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**FILLER MORPHOLOGY AND LOADING EFFECTS IN
CONDUCTIVE ELASTOMER SYSTEMS**

A Thesis

Presented to

**The Faculty of the Department of Materials Engineering
San Jose State University**

In Partial Fulfillment

**of the Requirements for the Degree
Master of Science**

by

Ileana Catalina Constantinescu

May 2002

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ABSTRACT

DEVELOPMENT AND CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE ELASTOMER SYSTEMS

by Ileana C. Constantinescu

This thesis addresses the topic of structure-properties relationships in two elastomer systems, a thermoplastic and a thermoset, fabricated by the addition of conductive fillers of different geometries to the elastomer matrix with the intent of lowering the volume resistivity to values similar to those of metals. Moderately conductive elastomers can be manufactured and used as electrically dissipative materials in electrostatic discharge prevention, whereas conductive elastomers can be used as electromagnetic shielding materials.

Filler concentrations exceeding 35 percent by volume decrease the resistivity of the matrix by approximatively 12 orders of magnitude compared to the unfilled elastomer, but have a reinforcing effect manifested in higher elastic modulus values. The objective of the current research is to establish the limits of elastic modulus and bulk resistivity in both elastomer systems, and evaluate their mechanical and electrical properties upon addition of increasing concentrations of silver-silica spheres , fibers, and mica flakes.

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Clearly, I would like to acknowledge the loving support of my parents, who were there from the beginning, always encouraging me to strive for the best I could do in everything I did and to always remember that my contribution will help the scientific community to move forward.

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TABLE OF NOMENCLATURE

Polymer	Long-chain molecule composed of a large number of repeating units (monomers)
Fillers	Metal or carbon particles added to an insulator in order to increase its electrical conductivity
EMI	Electromagnetic Interference
ESD	A spark discharge to "ground" from a surface that has accumulated an excess charge (+/-)
kPa	kilo Pascals
MHz	Mega Hertz
RF	Radio frequency
RTV	Rapid thermal vulcanization
SBS	Styrene-Butadiene-Styrene copolymer
SE	Log of ratio between transmitted and incident electromagnetic waves on a material; SE [=] dB
SIL	Silicone polymer containing silicon-oxygen bonds in the structure
ϕ_p	Packing factor; ratio between the densities of compacted powder and as-received powder
PTHR	Percolation Threshold - critical volume of conductive filler (V_c) that produces a sharp decrease in the resistivity of a matrix with randomly distributed particles.
TP	Thermoplastic Polymer
UTS	Ultimate Tensile Strength - maximum attainable stress in a material before break

CHAPTER 1

INTRODUCTION

1.1. Electromagnetic Shielding

Polymers have become the most desirable materials for electrical applications due to their ease of fabrication, low cost, light weight, and excellent insulating properties. The conventional uses of polymers as insulators in plastic-coated wires, terminals, industrial and household plugs, switches, and printed circuit boards have been extended to portable and wireless electronic devices. However, the main disadvantage of manufacturing electronic components using commonly available thermoplastics is that it makes them susceptible to damage from electrostatic discharge (ESD) or electromagnetic interference (EMI) because unfilled polymers (insulators) provide very little EMI shielding capability. In order to protect sensitive electronic components against ESD and EMI generated by various sources such as humans, computers, power cables, or unshielded electrical devices, the FCC (Federal Communications Committee) have placed restrictions on RF transmissions by computers and other electrical devices. The EIA (Electronic Industries Association) has formulated standards that apply to several different categories packaging materials that possess certain electrostatic properties such as to prevent triboelectric charging (antistatic), to dissipate a charge either by surface or volume conduction, or to act as shield material against electrostatic fields.⁽¹⁾

Electromagnetic energy is most effectively measured in terms of attenuation, defined as the amount by which the intensity of an electromagnetic signal is reduced by

the introduction of a shielding medium. The shielding effectiveness of a material is defined as percent attenuation of incident to transmitted electromagnetic radiation, and is proportional to its surface resistivity as depicted in Figure 1.⁽²⁾

Figure 1. Correlation between Surface Conductivity and Shielding Effectiveness for Conductive Composites. ⁽²⁾

The attenuation is measured in dB and represents the ratio of the field strength without the shield to the field strength with the shield. Shielding effectiveness measured in decibels is a logarithmic scale. Thus, an attenuation measurement of 50 dB is 10 times more effective than a measurement of 40 dB. The total electromagnetic shielding effectiveness for a material is given by the expression below:

$$EM_Shielding_Effectiveness = 10 * \log \frac{P_i}{P_t} (dB) \quad (1)$$

In the expression above, P_i represents the incident power in watts/m^2 , and P_t the transmitted power in Watts/m^2 . Among the four techniques developed for measuring the shielding effectiveness, which are, open-field, shielded box, coaxial transmission line and shielded room, the first two are the most effective in evaluating the EMI shielding performance of rubber gaskets. A more detailed description of the testing procedures is presented in the Handbook of Plastics Testing Technology.⁽³⁾

Effective, low-resistivity shield materials are manufactured by compounding a polymer with conductive fillers such as carbon black, Ag, Cu, Ni, stainless steel, carbon fiber, or metal-coated fibers that increase the electrical conductivity, dielectric constant, and EMI reflectance of the composite. Noble metal fillers such as silver have the added advantage that their compounds have good corrosion resistance and low contamination levels. The disadvantage is that they are usually more expensive to manufacture. One solution that has been adopted successfully for the design of cost-effective EMI shielding materials with improved performance was to substitute solid metal particles for silica (glass) particles of the same aspect ratio and coated with a thin film of the noble metal for maintaining good bulk conductivity. This resulted in significant weight and cost reductions for the silver-silica filled elastomers. Variations in polymer type, conductive filler geometry and concentration result in a range of surface and bulk resistivities. Composites with surface resistivity values between 10^5 - $10^{12} \Omega/\text{sq}$ are called dissipative, between 10^4 - 10^2 conductive, and between 10^1 - 10^{-3} ESD/EMI shielding. Figure 2 depicts a trend in surface resistivities from insulating polymers to metals.⁽⁴⁾

Figure 2. Surface Resistivity Values for Dissipative, Conductive, and ESD/EMI Shielding Composites.⁽⁴⁾

1.2. Thesis Outline

Chapter 1 of this report presents an overview of the electromagnetic interference phenomenon encountered in the electronics industry today, and the solutions adopted by the industry to develop new and improved composite materials. In addition, the chapter discusses ways by which the composite mechanical and electrical properties can be tailored to meet the current standards for shielding against electrostatic discharge and electromagnetic interference. The second chapter provides the materials background necessary for the development of new conductive composites containing conductive fillers embedded in two types of polymer matrices, thermoplastic and thermoset. Chapter 3 introduces the statement of purpose, or the objective of this study. In Chapter 4 the experimental methods used to fabricate the conductive compounds are described. In Chapter 5, the experimental results from the tensile, compressive, and resistivity tests performed on these compounds, and the discussion of the observed trends in the mechanical and electrical properties of TP and SIL gels as a function of the experimental variables are presented. The conclusions are summarized in Chapter 6, and the directions of future research in Chapter 7.

CHAPTER 2

BACKGROUND

2.1 Polymers

A polymer is defined as a long-chain molecule that is composed of a large number of repeating units of identical structure. Certain polymers (proteins, natural rubber, cellulose, and silk) are found in nature, whereas others (polystyrene, polyethylene, polyvinyl chloride) are synthetically produced. Most polymers are insulating materials with bulk resistivity values greater than $10^{13} \Omega\text{-cm}$.

