



# Compatibilization of silicone/fluorosilicone blends by dynamic crosslinking and fumed silica addition

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## ABSTRACT

The aim of this work is to study the compatibility of silicone/fluorosilicone blends by exploring two compatibilization strategies. First, the crosslinking of the blend under shearing conditions leads to a reduction in the size of the fluorosilicone domain and hence to an effective stabilization of the morphology under shear and long time annealing. The refinement of the morphology in the dynamic crosslinking step is most likely due to a decrease in the viscosity ratio coming from preferential crosslinking of the fluorosilicone phase. However, the formation of a copolymer between silicone and fluorosilicone at the blend interface cannot be totally excluded. Secondly, the silicone/fluorosilicone blend was compatibilized by the addition of silica particles whose surface is hydrophilic or hydrophobic. Fumed hydrophilic silica allows to reduce the size of the fluorosilicone phase up to 500 nm while its hydrophobic counterpart is ineffective. This observation has been attributed to the specific hydrogen and dipolar interactions of the silicone and the  $\text{CF}_3$  group with the silanol present on the surface of the hydrophilic silica. The compatibilization mechanism is supposed to be due to a decrease in the interfacial tension and to a reduction of the coalescence phenomenon.

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## 1. Introduction

From its intrinsic structure, poly (dimethylsiloxane) (PDMS) is of great interest in the industry. Indeed, it has excellent low temperature flexibility, heat resistance, dielectric and weathering properties [1]. It is widely used in medical applications because of its hydrophobicity, biocompatibility and high gas permeability [2]. Silicone chemistry is also widespread which gives access to a large panel of molar masses, chemical functionalities and structures [3]. As for fluorosilicone, the addition of trifluoropropyl groups increases resistance to fuels, oils and solvents especially non-polar such as hydrocarbons [4]. Fluorosilicone also exhibits low temperature flexibility and may serve as seals in the automotive industry because of its wide service temperature range from  $-50\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  [5].

The first approach to exploit the properties of both polymers is to tailor a high molar mass copolymer [6]. Xu et al. [7] achieved to manufacture a random copolymer with fine and homogeneous morphology and improved mechanical properties in comparison to

the silicone/fluorosilicone blend. Copolymer was found to swell less in lubricating and sealing oil but it swells more in kerosene and gasoline than the blend depending on the difference between the interaction parameters of the copolymers and the tested solvent. Bhuvanewari et al. [8] studied the silicone blends based on fluorosilicone and silicone rubber for seal applications in aeronautical fuel systems. They finally showed that such blends are promising for such applications.

Actually, polymer blending is an attractive way to take advantages of both polymers properties while reducing the cost [6,9]. Unmodified silicone/polymer blends are known to be difficult leading to unstable and coarse morphology with poor mechanical properties [10]. Li et al. [11] blended silicone and a random fluorosilicone oils and silicone resin to achieve an enhanced oil resistant composite with limited drawbacks in the mechanical properties. According to Kobayashi et al. [12], the fluorosilicone and silicone elastomers are difficult to blend because of their different solubility parameters leading to low surface adhesion and poor mechanical properties. They tailored random and block copolymers to successfully improve mechanical properties of the blend. The block copolymer was found to be the most effective, with 5 wt% of copolymers incorporated, in increasing by three the tensile strength. Liu et al. [13] studied the fluorosilicone/silicone blend in

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which a low molecular weight poly (methylsiloxane-co-fluorosiloxane) was used as an interfacial agent in order to improve phase morphology. The mechanical properties were improved by 10% by adding 4 phr of their copolymer. As expected, the oil-aging properties of the blend were improved when high fluorosilicone content is used. Industrially, fluorocarbon polymer and silicone rubber are blended and in situ compatibilized with hydroxyl end blocked methylvinylsiloxane oligomers [14] or vinyltris (*t*-butyl peroxy)silane [15]. Guo et al. [16] developed blends of fluororubber and silicone rubber which has been compatibilized by using 2,2,2-trifluoroethyl methacrylate grafted silicone rubber as a compatibilizer. Furthermore, the incorporation of fumed silica at different contents proved to be efficient for the improvement of the mechanical properties (tear and tensile strength, hardness and elongation at break).

Size reduction of the nodular phase is generally carried out by the addition of a compatibilizer by decreasing the interfacial tension but inorganic nanoparticles are recently used to effectively compatibilize a polymer blend [17,18]. When the particles are located at the interface between two polymers, coalescence and/or interfacial tension may be reduced [19,20]. The localization of the particles may be predicted by thermodynamics; however, blend compositions, melt viscosity, the shearing, the time and the sequence of mixing may prevent to reach this predicted equilibrium [17,18].

This article deals with two strategies of compatibilization of fluorosilicone/silicone blends. Firstly, the neat fluorosilicone/silicone blend morphology will be studied and the influence of crosslinking under shearing on the blend morphology will be discussed. Secondly, the addition of fumed silica, with two surface chemistries, on the blend morphology development will be also studied. Fumed silica was selected because of its wide use as reinforcement agent in the silicone industry.

