

Effect of Fumed Silica Filler on Rheological and Mechanical Properties of Polysulfide Sealant

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Abstract

In this paper, two types of filled polymers were prepared using gas-silicone and hydrophobic gas-silicon combined with liquid polysulfide rubber JLY155. The study investigated the impact of gas-silicon with specific surface areas ranging from 150-380 m²/g on the rheology of the filled polymer LP/SiO₂. The results indicated that the storage modulus (G') and composite viscosity (η) of both types of gas-silicon increased with the specific surface area, while the linear viscoelastic region narrowed, and the viscosity decreased significantly. When compared to hydrophilic gas silicon, hydrophobic gas silicon has a narrower linear viscoelastic region width. The mechanical properties of the filled polymers prepared using different gas silicones are vulcanized to create polysulfide sealants. Upon testing the mechanical properties, it was discovered that the tensile strength of hydrophobic HB150, HB200, and HB380 is higher. Additionally, the elongation at break increases with the decrease in specific surface area. This finding offers valuable insights into the process conditions of gas silicon in polysulfide sealant formulation and preparation.

Keywords

Fumed silica, filled with polymers, polysulfide sealant

1. Introduction

Polymeric materials often offer numerous advantages over the base polymer system when incorporating inorganic filler particles, including enhanced viscoelastic behavior, mechanical properties, and electrical conductivity [1-3]. In recent years, these aspects have attracted the attention of researchers due to their academic interest and practical significance in industrial fields such as sealants, paints, cosmetics, and automotive tire tread compounds. Sealants with liquid polysulfide rubber as the main component are widely used in aviation, aerospace, construction, automobiles, ships, machinery, and other industries [4-6]. Polysulfide sealants are primarily composed of liquid polysulfide rubber, along with fillers, plasticizers, coupling agents, etc. In the filler, fumed silica is primarily used as an additive and reinforcing agent, which significantly helps enhance the mechanical properties. Therefore, fumed silica plays a crucial role in the adhesive and sealant industry.

However, the incorporation of fillers complicates the processing of sealants. During the filler addition process, particles tend to aggregate and form clusters, leading to an increase in viscosity and modulus [7]. The flow properties of the filled liquid polysulfide rubber are influenced by various factors, such as particle characteristics (size, shape, distribution), dispersion state, particle interactions, and interactions between the filler and the liquid polysulfide rubber matrix [8-10]. Understanding the rheological behavior of the filler in the sealant can provide insights for selecting sealant fillers. Process parameters significantly influence the storage modulus (G') of the sealant during the preparation of polysulfide sealants. By monitoring the rheological behavior of the fillers, process parameters can be adjusted, aiding in enhancing the formulation and process conditions of the sealants [11, 12]. However, studies on the rheological properties of pyrogenic silica-filled polymers are rarely reported. In this

paper, the impact of particle size on the viscoelastic properties of LP/SiO₂ filled polymers was investigated through dynamic rheological tests. Polysulfide sealants were formulated using fumed silica with varying types and particle sizes. The study also delved into the influence of different types and particle sizes of gas-mediated silicon on the mechanical characteristics of polysulfide sealants.

2. Experimental Part

2.1 Experimental raw materials

Liquid polysulfide rubber JLY155: (SH%: 1.0-1.4%, Mn: 5000±400, 2% degree of cross-linking), Industrial grade, Jinxi Research Institute of Chemical Industry; Commercially available hydrophilic fumed silica (HL150, HL200, HL380) and hydrophobic fumed silica (HB150, HB200, HB380) are industrial-grade products. The numbers 150, 200, and 380 represent the specific surface area of the gas-silicon in m²/g. Hubei HuiFu Nanomaterials Co., Ltd; Silane coupling agent (KH560), analytically pure, Sinopharm Chemical Reagent Co., Ltd; Manganese dioxide (MnO₂), industrial grade, Min Strontium Technology Co., Ltd; Dipentamethylene tetrasulfide (DPTT), McLean Biochemical Technology Co., Ltd; Diphenylguanidine, Sinopharm Chemical Reagent Co., Ltd; Hydrogenated terphenyls, industrial grade, Jiangsu Mantuo Chemical Co., Ltd. Carbon black N990, Tianjin Huayuan Carbon Black Co., Ltd.

