

MECHANICAL AND TRIBOLOGICAL PROPERTIES OF MICROPARTICULATE AND NANOPARTICULATE REINFORCED POLYMER COMPOSITES

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SUMMARY: It is well known that inorganic particles can improve the mechanical properties of polymeric materials. The state of dispersion, the size and the shape as well as the content of the particles determine hereby widely stiffness, toughness and wear performance of the composites. In the present study, micro- and nano-dimensional ceramic particles (SiC, $5\mu m$ and $10\mu m$; TiO₂, $300nm$) were introduced as reinforcing fillers into an epoxy matrix. The influence of the fillers on impact toughness, dynamic mechanical properties and block-on-ring wear behavior of the composites was investigated. To understand the mechanisms involved in the performance enhancement, the morphology of wear traces, wear debris and fractured surfaces were examined. The results clearly showed an improvement in stiffness and specific wear rate of the SiC micro-particulate filled epoxy, whereas the impact toughness suffered. The TiO₂ nanocomposites demonstrated an improvement of the general performance, stiffness, toughness and wear, where geometrical properties of the particles and their dispersion state mostly contribute to the increase in performance.

KEYWORDS: nanoparticle; nanocomposite; microparticles; polymer; wear; dispersion, mechanical properties.

INTRODUCTION

Incorporation of inorganic particles into polymers is known to be an effective way to produce composite materials with improved mechanical properties. This is especially important in applications under severe working conditions, such as load carrying slide bearings and calendar cover coatings for the paper making industry. The degree of filler reinforcement is generally determined by a series of factors, including component properties, composition, filler/matrix bonding, and microstructure represented by homogeneity of filler dispersion, filler size and shape.

As compared with the other influencing factors cited here, the interface between filler and matrix plays a critical role, since composite technology is based on yielding a combination of properties that cannot be achieved by either of the components acting alone. It is expected that the properties of a composite, which contains a large number of particles with high surface area, would be greatly affected because the interfaces constitute a rather high volume fraction of the bulk material. Figure 1 shows the ideal correlation between the relative number of particles and the particle size for a constant filler content of 3vol.%. Within a cross section of $50\mu m \times 100\mu m$, this leads to about 2 particles if the diameter amounts to $10\mu m$, 200 particles in case of $1\mu m$ diameter and roughly 20000 particles of $100nm$ in diameter. In this context, nanoparticles filled composites would prevail micrometer-sized particulate composites. Of course, this can be true provided the nanoparticles are well dispersed on a nanometer level in the surrounding polymer matrix [1]. Only in this case, the deficiency induced by the heterogeneity of conventional particles filled

composites can be avoided [2]. Recent advances indicated that polymer based nanocomposites possess reduced frictional coefficients and wear rates. Wang et al. [3-8] reported that the incorporation of nanosized ZrO_2 , SiO_2 , Si_3N_4 and SiC into polyetheretherketone (PEEK) caused a considerable improvement in the tribological characteristics. Reinforcement was reached by incorporating only a small amount of fillers (7.5wt.%) at a particle size below $15nm$. In some cases, the dominant wear mechanism changed from melting adhesive transfer wear to slight transfer wear, and finally to abrasive wear with increasing nano-filler content. Rong et al. [9]

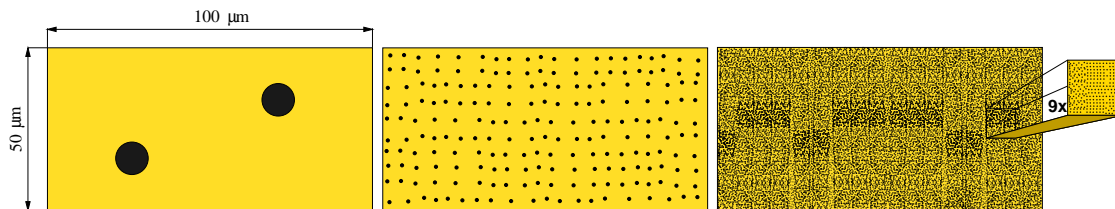


Figure 1: Correlation between relative number of particles and particle size (3vol.%, $5000\mu m^2$). **Left:** 2 particles, $10\mu m$; **Center:** 200 particles, $1\mu m$; **Right:** 20000 nanoparticles, $100nm$.

conducted tribological experiments on epoxy/ TiO_2 nanocomposites and showed that the performance significantly depended on the dispersion state and micro structural homogeneity of the fillers. An improvement of the dispersion state and the mechanical properties was reached by Ng et al. [10] who successfully applied an ultrasonic approach to disperse TiO_2 nanoparticles in epoxy, even when very small particles ($32nm$) were used. The resultant nanocomposites appeared not only to be tougher than the traditional micro-particle filled epoxy but also possessed a higher scratch resistance.

