Study of Laser Ablation and Mechanical Properties of Silicone Rubber Nano-composites

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***Abstract*— The use of nanofillers has increased significantly in many fields during the last few years with the growing interest in nanotechnology applications. In this paper nanocomposites with different amounts of surfactant and fillers were studied to determine the tensile properties of nanofilled samples. The results obtained show that it is essential to optimize the amount of surfactant used as otherwise the mechanical properties of the composites are negatively impacted in terms of reduced hardness and lowered tensile strength. An optimal amount of surfactant does not affect significantly the above-mentioned mechanical properties, however. In addition, laser ablation tests were done using a near infrared laser beam to assess the erosion resistance of all the samples. The laser tests confirmed that composites containing nano fumed silica have enhanced resistance to erosion as compared to natural nano silica or nanoalumina-filled composites.**

I. INTRODUCTION

Polymeric nanocomposites have attracted considerable attention over recent years. In particular, use of nanoparticles can lead to enhanced electrical and mechanical properties when incorporated in a soft matrix, due to the large number of interacting and/or cross-linking sites at the nanoparticle-matrix inter-face. Improvements in the materials' properties can only be achieved if the filler is well dispersed into the rubber matrix, however. In a previous study it was shown that a commercial surfactant could improve the dispersion of nanofillers in silicone rubber [1]. The level of matrix reinforcement achieved also depends on the extent of interaction between the organic and inorganic phases.

Reinforcing inorganic micro fillers such as alumina or silica is an important component to improve the performance of a silicone rubber matrix for outdoor insulation applica-

tions. It has been proposed that the reinforcement is due to the interactions of polymer chains with the filler surface through Van der Waals forces, hydrogen bonding, and/or by covalent bonding [2].

In the current investigation, different nanofillers were examined to reinforce silicone rubber for outdoor insulation applications in power systems. The inter-facial interaction between the silicone rubber matrix and the inorganic filler plays a key role in the reinforcement effect; another important point to consider is the particle size [3]. The addition of fillers results in improved tracking resistance, erosion resistance, and mechanical strength of the composite material.

To achieve good dispersion of the fillers in the nanocomposites, the commercial surfactant Triton X-100 was used. While better dispersion of the nanofiller improves the erosion resistance of the silicone, the surfactant also introduces another interface between the filler and the silicone matrix. It is, consequently, essential to optimize the amount of surfactant used to avoid any negative impact on the mechanical properties of the composite. The nature of the filler-matrix interface can affect properties such as the tensile strength, elongation at break, and hardness of the material.

Composites with different amounts of surfactant and fillers were investigated to determine the influence of nanofillers on the tensile properties and the ablation resistance of the samples.

II. METHODOLOGY

A. Materials and Sample Preparation

In this research nano fumed silica, natural nano silica, nanoalumina, and microsilica were used as fillers. The main characteristics of these materials are summarized in Table 1. The matrix is a two-part addition cure silicone rubber RTV 615 (SiR) manufactured by the General Electric Company. The surfactant Triton X-100^{TM} was used to improve the dispersion of the nanofillers.

A Ross model HSM-100LSK mixer with a high shear force was used to disperse the particles uniformly within the silicone rubber matrix. For most industrial applications, Degussa [4] suggests tip speeds (peripheral velocities) ranging from 8-10 m/sec to achieve adequate particle dispersion. For the Ross mixer, this corresponds to a mixing speed between 9550 and 11935 rpm. The wet-in time is defined as the time required for all the nanoparticles to be wetted by the dispersion medium; at this stage a low mixing speed was used (6,000 rpm). Once the nanoparticles were wetted, the mixing speed was increased to 12,000 rpm to begin dispersion. For samples with surfactant, the silicone rubber (SiR) was mixed with the surfactant prior to adding the nanofiller [1].

The samples were cured at room temperature for 24 h and then post-cured in an oven at 87ºC for 4 h.

TABLE 1: CHARACTERISTICS OF THE FILLERS

Fillers used	Average particle size (nm)	Surface area (m^2/g, BET*)	Density (g/mL) @25 ºC
Nano fumed silica	7	390±40	2.2
Nano alumina	2-4	350-720	4
Natural nanosilica	10	590-690	2.2-2.6
Microsilica	5000	5	0.58

* In honor of S. Brunauer, P. H. Emmett, and E. Teller

Samples were prepared with different compositions of nanofiller and a fixed amount of microfiller. Calcination for one hour at a temperature of 300°, 600°, or 900°C was used to break-up aggregates and pellets of nanofillers, and to eliminate adsorbed water [5].

