Controlled Methodology for Development of a Polydimethylsiloxane–Polytetrafluoroethylene-Based Composite for Enhanced Chemical Resistance: A Structure–Property Relationship Study

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ABSTRACT: Polydimethylsiloxane (PDMS) polymers are highly appreciated materials that are broadly applied in several industries, from baby bottle nipples to rockets. Momentive researchers are continuously working to understand and expand the scope of PDMS-based materials. Fluorofunctional PDMS has helped the world to apply in specialty applications. Efforts are taken to develop such siloxane–fluoropolymer composite materials with good thermal, solvent, and chemical resistance performances. We leveraged inherently flexible PDMS as the model matrix, whereas polytetrafluoroethylene (PTFE) was used as the additive to impart the functional benefits, offering great value in comparison to the individual polymers. The composites were made at three different mixing temperatures, that is, 0−35 °C, and different loadings of PTFE, that is, 0.5−8% (w/w), were selected as the model condition. A strong dependency of the mixing temperature against the performance attributes of the developed composites was noted. Mechanical and thermal stability of the composites were evaluated along with optical properties. X-ray diffraction demonstrated the change in the crystallite size of the PTFE particles as a function of processing temperature. Compared to the phase II crystallite structure of the PTFE, the fibrils formed in phase IV imparted a better reinforcing capability toward the PDMS matrix. A synergistic balance between higher filler loading and mechanical properties of the composite can be achieved by doping the formulation with short-chain curable PDMS, with 238% increment of tensile strength at 8 wt % PTFE loading when compared to the control sample. The learning was extended to check the applicability of doping such PTFE powder in commercial liquid silicone rubber (LSR). In the window of study, the formulated LSR demonstrated improved mechanical properties with additional functional benefits like resistance toward engine oil and other chemical solvents.

INTRODUCTION

Silicone-based elastomers are some of the most versatile functional materials with their stronghold in a vast array of applications since their commercialization in the 1940s. These elastomeric materials possess good tolerance with respect to a wide range of temperatures (~−50 to 300 °C).1 Additionally, the Si–O–Si backbone of these polymeric materials makes them less susceptible to UV radiations, heat, and ageing effects, compared to their carbon-based organic counterparts.2 These properties impart thermal and chemical stability to the elastomers. Furthermore, their low toxicity, low surface energy, chemical resistance, optical clarity, and dielectric properties have led to their utilization in coatings, adhesives, sealants, lubricants, insulators, cryogens, energy storage application, biomedical implants, and so forth.3 However, several of the
The aforementioned uses are difficult to achieve in their unmodified form. In order to achieve the desired properties, these elastomeric materials are subjected to bulk or surface modification. The modification methods include compositing, grafting, blending, and so forth, amongst which compositing of the polymer matrix with appropriate fillers has been identified as an inexpensive simple approach when compared with chemical modification such as grafting. Bulk modification of polymeric materials is utilized to alter physical properties that include elasticity and mechanical strength. Despite their several functionalities, one of the major impediments of silicone elastomers is their poor mechanical strength in the pristine state because of the low glass transition temperature and weak interactions among the silicon-based backbones. The enhancement of the mechanical properties of these silicone- or siloxane-based elastomeric materials is often achieved by reinforcing it with fillers such as fumed silica, carbon black, polyhedral oligomeric silsesquioxanes, and so forth. The effectiveness of the fillers in the matrix can be evaluated on the basis of their particle size, shape, and dispersion, along with the interfacial interactions of the filler particles with the matrix material. Furthermore, alternate routes that include addition of a cross-linker or curing materials have also been utilized for the increment of mechanical properties. Typically, the cross-link is obtained by the condensation of alkoxy groups using Sn, polyhedral oligomeric silsesquioxanes, and so forth. The link is obtained by the condensation of alkoxy groups using Sn, polyhedral oligomeric silsesquioxanes, and so forth. 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The presence of fluoro groups makes the polymer highly chemically stable, rendering it resistant toward organic solvents, water, and oils. Ruan et al. reported PDMS- and PTFE-based composite materials with improved durability and mechanical strength along with enhanced superhydrophobicity, extending the application of these composite materials in antifingerprint and anti-icing materials. Sun et al. reports the use of hydrophobic PDMS- and PTFE-based membranes for pervaporation of organic solvents from aqueous solution. They also report the enhancement of hydrophobicity, mechanical strength, and thermal stability of the membranes on addition of PTFE particles. The stronger C–F bond in perfluoropolyether and PTFE-type compounds imparts exceptional thermal stability to them at a very low loading. Furthermore, the strong electronegativity difference at the interface of two polymers, mainly between fluorine atoms in perfluoropolyether/PTFE and hydrogen atoms in PDMS, results in strong dipole–dipole interactions resulting in better cohesion between composite of these materials. Momentive Performance Materials, a specialty silicones company, has devoted research and developmental efforts over the past several years to the development of such silicone-based elastomeric materials, altering their properties to tailored applications providing performance and process simplification.

