Fluorination Effect on Anti-Penetration Performance of Polystyrene-*Block*-Poly(vinylmethylsiloxane)

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Primary CNF Tools Used: YES LP-III vacuum oven, Photolithography Spinners, DISCO Dicing Saw, Jelight 144AX UVO-Cleaner, Veeco Icon AFM, Woollam RC 2 Ellipsometer

Abstract:

A series of fluorinated polystyrene-*block*-poly(vinylmethylsiloxane) (PS-*b*-PVMS) polymers were synthesized by anionic polymerizations and thiol-ene reactions. The synthesized fluorinated PS-*b*-PVMS polymers were further characterized by nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS). The introduction of fluorine can enhance intra and intermolecular interactions, which limit the flexibility of polymer chains and improve polymers' anti-penetration performance.

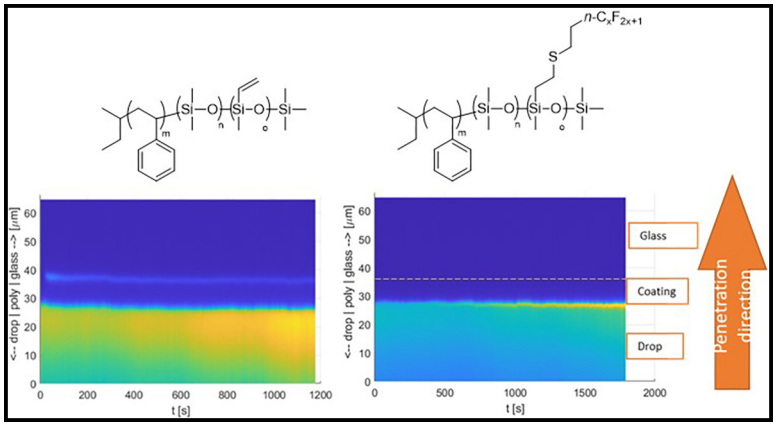

*Figure 1: Anti-penetration performance of nonfluorinated PS-*b*-PVMS (left) and fluorinated PS- PS-*b*-PVMS (right).*

Summary of Research:

Polydimethylsiloxane (PDMS) based surface coating materials are widely explored in antifouling and fouling release materials for marine vessels, as PDMS has low surface energy and elastic modulus, and is chemically stable and eco-friendly. Current research is highly focused on modifying PDMS with different functional groups to tune surface hydrophobicity, hydrophilicity, and amphiphilicity to adjust polymers' antifouling and fouling release performance on the surface [1].

Although fouler or contamination on the surface can be cleaned by water jet, the contamination just under the surface would be a problem that may damage the exposed surface performance and durability, as PDMS is a flexible backbone with nano-sized intermolecular spaces (free volume) and molecular level penetration into PDMS films can occur [2]. The introduction of fluorine is supposed to increase inter/intramolecular interactions [3], and is able to limit polymers' flexibility and movability of the free volume, which should restrict penetration theoretically.

In this research, a series of fluorinated alkyl chains with different lengths are attached to PVMS by thiol-ene click reaction to explore the fluorination effect on the penetration of PDMS.

NMR spectra show that the chemical shifts of fluorine shift to upfield and the chemical shifts of silicon shift to downfield after the fluorinated alkyl chains were grafted to PS-*b*-PVMS backbone, which indicates interactions between fluorine atoms and silicon atoms, as electron acceptors and donors, respectively. DSC results show that the glass transition temperature (T_g) for the PVMS block increases with the length of the fluorinated alkyl chain. SAXS results show that more ordered patterns of hexagonal columns can be observed after the fluorination. Fluorinated PS-*b*-PVMS polymers were dissolved, and spin-coated on glass slides, which were cleaned, and processed by YES LP-III vacuum oven. The test of contact angles of the films shows that fluorination increased the contract angle (water) from 92° of the nonfluorinated precursor to 111°. Penetration

tests on films of fluorinated PS-*b*-PVMS were recorded by a laser confocal microscope with aqueous solutions of Rhodamine B as a dye, which showed that fluorination can effectively improve the anti-penetration performance of PS-*b*-PVMS (see Figure 1).

Conclusions:

Our current results support that the introduction of fluorine in PS-*b*-PDMS enhances intra/intermolecular interactions, which can restrict the movements of free volumes in PVMS and improve its anti-penetration performance.

References:

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[3] Kim, S.; Saxena, A.; Kwak, G.; Fujiki, M.; Kawakami, Y. Chem. Commun. 2004, 538.539.