

# Thermoplastic vulcanizate based on poly(vinylidene fluoride) and methyl vinyl silicone rubber by using fluorosilicone rubber as interfacial compatibilizer



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## ABSTRACT

To successfully fabricate a thermoplastic vulcanizate (TPV) based on poly (vinylidene fluoride) (PVDF) and high loading level of methylvinyl silicone rubber (MVSr), stabilizing the phase structure during blending is a challenge due to the distinct interface properties of the two materials. Herein, we report a feasible method to fabricate a desired PVDF/MVSr TPV by using fluorosilicone rubber (FSR) as an interfacial compatibilizer. We found that the FSR was self-assembly migrated from MVSr phase toward PVDF phase and finally located at the interface between PVDF and MVSr, forming core-shell-like spherical particles with a rough surface, and surprisingly, the crosslinked rubber particles were connected by fiber-like elastomeric materials which bonded onto the surfaces of the particles. The excellent property of repeat processing of the PVDF/MVSr/FSR TPV with such novel phase morphology makes it a potential alternative of fluorosilicone rubber in future.

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## 1. Introduction

Fluorosilicone rubbers (FSR), which have drawn much attention because of their remarkable properties such as low surface tension, oil and solvent resistance, and thermal stability, are a kind of promising polymer for various commercial and military applications [1–3]. However, the harsh conditions and the high cost to synthesize high molecular weight FSR [4,5] hampered their commercial use [6,7]. Like most conventional rubbers, FSR must be crosslinked before practical application. The crosslinking makes them to be a thermoset material losing the processability and recyclability [8,9], which is somewhat a waste of raw fluorosilicone materials.

Thermoplastic vulcanizate (TPV) [10], a specific group of thermoplastic elastomers (TPE) prepared by reactive blending (namely dynamic vulcanization), give us some enlightenments to design and develop novel fluorosilicone elastomers. A successful TPV, usually consisting of high content of crosslinked rubber as dispersion phase and low content of thermoplastics as continuous phase, should have good interfacial compatibility [11,12] and thus be able to combine the good resilience of vulcanized rubber and processability and recyclability of thermoplastic [13]. Based on the concept of TPV, poly(vinylidene fluoride) (PVDF) and methyl vinyl silicone rubber (MVSr) are selected as the thermoplastic phase [14,15] and rubber phase, respectively. The former has a suitable melt process temperature (~170 °C) [14], excellent chemical

resistance, high barrier properties, good stability in high temperatures and harsh weather [16], and the later exhibits excellent common characteristics of silicone rubber [17]. However, the poor compatibility between PVDF and MVSr inevitably leads to a significant drop in the mechanical properties of the resultant blends and may cause it unsuccessful to fabricate a PVDF/MVSr TPV at a high loading level of MVSr, due to the distinct interface properties of PVDF and MVSr.

In this paper, we successfully demonstrated feasible method to fabricate a desired PVDF/MVSr TPV by using FSR to improve the interfacial compatibility between PVDF and MVSr. It was found that the FSR was self-assembly migrated from MVSr phase toward PVDF phase and finally located at the interface between PVDF and MVSr, forming a core-shell-like structure. To the best knowledge of us, there was no report on successful preparation of fluorosilicone TPV with high MVSr/PVDF ratio. The presence of the FSR significantly changed the surface of the crosslinked MVSr particles, which was the key to fabricate TPV.

## 2. Experimental

### 2.1. Materials

PVDF (density = 1.75 g/cm<sup>3</sup>, melting point = 172 °C) was purchased from Guangzhou Li Chang Fluoroplastics and used as received; the molecular weight and polydispersity of the PVDF sample, determined by gel permeation chromatography, are  $M_w = 209,000$  and  $M_w/M_n = 2.0$ , respectively. MVSr silicone gum (KE 571-U, Shin-Etsu, Japan) is a kind of transparent rubber with molecule weight of  $5.2 \times 10^5$  g/mol

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and density = 1.22 g/cm<sup>3</sup>. FSR (FE2801) was purchased from Shanghai 3F New Material Co., Ltd. (China). DCP was purchased from Sinopharm Chemical Reagent (Shanghai, China) and was purified by anhydrous alcohol recrystallization.

## 2.2. Preparation of PVDF/MVSR/FSR TPV

The PVDF/MVSR ratio was fixed at 30/70 (w/w) in this particular experiment. The FSR (10% weight of the MVSR) were first mixed with MVSR for 5 min to achieve a uniform compound in a two-roll at room temperature; then the MVSR/FSR (100/10) compound was blended with neat PVDF melt in a Haake torque rheometer at ~175 °C and a rotor speed of 90 rpm. The detail processing: PVDF was firstly melted mixed for 4 min and then the MVSR/FSR compound was added. About 2 min later, DCP (1.5 wt.% of the rubber content), the crosslinking agent, was added and the mixing was continued until the final stable torque was reached (the dynamic vulcanization time is ~5 min). It is important that the temperature for adding DCP was kept at or necessary below 175 °C as possible, avoiding quick decomposition of DCP at a higher temperature (since the half-life of DCP at 175 °C was less than 50 s). At the same time, feeding DCP must be careful to make sure it was involved into the inside of melt immediately. The above measurements were crucial to ensure that the MVSR phase was fully cured as possible. Subsequently, the resultant PVDF/MVSR/FSR TPV was removed from the cavity of rheometer and cooled down to the room temperature. To prepare test specimens, the cooled TPV were ground and compression molded to form sheets with ~1 mm thickness.