Polymers are divided into thermoplastics, thermosets, and elastomers based on their thermal process behavior. Thermoplastics are polymers that can be melt-processed by extrusion or molding. These include polyethylene, polypropylene, polystyrene, polyvinyl chloride, and various fibers like polyester, nylon and rayon. They are heat-softened in order to be processed into a desired form. Thermosets (epoxies, or phenol-formaldehyde resins) are network polymers that result from the chemical cross-linking of individual polymer chains during polymerization or during subsequent chemical or thermal treatment. Once formed, thermosets are infusible and insoluble materials that cannot be normally re-processed.⁽⁵⁾ Elastomers are network-like polymers that have low glass transition temperatures and low degrees of cross-linking. The glass transition temperature, T_g , of a polymer marks its transition between a rubbery, soft plastic state to a rigid, brittle glassy state. Elastomers are polymers that exhibit rubber-like properties at room temperature and have T_g values below 0°C . They are made up of flexible chains

that can unfold allowing the rubber material to extend 200% or more of its initial length at ambient conditions. The main categories of elastomers are diene, nondiene, and thermoplastic gels.⁽⁶⁾

Diene elastomers are polymerized from monomers that contain two alternating double bonds, diene, with the general structure:

In the chemical formula depicted above, R represents a hydrogen atom, a chlorine atom, or a methyl group. After polymerization, the repeating unit contains one double bond that can provide a site for cross-linking. The index 'n' represents the total number of repeating units in the polymer, or the degree of polymerization:

Examples of diene elastomers are natural rubber, SBR (styrene-butadiene), and NBR (nitrile rubber) a copolymer of butadiene and acrylonitrile. Of the three categories, only the silicone elastomers and thermoplastic gels are the most frequently used in the manufacture of gaskets and seals for electromagnetic shielding. Silicones, or elastomers having Si-O bonds instead of C-H bonds in their backbone, are well known for their ability to retain 90% or more of their elasticity at ambient temperature over a wide range of temperatures (-50 to 250°C). A review of the chemistry and properties of silicones and thermoplastic gels will be necessary prior to the study of the effects of matrix chemistry on the conduction mechanisms inside the composite.

Thermoplastic elastomers such as SBS (polystyrene-*block*-polybutadiene-*block*-polystyrene) are commercial elastomers that can be made to adopt a network structure similar to that of vulcanized rubbers. SBS elastomers contain soft (rubbery) and rigid (glassy) segments that can be easily compressed and restored when they are stretched. The glassy or crystalline phases are associated with the crystalline or glassy blocks of block copolymers or with the creation of hydrogen (physical) bonds between chemical groups in different molecules. When cooled from the melt below their glass-transition temperature, the butadiene rubbery blocks separate from the styrene glassy domains. The glassy domains then act as physical crosslinks for the elastomeric segments as depicted in schematic diagram in Figure 3. Since these domains are not chemical in nature, they are reversible and therefore elastomers from this class can be fabricated by conventional molding techniques. Thermoplastic gels are special types of elastomers in which the triblock polymer network is swollen with fluid, typically mineral oil.

Figure 3. Schematic Diagram of Styrene-Butadiene-Styrene Copolymer Chain (A), and SBS Thermoplastic Gel Structure with Physical Crosslinks (B).

Silicone rubbers are elastomers that have repeating units of silicon and oxygen in their backbone, as shown:

The symbols X and X' may be hydrogen atoms or bulky groups such as methyl (-CH₃) or phenyl (-C₆H₅). Of the many silicone elastomers, the most common is Poly-dimethylsiloxane, in which X, X' of the repeat units are methyl groups:

The polymer can be cross-linked at room temperature by the addition of an initiator (e.g., benzoyl peroxide), which reacts the methyl groups together with the elimination of hydrogen gas (H_2) to form $Si-CH_2-CH_2-Si$ bridges. Other types of silicones can be cured at higher temperatures (50 to $150^{\circ}C$), depending on the product and intended use. The chemistry of the silicone gel matrix used in this study is presented in greater detail in Chapter 4.

2.2. Conductive Fillers

A number of conductive materials such as metals, carbon black, and conductive carbon fibers may be added to plastics and elastomers to increase their surface and bulk conductivities and reinforce their matrix. Conductive polymer composites are obtained by mixing a polymer with conductive powders until it becomes conductive. Filled polymers have bulk conductivities exceeding those of intrinsically conductive polymers, and approaching those of metals.

The filler particles have the primary function to create conductive networks through the matrix and allow the transport and dissipation of incident electrostatic charge or electromagnetic radiation. The addition of small amounts of filler has little effect on the composite resistivity in the beginning, but adding filler particles beyond a critical concentration called the percolation threshold, produces a sharp decrease in resistivity and marks the transition from insulating to conducting behaviour of the matrix. The amount of filler required to reach the percolation threshold depends on the polymer-filler pair and the extent of interaction between the backbone and filler particles. In general, the

resistivity of an unfilled polymer decreases non-linearly with the addition of conductive filler and remains almost unchanged beyond the percolation threshold. On a microscopic level, the resistivity at low filler concentrations is proportional to the probability of formation of a limited number of conductive paths by particle-to-particle contact or electrons tunneling from one conductive surface to the next. At filler concentrations approaching the critical loading level, the resistivity of the compound drops exponentially as the number of new particle-to-particle contacts grows rapidly in the bulk of the material. At concentrations slightly beyond the percolation threshold, the resistivity shows a downward trend after which the profile flattens out as the matrix becomes saturated with filler. The graphical representation of this phenomenon is illustrated in Figure 4. ⁽⁷⁾

Figure 4. Percolation Resistivity Curve for Metal-Filled Polymer. ⁽⁷⁾

If filler particles of different geometry and aspect ratio are used, the critical volume of filler required to "switch" the electrical behavior of the matrix from insulative to conductive becomes a function of the packing efficiency and area-to-volume ratio of the filler. Specifically, flake compounds reach percolation values at lower loading levels than spheres and fibers. The reason is that flakes have highly irregular faces and large surface area-to-volume ratios which allow them to form many contact points between particles but at the same time have low packing fractions with a large number of voids between the layers. Spherical fillers have the smallest surface area-to-volume ratio and, thus, their packing fraction value approaches the ideal value of 0.74.

2.3 Electrical Conduction in Filled Polymers

The conductivity of a polymer filled with conductive particles such as metals, carbon black, or carbon fibers depends on the intrinsic conductivity of the particles and on the number of particles touching (or within 20-100 Angstroms of each other to allow electron tunneling) per unit volume. Most conductive polymers have surface resistivity values between 10^6 and $10^{-2} \Omega\text{-cm}$, seven orders of magnitude below those of insulators ($10^{13} \Omega\text{-cm}$). Once the volume fraction of conductive material exceeds the percolation threshold, the polymer-metal composite becomes conductive. If insulating polymers are considered organic semiconductors with very large energy gaps, then no charge transfer to a contacting metal will occur. Therefore, there would be no intrinsic states into which carriers at the metal Fermi level, ϕ_m , can be transferred. At low filler concentrations,

some electrons are capable to tunnel through small gaps or “hop” between conductive particles, but near the percolation threshold they “ride” along conductive paths formed by overlapping metal particles throughout the entire matrix. Thus, it is assumed that at higher filler loadings new states are created in the forbidden gap that accept or donate a charge to the contacting metal and determine the polymer “work function”, ϕ_p . These states could be due to chain-end groups, adsorbed molecules, additives, or impurities, or products of oxidation of the polymer surface. Figure 5 depicts the filled and empty extrinsic surface states as discrete levels, ϕ_c , and ϕ_{co} (before metal-polymer contact).⁽⁸⁾

Figure 5 – Energy Level Diagram of a Contact Between a Metal and Insulator with Surface States: (a) before contact, (b) after contact.⁽⁸⁾

2.4 Critical Review of Literature

The electrical conductivity of filled polymers has been extensively studied for more than four decades. Many researchers have reported that the electrical resistivity of polymer composites filled with carbon black does not increase continuously with increasing conductive filler content. At the critical filler loading (percolation threshold), the resistivity of the matrix drops by eight orders of magnitude.⁽⁹⁾ In order to increase the efficiency of the process and decrease economic costs, the amount of conductive phase for achieving high-conductivity materials should be as small as possible. The group of Pinto et al.⁽¹⁰⁾ have investigated the effects of filler content and processing parameters on the electrical resistivity, density, and hardness of composites prepared from carbon black and Nylon 6. (All samples were processed by mixing, melting, followed by compression molding.) Their study demonstrated that the composite resistivities decreased by 10^{12} ohm-cm for conductive black concentrations beyond the percolation value of nine percent by weight. This represents a significant shift in electrical properties for a rather small change in filler concentration.

Other research groups were able to demonstrate that the addition of carbon black beyond the percolation threshold can lower the modulus and strength of the material.⁽¹¹⁾ Because of additional contamination issues associated with the use of C-black in antistatic packaging materials in clean-rooms, carbon black fillers are being gradually replaced by metals, Ag, Cu, or Ni in flake or powder form, or carbon fibers coated with micron-thick films of these metals.

