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Method Development to Quantify the Reinforcing Properties of Silica Fillers

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METHOD DEVELOPMENT TO QUANTIFY THE REINFORCING PROPERTIES OF SILICA FILLERS

A Thesis Submitted to the Graduate School
in Partial Fulfillment of the Requirements
for the Degree of Master of Science

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METHOD DEVELOPMENT TO QUANTIFY THE REINFORCING PROPERTIES OF SILICA FILLERS

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Thank you!

METHOD DEVELOPMENT TO QUANTIFY
THE REINFORCING PROPERTIES OF SILICA FILLERS

An Abstract of the Thesis by
Hamid Reza Givehchi

Polysiloxane polymers are widely used as a high-temperature resistant materials with the ability to maintain flexibility at extremely low temperatures. Unfortunately, polysiloxane elastomers generally exhibit low strength and poor mechanical properties and have no practical use unless they are reinforced. These elastomers can be mechanically improved through the use of reinforcing silica-based fillers. It is known that silanol groups on the surface of silica filler particles can interact with the polysiloxane backbone. Interactions of silanol groups on the fillers' surfaces with the polysiloxane backbone through hydrogen bonding may hinder the mobility of the polymer chain and can improve thermal, physical, and rheological properties of the reinforced polysiloxane. Silica fillers can also undergo a filler-filler interactions, causing filler aggregation and agglomeration. These filler-filler interactions may improve or disrupt the overall properties of the filled polysiloxane based on a particular filler's surface area, silanol group orientation, or concentration. Therefore, the surface study of filler becomes critical in order to predict the reinforcing behavior of fillers with the polysiloxane polymer backbone and other filler particles.

This work seeks to quantify silanol group concentration on the surface of different silica fillers and investigate the effects of silanol group concentration on the rheological properties of filled polysiloxane polymers. Through the analysis of rheological data, this work can predict the reinforcing capabilities of each filler and will allow tailoring of

future materials based on those predictions. Silanol group concentration on a particular silica filler's surface depends on the synthesizing method, surface area, and surface hydrophobicity. In this study, silanol concentration on the surface of eight commercially-available amorphous silica fillers will be calculated by using Zhuravlev model via thermogravimetric analysis (TGA). Subsequently, fillers will be combined with vinyl-terminated polydimethylsiloxane (PDMS) to produce a filled polysiloxane material. Oscillatory rheometry and flow rheometry will be used to determine rheological responses and, therefore, determine the effects of silanol concentration on rheological properties in filled polysiloxane materials.

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LIST OF ABBREVIATIONS

µm – Micrometer

g/hr – Grams per hour

g/mol – Grams per mole

in/sec – Inches per second

J/g – Joules per gram

kg/hr – Kilograms per hour

L:D ratio– Length to diameter ratio

m^2/g – Meters squared per gram

mL/min – Milliliters per minute
mmol/g SiO_2 – Millimoles of hydroxyls per gram of silica
MPa – Mega Pascal

Med-High – Medium to high
OH nm^{-2} – Hydroxyl groups per square nanometer
Pa – Pascal

Pa·s – Pascal-second

PDI – Polydispersity index

PDMS – Polydimethylsiloxane

rpm – Revolutions per minute

sec –Second

TGA – Thermogravimetric analysis

Wt. % – Weight percent

CHAPTER I

1. INTRODUCTION

1.1 Polysiloxanes

Polysiloxanes polymers are made from long chains of alternating silicon and oxygen atoms with every silicon atom carrying two organic functional groups. Figure 1 shows the basic structure of a siloxane bond.[1] Silicon is located in Group IVA of the periodic table and exists as the most abundant element of group IVA. Silicon is rarely found naturally in elemental form, as it tends to bond with oxygen to form silicon dioxide (SiO_2) or silcate (SiO_4) which makes up roughly 77% of the Earth's crust.[3,4] Figure 1 indicates the general structure of a siloxane bond, silicon dioxide and silicate.

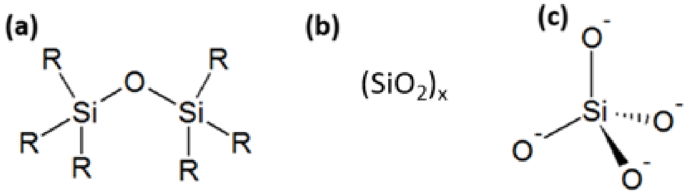

Figure 1. General structure of (a) siloxane bond, (b) silicon dioxide, (c) silicate.

Polysiloxanes retain extraordinary properties, such as high temperature stability and flexibility, at low temperatures due to its chemical structure.[6, 77] These unique properties make polysiloxanes applicable for variety of different applications that require performance in extreme conditions such as artificial organs, contact lenses, high-performance elastomers, electrical insulators, mold release agents, adhesives, and protective coatings.[1,3,5,77] Polysiloxane elastomers are unique among elastomeric materials. Polysiloxanes are capable of performing in an extended temperature range when compared to other elastomeric materials. For example, polydimethylsiloxane (PDMS) has an upper use temperature of 400°C and glass transition temperature ($T_{g)}$ of -123°C, while the highest performance temperature for natural rubber is 80°C and has a T_g at -72°C.[1,2] These versatile properties makes polysiloxanes viable in multiple applications such as gaskets, sealants, and O-rings in extreme environments where other elastomers are unstable.[1] It should be noted that polysiloxane elastomers generally exhibit poor strength and low mechanical properties and have no practical use unless they are combined with additives such as stabilizers and fillers. For example, the tensile strength of unfilled polysiloxane elastomer is 0.34 MPa, whereas silica-filled polysiloxane elastomers demonstrate an increase in tensile strength up to 14 MPa. It is possible to fill any typical polysiloxane elastomers up to 41% or higher depending on the nature of the filler.[1]

1.2 Fillers

Generally there are two main categories for fillers: extending fillers and reinforcing fillers. Extending fillers can perform as either semi- or non-reinforcing fillers. These fillers usually “extend” the formulation by reducing the cost of filled polymeric resins.[25] Filled polymeric material with reinforcing fillers can exhibit higher mechanical properties compared to unfilled materials.[26,27] Reinforcing fillers are also divided into two categories: active and inactive fillers. Inactive fillers such as chalks, calcium carbonates, natural silicates, and clays, are normally incorporated into elastomers for economic purposes and would only weakly reinforce elastomers. Chemically-treated silica fillers are known as active fillers, which strongly reinforce and extensively increase the physical properties of polysiloxane elastomers including abrasion resistance, tensile strength and heat-aging characteristics.

Precipitated and fumed silica filler are the two major types of reinforcing fillers. Precipitated silica is synthesized from the reaction of a mineral acid, such as sulfuric acid, with an alkaline silicate solution, such as a sodium silicate. The acid and silicate solution are combined and agitated until precipitation occurs. The porosity and particle size of precipitated silica filler depends on different factors including: temperature, amount of reactant, duration of the reaction, speed of agitation, pH, and concentration of the reaction. Sodium sulfate is the byproduct of this reaction and is removed from the actual particles. Finally, the particles are dried in order to reduce the majority of moisture present.[28] Precipitated silica filler may contain up to 7% of different impurities and moisture.[29] In comparison, fumed silica has a higher degree of purity. This commercially available silica filler contains up to 99.8% pure silica.[29] Fumed silica filler is produced by hydrolysis of a chlorosilane, such as silicon tetrachloride, which is burned in an oxygen and hydrogen flame to produce molten spheres of silicon dioxide and hydrogen chloride. During the production of fumed silica filler, hydroxyl groups on the particle surface create a hydrophilic surface which can subsequently undergo hydrogen bonding. In general, particles in precipitated silica fillers are larger than fumed silica fillers are more porous and have lower surface area.[30] For a given volume, smaller fumed particles can pack closer together and obtain higher total surface areas than larger, precipitated silica particles.[13,14,31.77]

Silanol groups (≡Si-OH) are polar groups present on the silica surface as well as inside the silica skeleton. Figure 2 shows the types of silanol groups: (a) isolated single silanols, (b) geminal silanediols, and (c) vicinal-bridged silanols through hydrogen bonding. Aside from the silanol groups on the surface of the silica, there are also surface siloxane groups and adsorbed water present.[32,33]

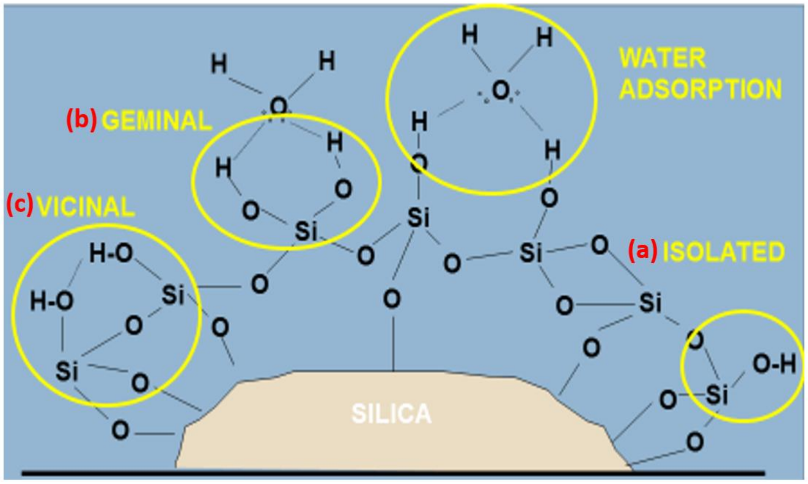

Figure 2. Silanol groups on the surface of silica: (a) isolated silanols, (b) geminal silanols, and (c) vicinal-bridged silanols. Also shown: adsorbed water.[33]

Silanols can undergo hydrogen bonding and interact with the polysiloxane polymer backbone. When the silica filler is wetted by polymer, polymer chains become adsorbed on the surface of the filler.[13,34,35,77] These interactions hinder the mobility of the polymer chains, thus reinforcing the filled material and improving mechanical, thermal and rheological properties.[27,36] Figure 3 displays the interaction between a surface-functional group of a silica particle and the polymer backbone.

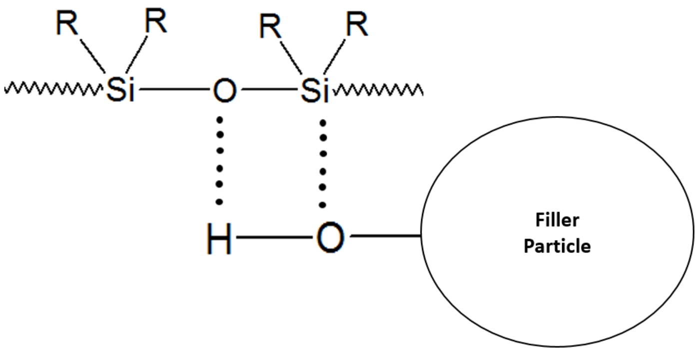

Figure 3. Interaction of a silica particle surface silanol group and the polymer backbone.

Surface silanol groups can also interact, or aggregate, with each other in addition to the polysiloxane polymer backbone. Aggregation can occur during the production of silica filler as well as during the compounding process when filler particles are distributed throughout the polymer matrix. This phenomena occurs as a result of the high surface area of silica filler. The high surface area of the silica fillers makes surface silanol groups available to interact with those on other silica particles through hydrogen bonding to create an aggregated network structure.[13,35,37-39,77]

Figure 4 shows an aggregated network structure of silica particles created by their surface silanol groups.[40] Smaller particles have the ability to pack closer to each other compared to larger particles and, therefore, they can create an aggregated network more readily than silica fillers with larger particles.

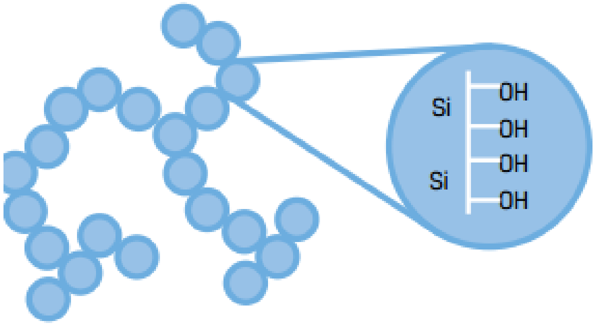

Figure 4. Aggregated network structure of silica particles with surface silanol groups.[40]

Even in an aggregated network, silica aggregates are still capable of interacting with the polymer backbone. Fillers with larger surface areas and smaller diameters normally exhibit better interaction and reinforcement of polysiloxane elastomers, compared to fillers with smaller surface areas, due to the possible presence of additional functional groups which could potentially interact with the polymer backbone.[13,14,31,77] The large number of interacting hydrogen bonds reinforces the filled material, which enhances the mechanical properties. The aggregated network structure hinders the mobility of the polymer chains to enhance the rheological properties. Finally, the network structure generates a protective barrier that disrupts release of the cyclic volatiles during thermal decomposition, thus the thermal stability increases.[13,15,39,41-51,77]

Despite the fact that the aggregation of silica filler can enhance the mentioned properties of polysiloxane elastomers, it also can disrupt these properties at higher aggregation levels. Silica particles prefer to interact with other silica particles, and aggregated network structures can interact to create a large agglomerates. An agglomerate is defined as a collection of silica aggregates. A filler network structure consist of aggregates and agglomerates is shown in figure 5.[44]

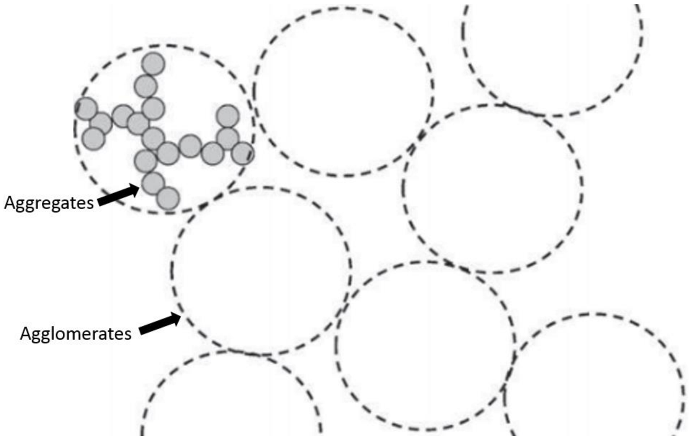

Figure 5. Filler network structure comprised of aggregates and aggloermates.[44]

Whenever filler particles are not evenly distributed throughout the polymer matrix, aggregates tend to interact with each other and assemble into a large particle instead of interacting with the polymer backbone and reinforcing the elastomer.[1,53,54,77] Large agglomerates can diminish the properties of filled material by disrupting the ability of the silanol groups on the filler particles to interact with polymer backbone. In fact, they are considered mechanical faults and reduce the mechanical and rheological properties as they occupy an extensive amount of space in the polymer matrix.[13,16,39,45,55-58,77]

The process of incorporating fillers into polysiloxanes to produce novel polysiloxane elastomers is called compounding. It would be cost prohibitive to synthesize novel polysiloxanes for each new application, so compounding allows polysiloxane materials to be tailored to different applications at a more reasonable cost. There are different methods of compounding that utilize various equipment, such as internal mixers, two-roll mills, torque rheometers, or twin screw extruders.[7-12,77] Versatility, efficiency, and the continuous nature of the process distinguishes the twin-screw extrusion compounding method from other known methods for the production of polysiloxane elastomers.[7,12]

The process of twin-screw extrusion is capable of mixing different additives, stabilizers, and fillers with various polymers to prepare specialized formulations.[7,12] Preventing filler particles from agglomerating is very important, but not easy to accomplish with all available compounding methods. Twin-screw extrusion creates mechanical shear to pulverize agglomerates into single particles and disperse them evenly throughout the polymer matrix.[13-19] Figure 6 illustrates the breakdown of the filler agglomerates into single particles by twin-screw extrusion.[18]

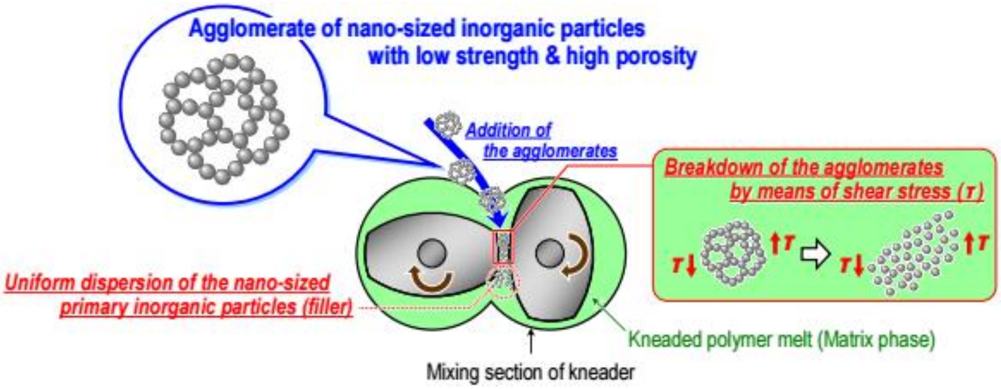

Figure 6. Breakdown of filler agglomerates into single particles by twin-screw extrusion.[18]

1.3 Quantifying SiOH groups on Silica Filler Surfaces

Hydroxyl groups on the surface of silica filler particles can interact with the polysiloxane backbone and other hydroxyl or silanol groups through hydrogen bonding and reinforce the polymer matrix during the process of compounding. As a result of these interactions, the thermal, mechanical and rheological properties of filled material increases.[13,35,39,41-51,77] Therefore, it is critical to quantify the number of hydroxyl groups on the surface of silica filler particles. The silanol number plays a significant role in the prediction of reinforcing behavior of different silica fillers with polysiloxanes.

