

A wear-resistant composite material based on polyvinyl alcohol

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Polyvinyl alcohol composites containing silicon-carbide particles that were modified by a silane coupling agent achieve enhanced mechanical and wear properties.

Today, polymeric nanocomposites are used for a wide range of tribological applications, most notably in machinery fields (e.g., in medical devices and artificial joint-bearing surfaces). The traditional polymers

used for tribological applications are polyethylene (PE),¹ polyamides (PAs),² and poly(ether ether)ketones.³

As a biodegradable and eco-friendly material, polyvinyl alcohol (PVA) is widely used in many industrial applications, such as in films, emulsifiers, paper coatings, adhesives, and textile sizing. PVA films with small-molecule plasticizers exhibit flexible characteristics. To further increase the mechanical strength of PVA, fillers—such as cellulose nanofillers⁴ and graphene oxide⁵—have been used, with good results. The compatibility and interactions between the filler and matrix are a key criterion for obtaining

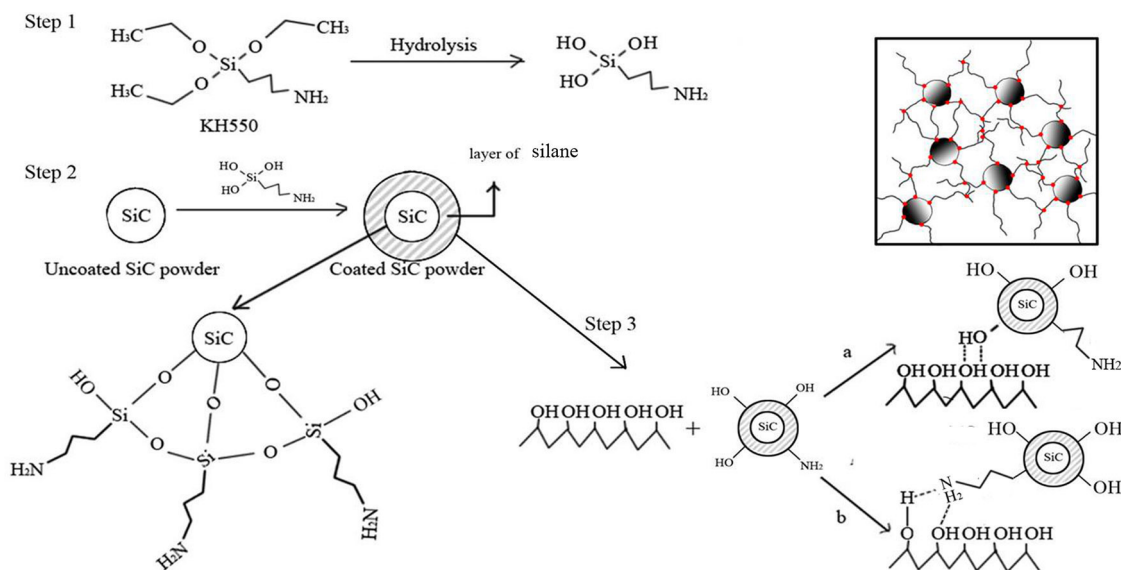


Figure 1. Schematic illustration of the silicon carbide-silane modification process, and the interaction mechanism between the silane coupling agent (KH550) and the polyvinyl alcohol (PVA) matrix. Si: Silicon. SiC: Silicon carbide. OH: Hydroxy group. NH₂: Amine group. In step 1, the silane coupling agent (γ -aminopropyltriethoxysilane, KH550) is hydrolyzed to generate silane with a large number of Si-OH bonds (which arise due to the acidic conditions introduced by acetic acid). In step 2, the reaction of dehydration with hydroxyl groups on the surface of SiC leads to the formation of siloxane (Si-O-Si) bonds, causing a layer of silane to be deposited on the SiC nanoparticles. Finally, in step 3, the filler and matrix are blended and the polar groups (on the modified SiC) and -OH groups (of the PVA) form strong hydrogen bonds.