Y. Ho and P. Schoen (1996) have investigated the microwave dielectric properties of composites made of nickel-coated graphite fibers (Cycom) in two different types of silicone elastomers (Sylgard 184/ Dow Chemical, and CF-421/ NuSil Technology).⁽¹²⁾ They showed that matrix viscosity plays a role on the fiber alignment and filamentation in the composites and influences the permittivity and loss tangent in the composite. Their work focused on the study of matrix dielectric charging mechanisms at filler levels that were one order of magnitude below the percolation threshold (25 wt%). The EMI shielding performance of the composites was not evaluated since the filler loading in the matrix was much below the percolation threshold. The second result of their research, although not so convincingly presented, was that the dielectric constant of the composites was a strong function of the dielectric constant (κ) of the matrix. Even if such a trend existed, it could not have been supported by this study because of the poor choice of matrix materials selected for comparison – the two elastomers used had almost identical physical properties. (The dielectric constants of the matrices were 2.67 and 2.5.) Therefore, any correlations between the dielectric constants of the filled and unfilled polymers could have been purely coincidental. Table 1 summarizes the dielectric performance and loss tangent values for the Nickel-filled silicone composites.

Table 1. Dielectric Constant and Loss Tangent Values for NuSil and Dow Sylgard Composites Filled with Low Concentrations of Cycom Fiber Fillers.⁽¹²⁾

Cycom Fiber wt.%	ϵ (dielectric constant)	$\tan\delta$ (loss tangent)
a) Nusil FC-4721, 0.75wt.% COS		
0	2.67	0.005
1	5.63	0.009
2.3	10.69	0.017
b) Dow Sylgard 184, 10wt.% COS		
0	2.5	0.022
2	9.45	0.031

The article provided no information about the number of samples analyzed or the confidence levels of the reported data.

CHAPTER 3

STATEMENT OF PURPOSE

The purpose of this work is to evaluate the effects of matrix chemistry, filler concentration, and filler geometry on the resistivity and elastic modulus of conductive elastomers and establish the limit of elastic modulus with an increase in conductive filler concentration to achieve EMI-shielding compatible resistivity values. The samples will be manufactured and their resistivity, elastic modulus, elongation at break, and strength in tension and compression will be measured to determine the optimum chemistry and processing parameters required for developing a composite with low resistivity and good elastic properties, in particular low modulus. The proposed research work attempts to explain which factors have a greater influence on the electrical resistivity and modulus of the conductive gel system. It is known that compressible, molded EMI gaskets and seals are currently difficult to manufacture in conductive form because the addition of metal fillers in excess of 40% by volume increases their surface conductivity and shielding effectiveness but reduces their elasticity and sealing performance. Thus, a 78% increase in hardness is measured for a commercial-grade silicone mixed with 40% by weight silver powder. All SE values were measured at 10 Mega Hertz incident-wave frequency. The maximum SE value, as presented in Table 2, is 140 dB.⁽¹³⁾

TABLE 2. Physical Properties for Six Commercial Conductive Elastomers.⁽¹³⁾

Filler	Unfilled	C	Ni	Ag	Ag-silica	Ag-Cu	Ag-Al
Volume Resistivity (Ω -cm)	9×10^{14}	6-8	0.100	0.005	0.006	0.004	0.008
SE (dB)	0	> 85	>100	>130	>130	>120	>120
Hardness (Shore A)	45	70	70	80	65	65	65
Tensile Strength (lb/in ²)	300	450	150	400	200	200	200
Tear Strength (lb/in)	20	15	40	60	30	25	30
Elongation (%)	150	160	300	290	280	300	300
Compression Set (%)	20	30	35	60	30	32	32
Specific Gravity	1.18	1.2	1.95	4.0	1.8	3.5	2.0

Substitution of Ag flakes with Ag-coated silica fibers in the same polymer matrix, leads to a hardness increase (or a loss in elasticity) of only 56%, while the surface conductivity remains constant. These facts indicate that the shielding performance of existing materials can be further improved through experiments in which matrix chemistry, and processing parameters, such as concentration and mixing time, are varied during the manufacture of the composite. Understanding and quantifying the influence of these changes on the three-dimensional structure, conductivity, and modulus of the metal-polymer networks can help one determine the optimum ranges for the above parameters and use them to design and develop elastic-conductive composites with higher shielding effectiveness.

CHAPTER 4

EXPERIMENTAL METHODS

4.1. Materials

4.1.1. Thermoplastic and Thermoset Elastomers

The TP gel matrix used in the present study was composed of a mixture of 20% weight SBS copolymer, and 80% weight mineral oil, with a total density of 0.88 grams per cubic centimeter. Since the typical use temperature of the gel is much higher than its T_g value (-120°C), it behaves like a soft and flexible material with very low modulus and high elongation-to-break values at ambient temperatures. The maximum temperature of use before the gel starts to flow is 60°C .

The thermoset gel, commercially known as Wacker 612 Sil Gel, was prepared by the reaction of A, B silicone parts as per the chemistry depicted in Figure 4. The viscoelastic properties of the matrix were controlled by adjusting the A:B ratio. A weight ratio of 1.2 : 1 (A : B) was found optimum for yielding 'Hardness B' values above 45. The bond between the siloxane chains is formed during the platinum catalyzed addition reaction between the methylsiloxane segment and vinylmethylsiloxane (prepolymer):

By using addition cure chemistry for formulating silicone elastomers, no byproducts are formed, which allows the system to preserve its dimensional stability. The platinum cure chemistry systems is used for room temperature cures and varies between a few minutes to hours.⁽¹⁴⁾

The cure reaction can be accelerated by mixing and heating the gel between 50 and 130°C. Silicone gels have weakly crosslinked structure, and contain a large fraction of "free" fluid, composed mainly of hydride functional fluids as depicted in the schematic diagram in Figure 6.

Figure 6. Catalyzed Two-Part Silicone Gel Reaction.

4.1.2. Conductive Filler Materials

The following materials from Potters Industries, Inc. were used as fillers: silver-coated silica spheres (Conduct-O-Fil S3000S2M), fibers (Conduct-O-Fil SF82TF8), and silver-coated mica flakes (Conduct-O-Fil SM600F55). The particles had average size distributions of 20-60 μm , 20-60 μm , 10-50 μm , and true densities of 2.6, 2.6, and 4.8 grams per cubic centimeter, respectively. The silver content was eight percent by weight for spheres and fibers, and 55% for flakes. Bulk powder resistivities decreased from fibers (0.004 ohm-cm) to flakes (0.003 ohm-cm) and spheres (0.0017 ohm-cm).

The SEM micrographs in Figure 7 depict the various morphologies of Conduct-O-Fil particles. The spheres and fibers have uniform particle geometries and aspect ratios of one and 10, respectively. In the case of flakes, the particle size and geometry are more irregular than for fibers and spheres, with less efficient packing. The average value for the aspect ratio (AR) of flake additives is 1.6.

Figure 7. SEM Micrographs of Conduct-O-Fil (A) Silver-Silica Spheres, (B) Fibers, and (C) Silver-Mica Flakes.

4.2. Test Specimen Preparation

Conductive thermoplastic and silicone gels are prepared by mixing the three types of rigid fillers with polymer (in viscous state) to ensure complete dispersion of the particles in the matrix. The mixing step differs for thermoplastics and silicone gels because of the different methods employed to partially interrupt the polymer network to introduce the filler particles. Thermoplastic gels are re-melted and mixed with the filler, whereas thermoset gels must first be prepared by mixing A and B silicone parts that are viscous fluids and undergo curing in the presence of a catalyst. The filler particles must be added and dispersed uniformly in the viscous matrix before the silicone system becomes fully cross-linked.

4.2.1. Compounding Thermoplastic Elastomers

The thermoplastic compounds were manufactured by first melting the thermoplastic matrix followed by compounding the filler and matrix at high temperature, and slowly cooling (solidifying) the product inside the mixer.. Filler loading levels were increased in increments of 10 volume percent until the maximum filler loading level was exceeded for each filler. The maximum loading level is the point at which there is not enough polymer to completely wet the filler surface. Filler type and loading level criteria are used to identify all thermoplastic compounds in Table 3. Formulations for which the maximum filler loading level was exceeded are listed in italics.