There are several different methods to determine the hydroxyl group content of silica including: thermogravimetric analysis (TGA), infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectrometry, and titration. The infrared spectrum of silica filler contains both qualitative and quantitative information on different types of hydroxyl groups. Quantitative analysis based on IR data is complex because it is difficult to distinguish between different types of hydroxyl groups, as well as trapped water.[32] Solid-state NMR can also be considered as a method to measure the total number of silanol groups of silica filler. This method is not always viable for quantifying silanol number due to the high cost of the required instrumentation and the procedure complexity.[59,60] Titration is a common chemical method to determine the hydroxyl content of silica filler. This method requires a series of time-consuming sample preparation steps and long experimental duration.[60] Thermogravimetric analysis (TGA) is a relatively inexpensive, relatively rapid, and precise method to calculate the surface hydroxyl content of silica filler. In addition to being cost-effective, fast, and precise, TGA also offers the opportunity to distinguish between dehydration and dihydroxylation which is difficult to measure via other methods.[59,60]

Zhuravlev was also able to show that the hydroxylation and dihydroxylation on the surface of silica fillers is critically important. Furthermore, his study suggested that a probable mechanism to calculate the silanol numbers based on the hydroxyls present on the surface of silica filler using thermogravimetric analysis. The Zhuravlev model is capable of calculating the hydroxyl number and subsequently, silanol number on the surface of silica fillers.[32]

There are two possible types of hydroxyl groups attached to silica fillers: physically-bonded and chemically-bonded. Water adsorbed on the surface of each filler can be considered physically-bonded hydroxyl groups which has no hydrogen bonding and can be removed at temperatures above 100℃. On the other hand, chemically-adsorbed hydroxyl groups are hydrogen-bonded with other hydroxyl groups on the surface of the filler which require more energy to disrupt.[59] Figure 7 shows the two types of hydroxyl groups in three steps on the TGA thermogram. Step 1 defines all the physically-adsorbed water which starts from room temperature and ends at approximately

120°C to insure that all water molecules have evaporated and no physically-adsorbed hydroxyl groups remain in the sample. Step 2 shows the presence of chemically-adsorbed hydroxyl groups in the sample, starting at 120°C (end of step 1) and continuing to 850°C. This step is much longer compared to step 1 and demands more time and energy to remove the chemically-bonded hydroxyl groups. Different variations of chemically-adsorbed hydroxyl group such as germinal, vicinal and isolated silanol groups causes this step to be long. [59]

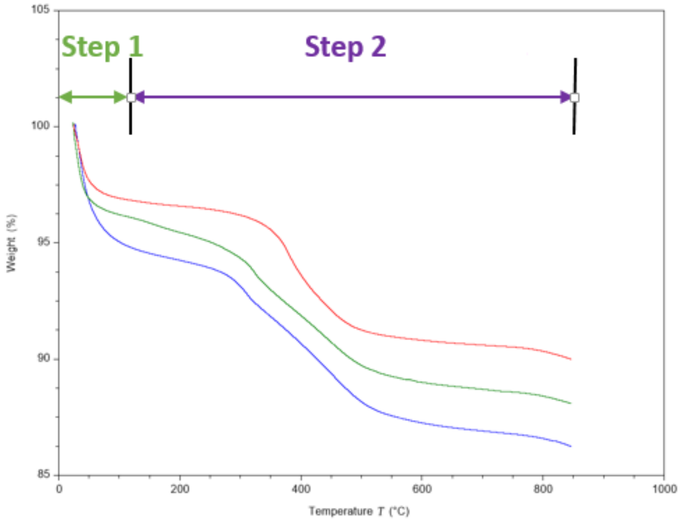

Figure 7. Distinguishing the physically-adsorbed (step 1) chemically-adsorbed (step 2) water.

The total surface hydroxyl group content in silica can be calculated from the entire second weight loss step, starting from the point where all the physically-adsorbed water is removed (T_0=120°C) and ending at the end point of measurement (T_{Final} =850 °C). An assumption is made that all silanol groups are removed at the end of the experiment, and the remaining sample residue is an oxide composed of only siloxane bridges. Figure 8 displays the condensation of silanol groups which occurs by the reaction of two silanol groups on the silica surface resulting in the release of one molecule of water and the formation of a siloxane bond.[59]

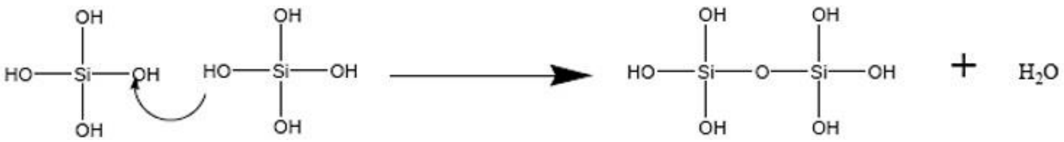

Figure 8. Condensation of silanol groups.[59]

The Zhuravlev method assumes that no volatiles are released from the sample besides water. The hydroxyl group, determined as millimoles of hydroxyls left per gram of silica at temperature T_0, can be calculated by using the following formula:

$$n\,OH = 2\,n\,H_2 0 = 1000 \times \frac{2\,[WL\,(T_0) - WL(T_{final})]}{100\,.\,M_{H_2O}} \tag{1}$$

Where the $WL(T_0)$ - $WL(T_{Final})$ is the weight percent loss in the temperature region of T_0 to T_{Final} and M_{H2O} is the molar mass of water.[32] Furthermore, the Zhuravlev model suggests the following formula to calculate the numbers of silanol groups on the surface:

$$\text{Number of Silanol Groups (OH nm}^{-2}\text{)} = k \times \frac{\text{OH number} \left(\frac{\text{mmol}}{\text{g}} \; \text{SiO}_2 \right)}{\text{Specific Surface Area}} \tag{2}$$

Where K can be calculated by the following formula: $k = N_A*10^{-21}$, $N_A = 6.022\times10^{23}$, and k= 602.2. Specific Surface Area can also be calculated by using Brunauer–Emmett–Teller (BET) method.[32]

1.4 Effect of Surface Silanols on Rheology

Rheology is the science studying the deformation and flow of matter. It is commonly reported that the incorporation of additives, such as fillers, can enhance rheological properties in the filled materials.[37,61] The filler can interact with the polymer backbone and restrict the mobility of the polymer chains. Regarding the polymer-filler interaction, a filler particle can be imagined as a hard core surrounded by a polymer shell that exhibits little mobility. Generally, filled materials only exhibit reinforcement characteristics as long as a parameter known as the *percolation threshold* is reached.[47,62] The percolation threshold is defined as the minimum critical amount of filler required for the material to convert from a liquid-like to solid-like material by promoting interactions between the filler and polymer matrix.[13,35,37,63,64,77] When the percolation threshold of the filled materials is reached, the material exhibits viscoelastic behavior.[62,65]

In addition to the interactions between the filler and the polymer matrix, aggregation of filler particles is another reinforcing mechanism in filled materials.[13,35,39,47-51,77] Aggregation is the supreme reinforcing mechanism in filled materials, as aggregates are dispersed throughout the matrix and interact with the polymer chains. Polymer adsorption on the aggregated filler particles restricts the mobility of the chains.[35,37,39,47,66,77] The creation of an aggregated network structure interacts with the polymer matrix to exhibit viscoelastic behavior in the materials.[13,47]

Rheometry investigates materials in simple flows, such as oscillatory-shear flow.[67] Oscillatory rheometry is a dynamic rheological technique that consists of applying a low-amplitude oscillatory shear stress that increases in a sinusoidal fashion to a material as the analysis progresses. The procedure measures the elastic and viscous behavior of the filled materials simultaneously by determining the storage modulus (G’) and loss modulus (G”).[47,68,69,77] The storage modulus expresses the elastic component of the testing material and represents the energy stored and recovered in the system. When the storage modulus is greater than the loss modulus, it indicates that the material is highly elastic. The loss modulus expresses the viscous component of the material and represents the energy lost in the system. When the loss modulus is greater than the storage modulus, it indicates that the material is more viscous than elastic.[48,69,70,77]

Oscillatory rheometry can also measure the yield stress of filled materials. The yield stress is the force at which the internal network structure of a filled material is adequately destroyed to initiate flow.[13,38,49,67,70,71,77] The yield stress is dependent on the network structure of the material and is the stress at which the material converts from solid-like to liquid-like.[62,71] During oscillatory analysis of a typical viscoelastic material, the viscosity, storage modulus, and loss modulus for a “typical” viscoelastic material begins to increase. This is the result of low shearing on the material that further distributes the silica particles throughout the matrix and further constructs an aggregated network structure.[51,72] As the analysis progresses, the yield stress is reached and the viscosity, storage modulus, and loss modulus begin to decrease and the material begins to flow. One approach to determining the yield stress of silica-filled materials is the point at which the storage modulus (G’) and the loss modulus (G”) curves intersect. This is demonstrated in Figure 9. The aggregates are destroyed as the analysis continues by elevated shearing until the yield stress is obtained and the aggregated network structure is dismantled.[49,51,66,68,61,73,77] Given enough time after the conclusion of the analysis, the network structure will eventually recover and return to its original state in a phenomenon known as thixotropy.[16,47,50,62,69,71,77]

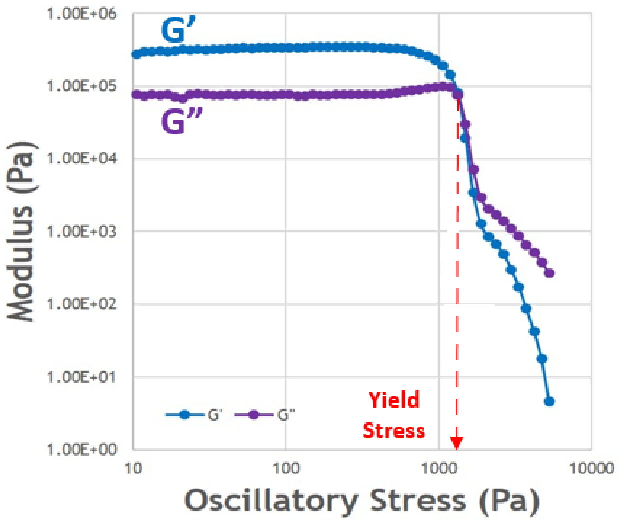

Figure 9. Storage and loss modulus versus oscillatory stress for a typical filled material. Yield stress is determined by the point where the G’ (●) and G” (●) curves intersect.

Thixotropy is a material property demonstrated by a time-dependent decrease in viscosity under a constant shear stress or shear rate that is followed by a gradual recovery in viscosity when the shear stress is removed. The flow properties and the thixotropic behavior of filled materials are generally dependent on the size of the filler, the filler loading amount, the interactions between the filler and the polymer matrix, and the interactions between the filler particles.[73] Flow rheology is a dynamic rheological technique that evaluates the thixotropic behavior of a filled material by controlling the shear rate in two stages to generate a thixotropic or hysteresis loop. Figure 10 displays a typical thixotropic loop.[74] The first stage of analysis consists of increasing the shear rate over time until a maximum shear rate is obtained, generating an “up” curve. The second stage consists of decreasing the shear rate to zero, generating a “down” curve. The area between the up and down curves make up the thixotropic loop. A large thixotropic area between the up and down curves demonstrates that the filled system requires a longer time for the network structure to be reconstructed.[75]

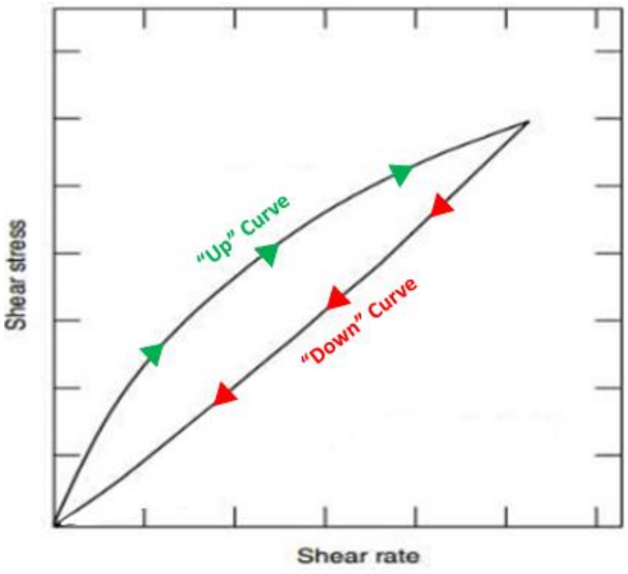

Figure 10. A typical thixotropic loop.[74]

During the first stage of the flow rheology procedure, the viscosity of the filled materials decreases as the shear rate increases. This is attributed to the destruction of the filler network structure by the increased shear rates that break the hydrogen bonds between the filler and polymer matrix, as well as the bonds between the filler particles. During the second stage of the flow rheology procedure, the viscosity of the filled materials increases as the shear rate decreases. This is attributed to the reconstruction of the filler network structure over time. The hydrogen bonds between the filler and polymer, as well as the bonds between the filler particles, begin to reform until the original network structure is obtained.[13,75] The particle interactions in thixotropic materials are displayed in Figure 11.[76]

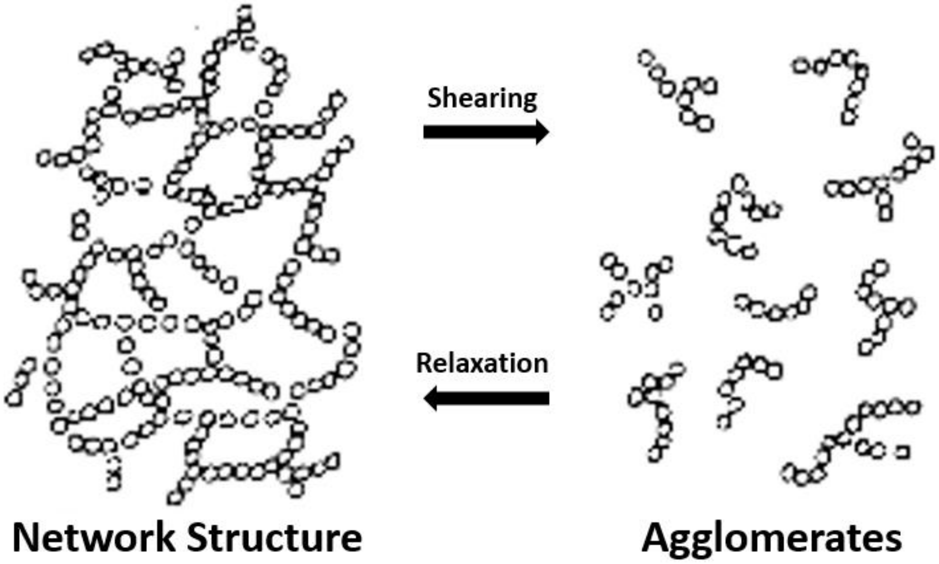

Figure 11. Particle interactions in thixotropic materials.[81]

This work seeks to quantify silanol group concentration on the surface of different silica fillers and investigate the effects of silanol group concentration on the rheological properties of filled polysiloxane polymers. Through the analysis of rheological data, this work can predict the reinforcing capabilities of each filler and will allow tailoring of future materials based on those predictions. Silanol group concentration on a particular silica filler's surface depends on the synthesizing method, surface area, and surface hydrophobicity. In this study, silanol concentration on the surface of eight commercially-available amorphous silica fillers will be calculated using the Zhuravlev model via thermogravimetric analysis (TGA). Subsequently, fillers will be combined with vinyl-terminated polydimethylsiloxane (PDMS) to produce a filled polysiloxane material. Oscillatory rheometry and flow rheometry will be used to determine rheological responses and, therefore, determine the effects of silanol concentration on rheological properties in filled polysiloxane materials.

CHAPTER II

2. OBJECTIVES

2. 1 Quantification of silanol group concentration on the surface of silica filler

The number of silanol groups on the surface of eight commercially-available amorphous silica filler were investigated using the Zhuravlev model via thermogravimetric analysis (TGA). This study calculated, evaluated, and compared the concentration of silanol groups on the surface of three precipitated silica filler with no surface treatment, three surface-treated precipitated silica fillers, a fumed silica filler with no surface treatment and a surface-treated fumed silica filler. A list of precipitated and fumed silica filler with and without surface treatment is presented below:

- Hi-Sil™ 135 (Hi-Sil-135): synthetic reinforcing precipitated silica filler with no surface treatment
- Hi-Sil™ 233 (Hi-Sil-233): synthetic reinforcing precipitated silica filler with no surface treatment
- Hi-Sil™ 233-D (Hi-Sil-233-D): synthetic reinforcing precipitated silica filler with no surface treatment
- Amsil 66 : synthetic reinforcing precipitated silica filler surface-treated with PDMS (standard hydrophobicity)

- Amsil 665 : synthetic reinforcing precipitated silica filler surface-treated with PDMS (medium-high hydrophobicity)
- Amsil 668 : synthetic reinforcing precipitated silica filler surface-treated with PDMS (high hydrophobicity)
- Cab-O-Sil® M-7D (Cab-O-Sil): synthetic reinforcing fumed silica filler with no surface treatment
- Aerosil R 8200 : synthetic reinforcing fumed silica filler surface-treated with trimethylsilyl functionality

In order to gain a better understanding of the behavior and effects of adsorbed water molecules on the surface of silica fillers, different drying methods were developed. The developed drying methods are listed as followed:

- Undried material: Each filler was used as received with no pretreatment.
- Oven-dried material: A conventional laboratory oven was used to dry each filler.
- Vacuum-dried material: A vacuum oven was to dry each filler under vacuum.

The drying methods were applied to all the filler materials prior to the calculation of silanol concentration.

2.2 Effects of the silanol group concentration on rheological properties of compounded materials

Subsequently, the effects of silanol concentration on the compounded material were investigated. A model polysiloxane was compounded with various pretreated silica fillers by twin-screw extrusion. The Process 11 was used to compound a commercially-available vinyl-terminated polydimethylsiloxane (PDMS) (Gelest DMS-V31) with a molecular weight of 28,000 g/mol, with 24 pretreated synthetic, amorphous silica fillers to produce well-mixed silica-filled polysiloxane extrudate materials.

Prior to compounding, the silica fillers were premixed with PDMS in order to feed the materials into the extruder more efficiently. The premixed materials were hand-fed into the Process 11 to be further mixed and processed into extrudate materials. The filler dispersion for compounded materials was characterized using thermogravimetric analysis (TGA). The rheological behavior and effect of the concentration of surface silanol groups of the filled PDMS was evaluated by oscillatory rheometry and flow rheology.

2.3 Prediction of reinforcing capabilities based on silanol group as determined by the Zhuravlev model

By using the Zhuravlev model via thermogravimetric analysis, it is possible to predict the reinforcing capabilities of precipitated fillers based on the concentration of silanol groups on the filler particle surface. This method has the ability to be tailored for the prediction of reinforcing capability of other precipitated silica fillers. Fumed silica fillers may require further investigations in order to predict the reinforcing capabilities based on the silanol concentration on the surface of silica particles produced through fumed synthetic methods.

CHAPTER III

3. EXPERIMENTAL

3.1 Materials

3.1.1 Commercial fillers

Eight commercial synthetic amorphous silica fillers were utilized to calculate the silanol numbers on the filler surface and to compound with the model polydimethylsiloxane in order to evaluate the rheological responses. Hi-Sil™ 135 (Hi-Sil-135), Hi-Sil™ 233-D (Hi-Sil-233D), and Hi-Sil™ 233 (Hi-Sil-233) synthetic precipitated silica fillers were donated by PPG (College Station, TX, USA).[78] Amsil 66, Amsil 665 and Amsil 668 are PDMS surface-treated synthetic precipitated silica fillers with different levels of hydrophobicity. These fillers were donated by Applied Material Solutions (Elkhorn, Wisconsin, USA).[79] Cab-O-Sil ® M7D amorphous fumed silica filler was donated by Cabot Corporation (Alpharetta, Georgia, United States).[81] Aerosil ® R 8200 amorphous fumed silica filler was donated by from Evonik Industries (Birmingham, Alabama, USA).[80] Table 1 displays the synthesis type, surface functionality, hydrophobicity, after treatment, and surface area for each filler.