## 2.3. Scanning electron microscopy (SEM)

The morphology of the TPV was studied by Nova NanoSEM 430 (FEI Company). In order to observe the crosslinked MVSR phase, the TPV sample was first extracted with hot N, N-Dimethylformamide (DMF) for 3 days to selectively remove the PVDF phase. Then the residue, namely the crosslinked rubber phase, was dried completely and sputter coated with gold to prevent electrostatic charging build-up during SEM observation.

## 2.4. Tensile test

The stress–strain behavior of the PVDF/MVSR/FSR TPV was determined using a Computerized Tensile Strength Tester (UT-2080, U-CAN Dynatex Inc., Taiwan) with a crosshead speed of 500 mm/min according to ISO 37-2005.

## 2.5. Fourier transform infrared (FT-IR) spectra

The absorption spectra were recorded using a Tensor 27 Spectrometer (Bruker, Germany) with a resolution of 4 cm<sup>-1</sup> and 32 scans. Similar to the sample preparation for SEM, TPV was first extracted by hot N, N-Dimethylformamide for 3 days to remove the PVDF completely. The residue after extraction was compressed into disks for the FT-IR test, using the attenuated total reflectance (ATR) model. All of the FT-IR samples were oven-dried under a vacuum prior to testing to eliminate the effects of residual solvent and moisture.

## 2.6. Contact angles measurement

Static contact angles were taken out using an apparatus model by OCA 15 PLUS, DATAPHYSICS. PVDF, MVSR and FSR films for contact angle measurement were compression molded between clean polyester films to ensure the smooth and clear surface as much as possible. Ten points of each sample were recorded and contact angles results were the mean values of 10 data.

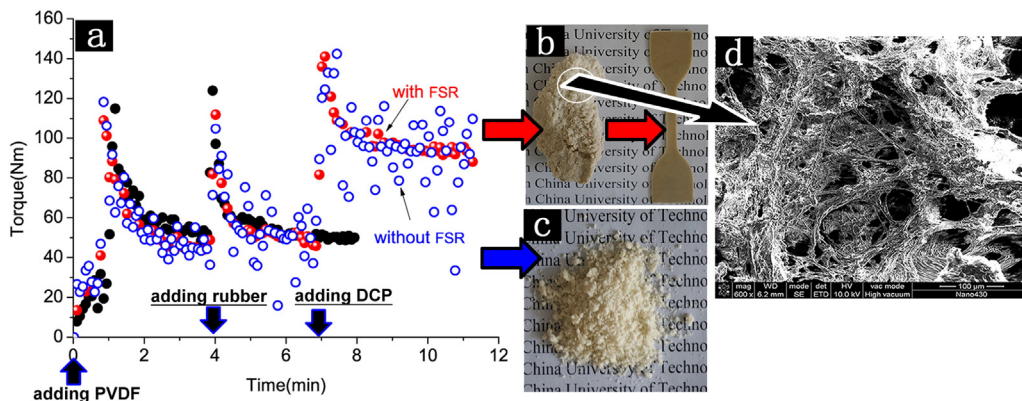
## 2.7. Melt rheological behavior

Melt rheological behavior of the PVDF/MVSR/FSR TPV were determined on a Rubber Process Analyzer (RPA 2000, Alpha Technologies, USA). The performing temperature was set at 210 °C. The frequency was logarithmically increased from 10<sup>-1</sup> to 10<sup>2</sup> Hz at a constant strain amplitude of 1°.

## 3. Results and discussion

### 3.1. Dynamic vulcanization of the TPV

The torque change usually reflects the variation of structure [18], which helps us to understand the evolution of the phase structure of the PVDF/MVSR/FSR TPV during dynamic vulcanization. Fig. 1a shows the real-time change of mixing torque during melt blending performed in the Haake rheomix. The torque of each curve initially displays two sharp and strong peaks which are attributed to the melting of the PVDF pellets and MVSR (or MVSR/FSR premixed compound), the red curve in Fig. 1a), respectively. Afterward, the mixing torque of the PVDF/MVSR without FSR (the blue one in Fig. 1a) shows a random fluctuation, indicating a heterogeneous blending system existed in the Haake rheomix. In contrast, the torque of PVDF/MVSR/FSR TPV reaches a constant level, suggesting a full homogenization of the blend [19]. A sharp increment in torque was observed immediately after adding DCP, which suggesting the occurrence of cross-linking [20] of the rubber



**Fig. 1.** (a) Torque change of the TPV during dynamic vulcanization; (b) the photographs of the successfully prepared TPV; (c) the photographs of the failed TPV without FSR; (d) SEM image of the successfully prepared TPV at low magnification. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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