-linking of sealants resulted in the increase of molecular weight and the small molecules have either been released or combined by cross-linking reactions during the aging procedure. Thus, the weight loss of the aged specimens shows a decrease.

TGA studies on PDMS/montmorillonite nanocomposites exposed to accelerated aging under dry  $\text{N}_2$  and air saturated with moisture, were carried out by Lewicki et al.<sup>10</sup> It was demonstrated that there was a significant increase of  $26^\circ\text{C}$  in the onset degradation temperature of unfilled elastomer under dry  $\text{N}_2$ . The Cloisite filled systems do not show such a spectacular increase under the same conditions. Moist air is inducing large increase in onset degradation temperatures, for both filled and unfilled PDMS systems exposed to aging. The mass analysis of the model

**TABLE IV**  
**TGA Data of OMMT/PDMS Nanocomposites After 400 h Exposure to Accelerated Aging in Comparison with Unexposed (Reference) Specimens**

Samples	$T_{\text{onset}}$ (°C)	$T_{\text{peak}}$ (°C)	Residue (%)
PDMS, reference	411.06 ± 4.98	462.35 ± 4.48	6.98 ± 0.46
PDMS after 400 h of exposure	402.63 ± 0.04	433.91 ± 8.61	4.23 ± 0.91
2 phr OMMT/PDMS, reference	455.14 ± 7.00	525.59 ± 6.60	10.19 ± 0.65
2 phr OMMT/PDMS after 400 h of exposure	446.22 ± 0.92	516.80 ± 1.60	9.48 ± 0.86

systems had clearly demonstrated a trend of progressive mass loss with aging, and the most significant levels were reported in the model nanocomposite systems aged in the air.

The incorporation of polyhedraloligomeric silsesquioxane (POSS) molecular silica, as a nanoscale modifier in polysiloxane, leads to significant improvement of mechanical properties of the elastomer but did not improve its thermal stability, as it was concluded from the TGA test results.<sup>7</sup>

### Tensile tests

The tensile characteristics, in terms of strength, modulus, and elongation at break are shown in Table V and Figure 3. The exposure to the combined action of UVB irradiation and humidity for 400 h, reduces to about 21% the tensile strength of pure PDMS, whereas the decrease of elongation exceeds 30%. Montmorillonite nanoparticles have a strong reinforcing effect on the mechanical properties of the unfilled silicone resin and, furthermore, seem to have a protective action against UV radiation for the reinforced specimens. From Table V, it can also be observed that incorporation of OMMT reinforcement significantly increases the elongation at break and, again, confines the observed decrease of this parameter during the aging process. Obviously, this effect can be attributed to the already mentioned structural changes of PDMS caused by aging. On the other hand, it seems that the property improvement due to OMMT nanofiller is very high overlapping any decrease due to UV aging.

Similarly, exposure of commercial maxillofacial silicones to accelerating aging in xenon ultraviolet light, at 90% relative humidity for 900 h, resulted in decreased or constant values of tensile strength.<sup>18</sup>

From the results of this study, we can conclude that the incorporation of montmorillonite particles

increases the apparent cross-linking density of silicone rubber during exposure to the accelerating aging conditions and, subsequently, the modulus of elasticity of the material.

Higher density of cross-links for silica-filled PDMS, in comparison with unfilled specimens, due to formation of links at the polymer-silica interfaces after electron irradiation, was also reported by Stevenson et al.<sup>3</sup> A further enhancement of the network density was obtained for surface treated silica fillers. On the other hand, the formation of higher number of cross-links is reasonable to restrict crystallization of PDMS, as it was confirmed by DSC, with obvious consequences to the mechanical properties of the elastomer.

Chien et al.<sup>5</sup> studied the changes of cross-linking density and chemical structure of silica-reinforced silicone composites due to aging in gamma radiation. Their results show that samples irradiated in air displayed an initial softening due to the loss of hydrogen bonding at the interface between the polymer matrix and filler, whereas samples irradiated under vacuum were stiffened upon irradiation, due to an increase of network density and hydrogen bonding at the polymer/filler interface.