TABLE 3 - Characteristics of Conductive Thermoplastic Gel Compounds

Conductive Filler (volume %)	Filler Weight (g)	Compound Weight (g)	Compound Density (g/cc)
10% sphere	10.92	33.26	1.05
20% sphere	21.84	29.57	1.22
30% sphere	32.76	25.87	1.40
40% sphere	43.68	22.18	1.57
50% sphere	54.6	18.48	1.74
60% sphere	65.52	14.78	1.91
10% fiber	10.92	33.26	1.05
20% fiber	21.84	29.57	1.22
30% fiber	32.76	25.87	1.40
40% fiber	43.68	22.18	1.57
50% fiber	54.6	18.48	1.74
10% flake	20.16	33.26	1.27
20% flake	40.32	29.57	1.66
30% flake	60.48	25.87	2.06
40% flake	67.41	19.01	2.45
50% flake	100.8	18.48	2.84

The thermoplastic (TP) gel was loaded into a 60 cc Brabender mixer and masticated at 200°C and 30 rpm (rotor) speed until complete melting was achieved. The

filler was then slowly added at 200°C and 30 rpm mixer speed. After complete addition, isothermal mixing was continued for 10 minutes at 80 rpm speed. During the last minute of mixing the front-, middle-, and back-plate heaters were turned off, and the mixer speed was reduced to 30 rpm. After the mixing step was completed, the compound was allowed to slowly (air) cool to room temperature for 20 minutes and then unloaded from the bowl. A front view of the Brabender mixing equipment used in the experiments is depicted in Figure 8.

Figure 8. Brabender Plasti-Corder PL 2200 Mixing System (A) front view and (B) face plate removed. (Courtesy of Raychem Corporation)

4.2.2. Preparation of Silicone Gel Compounds

In thermoplastic compounding and molding methods time was not a critical parameter since no reaction was taking place between the system components. The polymer and filler particles are bonded by van der Waals forces. However, thermoset processing methods for silicone gels use a condensation reaction that involves the breaking and forming of chemical bonds between the dimethyl-siloxane oligochains leading to an increase in the linear chain length and the number of crosslinks (bridges) between the chains. The process is irreversible leading to the formation of a highly viscous, two-dimensional elastomer network that cannot be softened by melting, thus, a thermoset. Because of the large changes in physical properties undergone by the matrix during the polymerization process, especially the large and rapid increase in viscosity, the addition of the filler to the system must be done almost simultaneously in order to ensure a homogeneous entrapment of filler particles inside the crosslinked regions provided that the density of crosslinks is uniform throughout the elastomer network.

The steps taken to manufacture the filled silicone thermosets involved the mixing of silicone parts A and B in a ratio of 1.2 to 1 by weight and stirring the viscous mixture at 100 rpm for two minutes to initiate the condensation and crosslinking reactions. After two minutes, the mixing is stopped and the silicone gel (still undergoing curing) is transferred to a 200 cc mixing container. The filler is then added and stirred manually for a few seconds to break the agglomerates and improve dispersion. Then, the mixing bowl is placed inside a Keyence hybrid mixer, where the mixing and de-foaming steps can be

performed sequentially eliminating the need for de-gassing the compound separately in a vacuum chamber before it is cured in a mold.

In the Keyence system the mechanical mixing (typically achieved with blades) is replaced by a combination of rotation and revolution motions of the bowl. The centrifugal force generated is sufficient to initiate the dissolution of air bubbles introduced in the system by manual stirring and allow them to escape from the viscous polymer solution. The mixing is continued for two to three minutes at fixed rpm speed, followed by a de-foaming step of one minute. During the compounding step, there is an increase in the system temperature of 15 °C, which leads to premature curing of the compound. In order to maintain near ambient temperature in the system during curing, the mixing and de-foaming times for sphere and fiber compounds were reduced from 2-3 minutes to 30 seconds, which seemed sufficient to disperse the filler in the matrix.

All flake compounds failed during this step even after taking the required precautions to control the temperature and curing rate in the system. Flake-filled silicone elastomers could not be prepared by this method due to the poisoning of the platinum catalyst by the rich silver film on the mica flakes. Since the mica surface contains more silver per unit area than fibers and spheres, 55% by weight compared to 8% by weight, it is highly probable that using silver-rich fillers in the system leads to more platinum atoms being substituted by silver at the active polymer sites with the formation of stable silver complexes. As a result, the platinum-catalyzed reactions leading to network formation are terminated. The "poisoned" flake system retains its liquid-like properties and cannot be forced to cure by heating it or adding more catalyst. The silicone gel formulations

prepared by this method are tabulated in Table 4. Compounds shown in italics represent extrapolated property data.

TABLE 4. Identification and Composition of Conductive Silicone Elastomers

Filler Type and Loading (vol. %)	Weight of Filler (g)	Weight of Gel (g)	Density of Compound (g)
<i>10% sphere</i>	<i>10.92</i>	<i>33.26</i>	<i>1.10</i>
20% sphere	80.24	119.74	1.30
30% sphere	106.92	93.08	1.45
40% sphere	128.2	71.76	1.62
50% sphere	145.65	54.34	1.79
60% sphere	160.16	39.84	1.95
<i>10% fiber</i>	<i>69.4</i>	<i>134.7</i>	<i>1.21</i>
20% fiber	80.25	119.75	1.30
30% fiber	106.92	93.08	1.46
40% fiber	128.24	71.76	1.62

At the end of the mixing and degassing steps, the viscous compounds were unloaded from the mixing container and poured immediately, while still in liquid form, and molded in the appropriate geometries for tensile, compression, and electrical resistivity tests. The gels were cured in the mold under a constant load of 3000 lb_f at 120°C for 45 minutes.

4.2.3. Compression Molding

All compounds were molded under the same conditions using a melting/ hot-forming step followed by a cold-forming step. The molding equipment used was composed of two PHI (Pasadena Hydraulics Inc.) presses mounted on the same base. The filled gel was placed inside the appropriate mold and supported between two Teflon sheets. Three types of molds were used to manufacture sheet, disk, and rectangular specimens for tensile, compression, and bulk electrical resistivity tests, respectively. The mold used to fabricate sheets was a stainless steel frame with inner dimensions of 15.24 cm, 15.24 cm, and 0.110 cm thick. The one used to fabricate compression disks was made of a 0.65 cm thick aluminum sheet with 10 circular dies stamped in it, each die having an ID (inner diameter) of 1.26 cm. A rectangular frame with inner dimensions of 2.54 cm, 10.16 cm, and thickness of 0.055 cm was employed to manufacture a strip, which was then cut into four identical square specimens for bulk resistivity measurements. The process was repeated in order to produce a total of eight specimens out of which five were tested, and three were used as a backup.

The molding step begins by supporting the mold and Teflon sheets between two stainless steel plates (side of 28 cm) and placing the stack inside a hydraulic press at 210°C (Figure 9). The compound is allowed to melt and evenly fill the mold cavity. Intimate contact between the plates is maintained by bringing the press rams closer together to eliminate the gap formed during melting of the compound. During the high pressure step a pressure of 1.25 MPa is applied on the plates for 5 minutes to form the compound into the desired shape (square). Then, the pressure is released and the hot

assembly is removed and placed inside a water-cooled press where the cold-forming step takes place at 625 kPa ram pressure. After five minutes, the mold is removed from the press and the top Teflon sheet is removed from the filled gel (the bottom sheet is left to provide support to the rather soft and rubbery material). The top surface is covered with a matte Nylon sheet to prevent surface contamination. The compound sheets are stored at room temperature (22-24°C) and 50% relative humidity until they are cut into appropriate size specimens for electrical and mechanical tests.

Figure 9. Hydraulic Press System for Compression Molding of TP and SIL Gel Compounds. (Courtesy of Raychem Corporation)

4.3. Tensile Measurements

The mechanical properties of filled thermoplastic and silicone gels were measured using an Instron tensile tester machine, Series 4500, interfaced with a Series IX computer control and analysis system. Load versus strain data were used to calculate elastic modulus (300% elongation modulus), tensile strength, elongation at break, and toughness parameters, and evaluate the reinforcing effect of sphere, fiber, and flakes on each type of matrix. The comparative reduction in strength and compliance for thermoplastic versus silicone matrices was also evaluated. Mechanical parameters of filled gels were reported as function of unfilled gel properties. A total of 13 formulations of TP gel and 8 of SiL gel were characterized in tensile tests, with five specimens manufactured and tested for each formulation. Test specimens were prepared by cutting out rectangular strips of compound of dimensions 2.54 cm x 1.27 cm x 0.11 cm from a mold of dimensions 15.24 cm x 15.24 cm x 0.11 cm (or 6 inch x 6 inch x 0.04 inch). The strips were secured in the Instron grips with a jaw separation of 1 inch. Setting up the Instron consisted of installing and calibrating a 100 Newton +/- 1% load cell, using a full scale setting of 2000 grams (dictated by the strength of the gel), and a crosshead speed to 500 mm/min.

4.4. Compression at 50 Percent Deflection Measurements

Compressive properties describe the behavior of materials when they are subjected to a compressive load at a relatively low and uniform rate of loading. The data obtained from them serves as a standard for the research and development of new materials and for quality control of commercial ones.