Table 1. Properties of Eight Commercial Fillers

Filler Name	**Silica Type**	**Surface**	**Surface area (m^2/g)**
Hi-Sil-135	Precipitated	Silanol	150
Hi-Sil-233	Precipitated	Silanol	135
Hi-Sil-233D	Precipitated	Silanol	151
Amsil 66	Precipitated	Hydrophobic	140
Amsil 665	Precipitated	Hydrophobic	140
Amsil 668	Precipitated	Hydrophobic	140
Cab-O-Sil® M7D	Fumed	Silanol	203.1
Aerosil ® R8200	Fumed	Hydrophobic	160

3.1.2 Commercial Polysiloxanes

A commercially-available vinyl-terminated polydimethylsiloxane (PDMS) polymer DMS-V31 with a molecular weight of 28,000 g/mol was used to investigate the effects of the concentration of silanol groups on the rheological properties of compounded material. The model polysiloxane was purchased from Gelest (Morrisville, PA, USA).[82]

3.2 Methods

3.2.1 Filler Drying Methods

Each filler was used as received with no pretreatment and designated “undried”. A conventional oven was used to dry each filler. Fillers were dried for 24 Hours at 120°C using a conventional laboratory oven and designated “oven-dried”. A vacuum oven (NAPCO vacuum oven, Model 5831) was also used to dry each filler under vacuum. Fillers were dried at 120°C for 24 hours under vacuum.

3.2.2 Materials Processing

3.2.2.1 Premixing Silica-Filled PDMS

Prior to compounding, the silica fillers were premixed with PDMS to prepare a paste-like material for proper feeding into the Process 11 twin-screw extruder. Each of the silica-filled PDMS samples were calculated to contain 25 wt. % of filler. Premixing of PDMS with silica filler consisted of pouring the polysiloxane into a KitchenAid Classic 4.5 quart Mixer, Model K45SSWH (Benton Harbor, MI, USA), adding the filler to the mixer at the desired loading level (25 wt.%), and stirring the formulations with the mixer until a visually homogenous mixture was obtained. Each pre-mixed PDMS/filler mixture was approximately 50 g total.

3.2.2.2 Compounding Silica-Filled PDMS

The ThermoFisher Scientific Process 11 Parallel Twin-screw Extruder, Model 11 (Karlsruhe, Germany) [83] is a bench-top, lab-scale twin-screw extruder. Figure 12 displays the Process 11 twin-screw extruder. The throughput rates can range from 20 g/hr to 2.5 kg/hr with realistic screw geometry and processing conditions that can be scalable for industrial compounding. The Process 11 contains a 40:1 L:D ratio barrel with two 11 mm fully segmented, co-rotating screws. The Process 11 includes a chiller unit that circulates water through the feed throat of the extruder to maintain a consistent feed throat temperature.[6]

Figure 12. ThermoFisher Scientific Process 11 twin-screw extruder.[6]

The premixed PDMS with pretreated (undried, oven-dried, vacuum-dried) silica fillers were compounded through the Process 11 twin-screw extruder. Each commercial filled PDMS formulation was processed at 25°C. The chiller was set to 25°C, and a screw speed of 75 rpm was used for extrusion.

3.3 Characterization Methods

3.3.1 Thermal Characterization

3.3.1.1 Thermogravimetric Analysis of Fillers for Silanol Concentration

Thermogravimetric analysis (TGA) was used to monitor the weight loss between the temperature of 100°C to 850°C of each filler by using a TA Instruments Thermogravimetric Analyzer, Model Q550 (New Castle, DE, USA).[32] In this temperature range, the OH number and silanol number on the surface of each filler can be determined using the Zhuravlev model.[32] All experiments were purged with nitrogen gas (30 mL/min purge flow rate), using standard platinum pans at a heating rate of 5°C/min to 850°C. The onset of degradation temperatures for each material was recorded by TA Universal Analysis software. A weight loss between 120 °C and 850 °C was observed for each filler. Three sample runs were performed for each filler and each type of pretreatment.

Subsequent to TGA analysis, the OH number and silanol number on the surface of each filler was calculated using the Zhuravlev model.[32] Undried samples, oven-dried samples and vacuum-dried samples were compared in order to determine the results of pretreatment on the filler powder.

3.3.1.2 Thermogravimetric Analysis of Filled PDMS

TGA was also used to evaluate the distribution of filler in the silica-filled PDMS materials by determining the percent residue present in three specimens per compounded extrudate material. All experiments were purged with nitrogen gas (30 mL/min purge flow rate), at a heating rate of 10°C/min to 700°C. The three specimens tested per extrudate material were taken from the beginning of the compounding process, middle of the compounding process, and end of the compounding process. The residue percentage were recorded by TA Universal Analysis software. Undried samples, oven-dried samples, and vacuum-dried samples were compared in order to determine the effect of filler pretreatment on the resulting compounded material.

3.3.2 Rheological Characterization

3.3.2.1 Oscillatory Rheometry

Oscillatory rheometry was used to determine the rheological responses and yield stresses of the filled PDMS materials using a TA Instruments Rotational Rheometer, Ltd AR2000EX (New Castle, DE, USA) with a 40 mm diameter steel flat plate and a 1 mm gap at 25°C. The frequency was held at 1 Hertz and an oscillatory stress sweep from 3 Pa to 10,000 Pa was applied to the filled PDMS material. The results were analyzed by TA Data Analysis software.

3.3.2.2 Flow rheology

Flow rheology was performed on the compounded materials, also. The TA Instruments Rotational Rheometer, Ltd AR2000EX (New Castle, DE, USA) used a 40 mm diameter steel flat plate and a 1 mm gap at 25°C. A linear shear rate from 0.01 sec^{-1} to 10 sec^{-1} was applied to the filled formulations, followed by a linear shear rate from 10 sec^{-1} to 0.01 sec^{-1}. The results were analyzed by TA Data Analysis software.

CHAPTER IV

4. RESULTS AND DISCUSSION

4.1 Fillers

Active fillers are chemically-treated silica fillers that strongly reinforce and significantly improve the physical properties of polysiloxane elastomers. Reinforcing fillers consist of precipitated and fumed silica fillers. It is also possible to chemically treat the precipitated and fumed silica fillers on the surface area which makes them suitable and selectable for wide variety of applications. We further examined the effects of pre-drying the fillers prior to extrusion to determine if this process has any effect on silanol number and/or rheological properties of the compounded material beyond the type of filler.

4.2 Zhuravlev model

Zhuravlev and his colleagues suggested a method to calculate the total hydroxyl group and silanol groups on the surface of different silica fillers by using TGA. The total hydroxyl group content in silica can be calculated from the entire second weight loss step which starts from the point where all the physically adsorbed water is removed (T_0=120°C) and ends at the end point of measurement (T_{Final} =850°C). It is assumed that all the silanol groups are released at the end point of heating, therefore, the residue of the sample is an oxide composed of only siloxane bridges. The Zhuravlev method assumes that no volatiles are released from the sample besides water. The hydroxyl group, determined as millimoles of hydroxyls left per gram of silica at temperature T_0, can be calculated by using the following formula:

$$n\,OH = 2\,n\,H_20 = 1000 \times \frac{2\,[WL\,(T_0) - WL(T_{final})]}{100\,.\,M_{H_2O}} \tag{1}$$

Where the $WL(T_0)$ - $WL(T_{Final})$ is the weight percent loss in the temperature region of T_0 to T_{Final} and M_{H2O} is the molar mass of water.[32] Furthermore, the Zhuravlev model suggests the following formula to calculate the numbers of silanol groups on the surface:

$$\text{Number of Silanol Groups (OH nm}^{-2}\text{)} = k \times \frac{\text{OH number} \left(\frac{\text{mmol}}{\text{g}}\ \text{SiO}_2 \right)}{\text{Specific Surface Area}} \tag{2}$$

Where K can be calculated by the following formula: $k = N_A * 10^{-21}$, $N_A = 6.022 \times 10^{23}$, and k= 602.2. Specific Surface Area can also be calculated by using Brunauer–Emmett–Teller (BET) method.[32]

4.3 Analysis of Silica Fillers

4.3.1 Synthetic Precipitated Silica Fillers

4.3.1.1 Precipitated Silica Filler With No Surface Treatment

4.3.1.1.1 Hi-Sil-135

4.3.1.1.1 Filler Appearance

Hi-Sil-135 synthetic precipitated silica filler with no surface treatment was used to evaluate the hydroxyl number and silanol number on the surface with particles ranging from 44 to 54 µm in size and a surface area of 150 m^2/g. Filler was used as received with no pretreatment and designated “undried”. A conventional oven was used to dry Hi-Sil-135. Fillers were dried for 24 Hours at 120°C using conventional laboratory oven and designated “oven-dried”. A vacuum oven was also used to dry Hi-Sil-135. Fillers were dried at 120°C for 24 hours under vacuum and designated “vacuum-dried”. Figure 13 exhibits the appearance of undried Hi-Sil-135, oven-dried Hi-Sil-135 and vacuum-dried Hi-Sil-135. All the fillers exhibit a white, flaky, and powder-type physical appearance.

Figure 13. Appearance of the undried Hi-Sil-135, oven-dried Hi-Sil-135 and vacuum-dried Hi-Sil-135 (left to right).

4.3.1.1.1.2 Zhuravlev model

Figure 14 displays the overlay of TGA runs of undried Hi-Sil-135, oven-dried Hi-Sil-135 and vacuum-dried Hi-Sil-135. Table 2 represents the second step weight change, pretreatment method, surface area, particle size, the total hydroxyl groups, and the silanol groups on the surface of undried Hi-Sil-135, oven-dried Hi-Sil 135, and vacuum-dried Hi-Sil-135 using the Zhuravlev model.

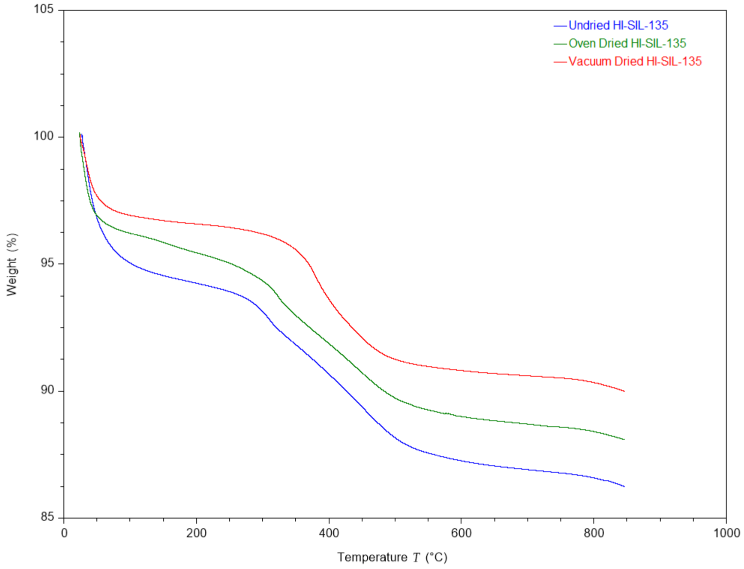

Figure 14. TGA thermograms of Undried Hi-Sil-135(—), Oven-dried Hi-Sil-135(—), and Vacuum-dried Hi-Sil-135 (—).

Table 2. Hi-Sil-135 Pretreatment method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	**Second Step Weight Loss (%)**	**Hydroxyl Groups (mmol/g SiO_2)**	**Silanol Groups (OH nm^{-2})**
Undried	8.81	9.78	39.25
Oven-dried	8.12	9.02	36.20
Vacuum-dried	6.93	7.69	30.88

The comparison of thermograms shows that the overall weight change in Hi-Sil-135 changes with the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler. Undried Hi-Sil-135 exhibits the highest overall weight change in comparison with oven-dried Hi-Sil-135 and vacuum-dried Hi-Sil-135. The weight loss of oven-dried Hi-Sil-135 is higher than vacuum-dried Hi-Sil-135. This different weight loss can be attributed to the designated drying method. In vacuum-dried Hi-Sil-135, water on the filler particle surface was extracted via the use of vacuum. Thus, it is expected to observe a reduction in weight loss compared to oven-dried and undried material. Oven-dried material exhibits more overall weight change than undried material. Evaporation of water molecules in oven drying method reduces hydroxyl groups on the filler surface that can be attributed to water therefore, less weight loss was observed in oven-dried Hi-Sil-135 compared to undried Hi-Sil-135.

The pretreatment method of Hi-Sil-135 plays a significant role in the amount of silanol groups on the filler particle surface. The calculation in Table 2 shows that the silanol number on the surface of Hi-Sil-135 precipitated silica filler decreases as the pretreatment method is changed from undried to oven-dried to vacuum-dried. Undried Hi-Sil-135 has 39.25 OH nm^{-2} silanol groups on its surface, while oven-dried Hi-Sil-135 bares 36.20 OH nm^{-2} silanol groups on its surface, and vacuum-dried Hi-Sil-135 filler has 30.88 OH nm^{-2} silanol groups on its surface.

4.3.1.1.2 Hi-Sil-233

4.3.1.1.2.1 Filler Appearance

Hi-Sil-233 synthetic precipitated silica filler with no surface treatment was used to evaluate the hydroxyl number and silanol number on the surface with particles ranging from 58 to 60 µm and surface area of 135 m^2/g. Hi-Sil-233 was treated in the same way described above for Hi-Sil-135. Figure 15 shows the appearance of undried Hi-Sil-233, oven-dried Hi-Sil-233 and vacuum-dried Hi-Sil-233. All the fillers exhibit a white, flaky and powder-type physical appearance.

Figure 15. Appearance of the Undried Hi-Sil-233, Oven-dried Hi-Sil-233 and Vacuum-dried Hi-Sil-233 (left to right).

4.3.1.1.2.2 Zhuravlev model

Figure 16 displays the overlay of TGA runs of undried Hi-Sil-233, oven-dried Hi-Sil-233 and vacuum-dried Hi-Sil-233. Table 3 represents the pretreatment method, second step weight loss, total hydroxyl groups, and total silanol groups on the surface of undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233 using the Zhuravlev model.

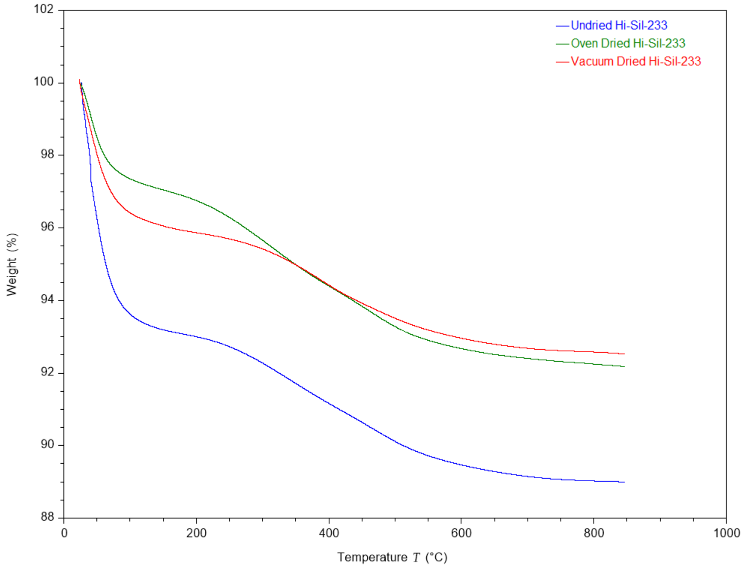

Figure 16. TGA thermograms of the Undried dried Hi-Sil-233 (—), Oven-dried Hi-Sil-233 (—), and Vacuum-dried Hi-Sil-233 (—).

Table 3. Hi-Sil-233 Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	**Second Step Weight Loss (%)**	**Hydroxyl Groups (mmol/g SiO_2)**	**Silanol Groups (OH nm^{-2})**
Undried	5.04	5.59	24.95
Oven-dried	4.39	4.87	21.73
Vacuum-dried	3.71	4.12	18.37

The comparison of thermograms in Figure 16 exhibits that the overall weight change in undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil 233 decreases by changing the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler, similar to that of Hi-Sil-135. This difference in weight loss can be attributed to designated drying method, also.

Type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 3 shows that the silanol number on the surface of Hi-Sil-233 precipitated silica filler decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Hi-Sil-233 has 24.95 OH nm^{-2} silanol groups on its surface, while oven-dried Hi-Sil-135 bares 21.73 OH nm^{-2} silanol groups, and vacuum-dried Hi-Sil-233 filler has 18.37 OH nm^{-2} on its surface.

4.3.1.1.3 Hi-Sil-233-D

4.3.1.1.3.1 Filler Appearance

Hi-Sil-233-D synthetic precipitated silica filler with no surface treatment was used to evaluate the hydroxyl number and silanol number on the surface with particles ranging from 64 to 77 µm and a surface area of 150 m^2/g. Hi-Sil-233-D was treated in the same way described above for Hi-Sil-135 and Hi-Sil-233. Figure 17 exhibits the appearance of undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D. All the fillers exhibit a white, flaky, and powder-type physical appearance.

Figure 17. Appearance of the Undried Hi-Sil-233-D, Oven-dried Hi-Sil-233-D, and Vacuum-dried Hi-Sil-233-D (left to right).

4.3.1.1.3.2 Zhuravlev model

Figure 18 displays the overlay of TGA runs of undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D. Table 4 represents the pretreatment, second step weight change, the total hydroxyl groups, and total silanol groups on the surface of undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D using the Zhuravlev model.

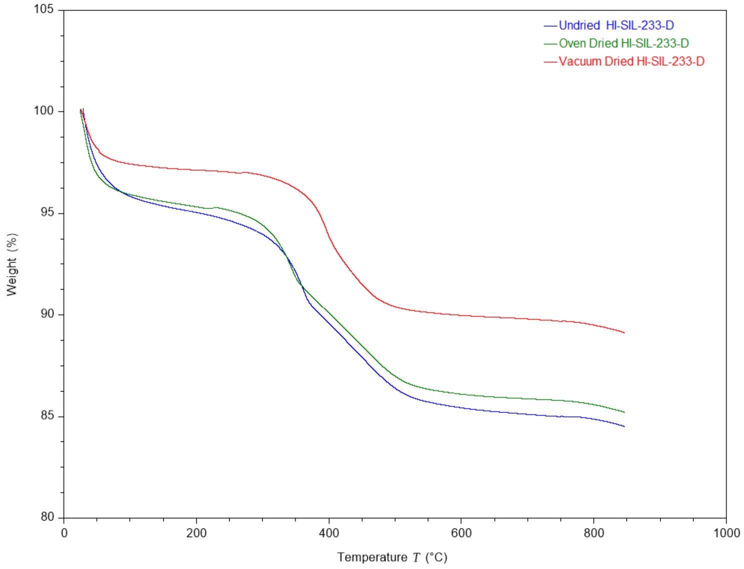

Figure 18. TGA thermograms of the Undried Hi-Sil-233-D (—), Oven-dried Hi-Sil-233-D (—), and Vacuum-dried Hi-Sil-233-D (—).