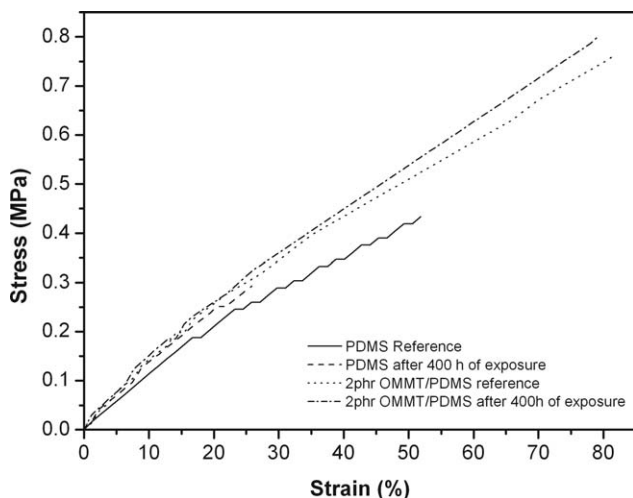
Similar behavior was reported by Maxwell et al.<sup>19</sup> for silica filled, RTV polysiloxane rubber exposed to gamma radiation. The authors found that radiation causes an increase in the cross-linking densities, as measured by solvent swelling, a decrease in segmental mobility assessed by nuclear magnetic resonance spectroscopy (NMR) relaxation times and a hardening as shown by DMA.

### Swelling

Swelling experiments with specimens from the reinforced silicone matrix, (PDMS nanocomposites), immersed in toluene, exhibited a decrease in solvent uptake, in comparison with that corresponding to

**TABLE V**  
**Tensile Properties of OMMT/PDMS Nanocomposites After 400 h Exposure to Accelerated Aging in Comparison with Unexposed (Reference) Specimens**

Samples	Tensile strength (MPa)	Modulus of elasticity (MPa)	Strain at break (%)
PDMS, reference	0.56 ± 0.009	1.09 ± 0.016	47.38 ± 4.950
PDMS after 400 h of exposure	0.44 ± 0.030	1.12 ± 0.025	32.25 ± 4.850
2 phr OMMT/PDMS, reference	0.81 ± 0.164	1.25 ± 0.017	81.85 ± 22.150
2 phr OMMT/PDMS after 400 h of exposure	0.80 ± 0.121	1.26 ± 0.038	74.39 ± 14.609



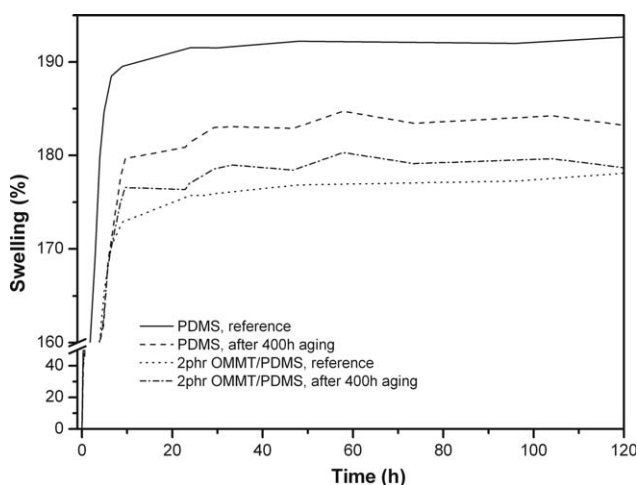
**Figure 3** Tension stress versus strain curves of OMMT/PDMS nanocomposites after 400 h exposure to accelerated aging in comparison with unexposed (reference) specimens.

the unfilled PDMS matrix, as can be seen in Figure 4. Toluene uptake by these specimens is controlled by Fickian diffusion for the first 8 h of the experiment and then a “plateau” can be observed.