The compression-deflection characteristics of filled thermoplaastic and thermoset gels was measured as per ASTM D575-91. Standard test specimens 28.6 +/- 1 mm in diameter, 650 mm² in area and 12.5 mm in thickness were molded from both TP and SIL gel compounds. A deflection rate of 1.27 cm (0.5 in) per minute and fixed deflection of 50% were used. The measurements were taken at room temperature and 50% relative humidity. Five samples were tested for each formulation and the average and standard deviation for compressive strength values were calculated.

Figure 10. Instron Compression Test System - (A) Tester console, (B) Setup for Testing Conductive Gel Disk Specimens. (Courtesy of Raychem Corporation)

4.5. Transverse Electrical Resistivity Measurements

The volume resistance is defined as the ratio of the direct voltage applied to two electrodes that are in contact with a specimen to that portion of the current between them that is in contact with the specimen. The volume resistance is the resistance to leakage through the body of the material. The volume resistivity is a material property defined as the ratio of the potential gradient parallel to the current in the material to the current density. It is the electrical resistance between the opposite faces of a cube of a given material that has a side length equal to 1 cm at a given temperature:

$$\rho = \frac{A}{t} (R_v) \quad (2)$$

where ρ is the volume or bulk resistivity, A is the area, t is the thickness of the specimen, and R_v is the volume resistance.

The surface resistance of a material is defined as the ratio of the direct voltage applied to the electrodes to that portion of the current between them that is primarily in a thin layer of moisture or other conductive material that may be present on the surface. The surface resistance of a material depends upon the quality of cleanliness of the surface of the sample. The test procedures to determine the surface and volume resistance values are rather complex. ASTM D257 and ASTM D4496 describe the required sample size, sample and electrode geometry, apparatus, and procedures required to carry out the test for DC resistance of insulating (ASTM D257) and moderately conducting (ASTM D4496) materials. The results of the tests are affected by the ambient temperature and humidity. Usually, the higher the temperature and humidity, the lower the resistance

value of the sample. Five specimens were tested for each formulation, and the test variables selected were voltage, temperature cycle, temperature range, and temperature increment size. The test setup used for measuring the transverse bulk resistivity of the specimens is presented in Figure 11.

**Figure 11. Transverse Electrical Resistivity Measurement Setup.
(Courtesy of Raychem Corporation)**

4.6. Environmental and Safety Issues

Silver fillers, silicones, and thermoplastic gels have been evaluated individually and in composite form in order to establish the safe limits of human exposure and possible health and safety issues involved with the handling and testing of these composites. The results of these evaluations can be found in the MSDS documents (Material Safety Data Sheets) that accompany the raw materials at the time of shipment from the manufacturer. No harmful effects on humans or animals have been detected as of yet for the above compounds. Since silicones are derived from the chemistry of sand (silica), they tend to be generally inert towards most chemicals or organic tissue. Silver is a benign metal with low reactivity, well-defined properties, and is safe to work with in general.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction

The mechanical and electrical properties of conductive elastomers are determined by the individual properties of the components, the shape of the filler phase, the morphology of the system, and the nature of the interface between the filler and matrix phases. A variety of properties such as elastic modulus at 300% elongation, tensile strength, elongation at break, compressive strength, and bulk resistivity have been measured for all formulations of thermoplastic and Wacker 612 silicone elastomers. The results are reported separately for reactive (silicone) and non-reactive (thermoplastic) systems, in order to separate the matrix effects from the geometrical and morphological aspects.

By altering the filler particle geometry, or volume fraction, one is able to change the properties of thermoplastic and silicone compounds in a gradual and controlled manner, until the right combination of resistivity and elastic modulus is achieved, and the composite meets the requirements set for electrostatic discharge or electromagnetic shielding applications. At present, these ranges for bulk resistivity are set between 10^2 and 10^{-2} ohm-cm. While a higher content of silver-silica or silver-mica particles is desirable because it makes the compound more conductive, an excess of filler can adversely affect the elastic and strength properties of the matrix by the same argument that any additive tends to "stiffen" the polymer matrix. Compositional and structural

factors can be varied within certain limits in both reactive and non-reactive systems studied in order to establish the optimum range of electrical and mechanical properties. In particular, when evaluating two compounds with similar bulk resistivity values, the one exhibiting lower modulus and higher compliance under tension-compression conditions is more appropriate for use as a flexible ESD/ EMI shielding compound.

5.2 Microstructural Characterization

The microstructures of sphere, fiber, and flake thermoplastic compounds were characterized using scanning electron microscopy. Fracture surfaces of TP gel specimens used in tensile tests were prepared for microscopic analysis by freeze-drying in liquid nitrogen to prevent off-gassing of organic volatiles or oils during analysis. Images of the tensile fracture surfaces were taken at an angle of 45 degrees from the vertical fracture plane. The microstructures are depicted in Figure 12 a, b, and c. Smooth top and side surfaces were observed for sphere and fiber composites, whereas the flake composite structure was porous with many sharp contact points between the flakes and the rubber molecules. It was also observed that in sphere and fiber compounds, the polymer molecules wet the filler particles almost completely (confirmed by the continuous polymer film covering the top surface of the sample), whereas the flakes seem to be only partially wetted by the polymer. This is due to the fact that the flake particle geometry is more irregular, with sharp ends, large roughness, and large surface-to-volume ratio. As a result of the large surface area of flakes, these fillers exhibit large interfacial interactions with the polymer chains leading to stronger filler-matrix physical bonds, increased

modulus (stiffness), and reduced strength and elongation at break. The lack of preferred orientation of fibers and flakes can be observed in the fracture plane x-z in which the particles have a completely random orientation.

**Figure 12 - Fracture Surfaces of 30% Volume Filler in TP Gel -
(A) Sphere, (B) Fiber, and (C) Flake Compounds.**

Thus, the final products exhibited homogeneous and isotropic structures despite the filler particle anisotropy, and processing conditions used. This is desirable when designing and manufacturing conductive elastomers for radiation shielding applications, because the processing direction can affect the compound properties and shielding performance along certain directions.

5.3 Elastic and Mechanical Strength Properties

5.3.1 Thermoplastic Elastomers

In general, the addition of fillers tends to reinforce the thermoplastic matrix, with the effect being more pronounced at higher loadings. Comparative measurements of elastic and mechanical strength properties for sphere, fiber, and flake compounds lead to the understanding of the influence of particle geometry on these properties and the correct selection of filler type for a certain application. Certain geometries are more efficient than others because they have the capacity to reach the desired levels of resistivity and modulus with less filler material.

Figure 13 depicts the average stress-strain profiles for five samples of 30% by volume of sphere, fiber and flake compounds. All compounds exhibit higher stress-strain responses than the unfilled gel having a nearly flat profile. For small tensile strains (less than 2), the elastic moduli increase from sphere (8.81 kPa), fiber (28.64 kPa), to flake (infinite slope), while the ultimate strengths decrease from 213 kPa, 192.4 kPa, to 132.4 kPa, respectively. In the case of flake compounds, the reinforcement is so severe that the compounds fail in brittle fracture mode. For these composites, the ultimate filler loading before break was set at 25 % by volume. The plateau in the stress versus strain profile for fiber compounds corresponds to filler re-orientation effects and parallel alignment with the stress field lines established inside the matrix.

Figure 13 - Stress-strain Profiles at 30 % Volume Filler in TP Gel Compounds.

While increasing the fraction of conductive component in the system increases the conductivity, the presence of a large number of particles in the voids between the polymer chains has a damaging effect on the bonding strength and elongation at break properties. Since the filler-polymer bonds have a smaller bond energy when compared to polymer-polymer bonds, occurs at the expense of a decrease in strength. Thus, an increased number of weaker bonds decreases the composite strength. The ultimate tensile strength (UTS) and elongation at break (EB) for spheres, fibers, and flakes at various loading levels are summarized in Table 5, in which each value reported represents the average of five measurements. The reduction in tensile strength at 30 % by volume of

filler as compared to the unfilled gel is 47% for sphere, 52% for fiber, and 67% for flake compounds. Similarly, the elongation at break limit decreases by 38%, 32%, and 94% for sphere, fiber, and flake composites, respectively. Nearly linear trends in ultimate tensile strength, toughness, and elongation at break were observed in sphere, fiber, and flake thermoplastic compounds (Figures 14, 15, and 16). Ultimate tensile strength data for thermoplastic compounds indicate a downward trend with the addition of rigid fillers, with a sharp drop in the property near the percolation threshold of the filler. For spherical fillers, the percolation threshold occurs between 20 and 30 vol.% loading, when the ultimate tensile strength drops by 94.5% from the unfilled gel value of 403.3 kPa. For fibers and flakes the thresholds are set at 20-30 vol.% fibers, and 10-20 vol.% flakes, and the percent reductions in UTS values from the unfilled gel are 78.1% and 36%. Thus, spherical fillers produce the most dramatic decrease in ultimate strength of the three types of fillers studied. Flake-filled compounds experience only a slight loss in strength, but a 76% increase in the modulus (stiffness) compared to the unfilled gel value of 1.47 kPa. The toughness decreases in all TP matrices with the addition of spheres, fibers, and flakes, remaining nearly unchanged for fiber compounds between 20 and 30% by volume of filler.