Table 4. Hi-Sil-233-D Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	**Second Step Weight Loss (%)**	**Hydroxyl Groups (mmol/g SiO_2)**	**Silanol Groups (OH nm^{-2})**
Undried	11.33	12.57	50.15
Oven-dried	10.71	11.90	47.45
Vacuum-dried	8.30	9.21	36.74

The comparison of thermograms in Figure 18 exhibits that the overall weight change in undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil 233-D decreases by changing the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler, similar to that of Hi-Sil-135 and Hi-Sil-233. This difference in weight loss can be attributed to designated drying method, also.

Type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 4 shows that the silanol number on the surface of

Hi-Sil-233-D precipitated silica filler decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Hi-Sil-233-D has 50.15 OH nm^{-2} silanol groups on its surface, while oven-dried Hi-Sil-233D bares 47.45 OH nm^{-2} silanol groups on its surface, and vacuum-dried Hi-Sil-233-D filler has 36.74 OH nm^{-2} on its surface.

4.3.1.2 Surface-treated Precipitated Silica Filler

4.3.1.2.1 Amsil 66

4.3.1.2.1.1 Filler Appearance

Amsil 66 PDMS surface-treated synthetic precipitated silica filler was used to evaluate the hydroxyl number and silanol number on the surface with particle size of 4 µm and a surface area of 140 m^2/g. Amsil 66 was treated in the same way described above for the “Hi-Sil” fillers. Figure 19 exhibits the appearance of undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66. All the fillers exhibit a white, flaky and powder-type physical appearance.

Figure 19. Appearance of Undried Amsil 66, Oven-dried Amsil 66 and Vacuum-dried Amsil 66 (left to right).

4.3.1.2.1.2 Zhuravlev model

Figure 20 displays the overlay of TGA runs of undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66. Table 5 represents the pretreatment method, the second step weight loss, the total hydroxyl groups, and the total silanol groups on the surface of undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 using the Zhuravlev model.

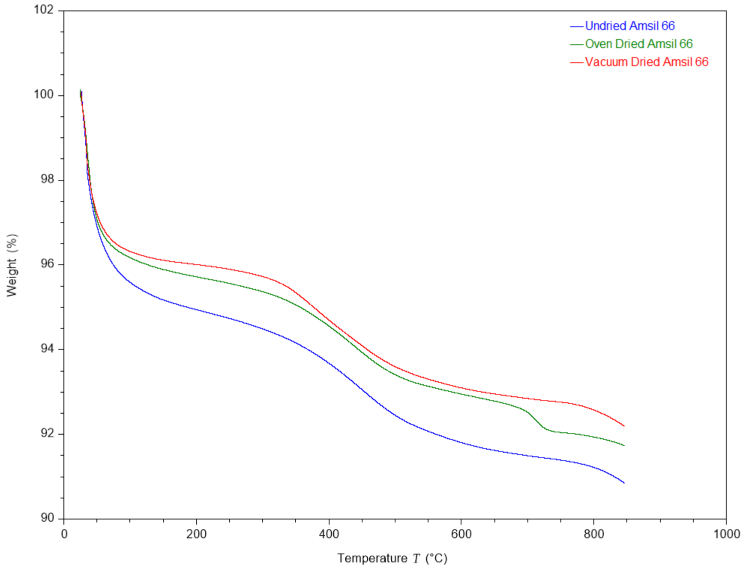

Figure 20. TGA thermograms of the Undried dried Amsil 66 (—), Oven-dried Amsil 66 (—), and Vacuum-dried Amsil 66 (—).

Table 5. Amsil 66 Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	Second step Weight Loss (%)	Hydroxyl Groups (mmol/g SiO2)	Silanol Groups (OH nm^{-2})
Undried	4.53	5.04	21.66
Oven-dried	4.31	4.78	20.56
Vacuum-dried	4.02	4.46	19.20

The comparison of thermograms in Figure 20 exhibits that the overall weight change in undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 decreases by changing the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler, similar to that of the Hi-Sil filler with no surface treatment. This difference in weight loss can be attributed to designated drying method, also.

The type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 5 shows that the silanol number on the surface of Amsil 66 surface-treated precipitated silica filler decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Amsil 66 has 21.66 OH nm^{-2} silanol groups on its surface, while oven dried Amsil 66 bares 20.56 OH nm^{-2} silanol groups, and vacuum-dried Amsil 66 filler has 19.20 OH nm^{-2} silanol groups.

4.3.1.2.2 Amsil 665

4.3.1.2.2.1 Filler Appearance

Amsil 665 PDMS surface-treated synthetic precipitated silica filler was used to evaluate the hydroxyl number and silanol number on the surface with particle size of 4 µm and a surface area of 140 m^2/g. Amsil 665 was treated in the same way described above for the “Hi-Sil” fillers and Amsil 66. Figure 21 exhibits the appearance of undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665. All the fillers exhibit a white, flaky, and powder-type physical appearance.

Figure 21. Appearance of Undried Amsil 665, Oven-dried Amsil 665, and Vacuum-dried Amsil 665 (left to right).

4.3.1.2.2.2 Zhuravlev model

Figure 22 displays the overlay of TGA runs of undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665. Table 6 represents the pretreatment method, the second step weight loss, the total hydroxyl groups, and the total silanol groups on the surface of undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665 using the Zhuravlev model.

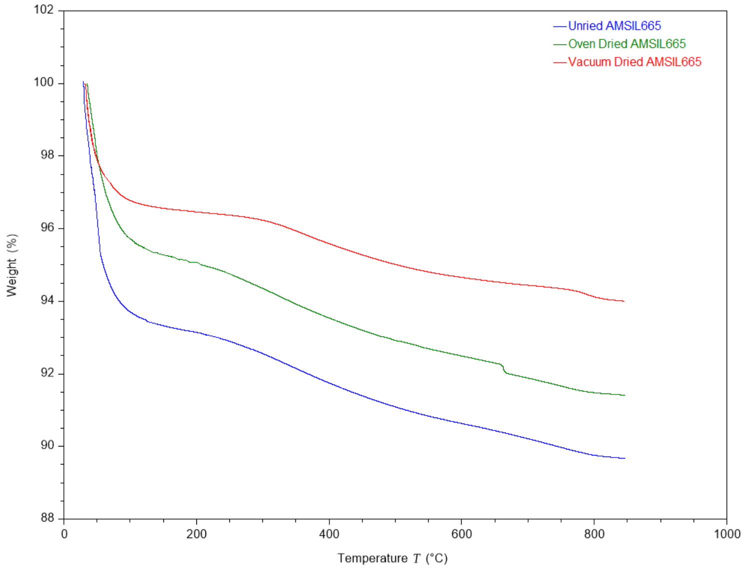

Figure 22. TGA thermograms of the Undried dried Amsil 665 (—), Oven-dried Amsil 665 (—), and Vacuum-dried Amsil 665 (—).

Table 6. Amsil 665 Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	Second Step Weight Loss (%)	Hydroxyl Groups (mmol/g SiO2)	Silanol Groups (OH nm^{-2})
Undried	4.31	4.78	20.58
Oven-dried	4.03	4.48	19.28
Vacuum-dried	3.10	3.44	14.82

The comparison of thermograms in Figure 22 exhibits that the overall weight change in undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665 decreases by changing the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler, similar to that of the Hi-Sil fillers with no surface treatment and Amsil 66. This difference in weight loss can be attributed to designated drying method, also. The type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 6 shows that the silanol number on the surface of Amsil 665 surface-treated precipitated silica filler decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Amsil 665 has 20.58 OH nm^{-2} silanol groups on its surface, while oven-dried Amsil 665 bares 19.58 OH nm^{-2} silanol groups on its surface, and vacuum-dried Amsil 665 filler has 14.82 OH nm^{-2} on its surface.

4.3.1.2.3 Amsil 668

4.3.1.2.3.1 Filler Appearance

Amsil 668 PDMS surface-treated synthetic precipitated silica filler was used to evaluate the hydroxyl number and silanol number on the surface with particle size of 4 µm and a surface area of 140 m^2/g. Amsil 668 was treated in the same way described above for the “Hi-Sil” fillers, Amsil 66, and Amsil 665. Figure 23 exhibits the appearance of undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668. All the fillers exhibit a white, flaky, and powder-type physical appearance.

Figure 23. Appearance of Undried Amsil 668, Oven-dried Amsil 668, and Vacuum-dried Amsil 668 (left to right).

4.3.1.2.3.2 Zhuravlev model

Figure 24 displays the overlay of TGA runs of undried Amsil 668, oven dried Amsil 668 and vacuum dried Amsil 668. Table 7 represents the pretreatment method, the second step weight loss, the total hydroxyl groups, and the total silanol groups on the surface of undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668 using the Zhuravlev model.

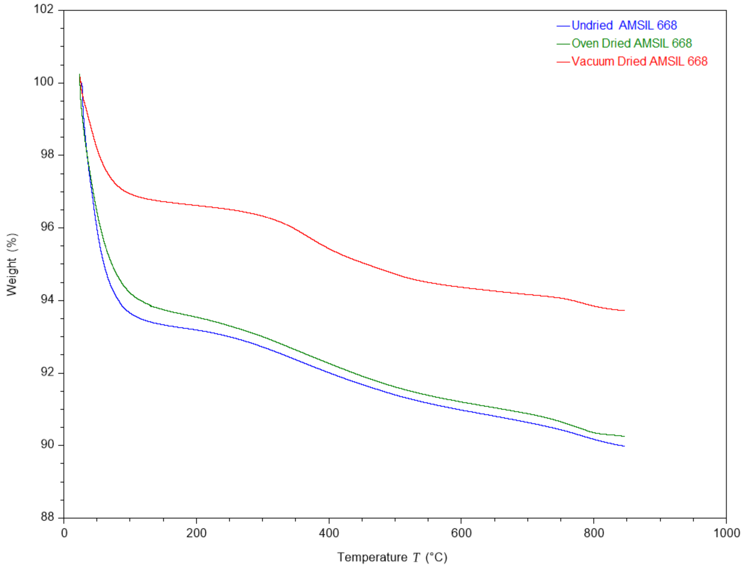

Figure 24. TGA thermograms of Undried dried Amsil 668 (—), Oven-dried Amsil 668 (—), and Vacuum-dried Amsil 668 (—).

Table 7. Amsil 668 Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	**Second Step Weight Loss (%)**	**Hydroxyl Groups (mmol/g SiO2)**	**Silanol Groups (OH nm^{-2})**
Undried	3.24	3.60	15.49
Oven-dried	3.48	3.86	16.63
Vacuum-dried	2.77	3.08	13.25

The type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 7 shows that the silanol number on the surface of Amsil 668 surface-treated precipitated silica filler decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Amsil 668 has 15.49 OH nm^{-2} silanol groups on its surface, while oven-dried Amsil 668 bares 16.63 OH nm^{-2} silanol groups on its surface, and vacuum-dried Amsil 668 filler has 13.25 OH nm^{-2} silanol groups on its surface.

4.3.2 Synthetic Fumed Silica Filler

4.3.2.1 Fumed Silica Filler with No Surface Treatment

4.3.2.1.1 Cab-O-Sil

4.3.2.1.1.1 Filler Appearance

Cab-O-Sil synthetic fumed silica filler with no surface treatment was used to evaluate the hydroxyl number and silanol number on the surface with particle size of 38 µm and a surface area of 203.1 m^2/g. Cab-O-Sil was treated in the same way described above for the “Hi-Sil” and “Amsil” fillers. Figure 25 exhibits the appearance of undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil. All the fillers exhibit a white, flaky, and powder-type physical appearance.

Figure 25. Appearance of Undried Cab-O-Sil, Oven-dried Cab-O-Sil, and Vacuum-dried Cab-O-Sil (left to right).

4.3.2.1.1.2 Zhuravlev model

Figure 26 displays the overlay of TGA runs of undried Cab-O-Sil, oven-dried Cab-O-Sil and vacuum-dried Cab-O-Sil. Table 8 represents the pretreatment method, the second step weight loss, the total hydroxyl groups, and the total silanol groups on the surface of undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil using the Zhuravlev model.

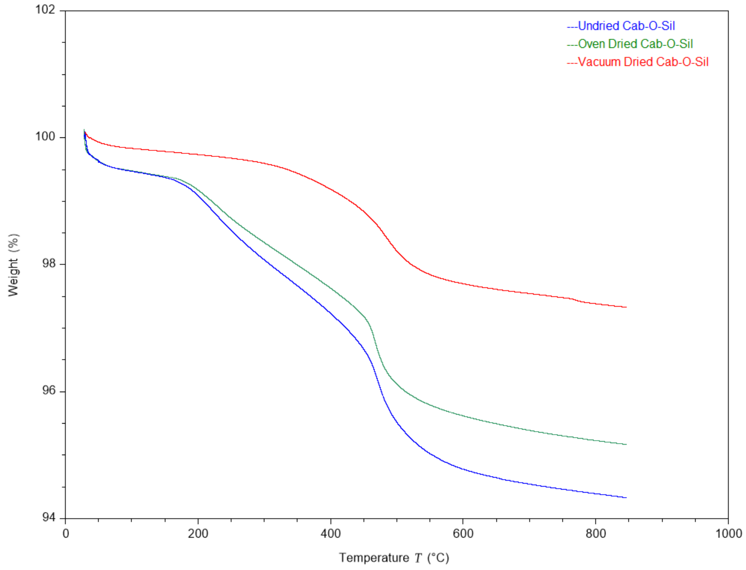

Figure 26. TGA thermograms of the Undried dried Cab-O-Sil (—), Oven-dried Cab-O-Sil (—), and Vacuum-dried Cab-O-Sil (—).

Table 8. Cab-O-Sil Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol groups Determined by the Zhuravlev model.

Pretreatment	**Second Step Weight Loss (%)**	**Hydroxyl Groups (mmol/g SiO2)**	**Silanol Groups (OH nm^{-2})**
Undried	5.11	5.67	16.81
Oven-dried	4.20	4.66	13.82
Vacuum-dried	2.48	2.76	8.18

The comparison of thermograms in figure 26 exhibits that the overall weight change in undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil decreases by changing the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler, similar to that of the Hi-Sil fillers with no surface treatment and surface-treated Amsil fillers. This difference in weight loss can be attributed to designated drying method, also.

The type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 8 shows that the silanol number on the surface of Cab-O-Sil fumed silica filler with no surface treatment decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Cab-O-Sil has 16.81 OH nm^{-2} silanol groups on its surface, while oven-dried Cab-O-Sil bares 13.82 OH nm^{-2} silanol groups on its surface, and vacuum-dried Cab-O-Sil filler has 8.18 OH nm^{-2} silanol groups on its surface.

4.3.2.2 Surface-treated Fumed silica filler

4.3.2.2.1 Aerosil

4.3.2.2.1.1 Filler Appearance

Aerosil R 8200 trimethylsilyl surface-treated synthetic fumed silica filler was used to evaluate the hydroxyl number and silanol number on the surface with the particle size of 26 µm and surface area of 160 m^2/g. Aerosil was treated in the same way described above for the “Hi-Sil” fillers, “Amsil” fillers, and Cab-O-Sil. Figure 27 exhibits the appearance of undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil. All the fillers exhibit a white, flaky, and powder-type physical appearance.

Figure 27. Appearance of Undried Aerosil, Oven-dried Aerosil, and Vacuum-dried Aerosil (left to right).

4.3.2.2.1.2 Zhuravlev model

Figure 28 displays the overlay of TGA runs of undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil. Table 9 represents the pretreatment method, the second step weight loss, the total hydroxyl groups, and the total silanol groups on the surface of undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil using the Zhuravlev model.

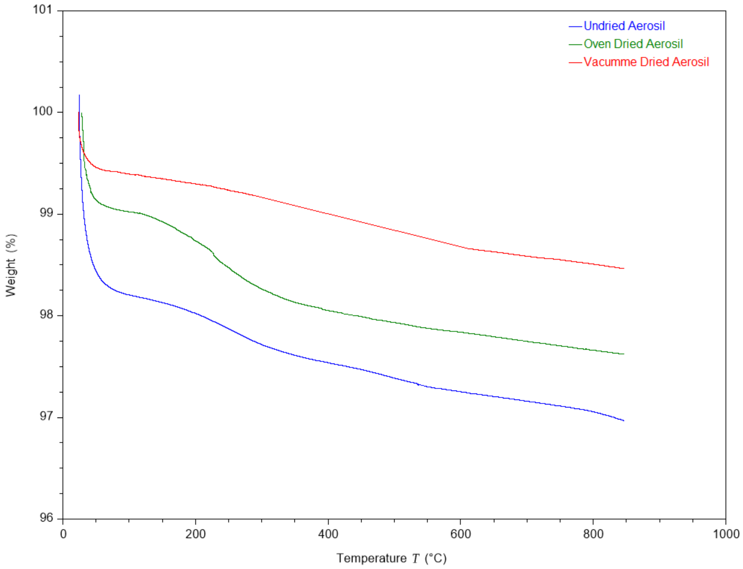

Figure 28. TGA thermograms of Undried dried Aerosil (—), Oven-dried Aerosil (—), and Vacuum-dried Aerosil (—).

Table 9. Aerosil Pretreatment Method, Total Second Step Weight loss, Total Hydroxyl, and Total Silanol Groups Determined by the Zhuravlev model.

Pretreatment	**Second Step Weight Loss (%)**	**Hydroxyl Groups (mmol/g SiO_2)**	**Silanol Groups (OH nm^{-2})**
Undried	1.38	1.53	5.77
Oven-dried	1.21	1.34	5.06
Vacuum-dried	0.91	1.01	3.81

The comparison of thermograms in Figure 28 exhibits that the overall weight change in undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil decreases by changing the pretreatment method and causes a decrease in hydroxyl groups on the surface of filler, similar to that of the Hi-Sil fillers with no surface treatment, surface-treated Amsil fillers, and Cab-O-Sil. This difference in weight loss can be attributed to designated drying method, also.

