

NOVEL ZIRCONIA NANOPARTICLE ENHANCING PERFORMANCE OF POLYMER MATRICES THROUGH NANOSCALE FILTERS

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Abstract - We were able to cover up the nano-concave-convex structure of the zirconia nanoparticle assembly by thermally treating a smooth surface and impregnating it with polymer, which is typical of the assembly's natural porous structure and large surface area. Mechanical strain tests revealed that a 0.2 percent zirconia and poly(N-isopropylacrylamide) nanoparticle assembly with the innate micro surface structure was the strongest polymer composite. To the contrary, mechanical tensile testing revealed lower strength and increased elongation at break in assemblies of sintered zirconia nanoparticles with zirconia nanoparticles and smooth surfaces with polymer obscuring the surface.

Keywords: polymer composite, Nano-concave-convex, impregnation, exterior changes, nanoparticle.

1. INTRODUCTION

The term "nanotechnology" has been used to describe a brand-new field of study that has emerged in recent years. Nanoparticle dispersion inside a polymer matrix is becoming an increasingly important technique for a wide variety of developing applications. A variety of qualities, including conductivity, strength, energetics, wear resistance, optical properties, and others, can be improved by incorporating dispersed particle systems into a composite material. Because nanoparticles have such a high ratio of surface-to-volume, more particle-medium interactions occur, which has a greater impact on the overall material properties. In many cases, a more desirable composite feature can be found in a widely dispersed system. [1] Friction and surface tension, two types of forces that attract small particles, increase in strength exponentially. At the subatomic level of nano-particles, quantum alterations are also occurring. A particle's shape has a complex set of geometric features. For example, it includes qualities like convexity and roughness on the surface. Other than these two, the word "shape" might denote "differences in roundness and convexity" (rounded versus angular form) (convex versus concave shape). [12] A particle with an isometric shape has a particle size that is nearly uniform in all directions. There are numerous applications where considering isotropic particles as spherical is a simple and natural assumption to make. Often, all that's needed to describe isometric particles is a single measurement of size (such as an analogous diameter). Although the phrase "(an-) isometric" is used to describe the external shape of objects (particles), the term "(an-) isotropic" is used to describe the interior structure of media (materials). Anisometric particles have a wide range of lengths. If a particle is centrally symmetric (at least approximately or statistically), it can be represented by an ellipsoid or a rectangular parallelepiped. At least three integers are needed to adequately

express the size and shape of such particles in the overall (triaxial) scenario (e.g., bioapatite platelets in bones).[11]

- **Nanoscale fillers and interfaces**

Fillers on the nanoscale come in a wide range of sizes and forms, and when attached to polymer matrices, they provide extremely large interfacial areas. These issues will be addressed first since they have the greatest impact on the characteristics of polymer nanocomposites.[10]

- **Nanoscale fillers that resemble sheets**

The layered silicates of the 2:1 phyllosilicate structural family are the first examples of the nano-fillers sheet frequently utilised in nanocomposites of polymer materials. Laid-back silicates like montmorillonite, hectorite, saponite, etc., are common in industrial applications. [2] The layers that make up their crystal lattice are flat. An alumina or magnesia octahedron is sandwiched between two silica tetrahedrons, with the octahedron's oxygen ions transferred to the tetrahedrons by fusion.[3] Layers can range in size from many tens of nanometers to several micrometres or larger in width and height. These layers will stack with interlayer or intergallery van der Waals gaps. The cation exchange capacity of this clay is moderate, and since the charge of the layer varies from layer to layer, it is necessary to take into account an average value for the entire crystal.

- **Nanofibers and nanotubes**

There is a structure of hexagonal graphite on the walls of carbon nanotubes, and the tubes are frequently capped on both ends. [4] A single graphene sheet can yield SWCNTs (single-walled carbon nanotubes), while many graphitic shells can yield MWCNTs (multi-walled carbon nanotubes) when rolled into a cylinder. Carbon atoms can create a single-walled nanotube through a process known as covalent bonding. MWNTs (Multiwalled nanotubes) can come in a broad variety of forms and sizes, depending on the manufacturing process. Graphene layers are separated by around 0.34 nm in thickness. The unique geometry and size of carbon nanotubes (CNTs) determine a variety of physical and mechanical properties.[5] The moduli and strength of these materials are out of this world. The theoretical tensile strength of a single graphene sheet is up to 200 GPa and the modulus is up to 1 TPa. In comparison to steel, carbon nanotubes (CNTs) have a potential specific strength ten-to-one hundred times stronger.