Schadler et al. [11] produced silica/polyamide nanocomposite coatings by using high-speed oxyfuel thermal spray processing. It was found that the surface chemistry of the nano-silica affected the final coating properties. Silica particles with a hydrophobic surface resulted in higher scratch resistance than those with a hydrophilic surface. The presence of nanosized fillers can affect the micro-morphology of the polymer and significantly improve the fracture toughness due to crack deviating processes [12, 13].

Riley et al. [13] found that the stiffness of mineral filled polypropylene is determined by the filler modulus and a favorably high aspect ratio of the particles. The impact strength, on the other hand, seems to be mainly enhanced by small particles with low aspect ratio. While large particles can act as crack initiators, the high aspect ratio particles are able to induce large stress concentration near their edges. Hussain et al. [14] stated that even the thermal contraction behavior of epoxy at low temperature can be controlled by the particle size. Nano-sized silica brought a lower contraction compared to micro-silica.

Surprisingly, very few papers have been presented up-to-date concerning comparative study of the relationship between micro structural details and tribological properties of polymer based micro- and nanocomposites. This topic is fundamentally significant for the development of nanocomposites for new technical applications. Therefore, the present work is focused on the mechanical and tribological performance of composites with differently sized and shaped reinforcing components, with the objective of understanding the geometric role of the inorganic fillers on micro- and nanometer scales.

EXPERIMENTAL

A commercially available epoxy resin matrix system (Araldit) was provided by Ciba Specialist Chemicals Ltd. and Vantico Ltd. It consists of the resin components cured by an amine curing agent. Different inorganic filler particles were introduced into the epoxy matrix: micron sized silicon carbide (SiC) ceramic with an average particle diameter of $10\mu m$ and $5\mu m$ were used in both virgin and silane treated state. The titanium dioxide (TiO_2) ceramic powder in a size range of 200 to $400nm$ was chosen because the particles possess a high specific surface area. In the unmixed condition (without the EP-matrix), the particles have a tendency to agglomerate in units of 2 to $12\mu m$ (Fig.2(d)). The filler content amounted to $17.5vol.\%$ but one batch was only incorporated with $7.5vol.\%$ TiO_2 . Typical filler morphologies and the averaged particle diameters are depicted below in Figure 2 on the next page.

To gain experience about the impact toughness of the composites, instrumented Charpy impact testing was performed in accordance to DIN-ISO-179/1eU using a Ceast pendulum ram impact testing machine and rectangular, unnotched specimens with $80mm$ in length, $10mm$ in width and $4mm$ in height. The distance between the supports was set to $62mm$. All specimens were crashed by an impactor mass of $2.19kg$ at impact speeds of $3.7m/s$ and impact energies of $15J$. Dynamic mechanical testing (DMTA) was performed using a Gabo Eplexor $150N$ in a three-point bending configuration to examine the dynamic mechanical responses. The complex elastic modulus and the glass transition temperature T_g were measured. The temperature range covered $-100^\circ C$ to $300^\circ C$ at a heating rate of $1^\circ C/minute$, and the amplitude of the static load was chosen to be $40N$ and that of the dynamic load $20N$ at a constant frequency of $10Hz$.

Unlubricated sliding wear tests to determine the friction and wear properties were carried out on a six-lever-block-on-ring apparatus designed and constructed at the Institute for Composite Materials (IVW). A smoothly polished and hardened carbon steel ring ($100Cr6$), $60mm$ in diameter, with an initial surface roughness of $R_a = 0.1\mu m$, served as a counter body. Under ambient conditions, after a running-in period of two hours, the ring was slid against the epoxy composite specimen for 24 hours at a constant speed of $1m/s$ and a pressure of $1MPa$. The specific wear rate was calculated by determining the specimens mass loss after the experiment. The worn surfaces, the morphologies of the wear traces and also the wear debris were examined by a JEOL 5400 scanning electron microscope (SEM) to receive information about the influence of fillers on the corresponding wear mechanisms.