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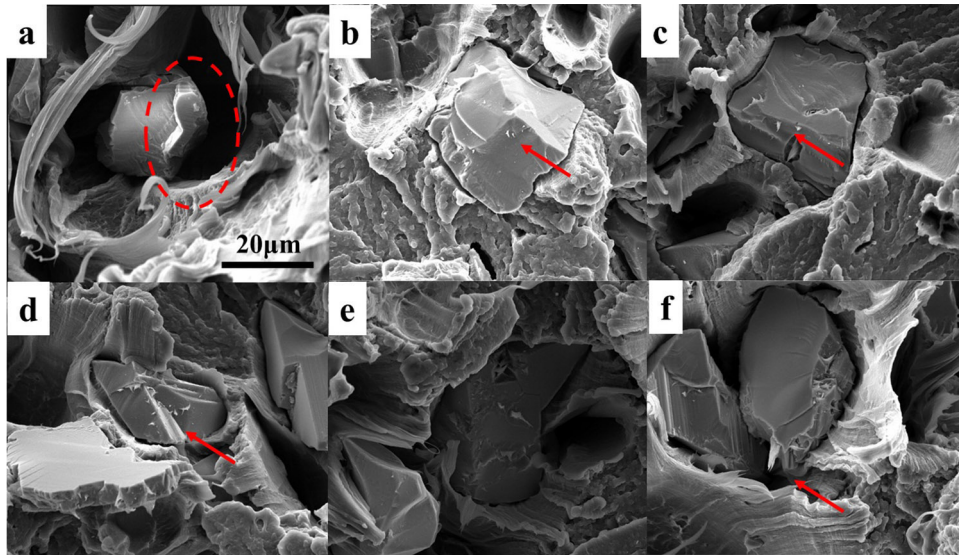


Figure 2. Scanning electron microscope images showing the fracture surface of the PVA/SiC composites after tensile tests. The results shown are for PVA/SiC samples composed of (a) unmodified SiC particles—the dashed circle indicates the presence of visible gaps between the two phases, and the smooth surface of these particles, reflecting unsatisfactory interfacial interaction—and SiC particles modified with the KH550 silane coupling agent at concentrations of (b) 1, (c) 1.5, (d) 2, (e) 3, and (f) 4wt% (arrows indicate areas where the PVA matrix is bonded tightly to the surface of the treated SiC particles).

composites with good mechanical properties.^{6,7} To achieve good compatibility between the filler and matrix, modification of the filler surface is usually recommended. By grafting or coating with a coupling agent (e.g., silane or titanate), the compatibility between the filler and matrix can be significantly improved, thus enhancing the mechanical properties of the resultant composite.⁸ No research has yet been carried out, however, on the tribological performance of PVA composites.

In our work, we therefore used surface-modified silicon carbide (SiC) as a filler in PVA to investigate its suitability for tribological applications. We chose SiC as a filler because it is a good abrasive and thus should improve the wear resistance of PVA. To prepare the surface-coated SiC, we dispersed the particles in silane coupling agent/ethanol solutions with different concentrations. We then fabricated the PVA/modified-SiC composites via a melt process and subjected the samples to a number of tensile tests to determine their mechanical properties.

To fabricate PVA/modified-SiC composites, we first hydrolyzed the silane coupling agent (γ -aminopropyltriethoxysilane, KH550) under acidic conditions. As a result, a large number of hydroxyl and amino groups were generated in the KH550. When introduced to the PVA during the melt process, these polar groups formed hydrogen bonds with the hydroxyl groups within the PVA molecular chains. Thus, the interactions between the filler and the matrix were improved with the

use of the coupling agent. We also found that the surface-modified SiC particles were well dispersed within the PVA, thereby enhancing their compatibility with the matrix. The surface-modification process of the SiC by KH550, and the mechanism by which interfacial interactions are improved between the modified SiC and PVA, are presented in Figure 1.

To determine the mechanical properties of the composites, we subjected them to tensile tests following the ASTM D638-2003 standard. We carried out the measurements at room temperature and implemented an extension speed of 100mm/min and an initial gauge length of 40mm. The samples were conditioned in a relative humidity (RH) of 35% and were saturated in magnesium chloride solution for two days before testing. Scanning electron microscope (SEM) images of the fractured surface (i.e., obtained after the tests) of SiC/PVA composites, with and without surface modification, are shown in Figure 2. For the control composite (composed of PVA and uncoated SiC particles), we observed visible gaps between the two phases and found that the surface of the SiC particles is smooth, without any adhesion—see Figure 2(a)—reflecting an unsatisfactory level of interfacial interaction. In contrast, the treated SiC particles were still tightly bound to the matrix after tensile tests and we detected no gaps at the filler–matrix

