

## Novel solid-lubricant materials for multifunctional applications

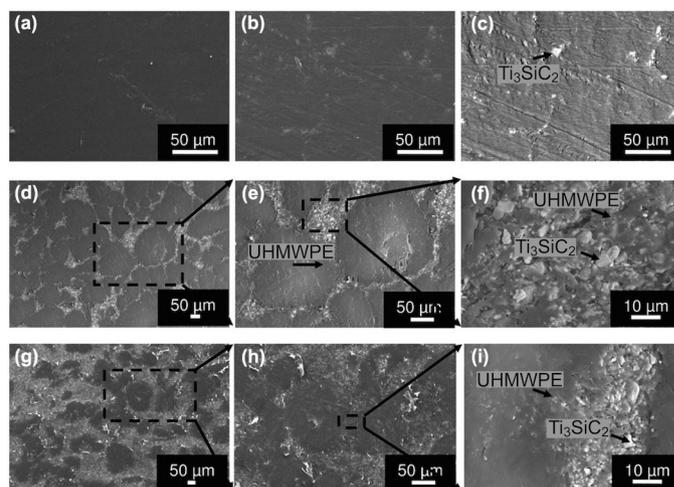
Surojit Gupta, M. F. Riyad, Sujan Ghosh, and Ross Dunnigan

*The addition of thermodynamically stable nanolaminates to thermosets and thermoplastics improves the performance of polymer matrix composites.*

Polymers and their composites possess excellent friction and wear characteristics, corrosion resistance, and mechanical properties that make them potential replacements for metals in many applications.<sup>1–6</sup> Self-lubricating composites are particularly attractive because of their simple design, easy operability, and low cost, among other things. Moreover, the use of additives such as kaolin,<sup>2</sup> molybdenum disulfide,<sup>3,7</sup> multiwalled carbon nanotubes,<sup>5,8,9</sup> calcium stearate,<sup>6</sup> wollastonite,<sup>10</sup> short fibers,<sup>11</sup> boron trioxide,<sup>12</sup> serpentine,<sup>13</sup> and silica<sup>14</sup> has been shown to further enhance the mechanical and tribological performance of polymers. In previous studies<sup>7–14</sup> it has been hypothesized that the addition of hard, machinable, conductive, and lubricious particles, such as  $\text{Ti}_3\text{SiC}_2$  (MAX phase) will significantly alter the mechanical and tribological behavior of polymer matrix composites (PMCs). Briefly,  $M_{n+1}AX_n$  (MAX) phases (more than 60 phases) are thermodynamically stable nanolaminates where  $n$  is 1, 2, or 3,  $M$  is an early transition metal element such as titanium (Ti),  $A$  is an A-group element such as silicon (Si), and  $X$  is carbon (C) or nitrogen. MAX phases are layered hexagonal, with two formula units per cell. These solids are highly damage tolerant, thermal shock resistant, and readily machinable.<sup>15–19</sup>

In a series of studies, we have reported that the addition of  $\text{Ti}_3\text{SiC}_2$  particulates, in both thermosets<sup>23</sup> and thermoplastics<sup>20–22</sup> enhances the mechanical performance and solid-lubrication behavior of PMCs. We have coined the term MAXPOL—composites of MAX phases and polymers—to designate this new generation of composites. Our detailed methods for fabrication and the characterization procedure are available elsewhere.<sup>19,23</sup> We have found that MAXPOL composites show solid-lubrication behavior during self-mating,<sup>20,21</sup> and here we review some of the important results from our recent studies.

Scanning electron microscopy (SEM) images of  $\text{Ti}_3\text{SiC}_2$ -UHMWPE (ultra-high-molecular-weight polyethylene) composites are shown in Figure 1.<sup>20</sup> We find that the  $\text{Ti}_3\text{SiC}_2$  particulates are well dispersed in the UHMWPE matrix when the concentration of  $\text{Ti}_3\text{SiC}_2$