The composites were prepared by applying conventional mechanical mixing methods using a commercially available laboratory mixing device. The particles were firstly dried in an oven at $60^\circ C$ for several hours. To lower the resin viscosity and to enable a better wetting of the filler particles, the epoxy resin components were preheated up to a temperature of $60^\circ C$. The mixing process was then conducted at the same temperature in a tempered water bath. The fillers were continuously filled into the resin followed by mechanical stirring for 30 minutes. Vacuum was applied during the whole process to eliminate entrapped air that would significantly lower the mechanical properties. Nanoparticles in general tend to agglomerate due to their high specific surface area. The particle attraction is hereby caused by adhesive forces emanating from the surface energy. To break down these agglomerates and to receive a finer particle distribution within the matrix, ultrasound vibration was applied. Finally, the hardener was added to the suspension followed by further mixing for 5 minutes. The mixture was filled into moulds by using a vacuum pump and cured in an oven. Test specimens were cut off from the cured composite plates.

RESULTS AND DISCUSSION

General morphologies of the particles: The sizes and shapes of different particles can be observed from Figure 2. SiC ($10\mu m$, Fig.2a) reveals a homogeneous size, a relatively smooth surface and some pointed corners. SiC ($5\mu m$, Fig.2b), in contrast, possesses peaky corners as well as needle- and plate-like structures. SiC ($5\mu m$, modified, Fig.2c) exhibits structures somewhere in between the shapes of (a) and (b). However, some of the particles are by far larger than $5\mu m$. The TiO₂ nanoparticles finally display an almost spherical structure, although they occur only as agglomerates.

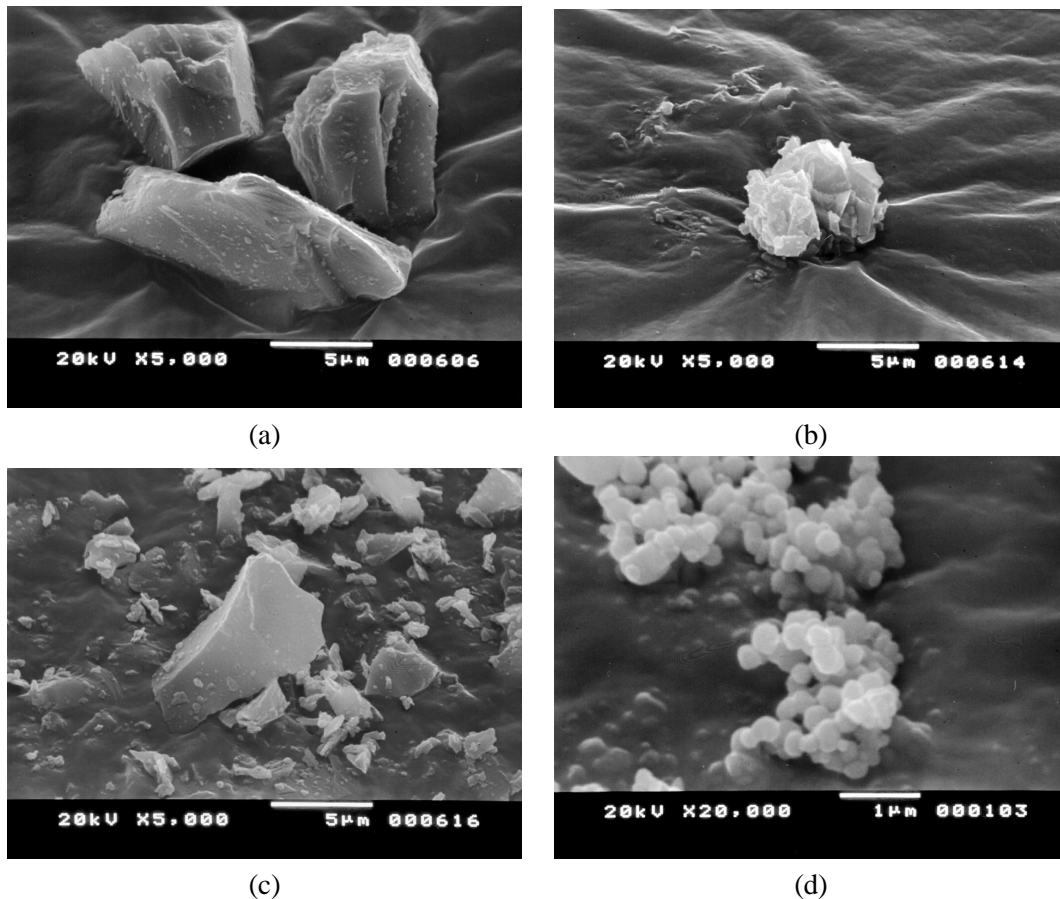


Figure 2: Typical shape and size of the filler particles: (a) SiC $10\mu m$, (b) SiC $5\mu m$, (c) SiC $5\mu m$, modified and (d) TiO₂, 200 to 400nm.