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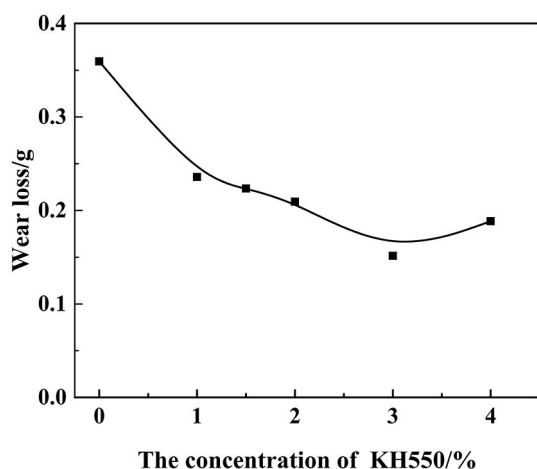


Figure 3. Graph showing the effect of the KH550 silane coupling agent on the wear resistance of PVA/SiC composites.

interface: see Figure 2(b–f). These SEM images show that the PVA matrix was bonded tightly to the surface of the treated SiC particles and that, as the coupling-agent concentration is increased (from 1 to 4wt%), this behavior is enhanced.

In the next stage of our experiments, we performed measurements of the wear behavior of our composites—to investigate the effect of coupling-agent concentration on their mechanical properties—using a wear-testing machine. The wear test is used to characterize the shear resistance of materials under the action of a shearing force. Figure 3 shows the effect of the silane coupling agent on the wear resistance of the PVA/SiC composites. We thus found that the wear-loss quality of the composites decreased and the resistance was increased at larger KH550 concentrations. Our results show that the best wear resistance is achieved by composites with a coupling agent concentration of 3% (an improvement of ~40% over PVA/SiC composites fabricated without KH550). At higher concentrations (4%), we found that the wear loss increased, and thus wear resistance had decreased. We attribute this result to excess KH550 forming aggregates or multi-molecular layers in the system, thus weakening the interfacial bonding force between the nanoparticles and the PVA matrix.

In summary, we have found that, by modifying SiC particles with a silane coupling agent (KH550), the interaction and thus the adhesion with a PVA matrix are increased. As a result, our PVA/SiC composites exhibited improved mechanical properties. For example, we found that the wear resistance was greatly improved (by ~40%) when a coupling agent was used at a concentration of 3wt%. In our future work, we plan to optimize the chemical bond of the fillers with the matrix to produce environmentally friendly composite materials with excellent mechanical properties and wear resistance.

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References

1. N. P. Suh, J. M. Mosleh, and J. Arinez, *Tribology of polyethylene homocomposites*, **Wear** **214**, pp. 231–236, 1998.
2. L. Zsidai, P. De Baets, P. Samyn, G. Kalacska, A. P. Van Peteghem, and F. Van Parys, *The tribological behaviour of engineering plastics during sliding friction investigated with small-scale specimens*, **Wear** **253**, pp. 673–688, 2002.
3. Z. P. Lu and K. Friedrich, *On sliding friction and wear of PEEK and its composites*, **Wear** **181**, pp. 624–631, 1995.
4. D. Liu, X. Sun, H.-F. Tian, S.-S. Maiti, and Z.-S. Ma, *Effects of cellulose nanofibrils on the structure and properties on PVA nanocomposites*, **Cellulose** **20**, pp. 2981–2989, 2013.
5. D. Liu, Q.-B. Bian, Y. Li, Y.-R. Wang, A.-M. Xiang, and H.-F. Tian, *Effect of oxidation degrees of graphene oxide on the structure and properties of poly (vinyl alcohol) composite films*, **Compos. Sci. Technol.** **129**, pp. 146–152, 2016.
6. P. Krishnaiah, C. T. Ratnam, and S. Manickam, *Development of silane grafted halloysite nanotube reinforced polylactide nanocomposites for the enhancement of mechanical, thermal, and dynamic-mechanical properties*, **Appl. Clay Sci.** **135**, pp. 583–595, 2017.
7. J. Feng, S. R. Venna, and D. P. Hopkinson, *Interactions at the interface of polymer matrix-filler particle composites*, **Polymer** **103**, pp. 189–195, 2016.
8. L. N. Carli, T. S. Daitx, G. V. Soares, J. S. Crespo, and R. S. Mauler, *The effects of silane coupling agents on the properties of PHBV/halloysite nanocomposites*, **Appl. Clay Sci.** **87**, pp. 311–319, 2014.