The present work reports a systematic and detailed study on the effect of loading of fluorine-based reinforcing agents in the PDMS matrix at different mixing temperatures along with the hydride cross-linker ratio, particle size of the filler, and length of cross-linker taking into account the composites’ thermal and mechanical properties. It was noted that the unique characteristics of crystallinity of the reinforcing materials at different mixing temperatures could result in changes in various properties of composites. Properties such as mechanical, optical, and so forth, were investigated for determining the changes involved. Subsequently, the filler concentration was increased up to 8 wt % and the effect of particle size in the composite was also determined. Two different particle sizes of filler powder, that is, 40 and 1 μm were used for the investigation of the particle size effect. The structure–property relationship of all composites was evaluated, and the model was applied to the commercial grade liquid silicone rubber (LSR) for enhanced chemical resistance applications.

**MATERIALS AND METHODS**

**Materials.** Karstedt’s catalyst, vinyl-terminated PDMS with a vinyl content of 0.026 mol/g and a viscosity of 65 Pa·s, octamethylcyclotetrasiloxane (D₄₅), and hydride containing the PDMS cross-linker with an active hydride content of 7.91 mmol/g were provided by Momentive Performance Materials GmbH, Leverkusen, Germany. Part A and part B of commercial grade of LSR 2050 were procured from Momentive Performance Materials, Bangalore, India. PTFE powders 1 and >40 μm particle size were procured from Sigma-Aldrich, St. Louis, USA, and used as received.

**Methods.** **Synthesis of Vinyl-Terminated PDMS Polymers.** D₄₅ (99.4 g, 0.34 mol) was taken in a two-necked round-bottomed flask, and 1,3-divinyltetramethyldisiloxane (2.5 g, 0.013 mol for D₄₅ = 100) was added to it followed by sulfuric acid (2 wt %) as a catalyst. The reaction was stirred at room temperature for 22 h. The progress of the reaction was monitored by solid content analysis. As the solid content of the reaction mixture reached above 85%, neutralization of the acid catalyst was carried out by slow addition of moist NaHCO₃.
Finally, sodium sulphate was added in the reaction mixture for removal of traces of moisture. The reaction mixture was then filtered to remove the solid impurities, and then, vacuum was applied to remove volatiles and low boiling impurities. The D length of the polymer was evaluated from $^{29}\text{Si NMR}$ and gel permeation chromatography (GPC) (Figures S5 and S6). The peak around $-4.0$ ppm could be assigned to the silicon attached to the vinyl group, and the peak around $-2.1$ ppm confirms the presence of silicon in Si-O-Si backbone. The actual D lengths were found to be 96 and 164 against the targeted D length of 100 and 150, respectively. $^{35} \text{Si NMR}$ (CDCl$_3$, 79.5 MHz; D$_{100}$): $\delta = -4.05$, $-21.9$. $^{29}\text{Si NMR}$ (CDCl$_3$, 79.5 MHz; D$_{150}$): $\delta = -4.10$, $-22.18$. GPC (polystyrene standard): $D_{100}$ $M_w = 11,471$ g mol$^{-1}$; $D_{150}$ $M_w = 16,877$ g mol$^{-1}$ (Table S1).

**Preparation of PDMS and PTFE Composites.** Vinyl-terminated PDMS ($\eta = 65$ Pa·s) and PTFE powder ($>40$ μm) were taken in a small batch reactor and were mixed together at high shear rate (150–200 rpm) for 5 h. Keeping the mixing time constant, the temperature of mixing was varied. The different mixing temperatures used were 0 ± 5, 25, and 35 °C. The formulations so prepared are shown in Table 1.