2.2 Experimental instruments

Scanning Electron Microscope SU8010 (Hitachi, Japan); Three-roller grinding machine ZYTR-80 (Suzhou Zhongyi Precision Technology Co., Ltd.); Electron microscope MS4 (Shenzhen Mai Kelong Technology Co., Ltd.); Dispersing machine LSFS550 (Changzhou Li'anbao Machinery Equipment Technology Co., Ltd.); Rheometer HR-1 (TA Instruments Waters, USA); Universal Proficiency Testing Machine SS-830 (Songshu Testing Instrument Co., Ltd.).

2.3 Experimental preparation

2.3.1 Preparation of LP/SiO₂ filled polymers

According to the ratio of m(LP):m(SiO₂) (HL150, HL200, HL380, HB132, HB612, HB630) = 100:6, the liquid polysulfide rubber JLY155 was added to the disperser, stirred for 10 minutes, and then fumed silica was slowly added to continue dispersing for 90 minutes to ensure even dispersion of the filler. The filled polymer LP/SiO₂ was prepared for later use. The formulation is shown in Table 1.

Table 1. The recipe for filled polymers LP/SiO₂

The name of the sample	Specific surface area	Hydrophilic/hydrophobic
LP-HL150	150	Hydrophilic
LP-HL200	200	Hydrophilic
LP-HL380	380	Hydrophilic
LP-HB150	150	Hydrophobic
LP-HB200	200	Hydrophobic
LP-HB380	380	Hydrophobic

2.3.2 Preparation of polysulfide sealant

The LP/SiO₂ filled polymer was added to the silane coupling agent KH560 to create the base paste. The sulfurization paste was then prepared by mixing MnO₂, the accelerator diphenylguanidine, DPTT, Carbon black N990, and heat transfer oil in specific proportions. The base paste and the sulfurized paste were ground using a tri-kun mill until the fineness reached 5-10 μm. The base paste and vulcanized paste are mixed evenly according to the mass ratio of 100: (8-12), and then the established polysulfide sealant is cured. The formula of the sealant is shown in Table 2.

Table 2. The recipe for polysulfide sealant

	LP/SiO ₂ filled polymers/g		Silane coupling agent KH560/g		
	base paste	LP-HL150	95		
LP-HL200		95			5
LP-HL380		95			5
LP-HB150		95			5
LP-HB200		95			5
LP-HB380		95			5
sulfurized paste	MnO ₂ /g	DPTT/g	Dibenzidine/g	Carbon black N990/g	Hydrogenated terphenyls/g
	2.4	0.3	0.3	1	5
	2.4	0.3	0.3	1	5
	2.4	0.3	0.3	1	5
	2.4	0.3	0.3	1	5
	2.4	0.3	0.3	1	5
	2.4	0.3	0.3	1	5

2.4 Testing and characterization

2.4.1 Scanning Electron Microscope (SEM)

Clean the metal sample stage for scanning electron microscopy. Gently sprinkle a small amount of dry sample particles on the conductive adhesive. Tilt the stage gently and blow on the edge of the electroplastic accurately and quickly with an ear wash ball to ensure that the sample is firmly glued. Spray the sample surface with gold for 150 seconds. Then, observe the surface morphology of the sample particles using the SU8010 cold field emission scanning electron microscope with an accelerating voltage of 0.5-30 kV and a vacuum degree of 10^{-4} Pa.

2.4.2 Rheological

The rheological tests were determined using an Anton Paar MCR301 rheometer equipped with a parallel-plate rotor with a diameter of 40 mm. The stress sweep frequency is 6.28 rad/s; In the viscoelastic region of the line, the strain was 0.1-1000%, and all experiments were performed at a constant temperature of 25 °C.