- **A nanoparticle sphere fills**

Since the early 1900s, spherical nanoparticles have been around; for instance, pyrolysis has made various surface area ranges of carbon black available. Surface areas range from 20 to 500 m² g⁻¹, and particle sizes are between 300 to 200 nm.[13] Many different techniques, such as a wet chemical process, have contributed to the accessibility of silica. The commercially available Ludox process, developed by DuPont, and the flame process Tetraethylortho-silicate (TEOS) in ethanol is used in flame techniques, with condensation of dispersion phase material following. Because of their small size, nanoparticles tend to

aggregate easily. To generate high-performance polymer nanocomposites, it is essential that nanoparticles be dispersed well within the polymer matrix, and dispersants are sometimes utilised to this end.[6]

2. METHODOLOGY

Methods:

FUJIFILM Wako Pure Chemical Corporation was the source for the TMEDA (N,N,N',N'-tetramethylethylenediamine), N-isopropylacrylamide (NIPAM), commercial zirconia (commercial ZrO₂), and potassium persulfate (KPS). All of the BMA, CHMA, HEMA, and HCPK (1-hydroxycyclohexyl phenyl ketone) came from Chemical Industry Co., Ltd in Tokyo. All components were used without any modifications. Ujiden Chemical Industry Co., Ltd. supplied the ZrO₂ MARIMO used in this study.

Fabricating ZrO₂ MARIMO Fillers Impregnated with BMA, NIPAM, HEMA, and CHMA

The HEMA impregnated ZrO₂ MARIMO filler was created by adapting an impregnation technique used to prepare supported nanometal catalysts. At 80 degrees Celsius and under vacuum for 12 hours, ZrO₂ MARIMO was dried. Then, 200 mg of ZrO₂ MARIMO of dried was added to 20 L of a HCPK/ HEMA (20/1, mol) combination and well mixed by hand using a mortar and pestle. The mixture was exposed to ultraviolet light for an hour while being stirred every 15 minutes. All three types of ZrO₂ MARIMO fillers, those impregnated with NIPAM, BMA, and CHMA, were made using the same methods.

Processing of PNIPAM Hydrogels containing ZrO₂ Fillers

An approach was developed to make hydrogels from PNIPAM and ZrO₂ fillers. Before adding 36 g, 30 wt percent of NIPAM, 24 mg, 0.02 wt percent of ZrO₂ MARIMO was dissolved in 115 mL of opposite osmosis aquatic with bubbling of N₂. After 30 minutes of stirring, 0.18 g, 0.67 mmol of KPS in 1.8 mL, 12 mmol of TMEDA and 5 mL of water were added in turn while the mixture was still in the glass beaker. The liquid was divided evenly among several glass tubes with a 1.0 cm internal diameter. After removing the upper dead volume with N₂, the crystal pipes were sealed with bolt lids and left at room temperature (25 °C). The polymer hydrogels were snipped out of the glass tubes after 3 days. Mechanical strength tests were performed on rods of hydrogel having a length of 3.0 cm. and diameter of 1.0 cm The PNIPAM composites containing the BMA-, NIPAM-, HEMA-, and CHMA-impregnated ZrO₂ MARIMO fillers were produced using the same methods.[7]

- **Tensile Mechanical Testing of Polymer Composites**

The specimens were subjected to axial mechanical tensile testing. AND MCT-2150 tensile tester with a crossheading hurry of 50 mm/min was used to determine the applied force (stress) and composite's deformed length (strain) the at room temperature. The maximum allowable elongation for the tensile tester is 930 percent, so this value must be used for all tensile tests on composite samples. Mechanical tensile testing was performed on a total of 10 composite samples, with at least seven of those being chosen for statistical analysis. To ensure the quality of the data, we remark that composites with bubbles, composites fractured

by glass, and composites cracked by the grasp of the tensile testing machine were not included in the analysis. The data is displayed as a mean and standard deviation.

Characterization Methods

For SEM (scanning electron microscopy), the Hitachi SU8020 FE-SEM microscope was employed (SEM). A JEOL JEM-2100F transmission electron microscope was used to take the images. An Oxford INCA X-max 80 EDX spectrometer was used to gather BF mode STEM-EDX mapping data. A Cu K radiation, D/teX Ultra 250 detector (Rigaku SmartLab diffractometer) was used for XRD experiments. A BEL Japan Inc. Belsorp Mini (II) gadget was used to measure the nitrogen adsorption–desorption isotherms. The Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods were employed to measure specific surface areas and the pore size distribution, respectively. For differential scanning calorimetry (DSC) from 0 to 100 degrees Celsius in nitrogen, the DSC7000X from Hitachi High-Tech Science Corporation was employed. Using a JASCO PU-2080 Plus pump, two gel columns (KF-804L and KF-806L), and a RI-2031 Plus Intelligent RI detector calibrated with polystyrene standards, SEC (size exclusion chromatography) was performed at 40 degrees Celsius. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) on an FT/IR-4600 from JASCO Corporation was used to transform the spectra.[8]

3. RESULTS

Table 1. The ZrO₂ fillers along with their primary particle size and specific surface area.