### Table 1. Formulation of the Composites with Different Rubber to Cross-Linker Ratio

| sample formulation | sample formulation II | silicone/PTFE (w/w %) | mixing temperature (°C) |
|-------------------|----------------------|-----------------------|-------------------------|
| UF-1              | B-UF-1               | 100:2                 | 0 ± 5                   |
| UF-2              | B-UF-2               | 100:1                 | 0 ± 5                   |
| UF-3              | B-UF-3               | 100:0.5               | 0 ± 5                   |
| 2SFU-1            | B-2SFU-1             | 100:2                 | 25                      |
| 2SFU-2            | B-2SFU-2             | 100:1                 | 25                      |
| 2SFU-3            | B-2SFU-3             | 100:0.5               | 25                      |
| 3SFU-1            | B-3SFU-1             | 100:2                 | 25                      |
| 3SFU-2            | B-3SFU-2             | 100:1                 | 35                      |
| 3SFU-3            | B-3SFU-3             | 100:0.5               | 35                      |

*aSilicone/PDMS to hydride ratio—1:1. bSilicone/PDMS to hydride ratio—1:2.5.*

with the samples named accordingly as UF-X, 2SFU-X, and 3SFU-X, respectively, where X denotes the PTFE loading ($X = 1$ for 2 wt %, $X = 2$ for 1 wt %, and $X = 3$ for 0.5 wt %, respectively). To obtain the moulded film, the composite was cured at elevated temperature (100–110 °C) with silicone hydride (1:1 and 1:2.5 molar ratios with silicone/PDMS) in the presence of Karstedt’s catalyst (5 μL, 11.4 ppm), and then, the cured material was compression-molded at 150 °C for 10 min (Figure S1). The samples with a higher silicone hydride content (1:2.5) have been denoted by B-UF-X, where X denotes the PTFE loading. Additionally, to study the effect of particle size, several composites were prepared in a systematic way, choosing different particle sizes (40 and 1 μm) and higher loadings of PTFE (2, 5, and 8 wt %) (Table 2). This set of composites prepared have been denoted as C3SFU-X, with particles prepared at constant temperature (35 °C) and where X denotes the PTFE loading. Finally, to study the effect of D-length of PDMS on composites, another set of composites were formulated, with PDMS, incorporating PTFE particles (40 μm) at mixing temperature of 35 °C. This set of formulated composites have been denoted as D 35UF DX, where X = 100 or 150, depending on the D-length of the crosslinker. Curing of these composites was performed at around 100–110 °C using the vinyl-terminated cross-linker (D length = 100 and 150) in 1:2.5 cross-linker to silicone/PDMS ratio (Table 3).

### Table 2. Formulation of the Composites with Increasing Load of Different Sizes of PTFE Particle at a Mixing Temperature of 35 °C

| sample name | PTFE particle size (in μm) | silicone/PDMS (w/w %) |
|-------------|---------------------------|-----------------------|
| C3SFU-1     | 40                        | 100:2                 |
| C3SFU-2     | 100:5                     |
| C3SFU-3     | 100:8                     |
| C3SFU-4     | 100:2                     |
| C3SFU-5     | 100:5                     |
| C3SFU-6     | 100:8                     |

### Table 3. Formulation of the Composites with Different Molecular Weight PDMS at a Mixing Temperature of 35 °C

| sample name | PTFE particle size (in μm) | silicone mixture (g) | silicone/PDMS (w/w %) |
|-------------|---------------------------|----------------------|-----------------------|
| D 35UF D$_{100}$ | 40                     | 90 g vinyl-terminated PDMS + 10 g | 100:8               |
| D 35UF D$_{150}$ | 40                     | 90 g vinyl-terminated PDMS + 10 g | 100:8               |

### Preparation of Silicone and PTFE Blends.** Typically, the composites are prepared by mixing fluoro-based additive with the two-part LSR compositions. A two-component siloxane-based elastomeric material LSR 2050 and PTFE powder (>40 μm) were taken and blended together in various ratios, with PTFE loading varying from 5 to 10 wt % (Table 4). The LSR compositions are made up of vinyl-terminated PDMS, hydride-terminated PDMS, and Pt catalyst. The compositions prepared were denoted by acronym LSF for liquid silicone fluorinated. Various blended formulations from LSF 5 to LSF 10 were prepared, and their application was evaluated as solvent resistant materials.

