



A facile route to fluoroalkylsiloxane polymers having resistance to corrosive acidic conditions: Synthesis and characterization

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ABSTRACT

Polysiloxanes having 3,3,3-trifluoropropyl (TFP) groups attached to the silicon atom are highly attractive by virtue of their unique properties such as extreme solvent resistance and broad service temperatures. Though fluoroalkylsiloxane polymers are known for their resistance to hydrocarbon solvents and oils, reports on room temperature curable fluoroalkylsiloxane polymer based coatings that are resistant to corrosive acidic and oxidative environments are very rare. In this paper, for the first time, we report the synthesis of vinyl terminated fluorosilicone copolymer, poly(methyltrifluoropropyl-co-methylvinyl) siloxane (V-PFMVS) with very high TFP content (77 mol%) and 23 mol% vinyl content, and its comparison of properties with non-fluorinated counterpart, vinyl terminated poly(dimethyl-co-methylvinyl) siloxane (V-PDMVS). The synthesised copolymers were obtained in high yields of 70–75% with number average molecular weight (M_n) of 65,000 and were cured using cyclic hydridosiloxane via hydrosilylation route. Cured V-PFMVS exhibited increased hydrophobicity compared to cured V-PDMVS (contact angle 113° vs. 91°). The corresponding silica reinforced composites also were processed and evaluated for dynamic mechanical and thermal properties as well as response to various environments including hexane, conc. HNO₃ and HF. Swelling studies proved the role of -CH₂CH₂CF₃ groups in imparting excellent resistance to hexane and better resistance to corrosive acidic environments as illustrated by the low weight loss after exposure to conc. HNO₃ and HF in the case of V-PFMVS/composite. Lap shear strength (LSS) evaluation on aluminium substrate proved its capability as a promising adhesive. The superior properties of the V-PFMVS/composite are correlated to its chemical composition.

1. Introduction

Fluorosilicones constitute a unique class of polymers that combine the properties of both fluoropolymers and silicones [1–3]. While silicones are known to possess thermal stability, flexibility, low temperature resistance and reasonably good adherence to various substrates [4], fluorocarbons exhibit lower surface energies and better solvent and oil resistance [5]. Thus, it is worthwhile to explore the characteristics of fluorocarbon-silicone hybrids or fluorosilicones that are technologically promising with the desirable attributes of both materials incorporated in the single polymer structure.

Polysiloxanes having 3,3,3-trifluoropropyl (TFP) groups on the silicon atom are being widely used as an important class of fluorosilicones by virtue of their unique properties such as extreme solvent resistance and broad service temperature [6–10]. 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane (F3) is the most common precursor for polymeric fluoroalkyl siloxanes. For many applications,

the convenience of addition-type room temperature vulcanisable (RTV) fluorosilicones, especially the fluidity, outweighs their lower mechanical properties compared to the corresponding heat-cured silicones. The RTV silicone consists of vinyl-terminated polysiloxane where the vinyl content is usually maintained at a low concentration of about 0.2–0.5 wt%. However, very often, the low vinyl content results in cured polysiloxane elastomer without appropriate crosslink density and calls for further cure activation by heat. Hence, more vinyl groups need to be introduced into the polysiloxane backbone to realize useful RTV elastomeric products [11,12]. Therefore, 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D₄V) is often involved in the copolymerization of F3 and dimethylcyclosiloxane (Dn) [13].

When a crosslinked polymer is in contact with a solvent, the network absorbs a certain amount of solvent, the process of which depends strongly on the polymer/solvent interactions, the crosslink density of the polymer and the temperature [14–18]. Though there are a few reports available on the solvent resistance properties of fluorosilicones

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[5,19–21], studies pertaining to the resistance of such polymers towards corrosive acidic and oxidative environments are scanty. Hence, exploration of novel fluorosilicone polymeric systems resisting acidic and oxidative environments is worth pursuing.

In this work, a room temperature curable fluorosilicone with high TFP content was synthesized using F3 and D₄V as monomers and a corresponding non-fluorinated counterpart with equivalent molecular weight was synthesized using D4 and D₄V. To the best of our knowledge, this is the first time that an RTV fluorosilicone system with high TFP content is realised, having excellent resistance to corrosive acids. The novel copolymer exhibited interesting hydrophobic and lipophobic characteristics along with promising adhesive characteristics.

