Synthesis and characterization of novel polysiloxane-grafted fluoropolymers

Bilal Baradie, Patricia H.M. Lai, and Molly S. Shoichet

Abstract: Fluorosilicone polymers combine the properties of both fluorocarbons and siloxanes, yielding materials with unique properties. Novel crosslinked fluorosilicone polymers were synthesized by grafting diisocyanate-terminated polydimethylsiloxane (PDMS) to hydroxyl-functionalized fluoropolymers of poly(tetrafluoroethylene-co-vinyl acetate-co-vinyl alcohol) (PTFE-V Ac-VA), as confirmed by elemental bulk and surface analysis. The fluorosilicone polymers containing 34 mol% of TFE were thermally stable with a degradation temperature of 267 °C. Fluorosilicone films were found to be more hydrophobic than the parent, non-grafted fluoropolymers; dynamic advancing and receding water contact angles for PTFE-co-V Ac-co-V A-g-PDMS were 104° ± 1° and 61° ± 1°, respectively, whereas for PTFE-co-V Ac they were 90° ± 2° and 59° ± 2°. The combined properties of thermal stability and hydrophobicity suggest that these fluorosilicones may be useful for coating and paint applications.

Key words: fluoropolymers, fluorosilicone, polydimethylsiloxane, supercritical carbon dioxide.

Introduction

Fluorosilicones consist of fluorocarbons and siloxanes and are generally thought of as siloxane backbone polymers with fluorocarbon pendant groups. Fluorosilicones are generally considered resilient within a working temperature range from −60 to 200 °C. They have low surface tension (2.0–2.5 μN cm^−1) (1), low volatility, and excellent chemical inertness, resulting in good release properties. Moreover, fluorosilicones have low glass transition temperatures (i.e., −75 °C for polymethyl-trifluoropropylsiloxane (PMTFPS)), low brittle points (i.e., of −59 °C), and do not crystallize at low temperatures (e.g., PMTFPS does not crystallize at −40 °C). Thus, fluorosilicones combine the high thermal stability and low surface tension of fluoropolymers with the high thermal stability, low adhesion, and good low-temperature flexibility of silicones (2, 3).

Fluorosilicone elastomers are used as lubricants for pumps and compressors where harsh chemical solvents are utilized. Fluorosilicone rubber is fuel resistant and, therefore, widely used in the automotive and aerospace industries to make O-rings, gaskets, washers, and sealants that are used in fuel line connections, as well as exhaust gas recirculating diaphragms for automobiles (2).

Several types of fluorosilicones have been synthesized, most of which are conceptually similar to PMTFPS — that is, with a siloxane backbone and a fluorocarbon pendant group — yet some are different. For example, Mascia et al.
(4) blended poly(vinylidene fluoride) with a fluorosilicone elastomer with the thought that the vinylidene fluoride would reinforce the mechanical and thermal properties of the fluorosilicone polymer. This experimental compatibility was proven to be successful, and the polymer exhibited a peak melting temperature of approximately 120 °C (4). In a separate example, Kim et al. (5) synthesized a fluorosilicone polymer with a hydrocarbon backbone and fluorinated and siloxane pendant groups covalently bound by urethane bonds (5). Interestingly, Suzuki et al. (6) grafted polydimethylsiloxane (PDMS) onto a poly(chlorotrifluoroethylene) (CTFE) via an epoxide, yet this ether bond is non-ideal, with a low cohesion energy of 4.2 kJ mol–1 vs. that of a urethane bond at 36.5 kJ mol–1 (6, 7). In both Kim and Suzuki papers, the polymer surfaces were found to be hydrophobic. While these two systems use graft polymers as a way to achieve fluoro-silicones, neither approach is ideal for thermally stable fluorosilicones because Kim’s polymers have a hydrocarbon backbone and Suzuki’s polymers use an ether bond for grafting. To overcome this void in thermal stability, we synthesized fluorosilicone polymers consisting of a fluorocarbon backbone and siloxane pendant groups, where urethane chemistry was utilized for the grafting.