### Characterization of the Composites and Blends.** Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) were conducted by using the instrument TA Q5000 under air environment. The sample was heated from 30 to 800 °C at 20 °C/min with a purge rate of 25 mL/min. Differential scanning calorimetry (DSC) was done to check the melting point of the silicone/PTFE composites. DSC studies were carried out by the TA DSC Q2000 instrument in the temperature range of 50–400 °C under nitrogen atmosphere. Three cycles were studied, where the heating ramp in the first and second heating cycle was 10 °C/min. In the cooling cycle, the ramp was 5 °C/min. A LEICA DM 2500P (Leica optical microscope) was used to observe surface microstructures of the composite and dispersion of PTFE particles in composite at 10X resolution. The effect of PTFE loading and the mixing temperature on the mechanical properties such as tensile strength, % elongation at break, and tear strength was investigated. ASTM D 412 and ASTM D 624 were used for the tensile test and tear strength, respectively. X-ray powder
diffraction spectroscopy of the composite was performed on a Bruker D2 2nd generation Phaser. The diffraction studies were carried out at room temperature with a tube voltage of 30 kV and tube current of 10 mA. The range of 2θ was from 5 to 60°. The synthesized vinyl-terminated PDMS was characterized by 1H and 29Si nuclear magnetic resonance spectroscopy (NMR) using CDCl3 as the solvent. The NMR spectra were utilized to determine the degree of polymerization. GPC was used to determine the number-average (Mn) and weight-average (Mw) molecular weights, using polystyrene as the standard. The optical properties such as transmittance and haze of all the film samples were analyzed by the “Haze-Gard Plus” BYK-Grander USA (Made in Germany) under the standard of ASTM D1003. For the estimation of the resistance toward the engine oil and solvent, the cured LSR sheet and the cured PTFE-LSR sheet were punched out in to a circular disc of 10 mm size. The initial weight of material punched derivatives were recorded. These were then immersed in the engine oil and different organic solvents for attaining equilibrium. After 72 h, the change in weight was recorded. The data obtained for the blends were compared against the pure cured LSR film.

**RESULT AND DISCUSSION**

**PDMS-Fluoro Composites.** Fluoropolymers, in its native form, bring thermal, chemical, and solvent stability and extreme temperature performances, but are not environmentally benign and expensive to produce. PDMS polymers are environmentally benign and brings flexibility, elasticity, biocompatibility, glossiness, weatherability, and so forth; however, they lack in terms of mechanical strength and solvent resistance. The mixing of fluorobased materials with the PDMS materials can bring new materials with overall balanced properties. Based on this hypothesis, the following list of fluoro polymers was selected for studying the composite formations (Table 5).

| s. no. | silicone polymers | fluoropolymers | observations |
|-------|------------------|----------------|--------------|
| 1     | PDMS             | PVD            | haze issues  |
| 2     | PDMS             | PTFE           | good up to 10% |
| 3     | PDMS             | PFPE-CH2OH-terminated | haze issues |

At first, as one of the primary physical characteristic of silicones, opacity was evaluated for the composite formulations. It decreased with considerable haze in the case of PDMS- and PVDF-based composites. Additionally, the composites of CH2OH-terminated PFPE with PDMS also resulted in hazy samples. However, the PTFE–PDMS-based products were identified as the potential candidates to form good composite products with a potential for diverse applications. A detailed investigation of this PTFE–PDMS composite system was performed and reported in following sections.

**Thermal Analysis.** The thermal performances of the composites are very critical in defining the industrial applicability. TGA was performed for the composites to study the effect of mixing temperature, particle size of PTFE, and the PTFE loading. The thermogram (Figure S2) obtained for the composites shows single-step degradation. The onset temperature for control PDMS film was found to be 321 °C (Figure 1). The addition of PTFE leads to increased thermal stability in the composites with increase in the onset temperature to 339 °C as the PTFE loading increased from 0 to 8 wt %. This could be attributed to better thermal conductivity of PTFE (0.25 W m⁻¹ K⁻¹) than PDMS (0.15 W m⁻¹ K⁻¹). Higher thermal stability was observed in the composites formulated at higher mixing temperature, which could be because of better heat dissipation with the addition of PTFE. Further, the thermal stability was induced by the formation of localized island by the dispersed PTFE. This will effectively shield the effective heat which the PDMS chain will face. Hence, an increase in the thermal stability of the composite was noted. However, in samples UF-2 and 25UF-3 with filler loading of 1 w/w % mixed at 0 °C and 0.5 w/w % loading mixed at 25 °C, respectively, an unexpected decrease in thermal stability was observed, which could be attributed to the nonuniform dispersion of PTFE in the composite (Table 6). The limiting oxygen index (LOI) was calculated from van Krevelen eq 1, to understand the correlation between the char residue (CR) of the polymer and LOI.

\[ \text{LOI} = 17.5 + 0.4\text{CR} \]  

where LOI and CR are in percentage.