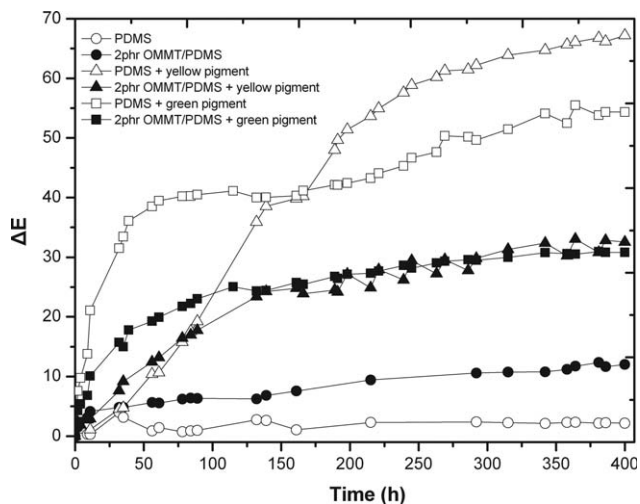
Two mechanisms might control the toluene diffusion in the PDMS matrix:

- a. Increase in the tortuosity path, because of the presence of the dispersed nanoparticles in the PDMS matrix.
- b. Network density of the cross-linked elastomer.

As already stated above, for the nanocomposite systems studied in this work, the increased surface area of nanoparticles might promote some interactions with the silicone matrix and, therefore, it may lead to the formation of additional cross-links, i.e., to an increased network density of the final product.



**Figure 4** Swelling of pure PDMS and OMMT/PDMS composites, immersed in toluene.



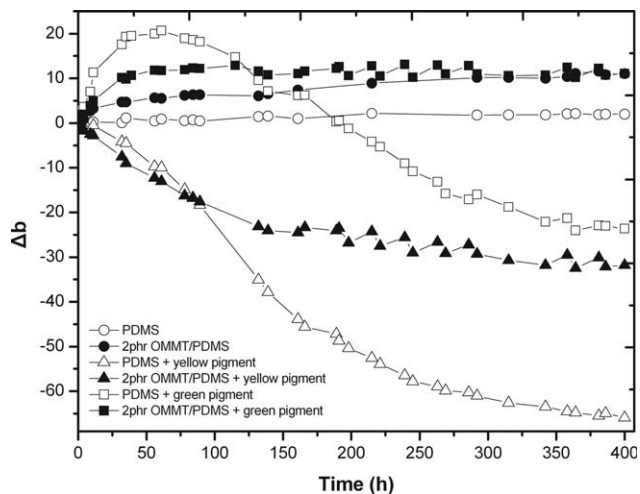
**Figure 5** The total color change  $\Delta E$  as a function of time of during accelerated aging of silicone elastomers colored with dry pigments.

This is associated with lower solvent uptake and leads to lower swelling for the filled nanocomposite.

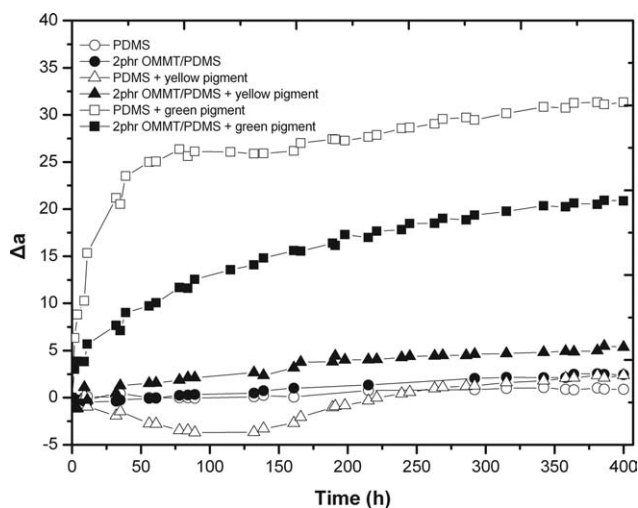
Exposure to accelerating aging conditions of PDMS decreases to a greater extent the swelling ratio in toluene, in comparison with the 2 phr OMMT/PDMS nanocomposite. In this latter case, the density of cross-linking remained almost unchanged during exposure. These results are in agreement with the data of Table V concerning the modulus of elasticity, where an increase was recorded for pristine PDMS specimens. However, in the case of 2 phr OMMT/PDMS nanocomposites, the modulus of elasticity remained almost constant after 400 h accelerated aging.