Filler	Exact surface are ^a (m ² g ⁻¹)	Pore size ^b (nm)	Primary particle size ^c (nm)
Sintered ZrO ₂ MARIMO	5	11	21
Commercial ZrO ₂	21	32	30
ZrO ₂ MARIMO	283	2	1

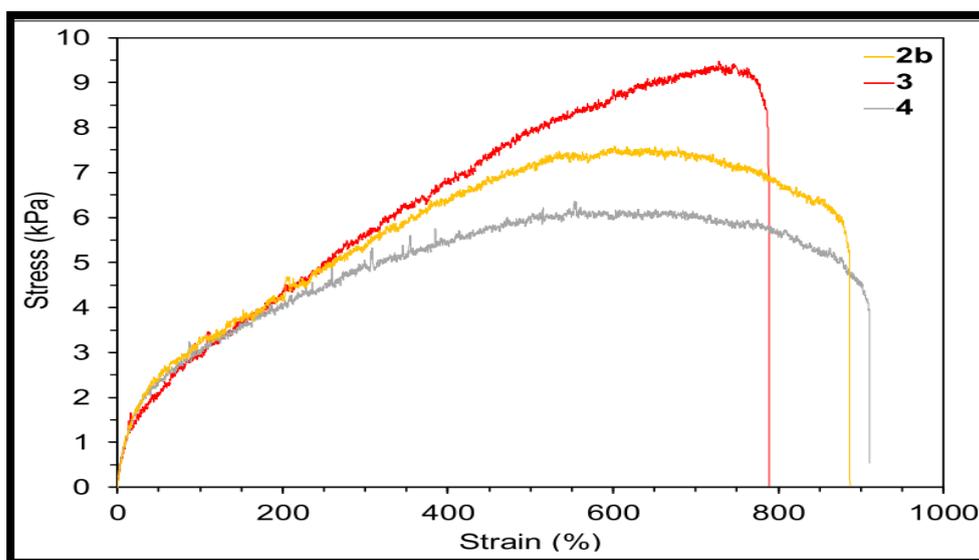


Fig 1. Tensile stress-strain plots of PNIPAM hydrogel composites containing 0.02 weight percent ZrO₂ fillers at 30% weight percent.

Table 2 PNIPAM hydrogel composites with 0.02 wt percent ZrO₂ nanoassembly at 30 wt percent elongation and tensile strength

Composite	Filler	Stress Max (kPa)	Strain Max (%)
4	Sintered ZrO ₂ MARIMO	6.6 ± 0.4	903 ± 20
3	ZrO ₂ MARIMO	9.2 ± 0.3	746 ± 38
2b	Commercial ZrO ₂	7.7 ± 0.3	902 ± 29
1	-	7.8 ± 0.3	716 ± 107