An LOI value of less than 20.95% indicated that the material is highly inflammmable as the oxygen makes up 20.95% of the atmosphere composition. From the calculation of LOI values of the composites, it was found that all samples showed LOI values higher than 20.95%, indicating their nonflammable nature (Table 6). However, the increased loading of PTFE showed only minor improvements in the LOI value indicating that nonflammable nature of the composites is primarily because of the PDMS matrix. From the DSC studies, the melting point of the composite was found to be in the range of 327−329 °C, which is characteristic of PTFE as PDMS does not give endothermic melting peak in the abovementioned range (Figures S3 and S4). This is indicative of higher thermal stability of the composites. Also, a decrease in enthalpy with increase in PTFE loading was observed. This observation could be ascribed to decreased surface area because of the agglomeration of the PTFE particles upon increased PTFE loading.

**X-ray Powder Diffraction.** To probe the effect of mixing temperature on the mechanical properties of the composites, X-ray diffraction (XRD) studies were performed and examined the effect of crystallite size of PTFE filler. The size of the crystallites were correlated with the mechanical properties of the composites. The Scherrer’s eq 2 was used for determination of crystallite size

\[ L = \frac{K\lambda}{b \cos \theta} \]  

where \( L \) is the crystallite size in Å, \( \lambda \) is the wavelength of the X-ray beam, \( b \) is the full width at half-maximum in radians, \( K \) is the dimensionless shape factor (value is from 0.89 to 0.9), and \( \theta \) is the Bragg’s angle.

The \( d \) spacing between the crystal planes was calculated by the Bragg’s equation as given below

\[ n\lambda = 2d \sin \theta \]  

where \( n \) is a positive integer, \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the interplanar distance in the crystal lattice plane, and \( \theta \) is Bragg’s angle.

Figure 2 shows XRD spectra of the composites along with the control PDMS sample. The peak at \( 2\theta \approx 10−12^\circ \) was observed in all the composite samples because of the presence of
of an amorphous PDMS. Additionally, the peak seen at $2\theta \approx 18^\circ$ corresponds to the PTFE crystal of the composite materials. With an increase in mixing temperature, the intensity of the peaks for PTFE was found to be increased, whereas the $d$ spacing was found to be constant.$^{23,32}$ Table 7 shows the crystallite size and $d$ spacing values at different mixing temperatures. The crystallite size increased significantly against the mixing temperature (0 to 35 °C), indicating Phase II < Phase IV < Phase I.

**Morphological Studies.** The morphological studies of the composite samples were performed through optical microscopy to observe the dispersion modes in the samples prepared (Figure 3). As the PTFE loading is increased from 0.5 to 2 wt %, the reinforcement could be seen more clearly with higher density. However, with increase in the mixing temperatures from 0 to 35 °C, the change in the crystal phase of PTFE was not detected. This is due to the fact that the resolution of the optical microscope could capture the phase transition along with fibril formation after the temperature of 30 °C. In the composites with lower PTFE loading of 0.5 wt % or below, a better matrix uniformity was observed through the optical microscopy. Overall, the PTFE particles in the PDMS matrix look well dispersed, with minimal agglomeration up to 2 wt % of the loading. This could be attributed to a strong electronegativity difference at the interface of two polymers, mainly between fluorine atoms of PTFE and hydrogen atoms in PDMS, resulting in strong dipole−dipole interactions, and thereby giving better cohesion and dispersion of PTFE in the matrix.

**Optical Studies.** PTFE is a unique thermoplastic crystalline material that exhibit different crystalline structures with variation in the processing temperature. A strong dependency of the processing temperature maintained during the preparation of the PDMS-PTFE blend on the physico-mechanical properties of the composite was noted. At first, the

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**Table 6. Thermal Properties of the Silicone/PTFE Composites Prepared at Different Mixing Temperatures**

| sample           | TGA onset temperature (°C) | LOI (CR,%) | LOI | ΔH (J/g) | DSC melting temperature (°C) |
|------------------|----------------------------|------------|-----|----------|------------------------------|
| PDMS-control     | 321                        | 25.5       | 27.7|          |                               |
| UF-1             | 323                        | 36.6       | 32.2| 11.57    | 329                           |
| UF-2             | 310                        | 20.7       | 25.8| 9.81     | 327                           |
| UF-3             | 339                        | 26.5       | 28.1| 20.70    | 327                           |
| 25UF-1           | 328                        | 19.8       | 25.2| 5.30     | 327                           |
| 25UF-2           | 325                        | 28.0       | 28.7| 4.04     | 328                           |
| 25UF-3           | 317                        | 30.5       | 29.7| 10.70    | 327                           |
| 35UF-1           | 332                        | 22.1       | 26.3| 7.46     | 328                           |
| 35UF-2           | 326                        | 21.7       | 26.1| 35.60    | 327                           |
| 35UF-3           | 323                        | 25.6       | 27.8| 13.68    | 327                           |