The type of pretreatment method on the precipitated silica filler with no surface treatment plays a significant role in the amount of silanol groups on the surface of the filler particles. The calculation in Table 9 shows that the silanol number on the surface of surface-treated Aerosil fumed silica filler decreased as the pretreatment method is changed from undried to oven-dried and from oven-dried to vacuum-dried. Undried Aerosil has 5.77 OH nm^{-2} silanol groups on its surface, while oven-dried Aerosil bares 5.06 OH nm^{-2} silanol groups on its surface, and vacuum-dried Aerosil filler has 3.81 OH nm^{-2} on its surface.

4.3.3 Summary Table

Table 10 details the surface area, level of hydrophobicity, particle size, pretreatment method, and amount of silanol groups on the surface of Hi-Sil-135, Hi-Sil-233, Hi-Sil-233-D, Amsil 66, Amsil 665, Amsil 668, Cab-O-Sil and Aerosil R 8200 using the Zhuravlev model.

Table 10. Calculation of Silanol Number on Filler Surfaces as Determined by the Zhuravlev Model for All Fillers and All Pretreatment Methods

Filler Name	**Type**	**Surface**	**Surface Area (m^2/g)**	**Particle Size (μm)**	**Pretreatment**	**Silanol Groups ($OH\ nm^{-2}$)**
Hi-Sil-135 [25]	Precipitated	Silanol	150	44-54	Undried	39.25
					Oven-Dried	36.20
					Vacuum-Dried	30.88
Hi-Sil-233 [26]	Precipitated	Silanol	135	55-60	Undried	24.95
					Oven-Dried	21.73
					Vacuum-Dried	18.37
Hi-Sil-233-D [27]	Precipitated	Silanol	150	64-77	Undried	50.18
					Oven-Dried	47.45
					Vacuum-Dried	36.74
Amsil 66 [28]	Precipitated	Hydrophobic	140	4	Undried	21.66
					Oven-Dried	20.56
					Vacuum-Dried	19.20
Amsil 665 [29]	Precipitated	Hydrophobic	140	4	Undried	20.58
					Oven-Dried	19.28
					Vacuum-Dried	13.25
Amsil 668 [30]	Precipitated	Hydrophobic	140	4	Undried	17.68
					Oven-Dried	16.63
					Vacuum-Dried	14.82
Cab-O-Sil [31]	Fumed	Silanol	203.1	38	Undried	16.81
					Oven-Dried	13.82
					Vacuum-Dried	8.18
Aerosil [32]	Fumed	Hydrophobic	160	26	Undried	5.77
					Oven-Dried	5.06
					Vacuum-Dried	3.81

Specific surface area and filler particles size play a significant role in the amount silanol groups on the surface of filler particles. The calculation in table 10 shows that the silanol number on the surface of precipitated filler particles decreases with decreasing the surface area. This trend can be observed by comparing the of silanol number of undried Hi-Sil-233-D with that of undried Hi-Sil-233. Undried Hi-Sil-233-D has the surface area of 150 m^2/g and has 50.18 OH nm^{-2} silanol groups on its surface. In comparison, undried Hi-Sil-233 has the surface area of 135 m^2/g and has less than half the silanol groups on its surface: 24.95 OH nm^{-2}.

Additionally, it was determined that the higher specific surface area and filler particle size can result in a higher amount of silanol group on the surface. Hi-Sil-233-D and Hi-Sil-135 share the same surface area surface area (150 m^2/g). The particle size in Hi-Sil-233-D ranges from 64 to 77 µm which is higher than of Hi-Sil-135 with the particle size of 44 to 54 µm. Therefore, it was expected that Hi-Sil-233-D would have a higher number of surface silanol groups compared to Hi-Sil-135. Hi-Sil-233-D has a silanol number of 50.18 OH nm^{-2}, which is higher than that of Hi-Sil-135 with 39.25 OH nm^{-2}. Level of hydrophobicity can also change the amount of silanol groups on the surface of filler particles. Amsil 66, Amsil 665 and Amsil 668 share the same specific surface area (140 m^2/g) and particle size (4 µm) with different levels of hydrophobic agent (PDMS) on their surfaces. By increasing the level of surface hydrophobicity, silanol number decreases. Undried Amsil 66, which has the standard amount of hydrophobic agent on its surface, exhibits a silanol number of 21.66 OH nm^{-2}, which is higher than undried Amsil 665 with medium-high level of hydrophobic PDMS (silanol number of 20.58 OH nm^{-2}). Amsil 668, with the highest level of hydrophobic agent on the surface, has the lowest silanol number of all three Amsil-type fillers: 17.68 OH nm^{-2}.

Different pretreated fillers show a decrease in silanol number as the material progressed from undried filler to oven-dried filler to vacuum-dried filler. Drying the material in 120 °C for 24 hours causes the evaporation of water which reduces the apparent surface hydroxyl groups and, consequently, the silanol groups on the surface show a decrease throughout all the examined fillers. Undried fillers had no pretreatment and all the hydroxyl groups were present on the filler particle surfaces. Thus, they exhibit the higher value of hydroxyl groups and, consequently, silanol groups on the surface. Drying the filler in a conventional laboratory oven causes the evaporation of hydroxyl groups on the surface of the filler, but some water is retained within the oven, and can be reabsorbed by the filler. Oven-dried fillers show a reduced silanol number compared to undried fillers for this reason. In vacuum drying, water is constantly extracted from the fillers and has no chance of readsorption. The resulting surface silanol number is decreased, compared to oven-dried fillers.

The synthesis method of silica fillers also plays a role in the surface silanol concentration. Fumed silica fillers have a large specific surface area however, they exhibit very small silanol numbers compared to their precipitated counterparts. Undried Cab-O-Sil has the surface area of 203.1 m^2/g and has 16.81 OH nm^{-2} silanol groups on its surface, compared to precipitated Hi-Sil-233-D, with a surface area of 150 m^2/g and silanol number of 50.18 OH nm^{-2}. The high level of hydrophobicity and fumed synthesis method of trimethylsilyl-surface treated Aerosil results in the lowest silanol numbers of the fillers studied. Undried precipitated PDMS surface-treated Amsil 668 with a specific surface area of 140 m^2/g has a silanol number of 17.68 OH nm^{-2}. Undried Aerosil with a specific surface area of 160 m^2/g has a silanol number of 5.77 OH nm^{-2}.

CHAPTER V

5. RESULTS AND DISCUSSION

5.1 Compounding process

The Process 11 twin-screw extruder was utilized to compound PDMS with eight synthetic amorphous silica fillers and three types of pretreatment (undried, oven-dried, and vacuum-dried) to determine the reinforcing properties of each filler based on the calculated number of silanol groups on the surface of each filler. All formulations consisted of PDMS and 25 wt. % synthetic amorphous silica filler. PDMS and pretreated filler were premixed for proper feeding into the extruder. When the fillers were first introduced into the PDMS, the mixtures would thicken into a ball, but as the mixtures were continuously mixed for one minute, the viscosity decreased and the mixtures began to flow to the bottom of the mixing bowl. The premixed PDMS with pretreated silica fillers were hand-fed into the Process 11 twin-screw extruder. During the compounding process of each formulation studied, all commercial filled PDMS formulations were processed at 25°C. The chiller was set to 25°C, and a screw speed of 75 rpm was used for extrusion. While compounding the PDMS with pretreated silica fillers, the torque reached up to 1.0 N m.

5.2 Observations and Filler Distribution of Filled PDMS

5.2.1 Synthetic Precipitated Silica Fillers

5.2.1.1 Precipitated Silica Filler with No Surface Treatment

5.2.1.1.1 Hi-Sil-135

The compounded PDMS with 25 wt. % of undried Hi-Sil-135, oven-dried Hi-Sil-135, and vacuum-dried Hi-Sil-135 was soft, paste-like material. The color of compounded material for undried Hi-Sil-135 was white and clear, but oven-dried material exhibited a darker color, and vacuum-dried material displayed a yellow color. This change in the color seems to be due to the pretreatment method of filler. Figure 29 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried and vacuum-dried, Hi-Sil-135 silica filler and PDMS.

Figure 29. Appearance of the filled PDMS compounded materials after extrusion: Undried Hi-Sil-135, Oven-dried Hi-Sil-135, and Vacuum-dried Hi-Sil-135 (left to right).

Figure 30 displays the TGA thermograms of the filled PDMS compounded with undried Hi-Sil-135, oven-dried Hi-Sil-135, and vacuum-dried Hi-Sil-135. The curves in Figure 30 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Hi-Sil-135, oven-dried Hi-Sil-135, and vacuum-dried Hi-Sil-135 are presented in Table 11. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

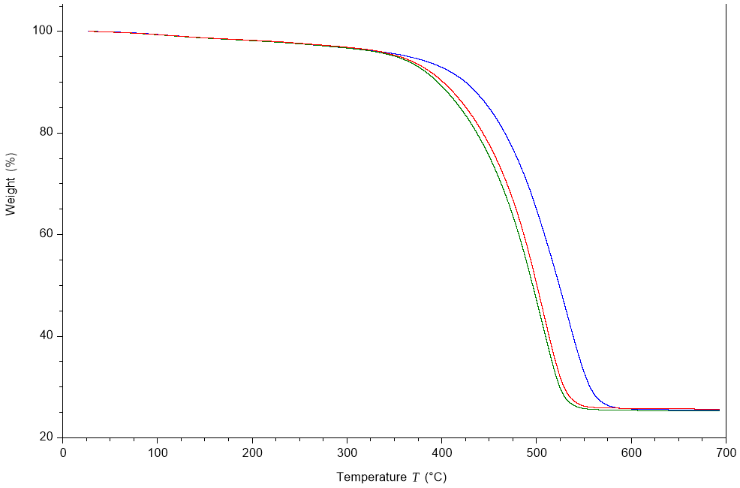

Figure 30. TGA thermograms of the Undried Hi-Sil-135 (—), Oven-dried Hi-Sil-135 (—), and Vacuum-dried Hi-Sil-135 (—).

Table 11. Hi-Sil-135-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	25.14
Oven-dried	25.16
Vacuum-dried	25.20

The consistent residue percentage resulting from thermograms of undried Hi-Sil-135, oven-dried Hi-Sil-135, and vacuum-dried Hi-Sil-135 determined that fillers were distributed evenly throughout the polymer matrix and were similar to the calculated percentage of filler.

5.2.1.1.2 Hi-Sil-233

The compounded PDMS with 25 wt. % of undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233 was soft, paste-like material similar to that of Hi-Sil-135. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 31 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried, and vacuum-dried Hi-Sil-233 silica filler and PDMS.

Figure 31. Appearance of the filled PDMS compounded materials after extrusion: Undried Hi-Sil-233, Oven-dried Hi-Sil-233, and Vacuum-dried Hi-Sil-233 (left to right).

Figure 32 displays the TGA thermograms of the filled PDMS compounded with undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233. The curves in Figure 32 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233 are presented in Table 12. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

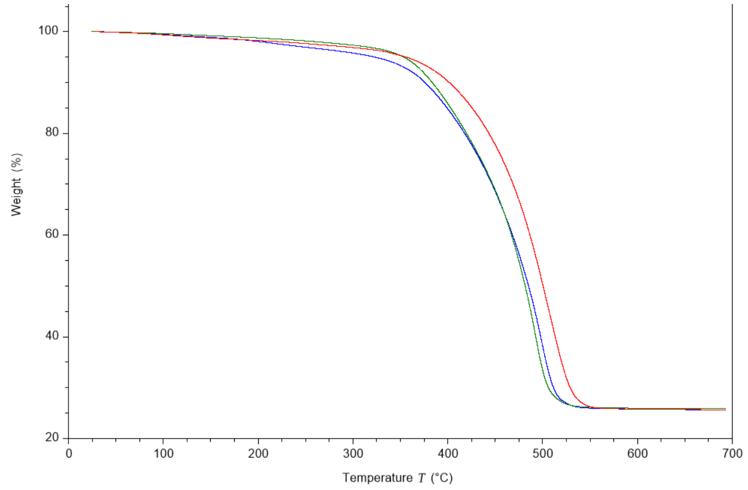

Figure 32. TGA thermograms of the Undried Hi-Sil-233 (—), Oven-dried Hi-Sil-233 (—), and Vacuum-dried Hi-Sil-233 (—).

Table 12. Hi-Sil-233-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	25.67
Oven-dried	25.87
Vacuum-dried	25.53

The consistent residue percentage resulting from thermograms of undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233 determined that fillers were distributed evenly throughout the polymer matrix and were similar to the calculated percentage of filler.

5.2.1.1.3 Hi-Sil-233-D

The compounded PDMS with 25 wt. % undried Hi-Sil-233D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D was soft, paste-like material similar to that of Hi-Sil-233-D. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 33 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried, and vacuum-dried Hi-Sil-233-D silica filler and PDMS.

Figure 33. Appearance of the filled PDMS compounded materials after extrusion: Undried Hi-Sil-233-D, Oven-dried Hi-Sil-233-D, and Vacuum-dried Hi-Sil-233-D (left to right).

Figure 34 displays the TGA thermograms of the filled PDMS compounded with undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D. The curves in Figure 34 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D are presented in Table 13. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

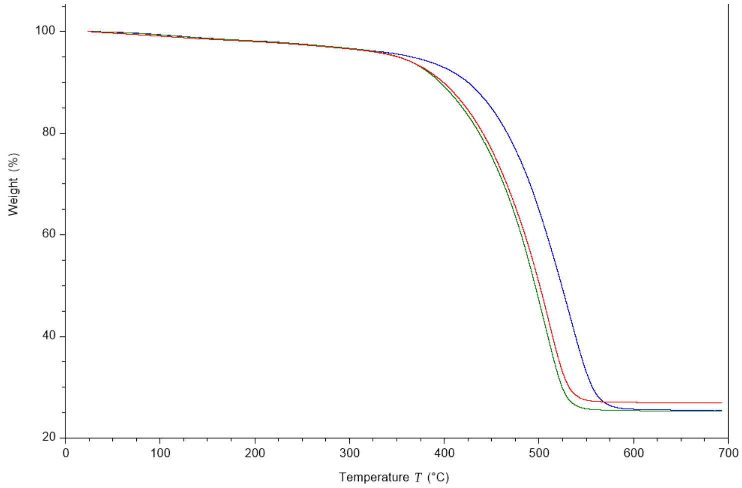

Figure 34. TGA thermograms of the Undried Hi-Sil-233-D (—), Oven-dried Hi-Sil-233-D (—), and Vacuum-dried Hi-Sil-233-D (—).

Table 13. Hi-Sil-233-D-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	25.32
Oven-dried	25.40
Vacuum-dried	26.43

The consistent residue percentage resulting from thermograms of undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D determined that fillers were distributed evenly throughout the polymer matrix and were similar to the calculated percentage of filler.

5.2.1.2 Surface-treated Precipitated Silica Filler

5.2.1.2.1 Amsil 66

The compounded PDMS with 25 wt. % undried Amsil 66, oven-dried Amsil 66 and vacuum-dried Amsil 66 silica filler was soft, liquid-like material with no dimensional stability. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 35 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried, and vacuum-dried Amsil 66 silica filler and PDMS.

Figure 35. Appearance of the filled PDMS compounded materials after extrusion: Undried Amsil 66, Oven-dried Amsil 66, and Vacuum-dried Amsil 66 (left to right).

Figure 36 displays the TGA thermograms of the filled PDMS compounded with undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66. The curves in Figure 36 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 are presented in Table 14. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

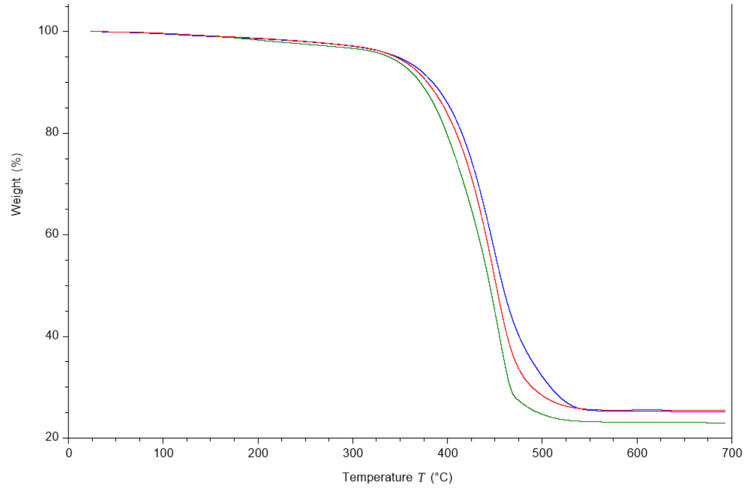

Figure 36. TGA thermograms of the Undried Amsil 66 (—), Oven-dried Amsil 66 (—), Vacuum-dried Amsil 66 (—).

Table 14. Amsil 66-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	25.22
Oven-dried	23.02
Vacuum-dried	25.31

The consistent residue percentage resulting from thermograms of undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 determined that fillers were distributed evenly throughout the polymer matrix and were similar to the calculated percentage of filler.

5.2.1.2.2 Amsil 665

The compounded PDMS with 25 wt. % undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665 silica filler was soft, liquid-like material with no dimensional stability. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 37 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried, and vacuum-dried Amsil 665 silica filler and PDMS.

Figure 37. Appearance of the filled PDMS compounded materials after extrusion: Undried Amsil 665, Oven-dried Amsil 665, and Vacuum-dried Amsil 665 (left to right).

Figure 38 displays the TGA thermograms of the filled PDMS compounded with undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665. The curves in Figure 38 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 are presented in Table 15. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

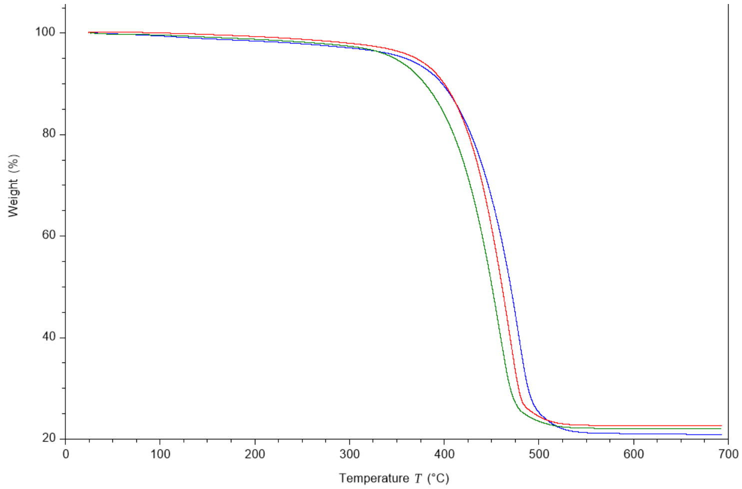

Figure 38. TGA thermograms of the Undried Amsil 665 (—), Oven-dried Amsil 665 (—), Vacuum-dried Amsil 665 (—).