2.4.3 Mechanical properties

The tensile strength and elongation at break are tested according to GB/T 528-2009 "Determination of tensile stress-strain properties of vulcanized rubber or thermoplastic rubber", and the tensile speed is 500 mm/min.

The peel strength test procedure involves placing the aluminum sheet into the groove of the lower template of the forming mold. A scraper is then used to apply the mixed sealant onto the aluminum sheet, ensuring a thickness of 3.0 mm in the mold groove. The aluminum plate is 100 mm long and 25 mm wide, with a gluing area of 25 mm × 75 mm. Subsequently, a canvas measuring 150 mm in length and 25 mm in width is laminated onto the glued surface of the aluminum sheet. The sealant is applied repeatedly on the canvas until it penetrates. The mold is then closed, bolts are tightened, and vulcanization is conducted at room temperature for 24 hours, followed by vulcanization at 70°C for another 24 hours for standby. The peel strength test refers to ASTM 2629. The unglued aluminum sheet end is clamped on the testing machine, the canvas without the glued end is flipped 180° vertically and clamped on the lower fixture, and the sample adhesive layer is cut along the specimen peeling line with a cutter to a depth of about 10 mm. The tensile machine is activated to peel off the specimen at a speed of 50 mm/min. The arithmetic mean of the peel strength of the three strips in each group of specimens represents the peel strength of the sample.

3. Results and Discussion

3.1 Microscopic morphology of fumed silica with different specific surface areas

In order to investigate the impact of fumed silica particles with varying specific surface areas in LP/SiO₂ filled polymers, we

utilized scanning electron microscopy to examine commercially available fumed silica particles. Figure 1 displays the scanning electron microscope images of hydrophilic HL150, HL200, and HL380 particles. We observed that particles with smaller specific surface areas were looser and larger in size, whereas particles with larger specific surface areas were more densely packed and smaller in size. The storage modulus G' of the filled polymer LP/SiO₂ increases [13, 14], resulting in higher tensile strength when used as a filler in preparing sealants [15]. This was also verified later.

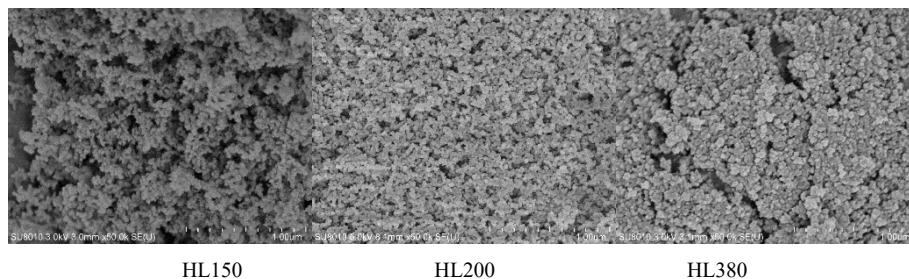


Figure 1. Morphology of fumed silica with different specific surface areas.