**Color measurements (lab)**

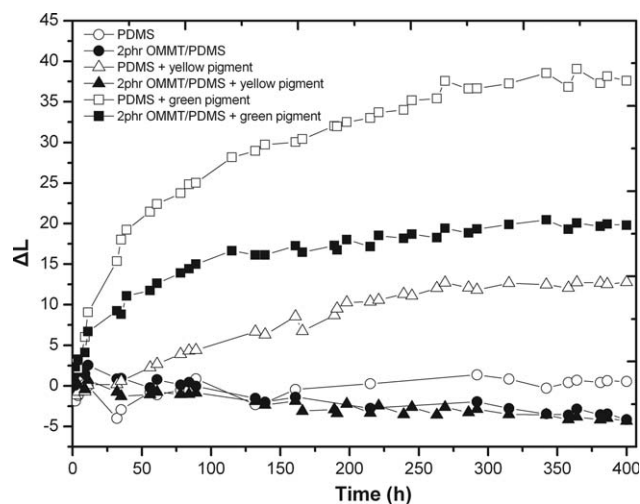
The color stability of silicone elastomer and its 2 phr OMMT nanocomposite, can be seen in Figures 5–8 and



**Figure 6** The red-green character  $\Delta b$  as a function of time of during accelerated aging of silicone elastomers colored with yellow and green dry pigments.



**Figure 7** The yellow-blue character  $\Delta a$  as a function of time of during accelerated aging of silicone elastomers colored with yellow and green dry pigments.



**Figure 8** The light-dark character  $\Delta L$  as a function of time of during accelerated aging of silicone elastomers colored with yellow and green dry pigments.

Table VI, in terms of the parameters determined by Lab chromatometry. A  $\Delta E$  value of two units was assumed as the minimum significant color change that could be visually detected.<sup>20</sup> It is obvious that the unpigmented samples present minor color variations after exposure to accelerated aging conditions. Small color changes, corresponding to 5 units  $\Delta E$ , were also reported for unpigmented silicone type A-2186, stored in darkness for 45 days, and this behavior was explained as a result of additional cross-linking caused by further polymerization of the elastomer or by side reactions initiated by catalyst and impurities present in the silicone system.<sup>21,22</sup> On the other hand, samples colored with yellow and green pigments underwent significant discoloration ( $\Delta E > 2.0$ ) from the early stages of exposure. As can be confirmed by the curves of Figure 5, unpigmented pure PDMS does not show any obvious changes during exposure to accelerating aging. The incorporation of 2 phr OMMT gives a milky appearance to the PDMS elastomer, that remains rather permanent during aging. Yellow and green colored specimens filled with 2 phr OMMT and unfilled PDMS specimens are more vulnerable to aging, with respect to the initial composite.

Color changes of silicone containing yellow pigment can be attributed to the strong effect of UV

radiation on  $\Delta b$  component (Fig. 6), representing the chromaticity coordinate for yellow/blue. On the other hand, discoloration of green colored silicone was mainly considered as a result of variations of the component  $\Delta a$  and  $\Delta L$  as it can be seen Figures 7 and 8, respectively. From Figure 5, it is obvious that the texture of green color changes during the first 60 h of exposure, whereas the change of yellow color is accomplished almost linearly during the first 300 h of aging. The incorporation of 2 phr OMMT increases significantly the color stability of yellow and green colored PDMS specimens.