Impact strength and dynamic mechanical properties:

Figure 3 (top) shows the impact strengths of the thermosetting epoxy (EP) composites investigated and its relation to the different particle sizes of the filler materials incorporated.

The micro-composites containing SiC exhibit a significantly lowered impact strengths, even below that of the neat matrix. The $5\mu m$ sized SiC particles seem to strongly increase the brittleness of the composite material, probably due to the inhomogeneous particle shape. Such an angularity can induce localized internal stress concentrations at regions of sharp edges and corners, which would, as a result, facilitate failure under impact conditions.

The impact strengths of the TiO₂ nanocomposites on the contrary are remarkably improved, especially at a low filler content of 7.5vol.% TiO₂. The relatively large scatter occurring for the 17.5vol.% TiO₂-filled material indicates that stress inducing particle agglomerates can still be

expected within the matrix, although ultrasound vibration was applied during the compounding process. At such high filler loadings, the nanoparticles must be very close to each other, so that these short interparticulate distances can generate an overlap and a resulting intensification of the stress fields around the particles. However, the average impact strengths of both materials still exceed the value of the neat matrix.

The fracture surfaces of the samples in Figure 4 indicate a relatively brittle failure behavior with smooth fracture planes in between the particles. The fracture surface of EP-SiC (Fig.4, left) appears to be much rougher than that of the EP-TiO₂ nanocomposite (Fig.4, right). In the latter, particle agglomerates can clearly be detected within the fracture surface. Figure 3 (bottom) contains some information about the dynamic mechanical behavior at a temperature of 23°C. The general tendency remains the same over the entire temperature range tested.

All composites examined show extended values of the complex modulus which can be twice as high as that of the neat matrix, especially in the case of SiC-micro-particle reinforced materials. The latter remain on a similar level at about 6000MPa, independent of the particle size. In addition, the fillers increase the glass transition temperature T_g , relative to the neat polymer.

Wear performance: Figure 5 shows the specific wear rate for the neat epoxy as compared to that of the micro- and nanocomposites. It is seen that a high impact toughness of the material (Fig.3, left) is not bound to result in a high wear resistance. Instead, the stiffness of the composites (Fig.3, right) seems to be more closely related to the wear performance. The wear rate of 10μm-SiC and 5μm-SiC filled composites reach half the level of the neat EP. It appears that the modification of the SiC (5μm) has only a little effect on the wear performance.

An interesting phenomenon seems to be induced by the nanoparticle fillers. One can observe a reduction of the wear rate by a factor of 5 for the 17.5vol.% filled EP-TiO₂ and, in fact, a factor of nearly 10 for the nanocomposite containing a low particle content: 7.5vol.%. In order to understand these effects, the wear surfaces were studied by SEM-examinations to provide knowledge about the wear mechanisms. Representative wear patterns are displayed in Figures 6 to 9 for EP, EP-SiC (5μm) and EP-TiO₂ composites, respectively. The wear patterns of EP-SiC (10μm) appeared to very similar to that of EP-SiC (5μm) and are therefore not depicted. The wear surface for the neat EP looks severely ploughed and abraded (Fig.6), whereas the surfaces of EP-SiC possess a system of rough and smooth striations parallel to the sliding direction (Fig.7 (left)). The rougher striations are deeper and contain indications of severe ploughing and therefore abrasive wear effects. On the smooth areas, consisting of compacted wear debris, cracking phenomena of the latter lead to the detachment of large, plate-like units. Such plates are depicted in Figure 7 (right) and are also representative for the morphology of the wear debris. Due to a greater appearance of the smooth areas on the wear surface of the composite containing 5μm-SiC, it seems that the formation of these compacted wear debris regions and their longer remaining on the specimen surface protects the material underneath and thus leads to lower wear rates. These smooth areas do also occur on the surface of the 17.5vol.% TiO₂ filled nanocomposite (Fig.8, left), and here they are even larger, which means that the deeper, rough wear grooves are much smaller. Here, the wear process delaminates thin and long board-like structures (100-200μm in length) as well as small plates from the specimen surface (Fig.8, right). According to the delamination theory of wear [16], it particularly means that relatively homogeneous stress concentrations can develop in a certain distance below the specimen surface. This depth appears to be around the thickness of a board (1 – 2μm). The EP-TiO₂ at a filler content of 7.5vol.% finally exhibits the lowest wear rate of all the materials tested. The wear grooves have a small depth (Fig.9, left) and the surface presents large, smooth areas where a relatively homogeneous distribution of nanoparticle agglomerates can be found at higher magnifications