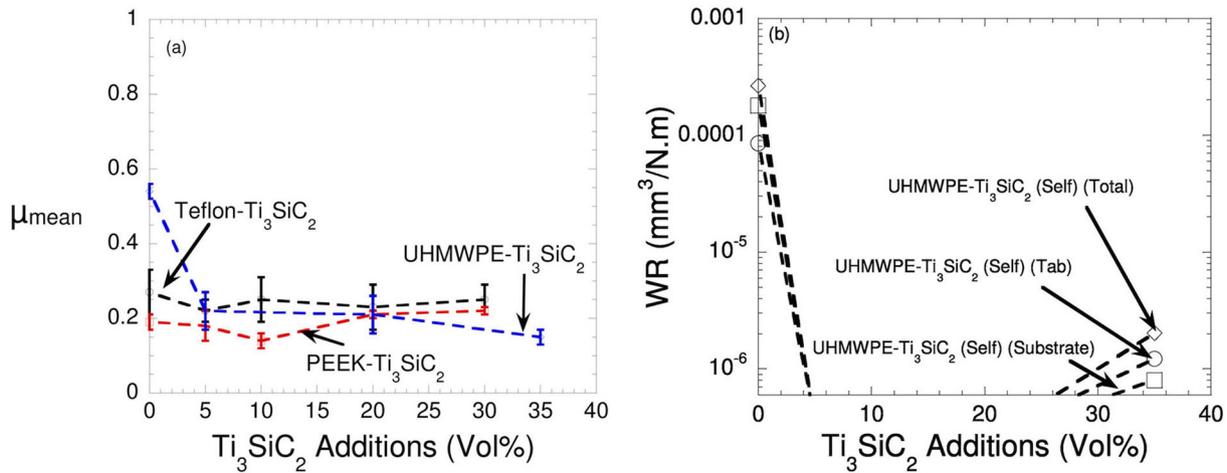


**Figure 1.** Secondary electron (SE) scanning electron microscopy (SEM) images of (a) pure ultra-high-molecular-weight polyethylene (UHMWPE), (b) 5vol.%  $\text{Ti}_3\text{SiC}_2$  (MAX phase)-UHMWPE, and (c) a backscatter electron (BSE) image of the same region. (d) and (g) are SE SEM images of 20 and 35vol.%  $\text{Ti}_3\text{SiC}_2$ , respectively. The same samples are shown at higher magnification in (e) and (h), and as BSE images of the same regions in (f) and (i).<sup>20</sup>

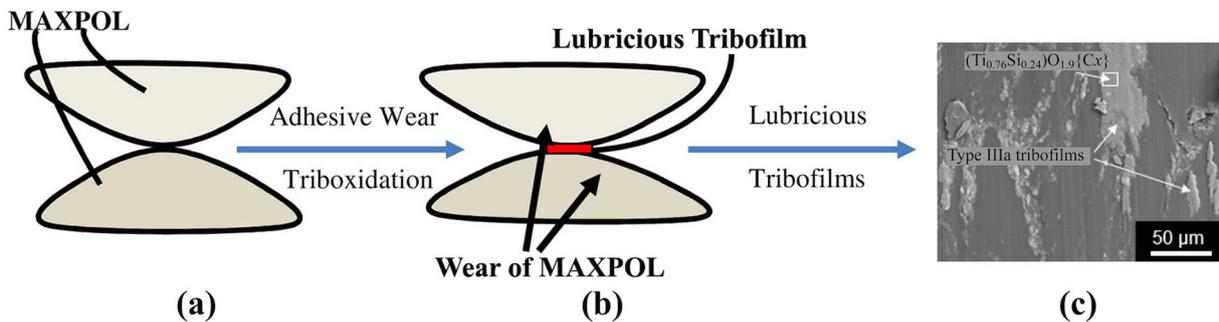
particulates is about 5vol.%, as shown in Figure 1(b) and (c). In contrast, the  $\text{Ti}_3\text{SiC}_2$  particulates segregate to form  $\text{Ti}_3\text{SiC}_2$ - and UHMWPE-rich interfaces around the UHMWPE matrix at higher concentrations of  $\text{Ti}_3\text{SiC}_2$ , as shown in Figure 1(d) to (i). At this juncture, we are not sure of the exact mechanism causing this behavior, but most probably, dewetting of  $\text{Ti}_3\text{SiC}_2$  particulates by the polymer causes the  $\text{Ti}_3\text{SiC}_2$  particulates to segregate in  $\text{Ti}_3\text{SiC}_2$ -rich polymer regions.