Elongation at break values reflect the limits of tensile strain before rupture of filled rubber compounds. Flake fillers are the most effective at weakening the matrix, and reducing its elastic limit under tensile strain, as shown in Figure 16. At 30% filler loading, the percent reductions in the EB value are 38.2% (spheres), 32.2% (fibers), and

94.1% (flakes) compared to the unfilled gel EB value of 2909% extension from the original length.

Table 5 - Effect of Silver Coated Spheres, Fibers, and Flakes on the Average Mechanical Properties of TP Gel Compounds.

Filler Type	Filler Volume Fraction	UTS (kPa)	Toughness (kPa)	300% Modulus (kPa)	Elongation at Break (%)	Compression at 50% Deflection (kPa)
unfilled gel	0	403.3	4033	1.47	2909	9.8
Ag _c -sphere	0.1	366.8	2386	12.15	2368	19.6
Ag _c -sphere	0.2	312.3	1889	15.55	2127	29.4
Ag _c -sphere	0.3	213.0	1207	8.81	1799	39.2
Ag _c -sphere	0.4	97.20	475.7	5.45	1360	39.2
Ag _c -sphere	0.5	97.90	551.6	26.34	1242	49.0
Ag _c -sphere	0.6	22.10	42.06	14.47	435	127
Ag _c -fiber	0.1	350.7	2455	22.42	2390	19.6
Ag _c -fiber	0.2	250.3	1558	25.09	2062	49.0
Ag _c -fiber	0.3	192.4	1434	28.64	1973	58.8
Ag _c -fiber	0.4	76.70	560.0	33.30	1340	142
Ag _c -flake	0.1	206.8	1303	23.88	1477	19.6
Ag _c -flake	0.2	180.6	806.7	99.63	773	189
Ag _c -flake	0.3	132.4	82	>9999	172	686

Figure 14. Ultimate Tensile Strength versus Filler Loading in TP Gel Compounds.

Figure 15. Toughness versus Filler Loading in TP Gel Compounds.

Figure 16. Elongation at Break versus Filler Loading in TP Gel Compounds.

The tensile and elongation-at-break profiles for sphere and fiber compounds nearly overlap at all loading levels. Both show a moderate decrease in strength and compliance with increasing filler content, with the sphere compounds exhibiting a plateau between 40 and 50 volume percent of filler. In the case of flake compounds, pronounced drops in strength and elasticity are noted even for low filler content (less than 20% by volume).

The elastic modulus at 300% elongation profiles for spheres, fibers, and flakes become divergent for loadings higher than 10% by volume. Spherical fillers lead to an increase in the composite modulus at first, followed by a recovery in this property at loading levels between 20 to 40% by volume. Hence, the 300 % modulus for sphere

compounds containing 40% vol. spheres is five times larger than that of the unfilled gel (Figure 17).

Figure 17. Elastic Modulus (300% M) versus Filler Loading in TP Gel Compounds.

Compression test results are important for evaluating the performance of materials to be used as gaskets or insulation between mating parts, and are required to withstand a certain level of compressive stress. They should also be able to revert back to their original shape in a relatively short period of time (min) after the removal of stress. Thus, a low compression modulus is desirable composites that are being evaluated as potential electrostatic discharge gasket or insulation materials.

As illustrated in Figure 18, the largest compliance in compression mode is exhibited by the sphere compounds whose strength remains unaffected by the addition of filler up to 50 % by volume. Beyond 50% by volume of fillers, the compression strength increases from 49 kPa (50% vol. spheres) to 127 kPa (60% vol. spheres).

Figure 18. Compression at 50% Deflection Versus Filler Loading in TP Gel Compounds.

5.3.2 Wacker 612 Silicone Elastomers

Silver-coated sphere and fiber silicone compounds exhibit similar mechanical behavior with their non-reactive counterparts (thermoplastic systems), but since their curing takes place in the presence of the filler, secondary reactions between the silicone parts and the metal on the filler particles are likely to occur and inhibit the curing process. As a result, these systems tend to be more sensitive to the type of metal that is used to coat the filler particles, and the surface concentration of metal in the coating. Silver-coated flake compounds could not be manufactured by this method. However, the curing problem can be eliminated if one uses a different grade of silver flakes that are less rich in silver, or substitute the silver for a different metal such as copper or nickel, which has excellent resistivity but does not interact with the platinum catalyst.

The ultimate tensile strength (UTS) and elongation at break (EB) for spheres and fibers at loading levels between 10 and 60 volume % are summarized in Table 6. Each value reported represents the average of five measurements. The percent decrease in the compounds' tensile strength at 30 volume% sphere and fiber (near the percolation threshold) as compared to the unfilled gel is 9.4 % and 4.3 %, respectively. Similarly, the elongation at break limits decrease by 22.5 % and 45.8 %, respectively.

Table 6 - Effect of Silver-coated Spheres and Fibers on the Average Mechanical Properties of Wacker 612 SIL Gel Compounds.

Filler Type	Filler Volume Fraction	UTS (kPa)	Toughness (kPa)	300% Modulus (kPa)	Elongation at Break (%)	Compression at 50% Deflection (kPa)
unfilled gel	0	148.4	474.5	0.017	895.1	8.52
Ag _c -sphere	0.1	-	-	-	-	-
Ag _c -sphere	0.2	99.28	223.4	0.177	634.5	25.48
Ag _c -sphere	0.3	134.5	355.1	0.257	693.4	41.21
Ag _c -sphere	0.4	244.76	650.2	2.518	479.7	176.5
Ag _c -sphere	0.5	91.70	308.2	0.746	585.1	90.37
Ag _c -sphere	0.6	>9999	53.85	0.000	55.1	297.1
Ag _c -fiber	0.1	-	-	-	-	-
Ag _c -fiber	0.2	77.91	250.3	0.726	556.9	34.05
Ag _c -fiber	0.3	142.0	482.6	2.234	485.0	118.1
Ag _c -fiber	0.4	124.8	206.8	2.135	251.0	303.6

The ultimate tensile strength, toughness, modulus at 300% elongation, and elongation at break profiles for silicone compounds show a higher degree of scatter in the data for low to medium loadings. (Figures 19, 20, 21, and 22). The maxima in strength and toughness for sphere and fiber compounds occur near 40 and 30% vol., respectively, as seen in Figures 19 and 20. Strength and toughness follow similar trends for both filler geometries. Sphere and fiber compounds at 40% loading levels exhibit high values of modulus, 25 kPa for spheres and 22 kPa for fibers, but low values in elongation at break. EB values for 40 vol.% spheres and fibers are 479.7 kPa and 251 kPa, respectively.

Figure 19. Ultimate Tensile Strength versus Filler Loading in Wacker 612 SIL Gel Compounds.

Figure 20. Toughness versus Filler Loading in Wacker 612 SIL Gel Compounds.

Figure 21. Elastic Modulus at 300% Elongation versus Filler Loading in Wacker 612 SIL Gel Compounds.

Figure 22. Elongation at Break versus Filler Loading in Wacker 612 SIL Gel Compounds.

Compression strength values for both sphere and fiber silicone gels display increasing and diverging trends for the two types of fillers. Fiber compounds exhibit a higher loss in compressive resilience than sphere compounds with the same volume percent of filler. The strength versus filler content profiles for both filler systems are depicted in Figure 23.

Figure 23. Compression at 50 Percent Deflection versus Filler Loading in Wacker 612 SIL Gel Compounds.

5.4 Electrical Resistivity

In their natural state, without any additives, the two types of elastomers studied are electrical insulators. The bulk resistivity value for the thermoplastic gel is 1.7×10^{12} ohm-cm for the thermoplastic gel and on the order of 10^{14} ohm-cm for the silicone gel. In this state, any surface charges generated by an electrostatic discharge are deposited on the polymer chains, and cannot be dissipated away. The longer the lifetime of the charge, the more likely it is to cause damage to electronics that come into contact with it.