For the laser test, the samples require a darker color to ensure identical spectral absorption of the laser radiation; this was achieved by including 2.5% wt of iron oxide in the mixture for all samples. Since Fe_2O_3 is stable at high temperatures, above the decomposition temperature of the SiR matrix, it may be considered otherwise inert [6].

B. Eroded Mass Assessment

In the evaluation of the eroded mass of nanocomposites under the influence of dry band arcing, a method that has been shown to give results equivalent to the inclined plane test is the laser erosion test developed by Meyer et al. [7]. Heat from dry band arcing is the main degradation factor in the use of SiR in outdoor insulation; consequently, the degradation is thermal and the laser test can be used to simulate the effects of dry band arcing. The eroded mass evaluation was conducted to differentiate between the different filled materials.

The method consists of delivering the same energy to each sample; in this case a Coherent model FAP infrared laser with an operating wavelength of 802 nm was used. The heat produces molecular vibrations causing the polymer to breakdown. Several tests were conducted to adjust the diode laser, which was operated in the continuous wave (CW) mode with a current of 17.5 A (power equivalent to 8.8 W) for 7 minutes (the calculated energy dose equals 3700 Joules). The sample was located 5 cm away from the laser source in all the tests.

The eroded mass of the samples was determined from the weight measured before and after testing using a Sartorius AC 211S-00MS balance with a readability of 0.1 mg. For each sample, 3 tests were carried out. The average of the 3 eroded mass values is represented in the plots.

C. Mechanical Tests

Stress–strain measurements were done at room temperature in the uniaxial extension mode and along the direction of increasing elongation. The tensile tester, a Minimat 2000, was used following the procedure described in ASTM D1708. For each formulation, 5 to 10 samples were tested. The testing speed was 100 mm/min (speed D) [8]. The stress, σ, was calculated as:

$$\sigma = \frac{f}{A_0} \qquad (1)$$

where f and A_0 are the measured force and the initial cross-sectional area, respectively.

The hardness was measured according to the ASTM D2240 standard [9] using a durometer Model 408 ASTM type A for applications in soft rubbers, elastomers, and flexible polyacrylics. Following the standard, 5 measurements were recorded for each sample and the mean and the standard deviation were reported. The objective of these tests was to evaluate the behavior after adding surfactant to the samples.

III. Results and Discussion

A. Eroded mass of nanofilled specimens using laser test

Three samples at each composition consisting of either 2.5 or 5 wt % of nanofiller and various Triton additions (expressed in parts per hundred, pph, of nanofiller by weight) were tested. Each point in Figures 1 and 2 corresponds to the average eroded mass for three samples at the different Triton concentrations.

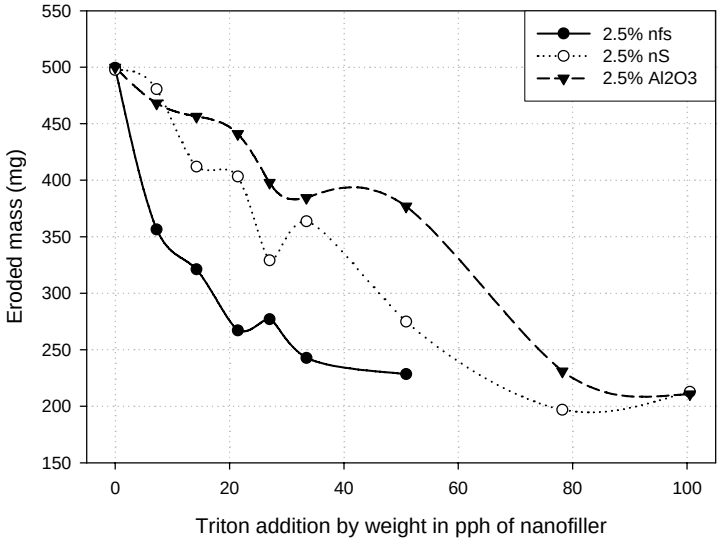


Figure 1: Eroded mass of samples with 2.5 wt % of different nano fillers for various Triton additions (in pph of nanofiller). Each data point shown is the average of three samples at each Triton concentration.