3.2 Micromorphology of hydrophilic/hydrophobic fumed silica

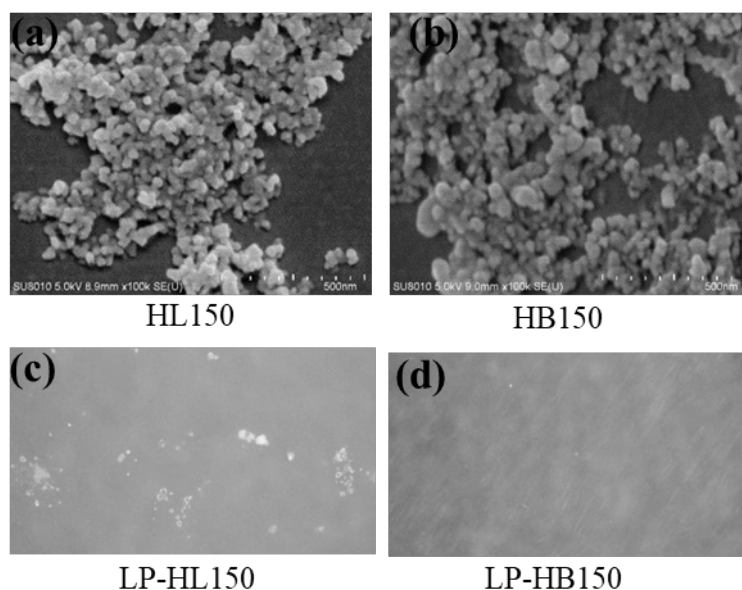


Figure 2. (a) and (b) show the morphology of HL150 and HB150, (c) and (d) display the morphology of the filled polymers LP-HL150 and LP-HB150.

Hydrophobic gas silicon is typically obtained by modifying hydrophilic gas silicon with silane. Consequently, the dispersion of the two types of gas silicon in liquid polysulfide rubber differs significantly, potentially impacting the performance of the subsequent sealant. For comparison, we selected HL150 and HB150 gas silicon. In Figures 2(a) and (b), it was observed that the modified hydrophobic gas phase silica particles exhibited a slight increase in size. This increase is primarily attributed to the presence of siloxy groups on the surface of the modified hydrophobic gas silicon [16], leading to a slight increase in particle size. Figures 2(c) and (d) demonstrate that the filled polymer LP-HB150, prepared using hydrophobic gas silicon, is uniformly dispersed. However, some agglomeration of gas silicon in the filled polymer LP-HL150 is still evident. This agglomeration is mainly due to the presence of numerous silicon hydroxyl groups that remain in the material. Hydrophilic gas silicon makes it difficult to soak and disperse in liquid polysulfide rubber [17]. However, when the hydrophobic gas silicon is modified, it increases the steric hindrance between the particles, thereby enhancing its compatibility and dispersion in liquid polysulfide rubber [18]. This modification has a significant impact on the mechanical properties of the resulting polysulfide rubber sealant.

3.3 Effect of hydrophilic/hydrophobic type and specific surface area on the viscoelasticity of LP/SiO₂ filled polymers

As a crucial aspect of preparing polysulfide sealants, the viscoelastic properties of filled polymers significantly influence the process conditions and mechanical properties of sealant preparation. Testing the rheological properties of filled polymers allows for the adjustment of process parameters by monitoring their rheological behavior. This helps in stabilizing the properties of the sealants [19, 20]. To investigate the impact of various gas-silicon types on the viscoelastic properties of LP/SiO₂ fillers, we chose two distinct fumed silica particles categorized as hydrophilic and hydrophobic. The gas-silicon specific surface area ranges from 150-380 m²/g, and the hydrophobic gas-silicon is altered using hydrophilic gas-silicon via siloxane modification.