Specifically, we investigated the use of supercritical carbon dioxide synthetized poly(tetrafluoroethylene-co-vinyl acetate) (PTFE-co-VAc) (8, 9), where the TFE-backbone polymers were found to be more thermally stable than those of CTFE and the vinyl acetate groups were hydrolyzed to vinyl alcohol (VA), yielding reactive functional groups for the covalent grafting of isocyanate-terminated PDMS. Monoallyl- and dihydroxy-terminated PDMS were modified with 1,4-phenylene diisocyanate, resulting in mono- and diisocyanate-terminated PDMS, respectively. As shown in Scheme 1, linear fluorosilicone polymers were synthesized by grafting monoisocyanate-terminated PDMS to PTFE-VAc-VA, whereas crosslinked fluorosilicone polymers were synthesized by grafting diisocyanate-terminated PDMS to PTFE-VAc-VA (as shown in Scheme 2). These polymers were characterized for bulk thermal stability and surface hydrophobicity of cast films.

Results and discussion

The ultimate goal of this research was to synthesize a crosslinked fluorosilicone with high thermal stability and high hydrophobicity; however, since crosslinked polymers are more difficult to analyze by, for example, 1H NMR, we first synthesized linear fluorosilicones as model systems for the crosslinked polymers.

Linear fluorosilicones

PTFE-VAc was synthesized in supercritical fluid CO2, as previously described, and found to have a linear backbone formed by hydrolysis of VAc repeats to VA (8). Three compositions of PTFE-VAc were examined for hydrolysis to PTFE-VAc-VA, each possessing TFE contents of 26 mol%, 34 mol%, and 63 mol%, respectively. However, only PTFE-VA copolymers with TFE contents of 26 mol% and 34 mol% could be hydrolysed to PTFE-VAc-VA because of the insolubility of PTFE-VAc with 63 mol% TFE in the hydrolysis solution of THF. Thus only these two compositions were further analyzed. PDMS-isocyanate was successfully synthesized, as determined by FT-IR, which was also utilized to demonstrate the grafting of PDMS-isocyanate to
PTFE-VAc-VA (shown in Fig. 1). The NH (3300 cm\(^{-1}\)) and C=O (1750 cm\(^{-1}\)) stretching vibrations correspond to the urethane bond, while the Si-O peak at 1260 cm\(^{-1}\) corresponds to PDMS and the CF\(_2\) peak at 1152 cm\(^{-1}\) reflects the fluorinated backbone of PTFE-co-VAc-co-VA. The disappearance of the NCO peak at 2250 cm\(^{-1}\) indicates that the PDMS-NCO functional groups were consumed and likely grafted to the fluorinated PTFE-co-VAc-co-VA, yielding the linear fluorosilicone polymer.

The grafting reaction was confirmed by \(^1\)H NMR, as shown in Fig. 2, where the peaks between 7.2 and 7.6 ppm correspond to phenyl protons of 1,4-phenylene diisocyanate. The three wide peaks between 5.2 and 6 ppm, as well as the two peaks between 1.9 and 2.8 ppm, correspond to the methine, methyl, and methylene protons of VAc. The peak at 3.7 ppm corresponds to the N-H proton from the urethane link. The resonance peak at ~0 ppm corresponds to the methyl protons of the PDMS repeat (CH\(_3\)-Si-CH\(_3\)), and the peaks labelled (d) correspond to the methyl and methylene protons in the PDMS end groups, specifically the terminal butyl and ethylene groups (e.g., HO-C\(_2\)H\(_5\)-PDMS-C\(_8\)H\(_9\)) found in PDMS.