2. Experimental

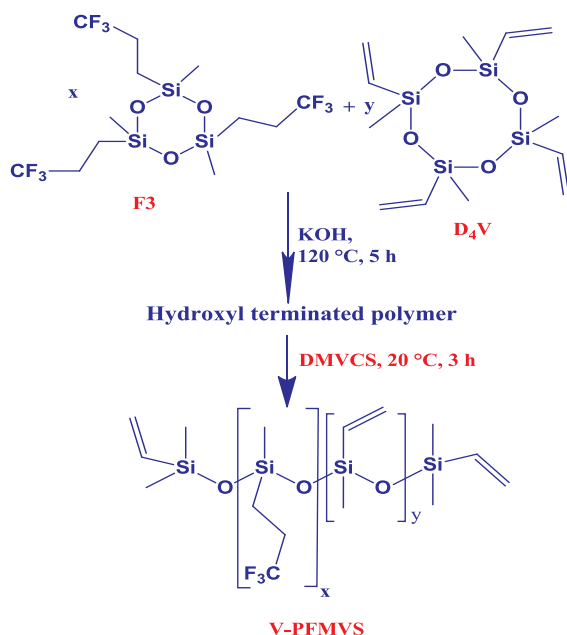
2.1. Materials

Monomers, octamethylcyclotetrasiloxane (D4), 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane (F3) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D₄V) were purchased from M/s. Gelest, M/s. Alfa-Aesar and M/s. Sigma Aldrich, respectively and used as received. The end-capping agent, dimethylvinylchlorosilane (DMVCS), the cross-linking agent 1,3,5,7-tetramethylcyclotetrasiloxane (D₄H) and polymerisation catalyst, KOH were obtained from M/s. Alfa-Aesar. Diethylether obtained from M/s. Qualigens was used as the solvent. The platinum catalyst, 0.05 M solution of Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in vinyl-terminated polydimethylsiloxane (V-PDMS) was procured from M/s. Aldrich and further diluted to 0.01 M using V-PDMS prior to use. The filler used was cristobalite silica obtained from M/s. CMET, Thrissur with particle size < 10 μm. It was used after drying at 150 °C for 4 h.

2.2. Synthesis of copolymers

2.2.1. Synthesis of vinyl terminated poly(methyltrifluoropropyl-co-methylvinyl) siloxane (V-PFMVS)

The fluorosilicone polymer, vinyl terminated poly(methyltrifluoropropyl-co-methylvinyl) siloxane (V-PFMVS) was synthesized by the ring opening co-polymerisation of F3 and D₄V in the molar ratio of 80:20 as depicted in Scheme 1. In our recent study, fluorosilicone copolymers having varying TFP content were synthesized in which

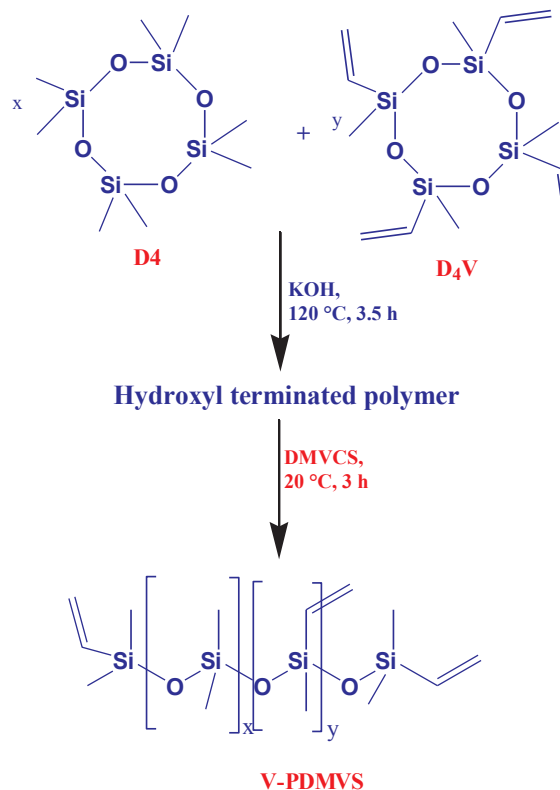


Scheme 1. Synthesis of V-PFMVS.

promising properties were obtained for the copolymer synthesized from 80 mol% F3 and 20 mol% D4 [21] and hence, in the present study, mole% of F3 is fixed as 80. A four-necked RB flask equipped with mechanical stirrer, condenser, N₂ inlet and outlet tubes was placed in an oil bath. 187.4 g (0.4 mol) of F3, 34.4 g (0.1 mol) of D₄V and 1.1 g KOH (0.5 wt% of total monomer) were added. The reaction mixture was kept under N₂ purging for 10 min and then heated to 120 °C. After 5 h, the system was cooled to around 20 °C and then 25 ml DMVCS, the chain end-capping agent was added. The reaction was continued further for 3 h. Finally, the whole reaction mixture was extracted with diethylether and the unreacted catalyst was removed out by repeated washing with distilled water. The system was then subjected to flash evaporation under vacuum at 70 °C to remove traces of solvent. As there is chance for the presence of unreacted cyclic siloxanes and low molecular weight oligomers, the polymer was subjected to drying at 145 °C for 2 h under vacuum. On cooling, the transparent resinous copolymer, V-PFMVS is obtained with 70% yield.

2.2.2. Synthesis of vinyl terminated poly(dimethyl-co-methylvinyl) siloxane (V-PDMVS)

The non-fluorinated silicone polymer, vinyl terminated poly(dimethyl-co-methylvinyl) siloxane (V-PDMVS) was synthesized from D4 and D₄V in the molar ratio of 80:20 as depicted in Scheme 2. Experimental set-up for the synthesis was same as that of V-PFMVS. 118.6 g (0.4 mol) of D4, 34.4 g (0.1 mol) of D₄V and 0.7 g KOH (0.5 wt% of total monomers) were taken and kept under N₂ purging for 10 min followed by heating to 120 °C. After 3.5 h, the system was cooled to around 20 °C and then added 25 ml DMVCS, the end-capping agent. The reaction was continued for further 3 h. The polymer formed was extracted with toluene and then subjected to repeated washing with distilled water to remove the catalyst followed by flash evaporation under vacuum at 90 °C for 1 h to remove the solvent. It was then dried at 145 °C for 2 h to remove the traces of unreacted cyclic siloxanes and low molecular weight oligomers, if any, present in the system. The final yield of the polymer, named as V-PDMVS, was 75%. The polymer was



Scheme 2. Synthesis of V-PDMVS.

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