**Table 7. PTFE Crystallite Size at Different Temperatures of Mixing in Composite of the 2 wt % PTFE-Filled PDMS**

| sample name | $2\theta$ | FWHM (radian) | crystallite size, $L$ (Å) | $d$ spacing (Å) |
|-------------|-----------|----------------|---------------------------|-----------------|
| UF-1        | 17.73     | 0.22           | 6.3                       | 1.55            |
| 25UF-1      | 18.09     | 0.08           | 17.6                      | 1.56            |
| 35UF-1      | 18.45     | 0.04           | 29.4                      | 1.56            |

**Figure 1.** DTG curves of PTFE in the silicone matrix at different mixing temperatures (a.) 2, (b.) 1, and (c.) 0.5 wt %.

**Figure 2.** XRD spectra of 2 wt % PTFE-filled PDMS composite at different mixing temperatures.

**Figure 3.** XRD spectra of 2 wt % PTFE-filled PDMS composite at different mixing temperatures.
Opacity test was leveraged to see the impact of processing temperature on the dispersion of the PTFE additive in the PDMS matrix. Compared to the unfilled system (control), all the PTFE-filled systems demonstrated decrease in the percent transmittance. This is because of the incorporation of large differences in the refractive index of PTFE and PDMS. Further, with increase in the loading of the PTFE additive, the percent transmission was found to decrease in the composites (Figure 4a). However, with an increase in the processing temperature, the percent transmission value was found to increase. Further to support the fidelity of the observations made, a complementary haze analysis test was performed on the same set of samples (Figure 4b). With an increase in the PTFE loading, the percent haze of the samples increased.

Figure 3. 10× optical microscope image PTFE/PDMS sample at different temperatures and different PTFE loadings from 0.5 to 2 wt %. A phase transition along with fibril formation after the temperature of 30 °C was observed.

Figure 4. (a) % Transmission and (b) haze; at different mixing temperatures (0, 25, and 35 °C) with different PTFE loadings, silicone/PTFE to cross-linker ratio of 1:1.

Figure 5. (a) % Transmission and (b) haze; at different mixing temperatures (0, 25, and 35 °C) with different PTFE loadings, silicone/PTFE to cross-linker ratio of 1:2.5.
However, upon increasing the processing temperature, the percent haze was noted to decrease under similar loading. The haze analysis was completely in agreement with the observation made in percent transmission analysis. Interestingly, similar observations following identical trends were seen when the silicone/PDMS to cross-linker ratio was increased to 1:2.5 (Figure 5a,b), with an overall decrease in the transmittance with an increase in PTFE loading, while increase in mixing temperatures led to increased transmittance. This confirms that primarily the opacity in these composites is governed by the reinforcing agent, with cross-linking density of the matrix playing a minimal role.

Furthermore, such an observation is made presumably because of the change in crystallite structure of PTFE as a function of processing temperature. Typically, below 19 °C, PTFE demonstrate a 13/6 helical phase II structure, whereas on increasing the temperature beyond 19 °C till 35 °C, 15/6 helical phase IV structure is noted. It is worth mentioning that in phase II, the PTFE demonstrates a nondeformable structure. While beyond 19 °C, the structure under shear mode tend to deform and unwind its crystallites to fibrils. As a result, because of the rigid structure of the phase II, they will have less tendency to deform and unwind its crystallites to fibrils. As a result, because of the compatibility and the dispersion of the PTFE in PDMS, the PTFE will be well dispersed. Further, on increasing the temperatures from 25 to 35 °C, the segmental dynamics of the PDMS chain increases because of the increased mobility of the chains. Hence, PTFE additives are well dispersed at elevated temperature (transition from 5 to 35 °C) and hence demonstrated with improved optical properties. Additionally, fibrillated PTFE reduces the scattering of lights. Such an impact of PTFE to act as an optical clarifying agent has been reported by Bernland and Smith. 