The mean friction coefficient ( $\mu_{\text{mean}}$ ) and wear rate (WR) of our composites, as a function of the addition of  $\text{Ti}_3\text{SiC}_2$  particulates, are summarized in Figure 2. UHMWPE sliding against itself exhibits a higher  $\mu_{\text{mean}}$  compared with the  $\text{Ti}_3\text{SiC}_2$ -UHMWPE composite sliding against itself, as shown in Figure 2(a). Teflon- $\text{Ti}_3\text{SiC}_2$  and polyetheretherketone (PEEK)- $\text{Ti}_3\text{SiC}_2$  composites showed a similar trend, which suggests that  $\text{Ti}_3\text{SiC}_2$  particulates may prove an effective solid-lubricant additive in a host of polymer matrices.

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**Figure 2.** Plot of (a) the mean friction coefficient ( $\mu_{mean}$ ) and (b) wear rate (WR), as a function of adding of  $Ti_3SiC_2$  to UHMWPE composites. PEEK: Polyetheretherketone. Tab: Test material.<sup>20–22</sup>



**Figure 3.** Schematic illustration of the formation of a type IIIa tribofilm. (a) Tribocontact formation during self-mating of MAXPOL (MAX phases plus polymers). (b) Formation of tribofilms by mild adhesive wear and tribooxidation of both surfaces during tribology studies. (c) SE SEM image of type IIIa tribofilms.  $Ti_{0.76}Si_{0.24}O_{1.9}\{Cx\}$ : Example chemical composition of a type IIIa tribofilm.<sup>19,20</sup>

The WR results—see Figure 2(b)—are also very promising. During self-mating, both surfaces showed wear. The total WR of the UHMWPE surfaces was less than about  $1.6 \times 10^{-4} \text{ mm}^3/\text{N.m}$ , whereas in 5vol.%  $Ti_3SiC_2$ -UHMWPE and 20vol.%  $Ti_3SiC_2$ -UHMWPE the WR was negligible (less than  $4 \times 10^{-7} \text{ mm}^3/\text{N.m}$ ). The WR then increased to about  $2 \times 10^{-6} \text{ mm}^3/\text{N.m}$  in 35vol.%  $Ti_3SiC_2$ -UHMWPE. We could not detect wear in the 5vol.%  $Ti_3SiC_2$ -UHMWPE and 20vol.%  $Ti_3SiC_2$ -UHMWPE compositions after cycling for 10,000m. This further indicates the long-term stability of these composites during self-mating.<sup>20</sup>

A detailed investigation of the wear tracks showed that the tribology of  $Ti_3SiC_2$ -UHMWPE composites is driven by the formation of tribofilms.<sup>19,23</sup> We have previously shown that the tribological behavior of MAX phases and their composites is driven by tribofilm formation.<sup>19</sup> The tribofilms formed during self-mating of

$Ti_3SiC_2$ -UHMWPE composites made thin layers over each tribosurface. Using a previously proposed classification,<sup>19</sup> we find that the tribofilms correspond to type IIIa. A simple schematic diagram, in which lubricious tribofilms are formed at tribocontacts, is shown in Figure 3.

In summary, we have synthesized and characterized novel MAXPOL composites. The addition of  $Ti_3SiC_2$  particulates enhances both the mechanical behavior and, especially, the tribological performance of the materials. Tribofilms that formed during self-mating of  $Ti_3SiC_2$ -UHMWPE composites were barely visible to the naked eye and formed thin layers over each tribosurface (as observed by SEM). We therefore classified these tribofilms as type IIIa.<sup>20</sup> Our tribological studies showed that the addition of  $Ti_3SiC_2$  in the UHMWPE matrix imparts

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self-lubricity to the composites and aids in decreasing adhesive wear during dry sliding of polymer-on-polymer tribocouples. In particular—when used in a polymer matrix to reduce adhesive wear— $Ti_3SiC_2$  particulates can lead to the development of polymer-on-polymer wear couples, which may provide engineers with novel approaches for designing devices.<sup>24</sup> We are currently conducting studies to investigate the wetting behavior of  $Ti_3SiC_2$  and polymers. We are also exploring novel polymer systems such as PEEK, Teflon, and polylactic acid. In addition, we are developing novel techniques for 3D printing of these composites.

*Surojit Gupta acknowledges start-up and Senate Scholarly Activities Committee funding from the University of North Dakota and from the NASA Experimental Program to Stimulate Competitive Research (grant NNX13AB20A). The authors would like to thank Kanthal Inc. for supplying the  $Ti_3SiC_2$  powders. North Dakota State University Electron Microscopy Center core facility is also acknowledged for the microscopy work. This article is also based on work supported by the National Science Foundation (grants 0619098 and 1229417). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.*

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