Table 15. Amsil 665-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	21.86
Oven-dried	22.19
Vacuum-dried	22.71

The consistent residue percentage resulting from thermograms of undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 determined that fillers were distributed evenly throughout the polymer matrix and were similar to the calculated percentage of filler.

5.2.1.2.3 Amsil 668

The compounded PDMS with 25 wt. % undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668 silica filler was soft, liquid-like material with no dimensional stability. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 39 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried, and vacuum-dried Amsil 668 silica filler and PDMS.

Figure 39. Appearance of the filled PDMS compounded materials after extrusion: Undried Amsil 668, Oven-dried Amsil 668, and Vacuum-dried Amsil 668 (left to right).

Figure 40 displays the TGA thermograms of the filled PDMS compounded with undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668. The curves in Figure 40 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668 are presented in Table 16. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

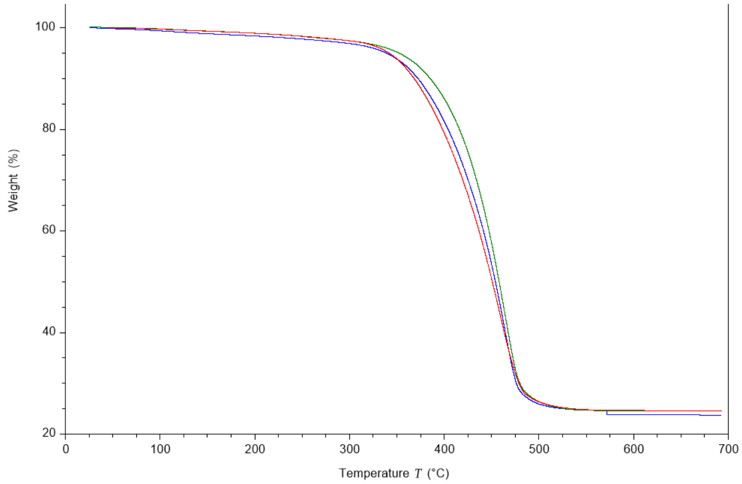

Figure 40. TGA thermograms of the Undried Amsil 668 (—), Oven-dried Amsil 668 (—), Vacuum-dried Amsil 668 (—).

Table 16. Amsil 668-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	23.97
Oven-dried	24.59
Vacuum-dried	24.57

The consistent residue percentage resulting from thermograms of undried Amsil 668, oven dried Amsil 668 and vacuum dried Amsil 668 determines that fillers were distributed evenly throughout the polymer matrix as it was calculated.

5.2.2 Synthetic Fumed Silica Filler

5.2.2.1 Fumed Silica Filler with No Surface Treatment

5.2.2.1.1 Cab-O-Sil

The compounded PDMS with 25 wt. % undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil was soft, paste-like material similar to that of Hi-Sil-233-D. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 41 exhibits the appearance of filled material with 25 wt. % undried, oven-dried, and vacuum-dried Cab-O-Sil silica filler and PDMS.

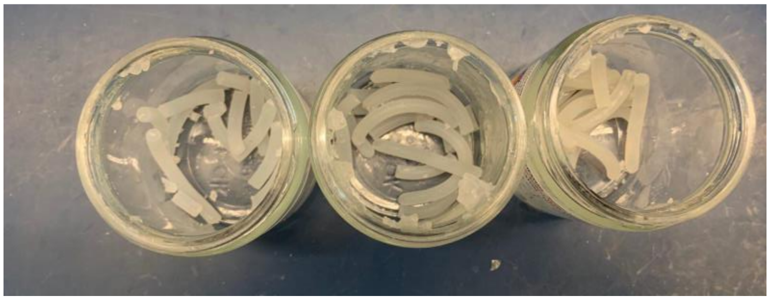

Figure 41. Appearance of the filled PDMS compounded materials after extrusion: Undried Cab-O-Sil, Oven-dried Cab-O-Sil, and Vacuum-dried Cab-O-Sil (left to right).

Figure 42 displays the TGA thermograms of the filled PDMS compounded with undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil. The curves in Figure 42 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil are presented in Table 17. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

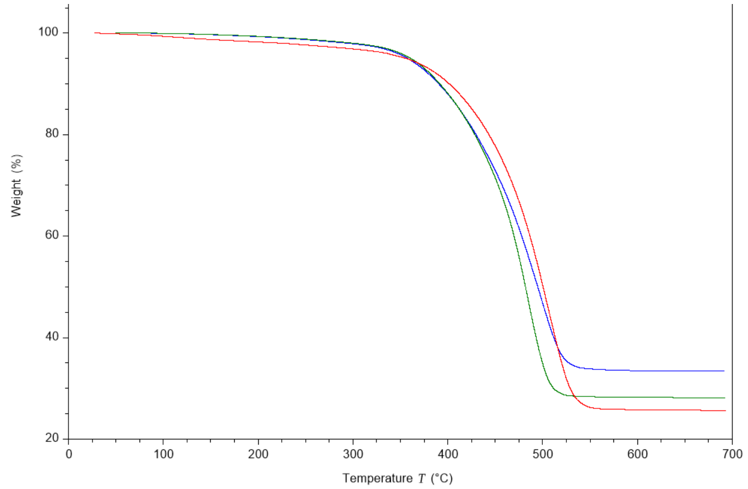

Figure 42. TGA thermograms of the Undried Cab-O-Sil (—), Oven-dried Cab-O-Sil (—), Vacuum-dried Cab-O-Sil (—).

Table 17. Cab-O-Sil-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	33.44
Oven-dried	29.72
Vacuum-dried	28.36

The increase in the residue percentage values could be attributed to the Cab-O-Sil filler. Cab-O-Sil filler is a fumed silica with a high surface area when compared to all other silica fillers analyzed. Higher surface area fillers have an abundance of silanol groups to enhance the interactions with the polymer backbone.[35,39,77,84] These interaction prevent volatilization of the polymer to monomer as the temperature rises to a greater degree than other fillers. The result is an apparent percent residue that is higher than the calculated value of 25 wt.%. The enhanced interaction of Cab-O-Sil filler with the PDMS resulted in higher residue that remained after TGA analysis.

5.2.2.2 Surface-treated Fumed Silica Filler

5.2.2.2.1 Aerosil

The compounded PDMS with 25 wt. % of undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil silica filler was soft, liquid-like material with no dimensional stability. The color of compounded material also showed a change in color from white in undried material to yellow in vacuum-dried material. Again, this change in the color is attributed to the pretreatment method of filler. Figure 43 exhibits the appearance of filled material with 25 wt. % of undried, oven-dried, and vacuum-dried Aerosil silica filler and PDMS.

Figure 43. Appearance of the filled PDMS compounded materials after extrusion: Undried Aerosil, Oven-dried Aerosil, and Vacuum-dried Aerosil (left to right).

Figure 44 displays the TGA thermograms of the filled PDMS compounded with undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil. The curves in Figure 44 resemble typical TGA curves of silica-filled PDMS materials.[41,84,85] The residue percentage values of PDMS compounded with 25 wt.% with undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil are presented in Table 18. The values presented are median values of the three specimens per compounded material taken at the beginning, middle, and end of the compounding process for each individually compounded material.

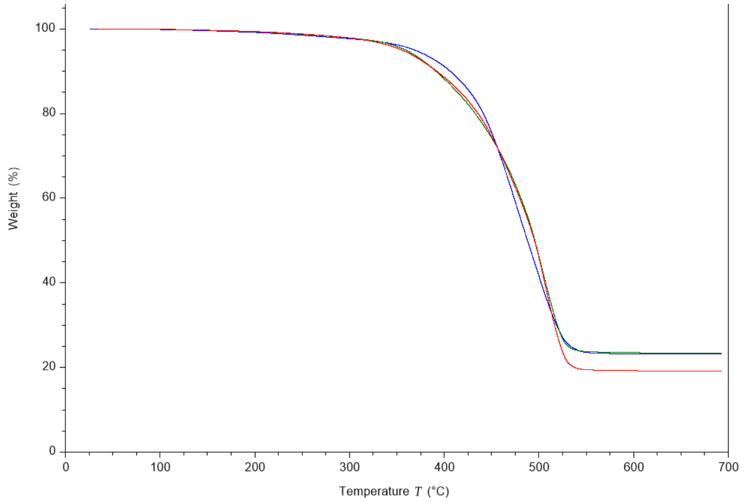

Figure 44. TGA thermograms of the Undried Aerosil (—), Oven-dried Aerosil (—), Vacuum-dried Aerosil (—).

Table 18. Aerosil-filled PDMS compounded with 25 wt.% of Undried, Oven-dried, and Vacuum-dried fillers.

Filler Pretreatment	**Residue (%)**
Undried	22.18
Oven-dried	22.40
Vacuum-dried	19.40

The consistent residue percentage resulting from thermograms of undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil determined that fillers were distributed evenly throughout the polymer matrix and were similar to the calculated percentage of filler.

5.3 Characterization

5.3.1 Oscillatory Rheometry of Filled PDMS

The yield stress of the silica-filled PDMS materials was analyzed by oscillatory rheometry. The yield stress of the silica-filled materials was determined by the point at which the storage modulus (G') and loss modulus (G") curves intersect. Thus, an oscillatory stress sweep from 3 Pa to 10,000 Pa was applied to all compounded formulations

5.3.1.1 Synthetic Precipitated Silica Filler

5.3.1.1.1 Synthetic Precipitated Silica Filler with No Surface Treatment

5.3.1.1.1.1 Hi-Sil-135

Table 19 displays the yield stress values of the filled PDMS compounded with undried Hi-Sil-135, oven-dried Hi-Sil-135, and vacuum-dried Hi-Sil-135 silica filler.

Table 19. Yield Stress of Hi-Sil-135-filled PDMS.

PDMS/ 25 wt.% Hi-Sil-135	**Silanol groups (OH nm^{-2})**	**Yield Stress (Pa)**
Undried	39.25	4754
Oven-dried	36.20	3710
Vacuum-dried	30.88	2965

These silica-filled materials exhibit similar rheological behavior to other silica-filled materials.[86,87,88] Evaluation of data presented in Table 19 shows that yield stress decreases as the number of silanol groups on the surface of filler particle decreases.

5.3.1.1.1.2 Hi-Sil-233

Table 20 displays the yield stress values of the filled PDMS compounded with undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233 silica filler.

Table 20. Yield Stress of Hi-Sil-233-filled PDMS.

PDMS/ 25 wt.% Hi-Sil-233	**Silanol groups (OH nm^{-2})**	**Yield Stress (Pa)**
Undried	24.95	2383
Oven-dried	21.73	2267
Vacuum-dried	18.37	1893

These silica-filled materials exhibit similar rheological behavior to other silica-filled materials.[86,87,88] Evaluation of data presented in table 20 shows that yield stress decreases as the number of silanol groups on the surface of filler particle decreases.

5.3.1.1.1.3 Hi-Sil-233-D

Table 21 displays the yield stress values of the filled PDMS compounded with undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D silica filler.

Table 21. Yield Stress of Hi-Sil-233-D-filled PDMS.

PDMS/ 25 wt.% Hi-Sil-233-D	**Silanol groups (OH nm^{-2})**	**Yield Stress (Pa)**
Undried	50.15	6325
Oven-dried	47.45	5622
Vacuum-dried	36.74	4710

These silica-filled materials exhibit similar rheological behavior to other silica-filled materials.[86,87,88] Evaluation of data presented in Table 21 shows that yield stress decreases as the number of silanol groups on the surface of filler particle decreases.

5.3.1.1.2 Surface-treated Precipitated Silica Filler

5.3.1.1.2.1 Amsil 66

Table 22 displays the yield stress values of the filled PDMS compounded with undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 filler.

Table 22. Yield Stress of Amsil 66-filled PDMS.

PDMS/ 25 wt.% Amsil 66	**Silanol groups (OH nm^{-2})**	**Yield Stress (Pa)**
Undried	21.66	--
Oven-dried	20.56	--
Vacuum-dried	19.20	--

Analysis of oscillatory rheometry data of undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 filler illustrates that these materials do not possess a yield stress. This is attributed to the filled materials not containing enough filler to reach the percolation threshold. The filler amount was too low to generate an aggregated network structure and disrupt the mobility of the polymer chains.[47,90,91] Various authors have shown that low silica concentration levels that do not approach the percolation threshold cannot obtain an accurate yield stress.[48,89] Low filler loadings can act as a plasticizer and decrease viscosity. The other reason for the lack of yield stress in these materials is low concentration of silanol groups on the surface. Low concentration of silanol groups on the filler surface limits the amount of hydrogen bonding in the compounded material, therefore no reinforcing capability can be observed.

5.3.1.1.2.2 Amsil 665

Table 23 displays the yield stress values of the filled PDMS compounded with undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665 filler.

Table 23. Yield Stress of Amsil 665-filled PDMS.

PDMS/ 25 wt.% Amsil 665	**Silanol groups ($OH\ nm^{-2}$)**	**Yield Stress (Pa)**
Undried	20.58	--
Oven-dried	19.28	--
Vacuum-dried	14.82	--

Analysis of oscillatory rheometry data of undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665 filler illustrates that these materials do not possess a yield stress for reasons similar to that of Amsil 66: inadequate filler amount to reach the percolation threshold required to disrupt the mobility of the polymer chains and a low concentration of silanol groups on the filler surface.[47,90,91]

5.3.1.1.2.3 Amsil 668

Table 24 displays the yield stress values of the filled PDMS compounded with undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668 filler.

Table 24. Yield Stress of Amsil 668-filled PDMS.

PDMS/ 25 wt.% Amsil 668	Silanol groups (OH nm^{-2})	Yield Stress (Pa)
Undried	15.49	--
Oven-dried	16.63	--
Vacuum-dried	13.25	--

Analysis of oscillatory rheometry data of undried Amsil 665, oven dried Amsil 665, and vacuum-dried Amsil 665 filler illustrates that these materials do not possess a yield stress for reasons similar to that of Amsil 66 and Amsil 665: inadequate filler amount to reach the percolation threshold required to disrupt the mobility of the polymer chains and a low concentration of silanol groups on the filler surface.[47,90,91]

5.3.1.2 Synthetic Fumed Silica Filler

5.3.1.2.1 Synthetic Fumed Silica Filler with No Surface Treatment

5.3.1.2.1.1 Cab-O-Sil

Table 25 displays the yield stress values of the filled PDMS compounded with undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil silica filler.

Table 25. Yield Stress of Cab-O-Sil-filled PDMS.

PDMS/ 25 wt.% Cab-O-Sil	Silanol Groups (OH nm^{-2})	Yield Stress (Pa)
Undried	16.81	8453
Oven-dried	13.82	8340
Vacuum-dried	8.18	8210

The yield stress of the PDMS compounded with 25 wt% undried, oven dried and vacuum dried Cab-O-Sil filler was evaluated by oscillatory rheometry. The yield stress enhancement can be attributed to the greater surface area of Cab-O-Sil. The surface area of Cab-O-Sil is 203.1 m^2/g, which is much larger than all other fillers. Larger surface areas enhance particle aggregation and interactions between the filler and the polymer matrix, resulting in increased yield stress values.[13,35,39,47,49]

5.3.1.2.2 Surface Treated Fumed Silica Filler

5.3.1.2.2.1 Aerosil

Table 26 displays the yield stress values of the filled PDMS compounded with undried Aerosil, oven-dried Aerosil, and vacuum-dried Aerosil silica filler

Table 26. Yield Stress of Aerosil-filled PDMS.

PDMS/ 25 wt.% Aerosil	Silanol Groups (OH nm^{-2})	Yield Stress (Pa)
Undried	5.77	--
Oven-dried	5.06	--
Vacuum-dried	5.06	--

Analysis of oscillatory rheometry data of undried Amsil 665, oven dried Amsil 665, and vacuum dried Amsil 665 filler illustrates that these materials do not possess a yield stress for reasons similar to that of Amsil-type fillers: inadequate filler amount to reach the percolation threshold required to disrupt the mobility of the polymer chains and a low concentration of silanol groups on the filler surface.[47,90,91]

5.3.2 Flow Rheology

5.3.2.1 Synthetic Precipitated Silica Filler

5.3.2.1.1 Synthetic Precipitated Silica Filler with No Surface Treatment

5.3.2.1.1.1 Hi-Sil-135

A flow rheology study was conducted on Hi-Sil-135-filled polysiloxane materials with each type of pretreated filler and compared to each other. The viscosity of the filled materials decreased as the shear rate increased, which was attributed to the destruction of the filler network structure by the increasing shear rates. The viscosity of the filled materials increased as the shear rate decreased, which was attributed to the reconstruction of the filler network structure over time.[75] Figure 45 displays the flow rheology data for the undried Hi-Sil-135, oven-dried Hi-Sil-135, and vacuum-dried Hi-Sil-135 materials.

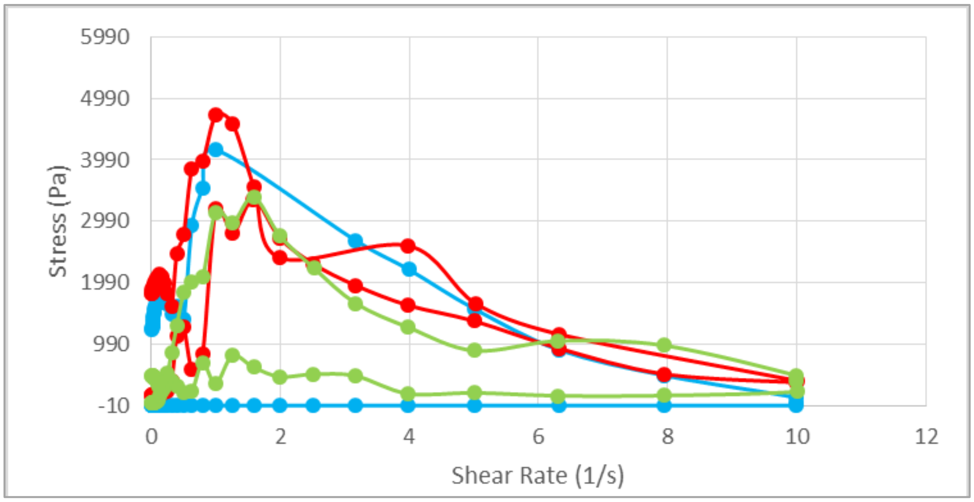

Figure 45. Flow rheology analysis for PDMS filled with Hi-Sil-135: Undried Hi-Sil-135 (●), Oven-dried Hi-Sil-135 (●), and Vacuum-dried Hi-Sil-135 (●).