A second disadvantage of unfilled elastomers is that they are "transparent" to electromagnetic radiation, meaning that the polymer chains do not interact with, and thus cannot absorb or reflect this type of radiation. Since the frequency of the electromagnetic radiation is significantly higher than the vibrational frequency of the polymer, coupling cannot occur and all radiation ends up being transmitted through the material. In order to reduce transmission and increase electromagnetic shielding effectiveness, conductive fillers are added to the insulating elastomer network in order to establish three-dimensional conductive paths through particle-to-particle contact. A simple shielding mechanism can be explained by the interaction of free electron "waves" from the conductive filler surface with the electromagnetic field which results in the incident radiation being reflected or absorbed by the shield material.

The most significant factors that influence composite resistivity, similar to those affecting mechanical properties, are: particle conductivity, particle shape, and loading level. However, when the loading level exceeds the percolation threshold for that filler type, a continuous conductive path is formed throughout the compound and the bulk

resistivity drops to that of a metal regardless of the filler morphology. For the present study, silver-coated powder, fibers, and flakes with resistivity of 1.5×10^{-6} ohm-cm were used to make elastomer compounds with volume resistivities as low as 9 ohm-cm. Increasing conductive filler content in the compound has as a result a sharp decrease in resistivity between 0 to approximately 30% volume for sphere and fiber compounds, and 15 - 20 % by volume of flake. The critical loading beyond which the electrical resistivity changes very little with filler loading marks the percolation threshold level for that filler geometry. Thus, flake compounds reach the bulk resistivity percolation threshold earlier than sphere and fiber compounds. However, for 30% volume loading, the resistivities of all compounds become equal. (Figure 24). This indicates that fact that, for a volume of filler nearly equal to a third of the total volume, the packing efficiency for all geometries studied is approximately the same. Beyond the percolation threshold, fiber compounds become slightly more conductive than sphere compounds. In Figure 24 the resistivity profiles for sphere and fiber SIL gel compounds are presented. There is a similar trend in both types of filler systems with the percolation threshold being delayed in sphere systems because the sphere-to-sphere electrical contacts are shorter than fiber-to-fiber. An advantage of fibers is that electrons can "race" across the conductive fiber surface without having to jump across from one conductive particle to another, the fiber acting as a resistor being the least-resistance path for surface electron conduction. As a result of the less regular arrangement of fibers in the bulk of the material, and the fact that it takes fewer of them than spheres to establish particle-to-particle contact inside the matrix, the inset of percolation threshold for fiber SIL occurs at about 10% vol. , whereas for spheres

at approximately 25% by volume. Fibers are, thus, more efficient than spherical fillers in establishing a conductive network through the matrix, fact confirmed by the more acute drop in resistivity for fiber (between 10 and 20% by weight) versus sphere compounds (between 20 and 40% by weight). It is important to note that the resistivity at 10% loading data were interpolated for both types of fillers, being assumed that the number of conductive paths formed in the system upon the addition of filler is a continuous function of the concentration of filler particles randomly distributed between the co-polymer chains, or bulky styrene functional groups.

Figure 24. Effect of Filler Geometry on the Volume Resistivity of TP Gel Compounds.

Figure 25. Effect of Filler Geometry on the Volume Resistivity of Wacker 612 SIL Gel Compounds.

Even though temperature was not, initially, one of the factors to be studied, it is important from an application standpoint to observe the qualitative effects of heat on the bulk resistivity of these compounds since heating induces visible volumetric expansions, thus increasing their resistivity. In general, all compounds, thermoplastic and silicone rubbers showed a very weak or no increase in resistivity with temperature. Actually in the case of 40 % by volume fiber - silicone compounds, the resistivity decreased by more than 50 % upon heating from room temperature (20°C) to 50° Celsius, as seen in Figures 25 and 26.

Figure 26. Temperature Dependence of Electrical Resistivity in TP and Wacker 612 SIL Gel Compounds.

CHAPTER 6

CONCLUSION

The structure and properties of thermoplastic and thermoset gels can be modified by adding variable amounts of conductive fillers made by the deposition of a continuous layer of silver on silica spheres and fibers, and mica substrates. Silicone gel matrices have a higher reactivity and sensitivity to filler content and chemistry because they are formed by the reaction between A and B silicone parts that are cured in the presence of a platinum catalyst. In silver-mica flake silicone systems the silver content in the system is sufficient to poison the platinum catalyst and inhibit the curing reaction of the matrix. Due to catalyst poisoning issues, flake-filled silicone gel compounds could not be manufactured, tested, and compared with flake-filled thermoplastic gels.

Sphere, fiber, and flake fillers added to thermoplastic and silicone gel matrices have a reinforcing effect on the matrix that is most visible in the case of flakes. At 30% volume of filler, the values of 300 percent modulus, or modulus at 300 percent elongation, are 8.81 kPa, 28.63 kPa, and 999 kPa for sphere, fiber, and flake TP gels, respectively. Additional losses in resilience in tension and compression, and tensile strength and elongation at break values were observed in both elastomer systems compared to the unfilled gels.

Low electrical resistivity values, approaching values of 0.1 ohm-cm for bulk compounds, were achieved in both systems at filler loading levels exceeding the percolation threshold values for each filler particle geometry. It was observed that at 30% by volume of spheres, the volume resistivity was 9.8×10^6 ohm-cm for SIL elastomers,

and 73.1 ohm-cm for TP elastomers, indicating that there are benefits associated with using a thermoplastic matrix for achieving lower compound resistivity. This result has been confirmed in fiber systems where the addition of 30% by volume of silver-silica fibers to TP and SIL matrices decreased the bulk resistivities to 96.7 ohm-cm and 58 ohm-cm for SIL and TP gels, respectively compared to the unfilled gel resistivities of approximately 10^{12} ohm-cm and 10^{14} ohm-cm for the thermoplastic and silicone gel, respectively. Thus, thermoplastic gel compounds have, in general, higher electrical conductivities, or conversely lower resistivities, than silicone gel compounds at the same volume percentage of filler. Sphere, fiber, and flake filled thermoplastic compounds exhibit lower elastic modulus and resistivity values than silicone systems, and have, thus, more desirable mechanical and electrical properties that can be used to design materials with higher electromagnetic and electrostatic discharge shielding performance.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE RESEARCH

The present study has limited its scope to the comparative evaluation of conductive thermoplastic and thermoset elastomers for electrostatic dissipation and electromagnetic shielding applications that pose limits on compound electrical resistivity and compression modulus of elastomer materials. However, since the homogeneity during compound is always an issue for these materials, and if affects the performance of the final composite, new research studies in the area of silver-silica filled thermoplastic and thermoset gels could focus on answering questions regarding the conservation of the filler and matrix properties during processing, and the degree to which compound homogeneity requirements are met.

Since the value of filler loading at which percolation threshold is manifested in a conductive elastomer system depends on the filler particle geometry, size and aspect ratio, and filler-polymer interaction forces, it might be appropriate to explore the limits of modulus and electrical conductivity for larger aspect ratio particles, or with irregular geometries that would help to randomize the filler dispersion in the matrix. It would also be appropriate to combine the results from both studies in order to determine which particle geometry and size would be most appropriate for initiating percolation thresholds at lower filler loadings, typically below 30% by volume. The results from both studies could be combined and used to design new compounds that are more cost-effective by using less filler material (of irregular geometry, and aspect ratio) to achieve

comparable resistivity and elastic modulus values to the ones reported in the present study. If such a compound was designed and tested by mechanical methods, additional tests such as dielectric strength, and shielding effectiveness would prove essential in assessing the conductive compound for commercial applications where performance and ease of processing issues must be balanced with cost issues. Shifting the conductive properties of elastomer compounds towards lower filler loadings has the advantage of preserving the elastic properties over a larger range, and at a reduced cost and processing time. Some disadvantages of low-filled compounds include inhomogeneity and non-uniform particle distribution inside the matrix, which can lead to anisotropic mechanical and electrical properties. Thus, care must be taken in using the appropriate compounding time and method to manufacture compounds with more random particle distributions, uniform structure, and isotropic properties.