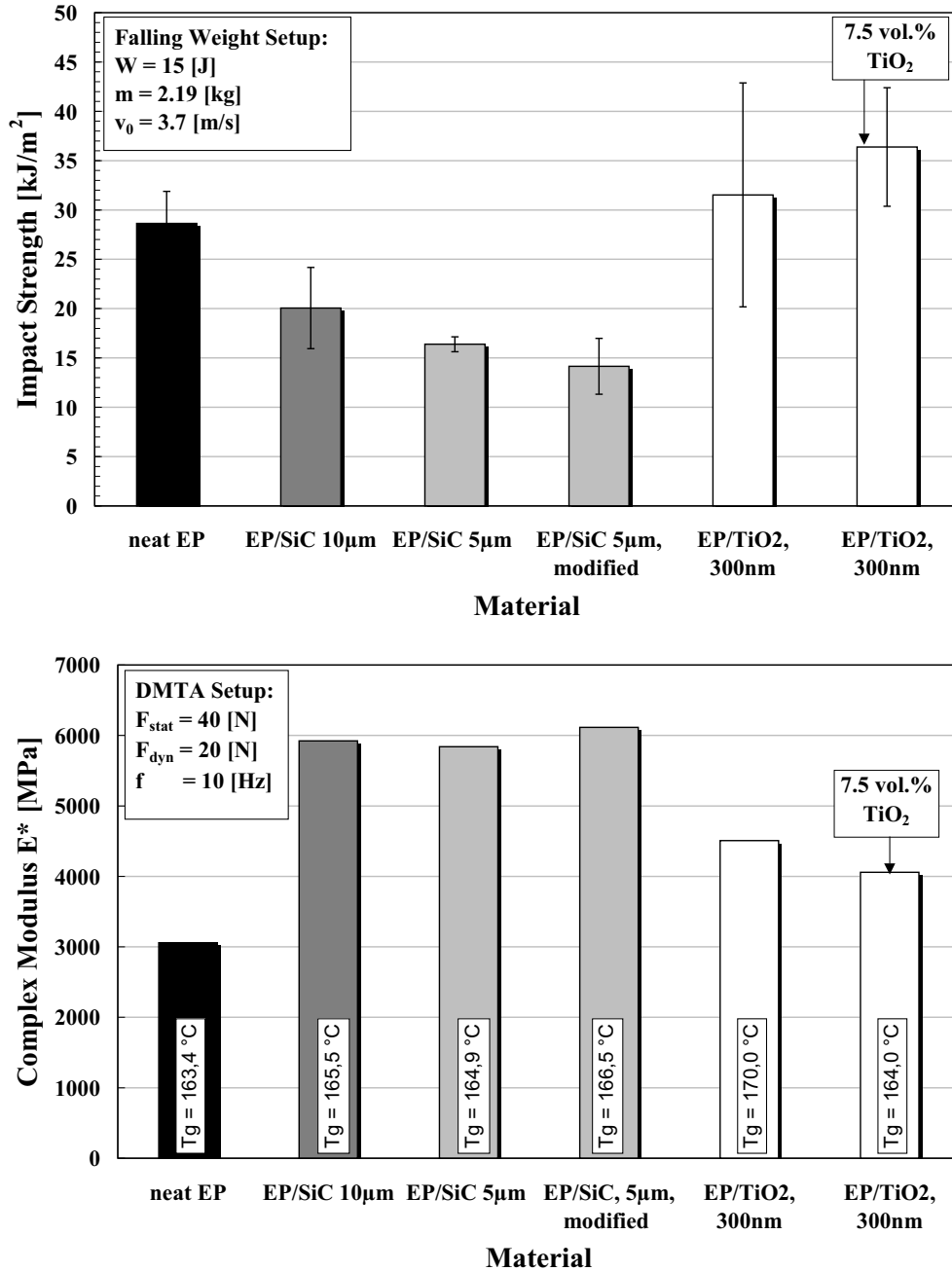


Figure 3: **Top:** Impact strength of epoxy(EP)/filler composites containing 17.5 vol.% of fillers. **Bottom:** Complex modulus of epoxy/filler (17.5 vol.%) composites at a temperature of 23°C.