The undried Hi-Sil-135-filled materials possessed greater thixotropic behavior than those filled with oven-dried Hi-Sil-135-filled and vacuum-dried Hi-Sil-135. This indicates that the undried Hi-Sil-135-filled materials required more time to reconstruct their network structures.[75,92,93] The undried Hi-Sil-135 filler's higher silanol group concentration on the filler surface enhances the thixotropic behavior.[13,34,35,39,47,49,94] It was also determined that by decreasing the silanol groups on the surface of filler the thixotropic behavior decreased.

5.4.2.1.1.2 Hi-Sil-233

A flow rheology study was conducted on the undried Hi-Sil-233-filled, oven-dried Hi-Sil-233-filled, and vacuum-dried Hi-Sil-233-filled polysiloxane materials and compared to each other. The Hi-Sil-233 materials demonstrated similar changes in viscosity with changes in shear rate as those observed for Hi-Sil-135. Figure 46 displays the flow rheology data for the undried Hi-Sil-233, oven-dried Hi-Sil-233, and vacuum-dried Hi-Sil-233 materials.

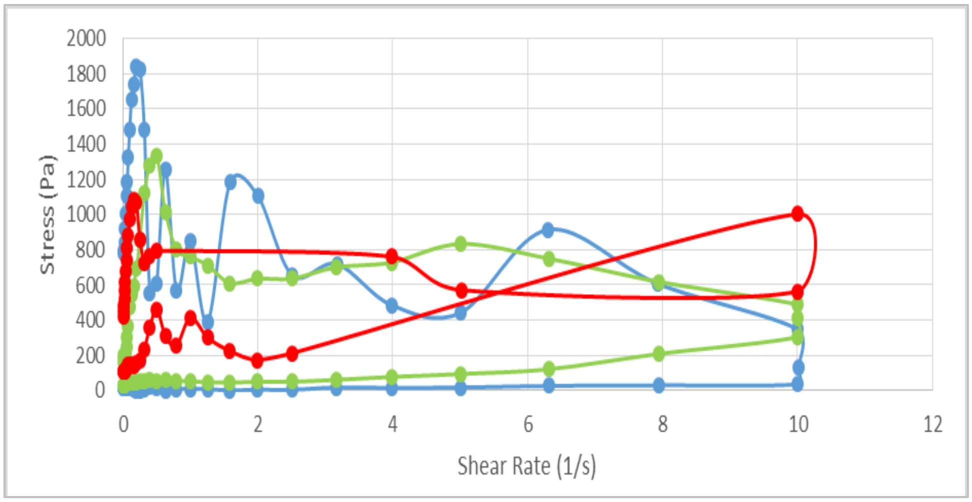

Figure 46. Flow rheology analysis for PDMS filled with Hi-Sil-233: Undried Hi-Sil-233 (●), Oven-dried Hi-Sil-233 (●), and Vacuum-dried Hi-Sil-233 (●).

The undried Hi-Sil-233-filled materials compared to oven-dried and vacuum-dried Hi-Sil-233 behaved in a manner similar to that of Hi-Sil-135 materials: undried materials required more time to reconstruct their network structures,[75,92,93] and decreased surface silanol groups on the filler surface resulted in a decrease in thixotropic behavior.

5.4.2.1.1.3 Hi-Sil-233-D

A flow rheology study was conducted on the undried Hi-Sil-233-D-filled, oven dried Hi-Sil-233-D-filled, and vacuum-dried Hi-Sil-233-D-filled polysiloxane materials and compared to each other. The Hi-Sil-233-D materials demonstrated similar changes in viscosity with changes in shear rate as those observed for Hi-Sil-135 and Hi-Sil-233. Figure 47 displays the flow rheology data for the undried Hi-Sil-233-D, oven-dried Hi-Sil-233-D, and vacuum-dried Hi-Sil-233-D materials.

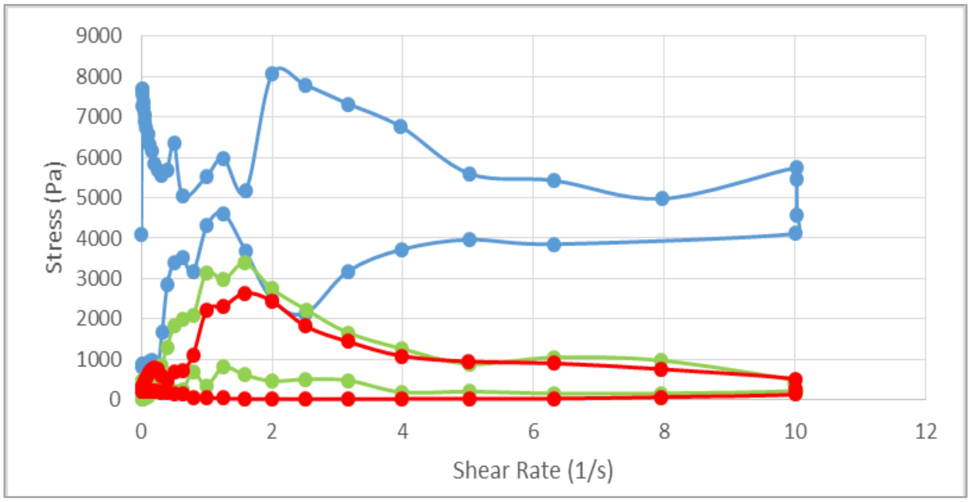

Figure 47. Flow rheology analysis for PDMS filled with Hi-Sil-233-D: Undried Hi-Sil-233-D (●), Oven-dried Hi-Sil-233-D (●), and Vacuum-dried Hi-Sil-233-D (●).

The undried Hi-Sil-233-D-filled materials compared to oven-dried and vacuum-dried Hi-Sil-233-D behaved in a manner similar to that of Hi-Sil-135 and Hi-Sil-233 materials: undried materials required more time to reconstruct their network structures,[75,92,93] and decreased surface silanol groups on the filler surface resulted in a decrease in thixotropic behavior.

5.3.2.1.2 Surface-treated Precipitated Silica Filler

5.3.2.1.2.1 Amsil 66

A flow rheology study was conducted on the undried Amsil 66-filled, oven dried Amsil 66-filled, and vacuum-dried Amsil 66-filled polysiloxane materials and compared to each other. The Amsil 66 materials demonstrated similar changes in viscosity with changes in shear rate as those observed for Hi-Sil-type fillers. Figure 48 displays the flow rheology data for the undried Amsil 66, oven-dried Amsil 66, and vacuum-dried Amsil 66 materials.

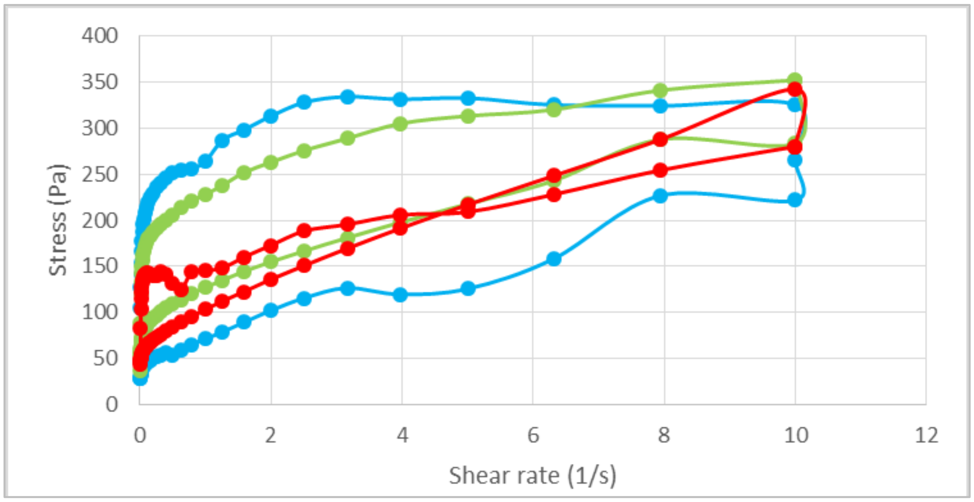

Figure 48. Flow rheology analysis for PDMS filled with Amsil 66: Undried Amsil 66 (●), Oven-dried Amsil 66 (●), and Vacuum-dried Amsil 66 (●).

The undried Amsil 66-filled materials compared to oven-dried and vacuum-dried Amsil 66 behaved in a manner similar to that of Hi-Sil materials: undried materials required more time to reconstruct their network structures,[75,92,93] and decreased surface silanol groups on the filler surface resulted in a decrease in thixotropic behavior. Overall, the Amsil 66 materials were more weakly thixotropic than the Hi-Sil materials.

5.3.2.1.2.2 Amsil 665

A flow rheology study was conducted on the undried Amsil 665-filled, oven dried Amsil 665-filled, and vacuum-dried Amsil 665-filled polysiloxane materials and compared to each other. The Amsil 665 materials demonstrated similar changes in viscosity with changes in shear rate as those observed for Amsil 66 and Hi-Sil-type fillers. Figure 49 displays the flow rheology data for the undried Amsil 665, oven-dried Amsil 665, and vacuum-dried Amsil 665 materials.

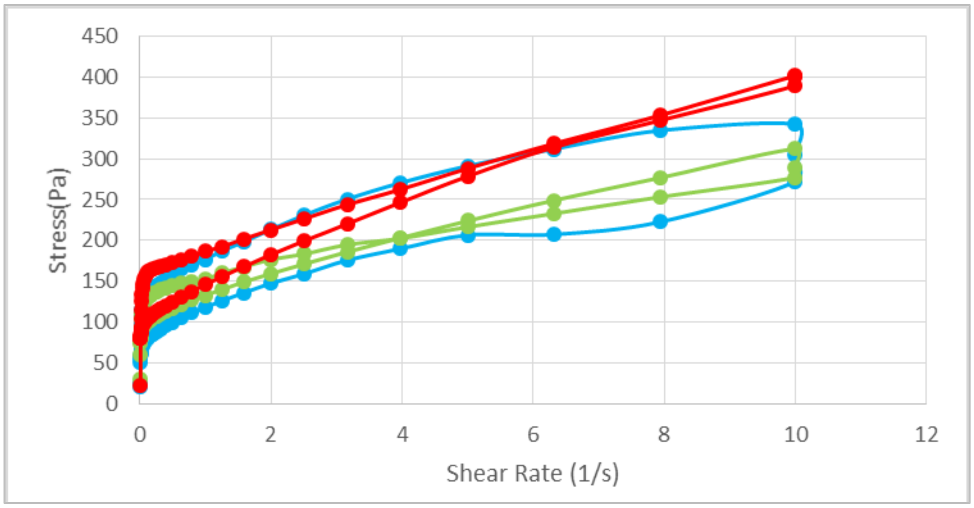

Figure 49. Flow rheology analysis for PDMS filled with Amsil 665: Undried Amsil 665 (●), Oven-dried Amsil 665 (●), and Vacuum-dried Amsil 665 (●).

The undried Amsil 665-filled materials compared to oven-dried and vacuum-dried Amsil 665 behaved in a manner similar to that of Amsil 66 and Hi-Sil materials: undried materials required more time to reconstruct their network structures,[75,92,93] and decreased surface silanol groups on the filler surface resulted in a decrease in thixotropic behavior. Overall, the Amsil 665 materials were more weakly thixotropic than both the Amsil 66 the Hi-Sil materials. Vacuum-dried Amsil 665 had the flow behavior more similar to a shear-thinning material than that of a thixotropic material. This is likely the result of all residual surface moisture being removed during the process of vacuum-drying and decreasing the reinforcing behavior below the point that a thixotropic loop would develop over the shear rate range analyzed.

5.3.2.1.2.3 Amsil 668

A flow rheology study was conducted on the undried Amsil 665-filled, oven dried Amsil 668-filled, and vacuum-dried Amsil 668-filled polysiloxane materials and compared to each other. The Amsil 668 materials demonstrated similar changes in viscosity with changes in shear rate as those observed for Amsil 66, Amsil 665, and Hi-Sil-type fillers. Figure 50 displays the flow rheology data for the undried Amsil 668, oven-dried Amsil 668, and vacuum-dried Amsil 668 materials.

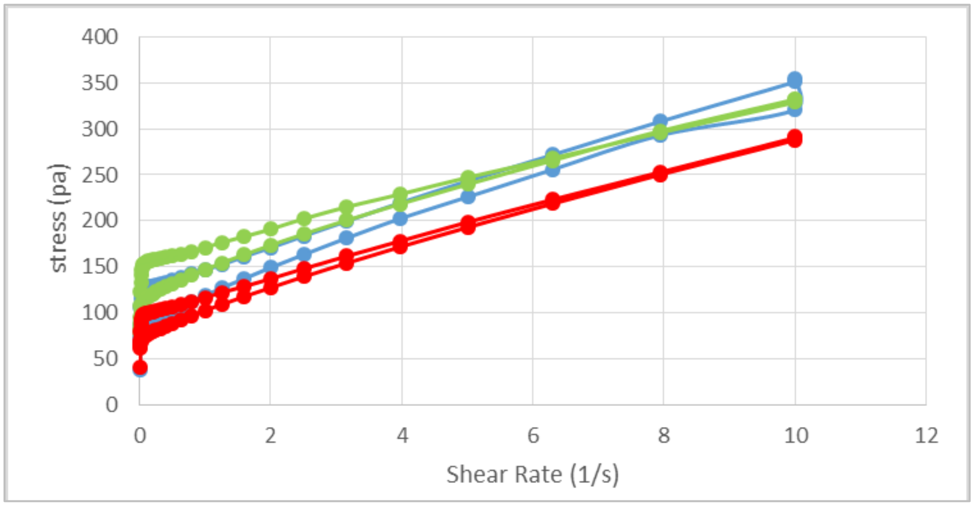

Figure 50. Flow rheology analysis for PDMS filled with Amsil 668: Undried Amsil 668 (●), Oven-dried Amsil 668 (●), and Vacuum-dried Amsil 668 (●).

The undried Amsil 668-filled materials compared to oven-dried and vacuum-dried Amsil 668 behaved in a manner similar to that of Amsil 66 and Hi-Sil materials: undried materials required more time to reconstruct their network structures,[75,92,93] and decreased surface silanol groups on the filler surface resulted in a decrease in thixotropic behavior. Overall, the Amsil 668 materials were more weakly thixotropic than the Amsil 66, Amsil 665, and the Hi-Sil materials. Vacuum-dried and oven-dried Amsil 668 had the flow behavior more similar to a shear-thinning material than that of a thixotropic material. This is likely the result of all residual surface moisture being removed during the process of oven-drying and vacuum-drying, preventing hydrogen-bonding with the polysiloxane backbone, and decreasing the reinforcing behavior below the point that a thixotropic loop would develop over the shear rate range analyzed.

5.3.2.2 Synthetic Fumed Silica Filler

5.3.2.2.1 Synthetic Fumed Silica Filler with No Surface Treatment

5.3.2.2.1.1 Cab-O-Sil

A flow rheology study was conducted on the undried Cab-O-Sil-filled, oven dried Cab-O-Sil-filled, and vacuum-dried Cab-O-Sil-filled polysiloxane materials and compared to each other. The Cab-O-Sil materials demonstrated similar changes in viscosity with changes in shear rate as those observed for the Amsil-type fillers and the Hi-Sil-type fillers. Figure 51 displays the flow rheology data for the undried Cab-O-Sil, oven-dried Cab-O-Sil, and vacuum-dried Cab-O-Sil materials.

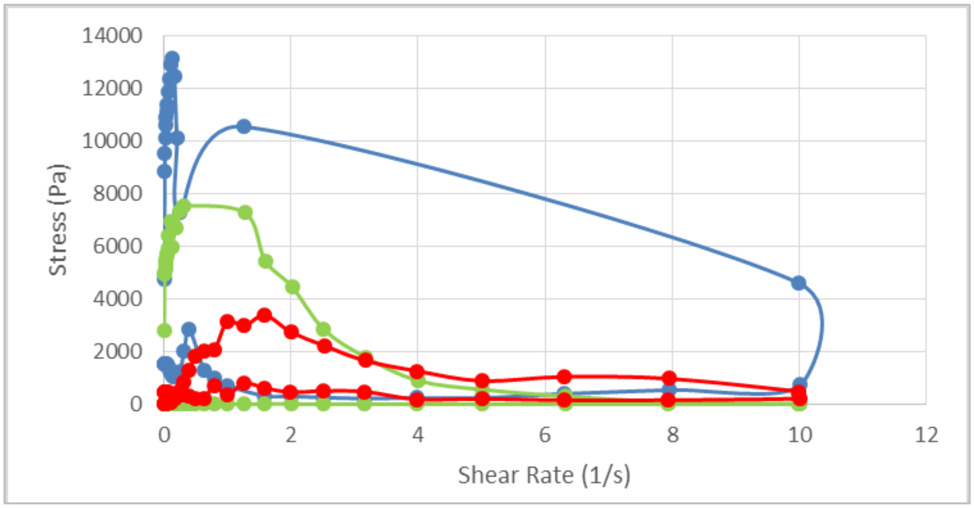

Figure 51. Flow rheology analysis for PDMS filled with Cab-O-Sil: Undried Cab-O-Sil (●), Oven-dried Cab-O-Sil (●), and Vacuum-dried Cab-O-Sil (●).

Cab-O-Sil behaved in a manner similar to that of Amsil 66 and Hi-Sil materials: undried materials required more time to reconstruct their network structures, and decreased surface silanol groups on the filler surface resulted in a decrease in thixotropic behavior.[75,92,93] Overall, the Cab-O-Sil materials were much more strongly thixotropic than the Amsil-materials and the Hi-Sil materials. Cab-O-Sil's high surface area and small particle size lend itself to strong aggregation behavior and ability to hydrogen-bond more strongly to the polysiloxane backbone, resulting in the greatest degree of thixotropic behavior observed in the fillers studied.[13,15,34,39,47,49,94]

5.3.2.2.2 Surface-treated Fumed Silica Filler

5.3.2.2.2.1 Aerosil

A flow rheology study was conducted on the undried Aerosil-filled, oven dried Aerosil –filled, and vacuum-dried Aerosil-filled polysiloxane materials and compared to each other. The Aerosil materials demonstrated similar changes in viscosity with changes in shear rate as those observed for Cab-O-Sil, Amsil-type fillers, and Hi-Sil-type fillers.