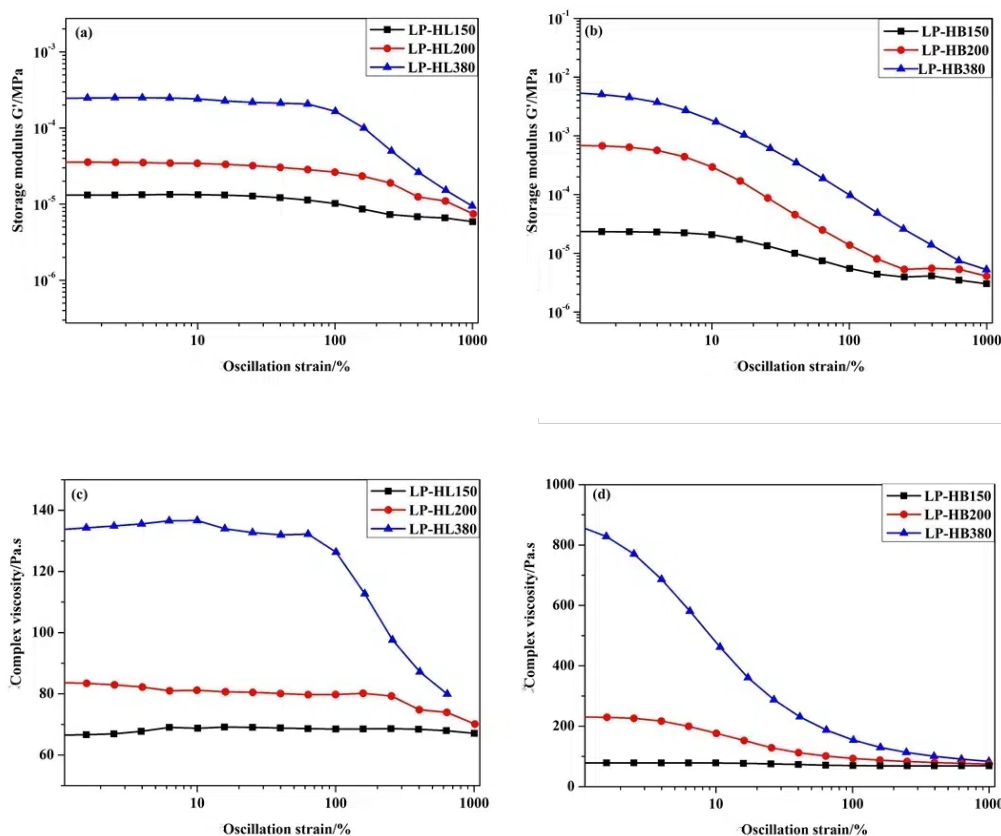


Figure 3. (a) and (b) show the G' curves of the filled polymers with different specific surface areas of hydrophilic and hydrophobic gas silicon, (c) and (d) display the viscosity curves of the filled polymers with different specific surface areas of hydrophilic and hydrophobic gas silicon.

Figs. 3(a) and (b) depict the dynamic storage modulus (G') versus strain of LP/SiO₂ fillers prepared by gas silicon with different specific surface areas of hydrophilic and hydrophobic types at 25 °C and 6.28 rad/s. It is evident that for all the samples in Figure 3(a), we find a modulus plateau occurring at 0-100%, remaining in the linear viscoelastic region. This phenomenon is mainly due to the formation of a packed polymer network between the filler gas silicon and the liquid polysulfide rubber JLY155 polymer, which limits the movement of the polymer segments. As the strain continues to increase (100%-1000%), G' gradually decreases after reaching the critical value. This decrease is primarily due to the gradual destruction of the interaction force between the gas-silicon filler particles, known as the "Payne effect" [19]. This effect reduces the energy storage modulus G' . Additionally, it is observed that when the specific surface area increases (LP-HL-150~380m²/g). With an increase in specific surface area, the storage modulus (G') gradually increases, and the width of the linear viscoelastic region gradually decreases. This phenomenon is attributed to the reduction in particle size as the specific surface area increases, leading to an enhanced interaction between particle sizes within the filled polymer. As a result, the elasticity of the filled polymer is improved [21].

However, as the strain continues to increase, the packing network formed between the particles of the gas silicon filler with smaller particle size is more likely to be decomposed, resulting in a narrower width of the linear viscoelastic region [22]. Figure 3(b) shows a similar trend to (a) for the G' of the gas silicon-filled polymer with different specific surface areas and the strain relationship. Nevertheless, the range of the linear viscoelastic region is narrower, and its G' decreases significantly in a small strain range. This is mainly attributed to the hydrophobic gas silicon in Figure 3(b) being surface-modified by the hydrophilic gas silicon in Figure 3(a) using siloxanes, etc. The modification alters the interface bonding properties between the gas silicon and the liquid polysulfide rubber matrix, reducing the polarity between the two. Phases improves the dispersion of the gas silicon in the liquid polysulfide rubber and have better fluidity [23, 24]. Therefore, the linear viscoelastic region is smaller, and the response to strain is more sensitive.