(Fig.9 right). Higher magnifications verify that small cracks occur perpendicular to the sliding direction (Fig.9, left, black arrow). They appear mainly at the interface between agglomerates and the matrix giving evidence of a weak bonding in these regions. The wear debris collected during the wear experiments possesses also a plate like structure, but the size is much smaller than the debris plates from the other composites.

For future experimental work, the wear mechanisms will be analysed in much more detail. In addition, an even dispersion state of the fillers is targeted, using a more sophisticated mixing technology.

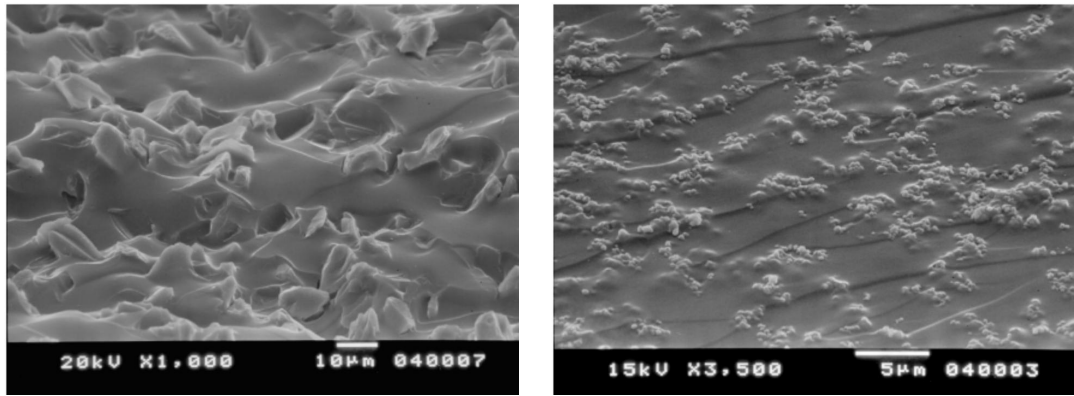


Figure 4: Sample fracture surfaces. **Left:** EP-SiC 10 μm (Magnification x1000), **Right:** EP-TiO₂, 300nm/7.5vol% (Magnification x3500).

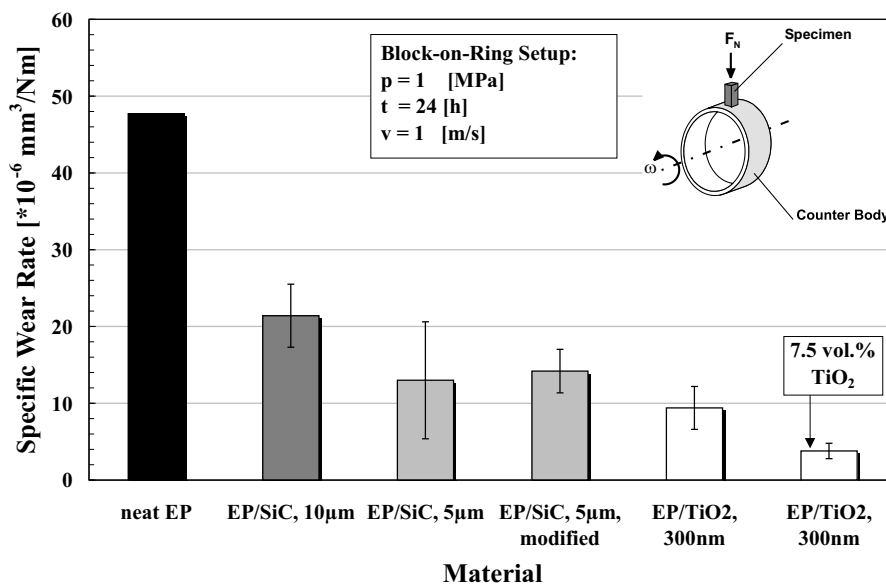


Figure 5: Specific wear rate of epoxy/filler composites containing 17.5vol.% of fillers.