Figure 52 displays the flow rheology data for the undried Aerosil 668, oven-dried Aerosil, and vacuum-dried Aerosil materials. The undried, oven-dried, and vacuum-dried Aerosil-filled material did not exhibit any thixotropic behavior, demonstrated by the lack of “loops” in the flow rheology data. The low concentration of silanol group on the surface and highly hydrophobic surface treatment causes this shear-thinning behavior in the Aerosil materials.[13,15,34,39,47,49,94]

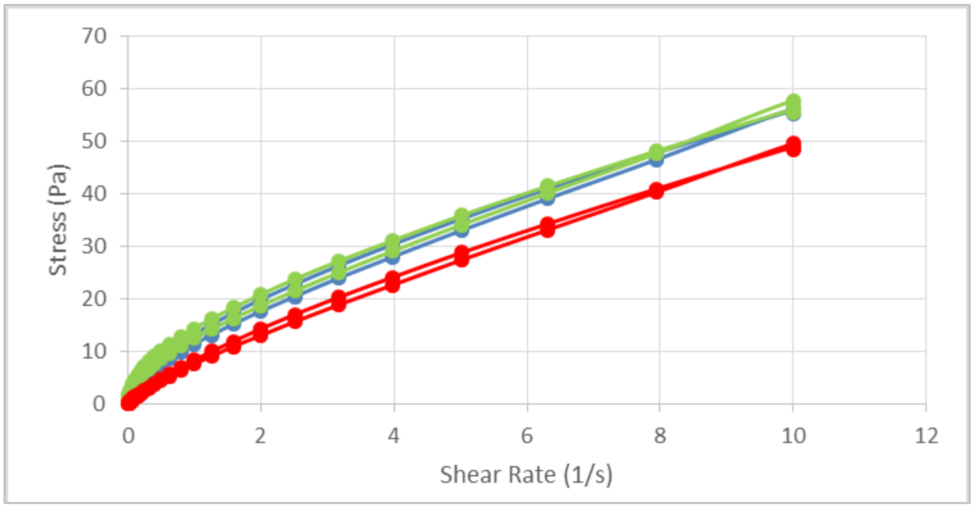

Figure 52. Flow rheology analysis for PDMS filled with Aerosil: Undried Aerosil (●), Oven-dried Aerosil (●), and Vacuum-dried Aerosil (●).

5.4 Summary Table

Table 27 displays the relationship between of number of silanol groups on the surface of silica filler, yield stress, and thixotropy.

It was determined that the yield stress is directly proportional to the number of silanol groups on the surface of precipitated silica filler with no surface treatment. As the silanol group on the silica filler surface increases, the reinforcing capabilities of the filler also increases. Data presented in table 27 also indicates that surface-treated precipitated and fumed silica fillers that were analyzed exhibited no yield stress. This is attributed to the filled materials not containing enough filler to reach the percolation threshold. The filler amount was too low to generate an aggregated network structure and disrupt the mobility of the polymer chains.[47,90,91] Low filler loadings can act as a plasticizer and decrease viscosity. The other reason for the lack of yield stress in these materials can be low concentration of silanol groups on the surface. Low concentration of silanol groups on the filler surface limits the amount of hydrogen bonding in the compounded material therefore, no reinforcing capability can be observed. Cab-O-Sil filled materials however, show the greatest yield stress among all other tested material. The yield stress improvement can be attributed to the greater surface area of Cab-O-Sil. The surface area of Cab-O-Sil is 203.1 m^2/g, which is much larger than all tested fillers. Larger surface areas increase particle aggregation and interactions between the filler and the polymer matrix, resulting in increased yield stress values.[13,35,39,47,49]

The large surface area and small particle size result in the greatest degree of thixotropy from Cab-O-Sil when compared to the other fillers, also. Hi-Sil-type fillers demonstrated moderate thixotropy, and Amsil-type fillers resulted in weakly thixotropic materials. The exception to this was the vacuum-dried Amsil 665 and oven-dried and vacuum-dried Amsil 668. Sufficient water had been removed from the fillers to result in shear-thinning materials as a result of inadequate filler particle aggregation and hydrogen-bonding with the polysiloxane backbone. Aerosil was purely shear thinning in its behavior in all pretreatment types analyzed. The hydrophobic surface treatment was sufficient to disrupt filler particle aggregation and prevent hydrogen-bonding with the polysiloxane backbone.

Table 27. Relationship between Silanol groups and Yield Stress for All Filler Types and All Pretreatment Conditions

Filler	Synthesis Type	Surface Type	Surface Area (m^2/g)	Pretreatment	Silanol Groups (OH nm^{-2})	Yield Stress (Pa)	Thixotropy
Hi-Sil-135	Precipitated	Silanol	150	Undried	39.25	4754	Yes
				Oven Dried	36.2	3710	Yes
				Vacuum dried	30.88	2965	Yes
Hi-Sil-233	Precipitated	Silanol	135	Undried	24.95	2383	Yes
				Oven Dried	21.73	2267	Yes
				Vacuum dried	18.37	1893	Yes
Hi-Sil-233-D	Precipitated	Silanol	150	Undried	50.18	6325	Yes
				Oven Dried	47.45	5622	Yes
				Vacuum dried	36.74	4710	Yes
Amsil 66	Precipitated	Hydrophobic	140	Undried	21.66	--	Yes
				Oven Dried	20.56	--	Yes
				Vacuum dried	19.2	--	Yes
Amsil 665	Precipitated	Hydrophobic	140	Undried	20.58	--	Yes
				Oven Dried	19.28	--	Yes
				Vacuum dried	13.25	--	No
Amsil 668	Precipitated	Hydrophobic	140	Undried	17.68	--	Yes
				Oven Dried	16.63	--	No
				Vacuum dried	14.82	--	No
Cab-O-Sil	Fumed	Silanol	203.1	Undried	16.81	8453	Yes
				Oven Dried	13.82	8340	Yes
				Vacuum dried	8.18	8210	Yes
Aerosil	Fumed	Hydrophobic	160	Undried	5.77	--	No
				Oven Dried	5.06	--	No
				Vacuum dried	3.81	--	No

5.5 Relationship between Silanol groups and Rheological Response

All precipitated silica fillers with no surface treatment that were used in this study exhibit thixotropic behavior. Degree of thixotropy varied based on the numbers of silanol groups presented on the surface of each filler. Undried Hi-Sil-233-D material with the highest number of silanol groups exhibit greater thixotropic behavior when compared to other precipitated silica fillers.[13,15,34,39,47,49,94] This indicates that the undried Hi-Sil-233-

D-filled materials required more time for the aggregated silica particle network to restructure after shearing.[75,92,93] Yield stress was also observed for Hi-Sil materials and the yield stress decreased with decreasing surface silanol groups. In precipitated silica filler surface-treated with PDMS (Amsil), thixotropic behavior was also observed. In this case, degree of thixotropic behavior was also directly proportional to number of silanol groups on the surface. The lower number of silanol groups on the surface, compared to Hi-Sil-type fillers, resulted in much more weakly thixotropic materials. While they required time to rebuild the aggregated network, the particle-particle interactions were reduced by the PDMS surface treatment. These material did not exhibit any yield stress since the percolation threshold was not reached and ultimately fillers acted as plasticizer in the compounded material.[48,89,47,90,91]

Fumed silica filler with no surface treatment correspondingly exhibit the same trend as observed with Hi-Sil type fillers. Cab-O-Sil-filled exhibited a greater degree of thixotropic behavior due to its large surface area and small particle size.[13,15,34,39,47,49,94] Larger surface areas enhance particle aggregation and interactions between the filler and the polymer matrix, resulting in increased yield stress values and thixotropic behavior.[13,,34,39,47,49] The yield stress in these material was also much greater than other filled materials. Aerosil-filled materials exhibited no thixotropic behavior, and instead, demonstrated shear-thinning behavior. The hydrophobic surface treatment sufficiently blocked surface silanols to prevent particle-particle aggregation and particle-polysiloxane interaction through hydrogen-bonding. As a result, different pretreatment drying methods had little effect on Aerosil materials. These filled materials also did not exhibit any yield stress. This lack of yield stress is the result of not reaching to the percolation threshold and fillers acted as a plasticizer as is commonly discussed in the literature.[47,48,89,90,91]

CHAPTER VI

6. CONCLUSIONS

Polysiloxanes are known as temperature-resistant materials with the ability to maintain flexibility at low temperatures. Their chemical properties make them suitable for different applications including gaskets, sealants, coatings, and adhesives. However, polysiloxane elastomers generally exhibit poor mechanical properties and have no practical use unless reinforced in some way. The elastomers can be mechanically improved through the use of reinforcing fillers. Active fillers are chemically-treated silica fillers that strongly reinforce and significantly improve the physical properties of polysiloxane elastomers. Reinforcing fillers consist of precipitated and fumed silica fillers. It is also possible to chemically treat the precipitated and fumed silica fillers on the surface area which makes them suitable and selectable for wide variety of applications.

The Zhuravlev model was employed to quantify the silanol group concentration on the surface of different silica fillers and investigate the effects of silanol group concentration on the rheological properties of filled polysiloxane polymers. The number of silanol groups on the surface of three precipitated silica fillers with no surface treatment (Hi-Sil-135, Hi-Sil-233 and Hi-Sil-233-D), three hydrophobic precipitated silica filler (Amsil 66, Amsil 665, and Amsil 668), one fumed silica filler with no surface treatment (Cab-O-Sil), and one surface-treated fumed silica filler (Aerosil) were measured. Each filler was used with three different pretreatment method (undried, oven-dried and vacuum-dried) and the silanol number on the surface was measured and compared to each other. It was determined that a larger number of silanol groups (higher silanol number) was present on the surface of fillers with no pretreatment (undried) compared to oven-dried and vacuum-dried fillers. The differences in the silanol number can be attributed to the type of drying method. In oven-dried pretreatment method, water molecules that are adsorbed on the surface evaporate, which reduces silanol groups on the filler particle surface compared to undried filler. Vacuum-dried fillers exhibit lower numbers of filler surface silanol groups compared to oven-dried material. The low concentration of filler surface silanol groups in vacuum-dried fillers can be attributed to the constant extraction of water molecules as they evaporate from the surface. Comparison of oven-dried and vacuum-dried filler shows that oven-dried filler had more silanol groups present on the surface due to the ability of evaporated water to reabsorb on the particle surface since it is not extracted by vacuum.

Specific surface area and filler particle size play a significant role in the amount of silanol groups on the filler particle surfaces. Silanol number on the surface of undried precipitated filler particles decreased with decreasing the surface area. This trend can be observed by evaluation of silanol number on the surface of undried Hi-Sil-233-D and undried Hi-Sil-233. Undried Hi-Sil-233-D has the surface area of 150 m^2/g and has 50.15 OH nm^{-2} silanol groups on its surface while undried Hi-Sil-233 has the surface area of 135 m^2/g and has 24.95 OH nm^{-2} silanol groups on its surface. It was also determined that the higher specific surface area and filler particle size can result in a higher amount of silanol group on the surface. Hi-Sil-233-D and Hi-Sil-135 are share the same surface area (150 m^2/g). The particle size in Hi-Sil-233-D is ranges from 64 to 77 µm which is higher than Hi-Sil-135 with the particle size of 44 to 54 µm. The higher number of silanol groups on the surface of Hi-Sil-233-D when compare with Hi-Sil-135 is attributed to larger particle size when surface areas are similar.

Surface treatment of the precipitated and fumed silica filler blocks the silanol groups on the surface of the filler particle and decreases the amount of silanol group on the fillers' surfaces. Hydrophobic surface treatment on the precipitated silica filler decreased the average silanol groups on the surface in when compared with precipitated silica filler with no surface treatment. Fumed silica filler with no surface treatment (Cab-O-Sil) also exhibited more silanol group on its surface when compared with surface-treated fumed silica filler (Aerosil).

Level of hydrophobicity can also change the amount of silanol groups on the surface of filler particles. Undried Amsil 66, Amsil 665 and Amsil 668 share the same specific surface area (140 m^2/g) and particle size (4 µm) with different levels of hydrophobic agent (PDMS) on their surface. By increasing the surface hydrophobicity, the silanol number on the surface decreases. The comparison of undried Amsil 66 with standard level of hydrophobicity, undried Amsil 665 with medium-high level of hydrophobicity, and undried Amsil 668 with high level of hydrophobicity demonstrates this trend. Undried Amsil 66, which has the standard amount of hydrophobic agent on its surface, has a silanol number of 21.66 OH nm^{-2}, which is higher than that of undried Amsil 665 with medium-high level of PDMS coating on the surface and a silanol number of 20.58 OH nm^{-2}. Undried Amsil 668 has the highest level of PDMS coating and, therefore, has the lowest silanol number of 17.68 OH nm^{-2}.

Synthesis method can also affect to the numbers of silanol groups on the surface of filler particles. It was determined that precipitated silica filler bare more silanol groups on their surfaces in comparison with fumed silica fillers. Precipitated silica filler have a more porous surface which may result in a larger number of surfaces that may contain silanol groups. Fumed silica particles are smoother, which may limit the numbers of silanol groups on the surface that are available for analysis.

Furthermore, through the analysis of rheological data, this work sought to predict the reinforcing capabilities of each filler and allow tailoring of future materials based on these predictions. In this study all the pretreated material were compounded via twin-screw extrusion with PDMS at 25 wt. % to evaluate their reinforcing capabilities. Oscillatory rheometry and flow rheometry was used to determine the rheological responses of the compounded materials. The yield stress of the silica-filled materials was determined by the point at which the storage modulus (G') and loss modulus (G") curves intersect. Thus, an oscillatory stress sweep from 3 Pa to 10,000 Pa was applied to the undried, oven-dried and vacuum-dried compounded materials. Flow rheology was also performed on the compounded materials with a linear shear rate from 0.01 sec^{-1} to 10 sec^{-1}, followed by a linear shear rate from 10 sec^{-1} to 0.01 sec^{-1}. Evaluation of collected data confirms that there is a close relationship between numbers of filler surface silanol groups and the reinforcing capability.

The average number of silanol groups on the surface of precipitated silica filler with no surface treatment is higher than those of surface-treated silica fillers. The silanol groups on the surface of precipitated silica filler with no surface treatment can participate in more hydrogen-bonding with other filler particles as well as the polymer backbone, resulting in greater reinforcing capabilities. This trend can be observed by comparison of the average yield stress in the precipitated silica filler with no surface treatment (Hi-Sil) and surface-treated precipitated silica filler (Amsil). The yield stress for precipitated silica filler with no surface treatment was observed by the range of 1893 – 6325 Pa while there was no yield stress measured for surface-treated silica filler. Compounded material with precipitated silica filler with no surface treatment exhibited a much higher degree of thixotropy compared to compounded material with surface-treated precipitated silica filler. The higher number of silanol groups on the surface of precipitated silica filler with no surface treatment enhances the thixotropic behavior, while surface treatment prevents filler particle aggregation and interactions with the polymer backbone that serves to reinforce the material.[4,13,17,18,19,20,24]

Specific surface area and filler particle size play a significant role in reinforcing capability as well. The comparison of Hi-Sil-135, Hi-Sil-233 and Hi-Sil-233-D shows that the reinforcing capabilities of the precipitated fillers with no surface treatment decreases as the surface silanol number decreased. Hi-Sil-233-D filler displayed a higher number of silanol groups on its surface, and, therefore it was expected to observe a higher yield stress and a greater degree of thixotropy compared with Hi-Sil-233. The yield stress range of Hi-Sil-233-D-filled materials (4710 – 6325 Pa) was much higher than the yield stress range of Hi-Sil-233-filled materials (2267 – 2965 Pa). Hi-Sil-233-D-filled materials also demonstrated a greater degree of thixotropy than Hi-Sil-233-filled materials. The higher yield stresses and greater degree of thixotropy in Hi-Sil-233-D-filled materials is attributed to higher numbers of filler surface silanol groups. The particle size in Hi-Sil-233-D ranges from 64 to 77 µm, which is higher than Hi-Sil-135 with the particle size range of 44 to 54 µm. Therefore, it was expected to see a greater degree of thixotropic behavior and higher yield stress values in Hi-Sil-233-D compared to Hi-Sil-135. Hi-Sil-135 filled material showed the yield stress values in the range of 2965 – 4754 Pa which is much lower than Hi-Sil-233-D with the yield stress range of 4710 – 6325 Pa. Hi-Sil-233-D-filled materials were also more thixotropic than Hi-Sil-135-filled materials.

The comparison of fumed silica filler with no surface treatment and surface-treated fumed silica filler also shows that number of silanol groups on the filler particle surface could result in differences in yield stress and thixotropic behavior. Cab-O-Sil-filled materials with higher numbers of surface silanol groups exhibit high yield stress values while no yield stress was obtained for Aerosil-filled material. Cab-O-Sil filled material with higher numbers of silanol groups on its surface also exhibit thixotropic behavior, compared with Aerosil-filled materials that are shear-thinning and do not demonstrated any thixotropy.

Comparison of surface-treated precipitated silica filler and surface-treated fumed silica filler showed an increase in thixotropic behavior. While neither type of filler resulted in materials that had measureable yield stresses, surface-treated precipitated silica filler-filled materials were weakly thixotropic compared to the shear-thinning surface-treated fumed silica filler-filled materials. Surface-treated precipitated silica filler had a larger number of silanol groups on their surfaces which promoted a greater degree of particle-particle interaction and interaction with the polymer backbone, resulting in a slight amount of thixotropy when compared to the lower silanol numbers of surface-treated fumed silica filler. [4,13,17,18,19,20,24]

The comparison of precipitated fillers with no surface treatment and fumed silica fillers with no surface treatment show that the average silanol groups on the surface of precipitated silica filler is much higher than that of fumed silica filler Cab-O-Sil. It was expected that precipitated silica fillers with no surface treatment would have higher yield stress values and a greater degree of thixotropy compared to fumed silica fillers with no surface treatment. This was not the case. Fumed silica filler materials exhibit higher yield stress and a greater degree of thixotropy. This can partially be attributed to the larger surface area of the fumed silica filler with no surface treatment. The surface area of Cab-O-Sil is 203.1 m^2/g, which is much larger than precipitated silica filler with no surface treatment (140 – 150 m^2/g). Larger surface areas in Cab-O-Sil enhances particle aggregation and interactions between the filler and the polymer matrix, resulting in higher yield stress values and a greater degree of thixotropy.[13.17,18,19,20] Porosity in precipitated silica filler causes hidden hydroxyl groups on the pores. The hidden silanol groups will not evaporate easily from the filler and cannot be counted by using the Zhuravlev model.[32] As a result, in precipitated silica fillers, good reinforcement is observed due to the participation of silanol groups hidden in the pores in hydrogen-bonding with polysiloxane backbone. However, in fumed silica filler, since the surface is smoother and no hidden silanol group are present, all the present silanol groups are measured by using Zhuravlev model. Therefore, the amount of reinforcement in Cab-O-Sil is much higher than was expected.[95]

In conclusion, it was confirmed that silanol group concentration on a particular silica filler’s surface depends on the synthesis method, surface area, and surface hydrophobicity. It was also shown by utilizing the Zhuravlev model with TGA analysis method, it is possible to predict the reinforcing capabilities of precipitated silica fillers and this method is tailorable for future precipitated material. However, fumed silica filler demands more study in order to have a better understanding of their rheological behavior and reinforcing capabilities.

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