Mechanical Properties. The impact of fibril formation is bound to affect the mechanical properties of the developed composites. Hence, the mechanical properties of the developed composites are very important to the study. In the window of the study, the tensile strength and the percent elongation at the break value for the PDMS–PTFE composites were found to be higher compared to the controlled sample. This was because of the compatibility and the dispersion of the PTFE particles in PDMS. However, it is worth mentioning that the composites processed at 35 °C demonstrated improved properties compared to its analogues produced at 0 and 25 °C, respectively. The tensile strength data and elongation at break values are represented in Figure 6a–c. The composite 35UF-1, with a PTFE loading of 2 wt % and mixing temperature of 35 °C, was found to have maximum tensile strength. At 35 °C, formation of anisotropic fibrillated layers assists in the formation of a unique PTFE–PDMS interface. The anisotropic PTFE fibrils provides a higher surface area compared to the undeformed PTFE particles processed at 0 °C. Hence, the PDMS–PTFE interaction is conjectured to be more in the case of composition processed at 35 °C. Conversely, the elongation at break (%) was found to decrease with the increase in mixing temperature and PTFE loading in the composites with a silicone/PTFE to cross-linker ratio of 1:1. This could be ascribed to the increased stiffness of the composite with increase in PTFE loading, as the elongation at break decreased to 203% for 35UF-1 when compared to 410% for the control PDMS sample. Furthermore, the tear strength of the samples was found to increase with increase in the PTFE loading and mixing temperature. The tear strength increased from 0.90 N mm⁻¹ for control PDMS sample to 1.90 N mm⁻¹ for 35UF-1. This increase implies that the PTFE particles strengthens the composite material in lateral direction as the
samples were prepared through compression molding. During compression molding, the force reduces the thickness of the film leading to better distribution of the PTFE particles in the direction of PDMS flow. With increased PTFE loading, the structure of the layer in the lateral direction is increased, ultimately reinforcing the strength of the composite material.

To study the effect of higher cross-linking in the composites, the silicone/PDMS to cross-linker ratio was varied from 1:1 to 1:2.5; this change led to some improvements in the tensile strength. In the case of PDMS–PTFE composites with increased silicone/PDMS to cross-linker ratios, the increased cross-linked density and absence of the terminal vinyl group mainly affects the mechanical properties. However, similar to the previous set of composites, here also the composite B35UF-1 with a PTFE loading of 2 wt % and mixing temperature of 35 °C showed the highest tensile strength (Figure 7). The composites prepared at mixing temperatures of 0, 25, and 35 °C show increments of 14, 25, and 34%, respectively, when compared to the control sample of PDMS. While comparing the tensile strength data from both the sets, it can be concluded that the best composition was obtained at 2 wt % loading, with a mixing temperature of 35 °C and having 8 wt % of PTFE (particle size ≥ 40 μm) breaking down into smaller irregular-shaped particles during the mixing process, playing an indispensable role in reinforcement of the silicones. This reinforcement resulted in increase of the tensile strength. The particles with 1 μm size were found to be spherical and having much more regular shape unlike bigger particles (40 μm), which resulted in smaller irregular particles because of shearing during the mixing step. There was insignificant change in the tear strength with increase in particle loading on the composites having a particle size of 1 μm. For the composites with a PTFE particle size of 40 μm, an increment of merely 1.7% was observed with increasing loading. However, when compared to the control sample of B35UF-1, the tear strength showed significant increase of 66% for C35UF-3 with 8 wt % of PTFE load. This could be ascribed to the reinforcement of the composite in lateral direction of tear with increased PTFE loading.

By and large, most of the commercial two part addition curable silicone elastomer contains mixture of PDMS of different chain lengths. Hence, to further study the impact of

![Figure 8. Mechanical properties of PDMS and PTFE composites with different PTFE particle sizes (40 and 1 μm). (a) Tensile strength, (b) elongation at break (%), and (c) tear strength (S.D ± 10%).](https://dx.doi.org/10.1021/acsomega.0c02585)

Scheme 1. Scheme of Polymerization of Vinyl-Terminated PDMS

![Scheme of Polymerization of Vinyl-Terminated PDMS](https://dx.doi.org/10.1021/acsomega.0c02585)
incorporation of PDMS of different chain lengths, divinyl-substituted PDMS polymers were synthesized and were mixed in the optimized formulation. The model “D” systems used for the same are $D_{100}$ and $D_{150}$. Acid-catalyzed ring-opening equilibration reaction was performed for the preparation of desired chain length of vinyl-terminated PDMS (Scheme 1). The effect of addition of vinyl-terminated PDMS linker containing different $D$ lengths ($D_{100}$ and $D_{150}$) showed that the addition of smaller vinyl-terminated polymer ($D_{100}$) was found to have a significant effect on the tensile strength, elongation at break, and tear strength of the material. The smaller cross-linker results in greater number of cross-linking points, thus influencing the mechanical properties to significant extent. In comparison to the control sample of B35UF-1, there was an increment of 50% in the tensile strength upon addition of a cross-linker of $D$ length 100 (Figure 9). Similarly, the tear strength also showed a dramatic increment of 90% when compared to the control sample. The results also indicated increased toughness of the composites. Thus, from the abovementioned experiments, it can be reasonably inferred that the shortcomings associated in terms of addition of higher PTFE loading can be counter balanced by having a mix of short and long PDMS cross-linkable systems.