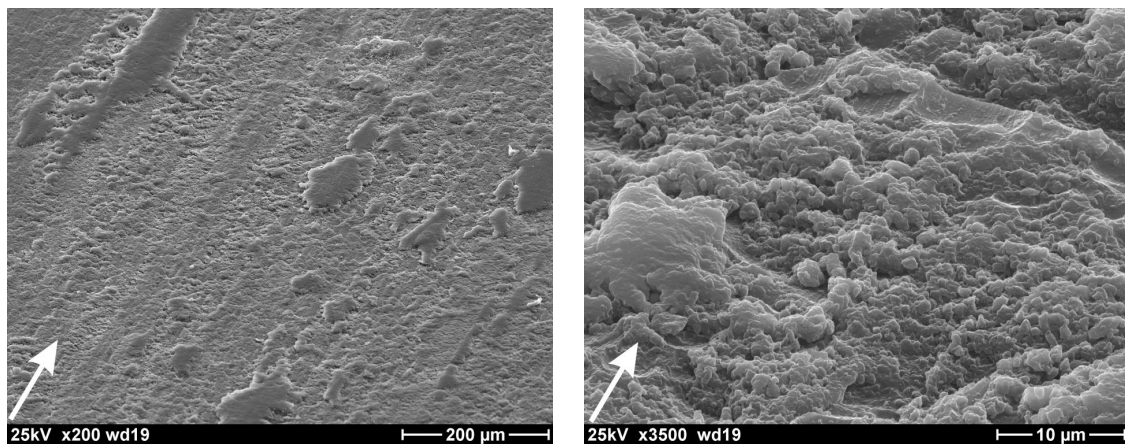


Figure 6: **Left:** Wear traces on the neat epoxy resin surface. Arrows indicate the sliding direction. **Right:** Worn and ploughed areas.

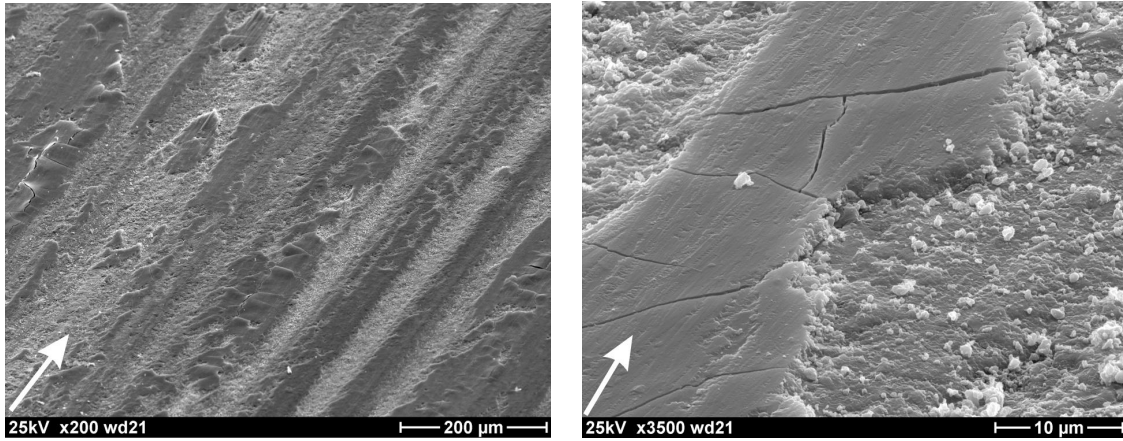


Figure 7: Wear traces of epoxy-SiC ($5\mu\text{m}$, 17.5vol.%) composites; **Left:** Wear traces on the specimen surface. Arrows indicate the sliding direction. **Right:** Worn areas.