In comparison to natural nanosilica (nS) and nanoalumina (Al_2O_3), for the same amount of surfactant, nano fumed silica (nfs) yielded the lowest ablated mass (highest resistance to ablation) under infrared laser heating. The performance of natural silica was intermediate, while the highest eroded masses were obtained with alumina. This may be due to a change in the protective mechanism brought about by the nano filler particles.

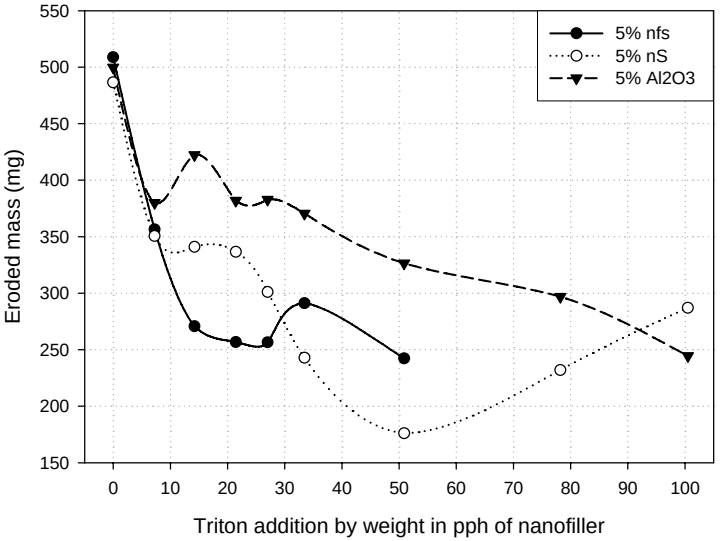


Figure 2: Eroded mass of samples with 5 wt % of different nano fillers for various Triton additions (in pph of nanofiller). Each data point shown is the average of three samples at each Triton concentration.

B. Eroded mass of micro- and nanofilled specimens in laser test

To examine the influence of the surfactant content, the erosion behavior was compared for samples containing 14 and 28 pph surfactant, i.e. amounts considered optimal and excessive, respectively [10]. Samples incorporating the nano fumed silica (nfs) filler in combination with 20 % microsilica filler, displaying the minimal eroded mass, were selected for the comparison.

Three samples of each composition consisting of 20 % microsilica filler with various amounts of nano size fumed silica (nfs) and the two different Triton contents were subjected to the laser ablation test. The results obtained are summarized in Figure 3, where each point is the average of the three samples tested. Both fillers were used without any pre-treatment. Five percent nfs was the upper loading limit used, since mixing became quite difficult to achieve above this concentration. It is nonetheless evident that the eroded mass decreased with increased nfs content. Furthermore, 28 pph of Triton was more efficient at reducing sample erosion than 14 pph. In all cases, the eroded mass for samples prepared with surfactant was lower than for samples with the same amount of filler but without surfactant.

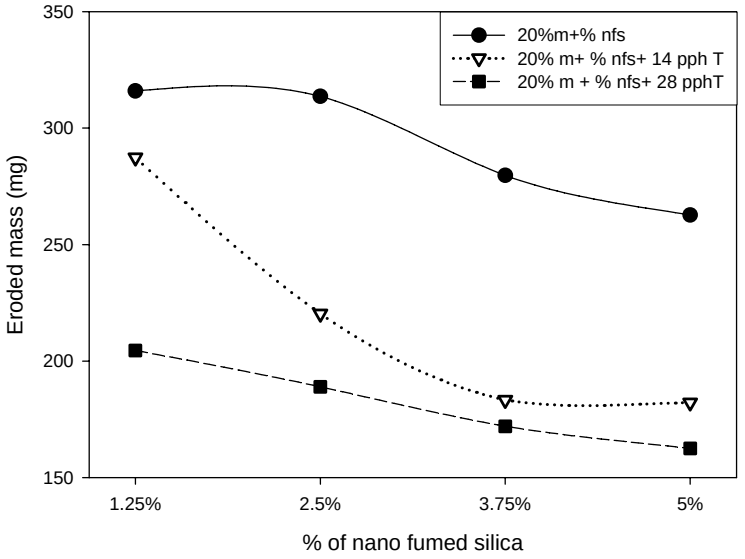


Figure 3: Average eroded mass of three samples with 20 % microsilica filler (m) for various additions of nano fumed silica (nfs) and Triton (expressed in parts per hundred, pph, of nanofiller by weight).

