Silicone fouling-release coatings: effects of the molecular weight of poly(dimethylsiloxane) and tetraethyl orthosilicate on the magnitude of pseudobarnacle adhesion strength

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A series of poly(dimethyl siloxane) (PDMS)/silica nanocomposites were synthesized utilizing a sol gel method. The samples were evaluated using pseudobarnacle adhesion and tensile strength tests. The effects of the molecular weight of the PDMS and the size and structure of the silica domains on biofouling release and the mechanical behavior of the PDMS/silica materials were investigated. Three different molecular weights (18,000, 49,000 and 79,000 g mol$^{-1}$) of hydroxyl-terminated PDMS (HT-PDMS) were used to prepare the nanocomposites with three different weight ratios (1:1, 3:1 and 5:1) of HT-PDMS to tetraethyl orthosilicate (TEOS). TEOS served as a crosslinker to form PDMS networks and as a precursor to form silica domains. Two different variants of TEOS with regard to its degree of polymerization ($n$) (monomeric type: $n \approx 1$ and oligomeric type: $n \approx 5$) were used for in situ formation of silica particles via the sol-gel process. The mechanical properties of the composites were characterized using stress–strain isotherms. All the mechanical properties evaluated (Young’s modulus, tensile strength, energy required for rupture, elongation at break) improved with increases in the molecular weight of the HT-PDMS and the silica content. The pseudobarnacle adhesion test was used to examine the fouling-release (FR) properties of coatings applied on aluminum plates. The rupture energy and tensile strength increased substantially when oligomeric TEOS was employed in the PDMS/silica composites. Scanning electron microscopy (SEM) was used to investigate the structure of the silica domains. It was found that the use of oligomeric TEOS in higher molecular weight PDMS samples with higher PDMS/TEOS weight ratios led to low pseudobarnacle adhesion strengths of $\approx 0.3$ MPa, which is in the range of commercial FR coatings.

Keywords: biofouling release; poly(dimethylsiloxane)/silica nanocomposites; pseudobarnacle adhesion; stress–strain isotherms, fouling-release coatings

Introduction

Biofouling is ubiquitous in the marine environment. This fouling that clings to the hulls of ships results in increased operational and maintenance costs by increasing the fuel consumption and frequency of dry-docking operations (Callow 1990; Townsin 2003; Yebra et al. 2004; Schultz et al. 2011). Toxic antifouling paints containing copper, tin and other biocides have been applied to ships to combat fouling (Rascio 2000; Thomas and Brooks 2010) until the use of tin-based paints was banned by environmental organizations (Champ 2000; Dafforn et al. 2011). This legislation led to the development of fouling-release (FR) coatings as an alternative nontoxic technology (Brady et al. 1987; Brady 1994, 1997, 2000; Adkins et al. 1996). Although organisms can attach to these coatings, they are removed by either mechanical or forceful water movement, which is caused by the motion of the vessel (Swain and Schultz 1996; Kavanagh et al. 2005).

Initially, both silicones and fluoropolymers were identified as FR surfaces because both polymers exhibit low critical surface tension and this character is considered crucial for foul releasing ability (Baier and Meyer 1992; Callow and Fletcher 1994). Baier and Depalma (1971) studied the relationship between the critical surface tension of the polymer surface and the relative amount of bioadhesion. The results were shown as the “Baier curve.” An important feature of this curve is that the minimum in bioadhesion does not occur at the lowest critical surface energy. The minimum of the Baier curve is attributed to poly(dimethylsiloxane), which has a very low elastic modulus (0.002 GPa). Later, it was found that the FR behavior of polymers depends not only on the surface energy but also upon mechanical properties such as the elastic modulus (Brady and Singer 2000; Singer and Kohl 2000; Brady 2001). Because of this, silicone polymers outperformed fluoropolymers (Brady 1999). Furthermore, fluoropolymers are porous, thus they allow