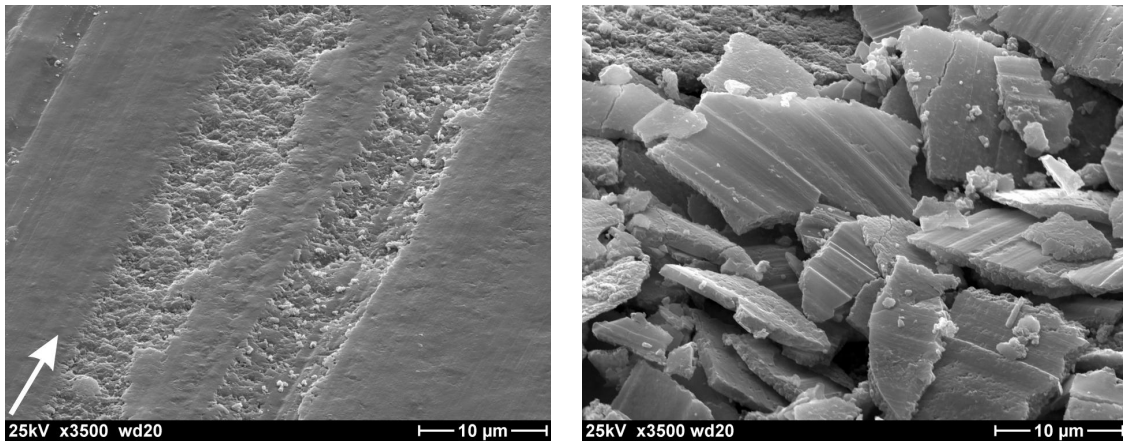


Figure 8: **Left:** Wear grooves; Epoxy-TiO₂ (300nm, 17.5vol.%) nanocomposite; **Right:** Plate like wear debris, collected after 24 hours of testing.

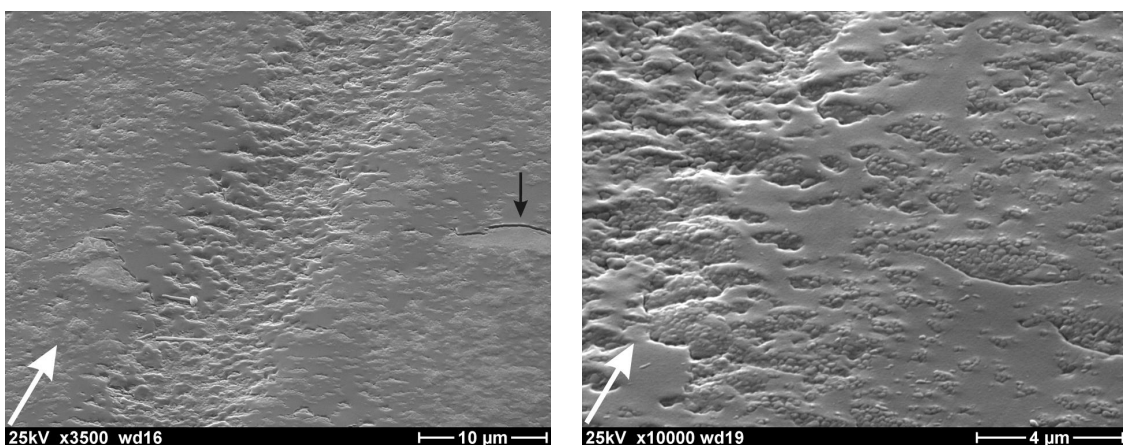


Figure 9: **Left:** Wear groove; Epoxy/TiO₂ (300nm, 7.5vol.%) nanocomposite. Cracking perpendicular to the sliding direction (black arrow). **Right:** Nanoparticle agglomerates.

CONCLUSIONS

This paper describes the influence of ceramic particles with different sizes on the mechanical, especially tribological properties of an epoxy resin matrix. The following conclusions can be drawn:

1. The wear properties of polymer based micro- and nanocomposites are strongly influenced by the particle size, their shape, and the amount of ceramic fillers incorporated. A uniform distribution of the particles helps to enhance the wear resistance.
2. Stiffness but not strength properties exert important influence on the wear behavior of polymer composites especially when nanoparticles are added, as evidenced by a recent study of nano- Al_2O_3 filled polyphenylene sulfide [17].
3. EP-TiO₂ nanocomposites exhibit an extensively improved performance: stiffness, impact toughness and specific wear rate. EP-SiC microcomposites in contrast sacrifice impact strength while stiffness and wear rate are improved.
4. In general, the ceramic nanoparticles are able to reduce the wear rate of the epoxy matrix. The corresponding mechanisms undergo a transition from severe abrasive wear to a mild abrasive wear with an enhanced amount of the formation of compacted wear debris layers that temporarily protect the composite surface from extreme wear. However, this contribution depends very much on the content and morphology of the filler particles. Nanosized particles at a volume content that favors the agglomeration tendency lead to the best results.
5. Based on the above findings, it can be reasonably expected that the mechanical and tribological properties would be further improved by a stronger coupling between nanoscale fillers and matrix. Further efforts will be made to upgrade the mixing technology for breaking up nanoparticle agglomerates and to receive a finer distribution of the particles within the matrix.

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