Figs. 3(c) and (d) show the viscosity curves of hydrophilic gas silicon and hydrophobic gas silicon. It can be observed that the viscosity of all samples remains essentially unchanged at small strain amplitudes, which fall within the linear viscoelastic region. Subsequently, the viscosity decreases as the strain increases. As the specific surface area increases, meaning the particle size decreases, the viscosity is observed to increase while the viscosity decreases simultaneously. The impact of particle size on flow behavior is determined by the particles' capacity to immobilize the polymer matrix. In regions with lower strains, the dominant role is played by the interaction forces between particles, leading to higher viscosity in particles with smaller sizes. As strain intensifies, the particle aggregate structure breaks down gradually, reducing the entrapment of the liquid polysulfide rubber matrix. Consequently, smaller particle sizes exhibit a more significant decrease in viscosity [25, 26]. However, in regions with higher strains, the viscosity of the sample is mainly determined by the properties of the polymer matrix, and the particle size effect is less significant. As a result, the viscosity curves of all samples are ultimately consistent with each other. The trend in Figure 3(d) is the same as in (c), but according to the above analysis, the hydrophobic gas silicon is more evenly dispersed due to its surface modification, better compatibility with the matrix, and thus more sensitive to strain response. Therefore, the downward trend is more pronounced.

Through the above analysis, it was observed that the greater the specific surface area, the higher the G' . However, the G' associated with the hydrophilic gas silicon as a whole, with varying specific surface areas, is higher. This indicates that the vulcanized filler network will be reinforced, potentially enhancing the tensile strength of the sealant. These findings are elaborated upon in the subsequent sealant preparation process.

3.4 Effect of hydrophilic/hydrophobic type and specific surface area on the properties of polysulfide sealants

Table 3 presents the mechanical properties of polysulfide sealants filled with various types and particle sizes of gas silica vulcanization. It can be observed that the samples filled with HL150, HL200, and HL380 exhibit nearly identical mechanical properties. However, the samples filled with HL150 demonstrate a relatively high elongation at break. This can be attributed to the interaction between the polymer matrix and the filler in the polymer-filler system, leading to a reinforcement mechanism caused by the filled particles forming physical cross-linking. Nonetheless, HL150 has a smaller specific surface area and larger particle size compared to other gas silicons, resulting in fewer contact points with the polymer matrix and consequently a lower physical crosslinking density [22]. As a result, the prepared polysulfide sealant exhibits high elongation. Further analysis reveals that the mechanical properties of the surface-modified HB150, HB200, and HB380 filled samples are similar. The HB150 samples still exhibit high elongation, similar to the reasons analyzed earlier. However, their tensile strength is higher than that of the HL150, HL200, and HL380 filled samples. This is primarily attributed to the good compatibility between the surface-modified gas silicon and the liquid polysulfide rubber matrix, which enhances the dispersion performance of the gas silicon in the liquid polysulfide rubber. Therefore, the tensile strength is higher [15]. And we found out. The higher the specific surface area, the higher the tensile strength, which is also confirmed in the rheology described above.

Table 3. Mechanical properties of polysulfide sealant

LP/SiO ₂ filled polymers	Tensile strength./MPa	Elongation/%	Peel strength/N/25mm
LP-HL150	1.52	309.2	148.2
LP-HL200	1.57	237.1	145.1
LP-HL380	1.64	206.7	132.3
LP-HB150	1.82	251.6	126.1
LP-HB200	1.83	199.8	132.5
LP-HB380	1.90	194.3	123.3

4. Conclusion

In this paper, the specific surface area and modification degree of various gas silicon samples were determined using SEM. The impact of gas silicon with a specific surface area ranging from 150-380 m²/g on the rheology of polysulfide sealant was investigated. The main reason can be attributed to the interaction forces between the particles, which lead to stronger particle interactions as the specific surface area increases. This can enhance the structure of the filling network. However, compared with hydrophilic gas silicon, hydrophobic gas silicon has a narrower linear viscoelastic region width. The storage modulus (G') and composite viscosity show a more pronounced downward trend, indicating that the modification effect improves the dispersion of gas silicon particles in liquid polysulfide rubber, resulting in higher fluidity and increased sensitivity to strain. This further provides a reference for the use of gas silicon in polysulfide sealant and the selection of process conditions.

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