Hitherto, two important perspective can be noted. Briefly, (i) processing the PDMS–PTFE composite at 35 °C resulted in the best performing composite, (ii) a synergistic balance between higher filler loading and mechanical properties of the composite can be balanced by doping the formulation with short-chain curable PDMS.

In order to check the fidelity and industrial applicability of the above mentioned proposition, the PTFE particles were blended with commercially available LSR 2050 using the protocol used for the development of above mentioned formulations. Because the formulation D 35UF D100 contained 8 g of PTFE/100 g of PDMS, two additional data points were taken as the reference point.

The mechanical properties of the developed formulation were compared against the unfilled system. As shown in Figure 10, the elongation at break properties of the developed composites was improved compared to the control sample. This is surmised due to the fact that commercial LSR contains silica particles as a reinforcing filler. The fibril of the PTFE so formed will tend to act as a lubricating agent and tend to slide along with the silica and thereby increase the elongation at break properties. However, tensile strength was found to be marginally decreased compared to the control sample. The reinforcing capability of the fibril of the PTFE might be compromised in the presence of silica at higher loading. Hence, such an observation was noted.

**Solvent Resistance.** The moisture and the solvent permeability are indispensable product attributes for the industry. In the preliminary studies of the hybrid blended materials of fluoropolymers with PDMS, the moisture permeability was found to be much lower compared to fluorosilicones (Figure S7). This opens up plethora of opportunities for such composites in various applications. These composite materials were also tested for solvent as well as engine oil stability and uptake (Table 8). A commercial grade Momentive LSR 2050 was chosen to study the solvent resistance and uptake. LSR 2050 is a two-component curable silicone-based elastomeric material. The material was cured into LSR sheets upon blending with PTFE filler particles. The cured elastic composite materials were studied for the uptake of solvents and engine oil.

| Table 8. Solvent and Engine Oil Resistance in LSR 2050 and PTFE Blends |
|---------------------------|----------------|----------------|----------------|
| sample       | % decrease in engine oil uptake | % decrease in MEK uptake | % decrease in chloroform uptake | % decrease in xylene uptake |
| LSF 5        | 2.26 | 9.65 | 6.3 | 1.62 |
| LSF 10       | 3.27 | 13 | 21.84 | 4.87 |
of solvents like methyl ethyl ketone, chloroform, and xylene, and so forth. The PTFE blending decreased the solvent uptake in elastomer sheets, significantly. The results of LSF 10, seen for chloroform, were very encouraging with >20% decrease in the solvent uptake when compared with control as shown in Table 8. These novel composite materials can be used in industry applications where solvent/oil resistant environment is needed.

■ CONCLUSIONS

A structure–property relationship of fluorine-based reinforcements for silicone polymers was made by evaluating the thermal, mechanical, optical, and morphological properties along with studying the effect of processing temperature, cross-linking ratio, filler loading and particle size, at various levels of the cross-linker. The thermal stability of PDMS got improved after the addition of PTFE. PTFE provides high thermal stability to the composite material with a degradation temperature of 350 °C. The melting point of the composite was found to be at 327 °C in DSC, corresponding to the PTFE component of the composite. To summarize, the unique capability of PTFE to have transition from one phase to other as function of processing temperature was explored. Such a phase transition of PTFE was found to work even under confinement in the PDMS matrix. A strong dependency of the mixing temperature against the performance attributes of the developed composites was noted. The addition curable PDMS system was used as the model matrix. Compared to the phase II crystallite structure of the PTFE, the fibrils formed in phase IV imparted a better reinforcing capability toward the PDMS matrix. A synergistic balance between higher filler loading and mechanical properties of the composites can be achieved by doping the formulation with short-chain curable PDMS polymer.

Thus, PTFE–PDMS composites can be utilized to mitigate the shortcomings of the unfilled PDMS and PTFE, leveraging these materials to be made in economic manner for varied applications. The learning was extended to check the applicability of doping such PTFE powder in commercial LSR. In the window of study, the formulated LSR demonstrated improved mechanical properties with additional functional benefits like resistance toward engine oil and other chemical solvents which are important to the industrial applicability.

■ ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02585.

Schematic of composite formation steps; DSC diagrams of different composites; 29Si NMR of vinyl-terminated silicone with different D length D100, D150, showing the moisture uptake of the PDMS; and GPC data of molecular weight of cross-linkers of different D length, D100 and D150 (PDF)

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