Some colorants seem to stabilize silicones against weathering, possibly by blocking light radiation and, thus, preventing it from diffusing through the entire elastomer mass.<sup>22</sup> It has also been reported that inorganic coloring agents are more stable to color changes in comparison with organic colorants.<sup>23</sup>

These interactions were further studied by Beatty et al.<sup>21</sup> who evaluated the color stability of elastomers, pigmented with five dry pigments, after exposure to UVA and UVB light. Cosmetic red and cadmium yellow pigments underwent substantial color change after 400 h, whereas mars violet and cosmetic yellow ochre remained stable after 1800 h. The authors claimed that it is possible that

**TABLE VI**  
Lab Values of Silanol Terminated PDMS Nanocomposites After 400 h Exposure to Accelerated Aging Conditions

Sample	$\Delta L$	$\Delta a$	$\Delta b$	$\Delta E$
Unpigmented PDMS	$0.534 \pm 0.126$	$0.878 \pm 0.001$	$1.985 \pm 0.058$	$2.170 \pm 0.139$
2 phr OMMT/PDMS	$-4.136 \pm 0.115$	$2.439 \pm 0.252$	$11.023 \pm 0.697$	$12.023 \pm 0.750$
PDMS + yellow dry pigment	$12.780 \pm 0.350$	$2.396 \pm 0.243$	$-74.244 \pm 0.319$	$67.207 \pm 0.708$
2 phr OMMT/PDMS + yellow dry pigment	$-4.355 \pm 0.297$	$5.369 \pm 0.173$	$-31.797 \pm 0.162$	$32.537 \pm 0.380$
PDMS + green dry pigment	$37.609 \pm 1.058$	$31.339 \pm 0.070$	$-23.610 \pm 0.735$	$54.351 \pm 1.290$
2 phr OMMT/PDMS + green dry pigment	$19.782 \pm 0.170$	$20.86 \pm 0.021$	$11.120 \pm 0.105$	$30.824 \pm 0.201$



the above results are due to compositional differences among various pigments. However, pigment composition is generally unknown in the related studies, as it often remains proprietary information of the manufacturer.

Taking into account the obtained data and the above literature, we can conclude that both types of the pigments used in this work are susceptible to discoloration upon aging. However, the discoloration of the above pigments could probably prevent the silicone elastomer from degradation during exposure to UV irradiation. On the other hand, the results obtained from mechanical testing and swelling experiments would allow the hypothesis that incorporation of 2 phr of OMMT filler into PDMS has some protective action to the elastomer system against photo-aging.

### CONCLUSIONS

From the evaluation of the results obtained in this work, the following conclusions may be drawn:

The exposure of silicone samples to UV radiation has no significant effect on IR absorbance and, more specifically, does not produce absorption bands that could suggest the formation of oxygen containing groups or other oxidation products. Also, the results obtained by DSC testing of silicone samples cannot establish any particular effect of the aging on the thermal properties of pure PDMS, whereas OMMT nanofiller seemed to rise silicone's  $T_g$ , probably because of the increase of cross-links-density and the decrease of the free volume of the polymer. Moreover, aging of the reinforced silicone elastomer results in a decrease of  $T_g$ , possibly due to structural changes, such as chain scission. As above described changes may be responsible for the decrease of thermal stability assessed by TGA, for pure and reinforced samples exposed to accelerating aging. Furthermore, remarkable decrease of tensile strength and elongation of pure silicone samples was observed after aging, whereas reinforced specimens showed resistance against aging. The results obtained by mechanical testing were again interpreted taking into consideration the two competitive reactions taking place during UV aging, i.e., chain scission and cross-linking. This was further confirmed by the data from swelling experiments in toluene, that can be directly correlated with the network density. The susceptibility of various pigments to discoloration upon exposure to UV radiation, varies from this of green color that shows changes

within the first 60 h of exposure to that of yellow presenting an almost linear change during the first 300 h of aging, whereas the incorporation of 2 phr OMMT significantly increases the color stability of yellow and green colored PDMS specimens. Finally, the investigated pigments did not show to prevent aging of silicone elastomers exposed to UV radiation, even though their fast discoloration could suggest a protective action.

The main conclusion of this work is probably the fact that the addition of montmorillonite nanofiller produces a significant reinforcing effect and might prevent the effect of aging of silicone elastomers, as recorded by mechanical tests and swelling measurements.

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