**Crosslinked fluorosilicones**

**Surface properties**

Reaction chemistries similar to those described for monoisocyanate-terminated PDMS (above) were repeated with diisocyanate-terminated PDMS with PTFE-VAc-VA, yielding crosslinked fluorosilicones. Diisocyanate-terminated PDMS 4000 and 700 were grafted to PTFE-VAc-VA, resulting in a product that possessed TFE:VAc:VA molar ratios of 34:44:22 and 26:48:26, respectively, as determined by a
combination of elemental analysis (for TFE:VAc molar ratio) and FT-IR (for VAc:VA molar ratio).

Films were cast from THF on glass slides, and the air–polymer surface was analyzed for hydrophobicity by dynamic advancing and receding water contact angles and for surface elemental composition by XPS. Moreover, the XPS surface composition was compared to the elemental-analysis-determined bulk composition. As shown in Table 1, PTFE-VAc-VA-g-PDMS films were hydrophobic, with greater contact angles measured for those polymers with both greater TFE molar content (i.e., 34 mol% vs. 26 mol%) and higher molar mass of PDMS (4000 vs. 700). Interestingly, the XPS elemental surface composition for both films had similar fluorine content (representative of TFE) yet different silicon content (representative of PDMS). The PDMS 4000 sample had more silicon at the surface than the PDMS 700 samples, which suggests that the greater contact angles measured reflect the greater siloxane surface composition. Interestingly, there was a surface enrichment of silicon relative to the bulk composition for both samples. Siloxane groups likely enrich the surface for several reasons, as follows: (a) PDMS has a lower critical surface tension (2.1 µN cm⁻¹)
than that of either TFE (2.4 μN cm⁻¹) or that of PVAc (3.65 μN cm⁻¹) (10); (b) the siloxane groups have greater mobility, being pendant to the main chain, than do the TFE groups, which form the backbone, and thus PDMS groups have greater free volume of rotation and can orient themselves more easily at the air–polymer surface (11); and moreover, (c) polarity differences between PVAc (0.329) and PTFE (0.089) and PDMS (0.042) likely act to drive PTFE and PDMS away from each other and away from PVAc, driving PDMS to the surface and away from the bulk.

Thermal properties

Thermal stability was measured by thermogravimetric analysis (TGA) for the crosslinked PTFE-VAc-V A-g-PDMS 4000 that was most hydrophobic, and this thermal stability was compared with those of PVAc and PTFE homopolymers. The polymer films were heated from room temperature to 600 °C at a fixed heating rate of 5 °C min⁻¹ in air, and mass loss vs. temperature was plotted, as shown in Fig. 3. While PTFE is clearly more stable than PTFE-VAc-V A-g-PDMS, the latter is more stable than PVAc.

To gain a greater understanding of the degradation behavior of crosslinked PTFE-VAc-V A-g-PDMS, its degradation behavior was compared to that of PTFE and PVAc at two specific degradation temperatures, as follows: (a) the temperature of the initial (1%) mass loss (T₁%) and (b) the temperature at 50% mass loss (T₅₀%). These data are summarized in Table 2. Given that PVAc has lower T₁% and T₅₀% values than the PTFE-VAc-V A-g-PDMS, this suggests that TFE likely influences the decomposition temperature.

In summary, we achieved our goal of creating a thermally stable, hydrophobic fluorosilicone possessing a fluorocarbon backbone and siloxane pendant group by grafting PDMS to PTFE-VAc-V A via urethane chemistry. This chemistry may be applied to other systems, thereby extending its utility beyond the specific polymers described herein. Moreover, these fluorosilicones may be useful in coating applications where thermal stability and hydrophobicity are desirable. In ongoing studies, we are investigating other fluorosilicone systems that build on the fluorocarbon backbone and siloxane pendant chain approach.