The eroded mass observed in laser ablation tests using calcinated fillers is shown in Figure 4 for several fillers and as a function of Triton content. It appears that calcination does not have as much influence on the eroded mass as the addition of Triton, and all the results tend to converge when adding 28 pph of Triton.

In these tests it was noticed that for the 2.5% nfs content treated at 900°C, a white layer developed in the sample during the test. As shown in Figure 5, this is likely to be a layer of silica formation; and such a protective mechanism decreasing sample erosion has been reported previously [11].

The decomposition of SiR in air is known to produce white silica particles [12]. The white layer is therefore attributed to filler residues and to the decomposition of the SiR matrix in air. For this reason, samples with 2.5% nfs thermally treated at 900°C were not evaluated by the laser technique, because the laser beam is likely reflected by the white layer, biasing the erosion level determined by laser ablation. It appears likely that this silica layer also forms a heat-resistant shield hindering further heat ablation of the underlying SiR matrix.

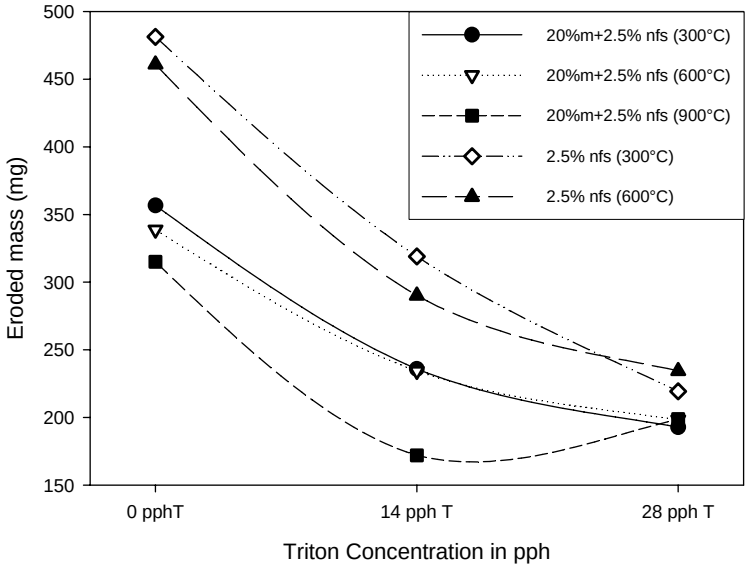
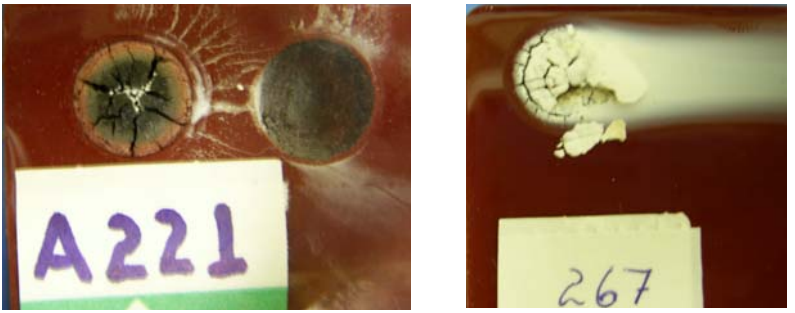


Figure 4: Average eroded mass of three samples with 20 % microsilica filler (m) and for 2.5 % nano size fumed filler (nfs) calcinated at different temperatures and for various Triton additions (expressed in parts per hundred, pph, of nanofiller by weight).



(a) (b)

Figure 5: Eroded samples (a) with normal charred surface and after the char was removed (b) with the formation of a white silica layer.