## 2. Experimental part

### 2.1. Materials

**Silicone polymers:** A methylvinyl dimethylsiloxane elastomer, named S, was kindly supplied by BlueStar Silicone. Its density is about  $0.97 \text{ g cm}^{-3}$ . Molar masses were determined by size exclusion chromatography (SEC) with toluene in universal calibration mode. Molar percentage of vinyl groups inside silicone backbone chain was determined by NMR in  $\text{CDCl}_3$ . (98–99% Methyl-3,3,3-trifluoropropylsiloxane)-(1–2% methylvinyl-siloxane) elastomer (named FS) was purchased from ABCR (AB116651). Its density is about  $1.30 \text{ g cm}^{-3}$ . The molar masses were determined by size exclusion chromatography (SEC) with THF. Molar percentage of vinyl groups inside silicone backbone chain was determined by NMR in *d*-THF. S and FS have 10.3 and 4.1 vinyl groups per chain respectively. As a consequence, the molar weight of molecular segment between two consecutive vinyl groups,  $M_0$ , for S and FS are equal to 37000 and  $15500 \text{ g mol}^{-1}$  respectively. The fluorosilicone is amorphous whereas silicone is a semi-crystalline

polymer. Elastomer properties are summed-up in Table 1.

Two fumed silica were used with two surface chemistries with the same specific area,  $200 \text{ m}^2/\text{g}$ , fumed silica R974 and A200. R974 silica is hydrophobic fumed silica after-treated with dimethyldichlorosilane while the A200 is hydrophilic silica [21]. It was added several content of silica in S+10 wt%FS+0.2 wt%DCP blend as listed in Table 2. Filler contents were verified by TGA and reported in Table 2.

The master curves of complex shear moduli and viscosities as function of frequency for both silicone elastomers are shown in Fig. 1,  $T_0 = 30 \text{ }^\circ\text{C}$ .

The zero shear viscosity was directly measured on the rheological curves at  $30 \text{ }^\circ\text{C}$ . The  $G'$ ,  $G''$  crossover defines the characteristic relaxation time,  $\tau_c$ . Rheological shift factors,  $a_{T/T_0}$ , were determined using TTS module of Trios software. Flow activation energy of polymers used was modeled by an Arrhenius law of the temperature dependence of the shift factors. These three material parameters are reported in Table 3. Williams-Landel-Ferry (WLF) model fits better the data for the fluorosilicone, as it is an amorphous polymer, even if temperatures are well above  $T_g + 100 \text{ }^\circ\text{C}$  suggesting large flowing units. WLF parameters are as follows:  $C_1 = 2.98$ ,  $C_2 = 142.6 \text{ K}$  and  $T_0 = 303 \text{ K}$ .

**Free-radical crosslinking:** Dicumyl peroxide (DCP,  $M = 270 \text{ g mol}^{-1}$ ) was used as the free radical initiator of the crosslinking reaction. It was purchased from Aldrich with an assay of 98% and used as received. The thermal decomposition of DCP was determined by Refs. [22,23]:

$$\frac{d[\text{DCP}]}{dt} = -Ae^{-\left(\frac{E_a}{RT}\right)} \cdot [\text{DCP}] \quad (1)$$

With  $A = 7.47 \times 10^{15} \text{ s}^{-1}$ ;  $E_a = 153.5 \text{ kJ/mol}$ .

### 2.2. Samples preparation

#### 2.2.1. Pre-mix procedure

Blends of silicone and fluorosilicone elastomers were prepared before the dynamic vulcanization step. First, silicone and fluorosilicone elastomers are mixed in a roll mill (cylinder diameter = 100 mm) at room temperature until homogenization, depending of the amount of fluorosilicone. Then, DCP crystals were added and the mixing goes on 5 min to ensure a good dispersion. Then if silica is used, the silica is added step by step. Once, all the content of silica is introduced, a homogenization step is carried out for 10 min. The gap was set to 0.4 mm, noted as  $L$ , a roll speed of 25 rpm and a friction ratio of 0.8. We estimated the shear rate between the two rolls with asymmetric rolls speed ( $U_1$  and  $U_2$ ) as follows [24]:

$$\dot{\gamma} = \frac{U_1 - U_2}{L} = 65 \text{ s}^{-1} \quad (2)$$

**Table 1**

Main properties of silicone and fluorosilicone.

Polymer	$M_n$ [kg/mol] <sup>a</sup>	$M_w$ [kg/mol] <sup>a</sup>	%mol vinyl groups <sup>b</sup>	$T_g$ [ $^\circ\text{C}$ ] <sup>c</sup>	$T_c$ [ $^\circ\text{C}$ ] <sup>c</sup>	$T_f$ [ $^\circ\text{C}$ ] <sup>c</sup>
S	380	600	0.22	-126	-90/-84 <sup>d</sup>	-46/-41
FS	63	434	1	-70	-	-

<sup>a</sup> SEC measurements.

<sup>b</sup> NMR results.

<sup>c</sup> DSC measurements.

<sup>d</sup> Cold crystallization.

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