Experimental

General information

All chemicals were purchased from Aldrich (Ontario, Canada) and used as received unless otherwise specified. TFE was prepared by vacuum pyrolysis of PTFE (12) and stored at room temperature over d-limonene in a 300 mL stainless steel sample cylinder fitted with an 1800 psi (1 psi = 6.895 kPa) safety rupture disk. The d-limonene inhibitor was removed by inline filtration through chromato-

<table>
<thead>
<tr>
<th>Polymer sample</th>
<th>T₁%</th>
<th>T₅₀%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE-VAc-V A-g-PDMS</td>
<td>267</td>
<td>356</td>
</tr>
<tr>
<td>PVAc</td>
<td>244</td>
<td>319</td>
</tr>
<tr>
<td>PTFE</td>
<td>475</td>
<td>534</td>
</tr>
</tbody>
</table>

Table 2. Thermogravimetric analysis of crosslinked PTFE-VAc-V A-g-PDMS 4000 vs. PTFE and PVAc.
bottom flask, 1,4-diazo[2,2,2]-bicyclo-octane (DABCO), PDMS, and THF were added to make a 40% mass fraction solution. Both flasks were continuously purged with N₂. THF was transferred into the flasks using a canula. The dissolved PhDI in THF was added to the flask that contained the PDMS via the canula.

Graft polymerization reaction

For both the linear and crosslinked fluorosilicone elastomers, PTFE-VAc-VIA was dissolved in THF to make a 40% mass fraction solution, and it was purged under N₂ for 1 h. Under continuous stirring, the pre-polymer was added via cannula to the dissolved fluorinated polymer. For the linear form, the reaction was monitored by taking samples every 30 min for 2 h and analyzing them using FT-IR. At the end of the reaction, the graft solution was precipitated in a solution of 30% methanol and 70% distilled water. The product was washed and centrifuged in the methanol–water solution three times for 10 min. The product was then dried in the vacuum oven at 60 °C. FT-IR data of PDMS-O(CO)NH-Ph-NCO was as follows: NH (3300 cm⁻¹) and C=O (1750 cm⁻¹) correspond to the urethane bond; free isocyanate (-NCO) (2250 cm⁻¹) corresponds to the functional group at the end of the pre-polymer; and Si-O-Si (1260 cm⁻¹) corresponds to the PDMS (14).

For the crosslinked films, after the pre-polymer was completely added via cannula to the hydrolyzed polymer, the graft solution was immediately cast onto an aluminum dish. Casting of the film was performed at 40 °C. After crosslinking, all films were soaked in methanol for 3 days and then dried under vacuum at 60 °C.

Bulk characterization

Infrared spectra were recorded using the Mattson, Galaxy Series FT-IR 5000. FT-IR was used to monitor the pre-polymer and grafting reactions over time. The attenuated total reflection (ATR) FT-IR was used to analyze the crosslinked films. Solution NMR analysis was performed using the Gemini 300 Spectrometer. ¹H and ¹⁹F NMR were used to analyze the structure of the linear fluorosilicone elastomers.

Degradation and thermal stability analysis was performed using the TGA Q50 by TA Instruments. To identify the 1% mass loss temperature, the elastomer was heated from room temperature to 600 °C at 5 °C min⁻¹.

Surface characterization

Advancing and receding water contact angles were measured on air–film surfaces using a Ramé-Hart NRL tele- scopic goniometer equipped with a Gilmont syringe and a 22-gauge flat-tipped needle. The data presented are the average and standard deviation of at least six measurements made at different areas on the film surface. All contact angles had standard deviations of 1°–3°.

Surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS, Leybold LHMax 200) using an AlKα X-ray source at 15 kV and 25 mA emission current; data were collected at a take-off angle of 90° (between the sample plane and detector). Samples were exposed to X-ray for less than 5 min using pass energies of 192 and 42 eV for survey and C₁s region spectra, respectively. X-ray damage of film surfaces is negligible under these conditions, but is not negligible with longer acquisitions.

Acknowledgements

We are grateful to Peter Odell, Xerox Corporation and the Natural Sciences and Engineering Research Council of Canada (NSERC CRD program) for financial support.

References


© 2005 NRC Canada