C. Mechanical Tests

The tensile strength, elongation at break, and hardness are bulk properties of silicone that are affected by the type and amount of filler particles, and their interactions (bonding) with the polymer matrix. Since the addition of surfactant to disperse the filler can have adverse effects on bonding, the mechanical properties may be negatively impacted.

In Figure 6 the ultimate tensile strength is shown for the samples combining nano fumed silica and microsilica (m+nfs) for several surfactant concentrations.

Although the tensile strength is somewhat higher for the micro- and nanofilled samples as compared to the nfs-filled samples, it is evident that the addition of 14 pph of surfactant has little effect on the tensile strength. A lower decrease is observed in samples with 28 pph surfactant. For these samples, a maximum reduction in the average tensile strength by about 4% was found with respect to the samples without surfactant. Although, 28 pph of surfactant is considered to be high and above that needed, 14 pph, for proper dispersion of the nanofillers, it seems that both concentrations can be used without a significant decrease in tensile strength [10]. The actual values of average tensile strength obtained are summarized in Table 2.

The hardness and elongation at break of the filled samples are also compared in Table 2. The variations observed in both parameters are similar to the tensile strength. Hence, it can be stated that for an addition of 14 pph surfactant, the mechanical properties are unaffected.

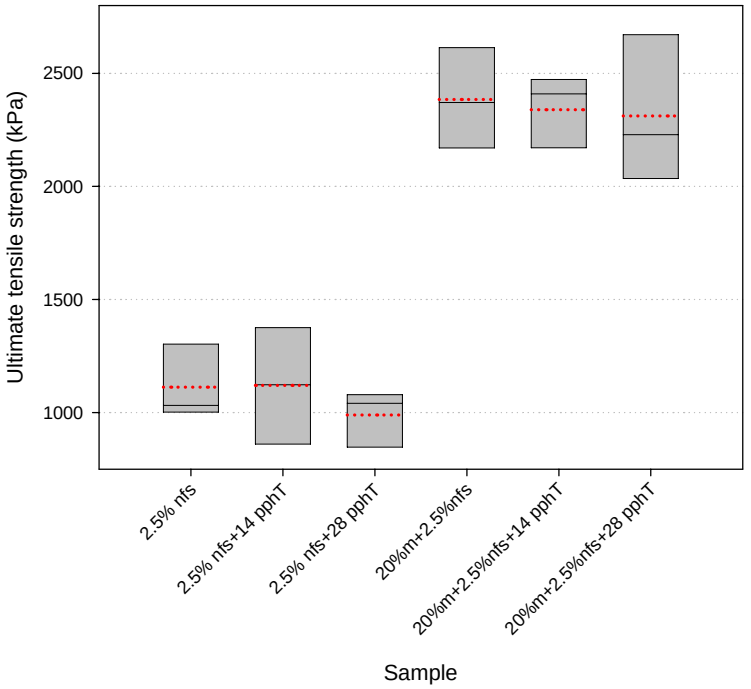


Figure 6: Ultimate tensile strength of nanofilled and micro-nanofilled samples, discontinuous line shows the average.

TABLE 2: SUMMARY OF MECHANICAL EVALUATION

Sample	Ultimate tensile strength (kPa)	Standard deviation	Elongation (%)	Hardness (Type A)
2.5% nfs	1112.3	165.8	238.5	51.5
2.5% nfs +14 pphT	1120.0	280.1	235.4	50.3
2.5% nfs +28 pphT	989.0	138.0	219.2	50.0
20%m +2.5%nfs	2385.0	222.3	213.6	61.9
20%m +2.5%nfs +14 pphT	2339.2	198.3	209.4	60.9
20%m +2.5%nfs +28 pphT	2311.8	343.9	226.5	57.6

IV. CONCLUSIONS

The laser ablation tests were done using a near infrared laser beam to assess the erosion resistance of silica-filled samples. Fumed silica was shown to impart greater heat ablation resistance than either natural silica or alumina. There was no significant difference in the erosion resistance of natural silica- or alumina-filled compositions. The ablation observed for nanosilica-filled specimens suggests that the silica accumulated at the surface forms a heat-resistant barrier preventing further erosion of the underlying silicone rubber.

The results obtained demonstrated that the amount of surfactant does not decrease significantly the tensile strength, elongation at break, and hardness of the filled samples.

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