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Appendix

TABLE A.1. - Average Elastic Properties for Silver-Silica Filled Thermoplastic Gel Compounds

Filler Content by Volume	Modulus Elongation at 300% (kPa)		Elongation at Break (%)	
	Average	STD (*)	Average	STD(*)
Unfilled Gel	1.47	1.24	2909	141
10% Spheres	12.15	1.20	2368	121
20% Spheres	15.55	1.34	2127	66
30% Spheres	8.81	3.02	1799	72
40% Spheres	5.45	3.37	1360	175
50% Spheres	26.34	1.84	1242	51
60% Spheres	14.47	1.16	435	146
10% Fibers	22.42	2.30	2390	163
20% Fibers	25.09	2.93	2062	67
30% Fibers	28.64	3.48	1973	19
40% Fibers	33.30	2.58	1340	173
10% Flakes	23.88	2.7	1477	23
20% Flakes	99.63	8.07	773	65
30% Flakes	0.00	0.00	172	39

* - Standard Deviation

TABLE A.2. - Average Elastic Properties of Silver-Silica Filled Wacker 612 SIL Gel Compounds

Filler Content by Volume	Modulus Elongation at 300% (kPa)		Elongation at Break (%)	
	Average	STD (*)	Average	STD(*)
Unfilled	0.017	0.0	895.1	33.6
10% Spheres	-	-	-	-
20% Spheres	0.177	0.084	634.5	53.5
30% Spheres	0.257	0.055	693.4	19.7
40% Spheres	2.518	0.109	479.7	41.7
50% Spheres	0.746	0.111	585.1	32.8
60% Spheres	0.000	0.000	55.1	18.4
10% Fibers	-	-	-	-
20% Fibers	0.726	0.151	556.9	56.8
30% Fibers	2.234	0.251	485	11.3
40% Fibers	2.135	0.271	251	46.2
10% Flakes	-	-	-	-
20% Flakes	-	-	-	-
30% Flakes	-	-	-	-

* - Standard Deviation

TABLE A.3. - Average Strength Properties of Silver-Silica Filled Thermoplastic Gel Compounds

Filler Content by Volume	Ultimate Tensile Strength (kPa)		Toughness (kPa)	
	Average	STD (*)	Average	STD(*)
Unfilled	403.3	27.6	4033	641.2
10% Spheres	366.8	20	2386	303.4
20% Spheres	312.3	26.2	1889	179.3
30% Spheres	213	17.2	1207	103.4
40% Spheres	97.2	24.1	475.7	151.8
50% Spheres	97.9	11	551.6	48.26
60% Spheres	22.1	1.4	42.06	24.82
10% Fibers	350.7	30.3	2455	268.9
20% Fibers	250.3	40.7	1558	227.5
30% Fibers	192.4	7.6	1434	27.58
40% Fibers	76.7	9	560	103.4
10% Flakes	206.8	15.2	1303	103.4
20% Flakes	180.6	13.1	806.7	144.8
30% Flakes	132.4	30	82	62.05

* - Standard Deviation

TABLE A.4. - Average Mechanical Strength of Silver-Silica Filled Wacker 612 SIL Gel Compounds

Filler Content by Volume	Ultimate Tensile Strength (kPa)		Toughness (kPa)	
	Average	STD *(kPa)	Average	STD *(kPa)
Unfilled Gel	148.40	0.820	474.50	0.017
20% Spheres	99.28	1.342	223.4	0.177
30% Spheres	134.45	3.447	355.1	0.257
40% Spheres	244.76	24.82	650.2	2.518
50% Spheres	91.70	4.137	308.2	0.746
60% Spheres	0.000	0.000	53.85	0.000
20% Fibers	77.91	1.379	250.28	0.726
30% Fibers	142.03	9.653	482.63	2.234
40% Fibers	124.79	6.895	206.84	2.135
10% Flakes	-	-	-	-
20% Flakes	-	-	-	-
30% Flakes	-	-	-	-

* - Standard Deviation

TABLE A.5. - Compression at 50 Percent Deflection for Silver-Silica Filled TP Gel Compounds

Filler Content by Volume	Compression Strength (kPa)	STD *(kPa)
Unfilled Gel	9.8	0.0
10% Spheres	21.3	19.6
20% Spheres	33.7	0.0
30% Spheres	43.2	0.0
40% Spheres	41.3	0.0
50% Spheres	51.8	9.8
60% Spheres	121.4	19.6
10% Fibers	19.6	0.0
20% Fibers	53.0	0.0
30% Fibers	56.9	0.0
40% Fibers	122.1	19.6
10% Flakes	20.8	0.0
20% Flakes	190.2	0.0
30% Flakes	680.2	39.2

* - Standard Deviation

**TABLE A.6. - Compression at 50 Percent Deflection for Silver-Silica Filled
Wacker 612 SIL Gel Compounds**

Filler Content by Volume	Compression Strength (kPa)	STD *(kPa)
Unfilled	-	-
10% Spheres	-	-
20% Spheres	25.48	0.0
30% Spheres	41.21	0.0
40% Spheres	176.52	19.6
50% Spheres	90.37	9.8
60% Spheres	297.05	9.8
10% Fibers	-	-
20% Fibers	34.05	0.0
30% Fibers	118.07	9.6
40% Fibers	303.58	9.6
10% Flakes	-	-
20% Flakes	-	-
30% Flakes	-	-

* - Standard Deviation

TABLE A.7. - Electrical Volume Resistivity Values (ohm-cm) for Silver-Silica Filled TP Gel Compounds

Filler Content by Volume	Sample 1 $\rho_1, \Omega\text{-cm}$	Sample 2 $\rho_2, \Omega\text{-cm}$	Sample 3 $\rho_3, \Omega\text{-cm}$	Sample 4 $\rho_4, \Omega\text{-cm}$	Sample 5 $\rho_5, \Omega\text{-cm}$	Average $\rho, \Omega\text{-cm}$	STD * $\rho, \Omega\text{-cm}$
10% Sphere	135.0	72.5	99.5	128.0	220.0	145.6	50.1
20% Sphere	147.0	141.0	88.2	108.0	166.0	140.5	28.4
30% Sphere	82.0	77.8	55.3	73.7	76.8	73.1	9.3
40% Sphere	52.4	62.6	61.0	56.0	49.1	56.2	5.1
50% Sphere	45.4	15.6	39.4	45.8	16.1	32.5	13.8
60% Sphere	6.18	9.96	4.72	4.59	6.60	6.41	1.9
10% Fiber	79.2	450.0	715.0	707.0	659.0	632.8	107.7
20% Fiber	689.0	765.0	805.0	602.0	61.1	715.3	77.5
30% Fiber	59.4	72.8	47.2	50.4	60.8	58.1	9.0
40% Fiber	25.4	10.9	12.9	26.6	12.0	17.6	6.9
10% Flake	593.0	352.0	73.2	556.0	354.0	463.8	128.8
20% Flake	64.4	54.6	58.5	49.5	55.8	56.6	4.9
30% Flake	64.4	54.5	41.5	59.7	66.9	57.4	9.0

* - Standard Deviation

TABLE A.8. - Electrical Volume Resistivity Values (ohm-cm) for Silver-Silica Filled Wacker 612 SIL Gel Compounds

Filler Content by Volume	Sample 1 $\rho_1, \Omega\text{-cm}$	Sample 2 $\rho_2, \Omega\text{-cm}$	Sample 3 $\rho_3, \Omega\text{-cm}$	Sample 4 $\rho_4, \Omega\text{-cm}$	Sample 5 $\rho_5, \Omega\text{-cm}$	Average $\rho, \Omega\text{-cm}$	STD ** $\rho, \Omega\text{-cm}$
10% Sphere*	3.30E+13	2.97E+13	3.39E+13	3.26E+13	2.97E+13	3.2E+13	1.7E+12
20% Sphere	7.30E+12	5.97E+12	7.39E+12	6.26E+12	6.97E+12	6.8E+12	5.7E+11
30% Sphere	3.54E+06	3.79E+07	1.61E+6	2.82E+06	3.13E+06	9.8E+06	1.4E+07
40% Sphere	64.0	64.6	104.0	43.3	57.4	66.7	20.2
50% Sphere	752.0	730.0	794.0	752.0	740.0	753.6	21.8
10% Fiber*	2.65E+11	2.75E+11	2.47E+11	2.03E+11	2.64E+11	2.51E+11	2.55E+10
20% Fiber	77.3	78.5	95.0	71.6	67.8	78.0	9.3
30% Fiber	155.0	34.4	104.0	74.9	115.0	9607	40.4
40% Fiber	499.0	588.0	786.0	497.0	604.0	594.8	105.3

* - Interpolated data

** - Standard Deviation