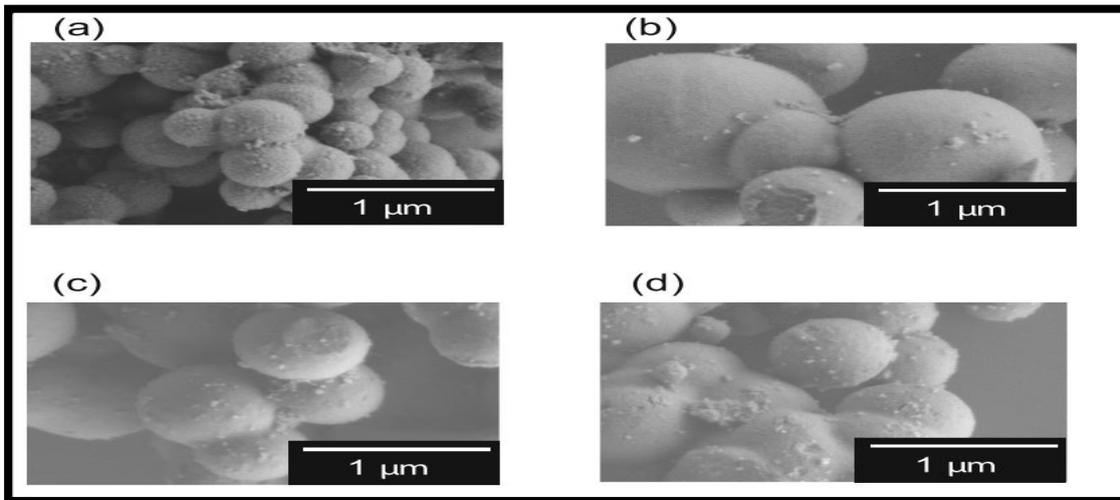


Fig. 2 Scanning electron micrographs

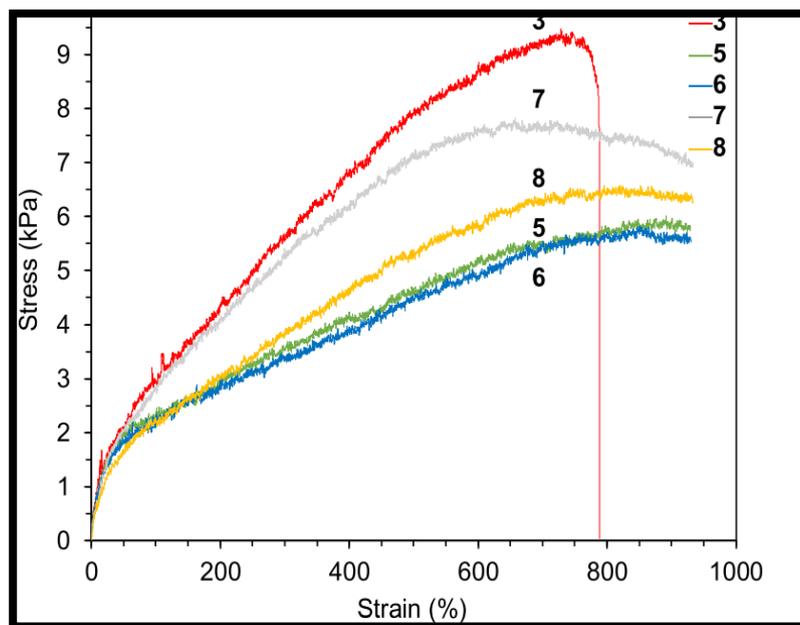


Fig. 3 Stress-strain plots for tensile samples containing 30% poly(N-isopropylacrylate) (PNIPAM) hydrogel composites with ZrO₂ nano-concave-convex surfaces; 0.02%

4. DISCUSSIONS

The physical properties of ZrO₂ fillers were studied using the BET method, XRD, and SEM. Commercial ZrO₂ nanoparticles, used as a reference, had a surface area of 20 m² g⁻¹ and were coarsely aggregated. [14] A mesoporous cylindrical form with a vast specific surface area (283 m² g⁻¹, 14 times greater than commercial ZrO₂ nanoparticles) was seen in ZrO₂ MARIMO. As expected, the low specific surface area of ZrO₂ MARIMO, measured after three hours of heating at 700 °C in the air, was found when samples were sintered. When permitted to sit at room temperature for 60 minutes, the 20% NIPAM gel transforms into a sol. On the other hand, gels made from 25 and 30 wt% NIPAM solutions did not alter the hydrogel shape. [9] To put it another way, the stress and strain values for hydrogels made up of 25 percent PNIPAM and 30 percent were 2.70 and 930 percent, respectively, but the values for hydrogels made up of 30 percent were 7.80 and 716 percent, respectively. MARIMO's nano-concave-convex surface provided the greatest results in composite 3, with an ultimate tensile strength and elongation of 92% and 37%, respectively. [15] When the Composite 4 material was sintered, it was found to be only capable of withstanding an average load of 6.8 to 3.0 kg/cm². 2b (902, 28%) and 4 (903, 19%) have almost equal elongation capabilities. The possible anchoring effect of ZrO₂ MARIMO's nano-concave-convex surface was investigated using mechanical tension testing. To make polymer composites using CHMA-impregnated ZrO₂ MARIMO, NIPAM-impregnated ZrO₂ MARIMO, BMA-impregnated ZrO₂ MARIMO, and HEMA-impregnated ZrO₂ MARIMO, the same procedures were utilised to prepare polymer composites.[16].

5. CONCLUSION

After a ZrO₂ MARIMO filler was surface modified to form a nano-concave-convex structure, mechanical stress testing revealed the relevance of nanoscale anchorin contacts between the filler surface and matrix polymer chains. [20] For this reason, we calcined the ZrO₂ MARIMO and impregnated polymers into the ZrO₂ MARIMO pores to smooth the nano-concave-convex surface in order to see how it affected the results. We then used this technique to disguise the nano-concave-convex surface. [17] Mechanical tensile testing was performed to approximate the interaction between filler surfaces and polymer chains in the polymer composites. While ZrO₂ MARIMO fillers impregnated with polymer exhibited the greatest tensile strength, nano-concave-convex ZrO₂ MARIMO fillers in polymer composites exhibited the greatest elongation. To improve tensile strength and elongation, the ZrO₂ MARIMO filler's nano-concave-convex surface reacted favourably with the matrix polymer chains and was polymer-masked to hide its nano-concave-convex surface.[19] Our filler surface was strategically designed so that we could gain a better understanding of nanoscale structures. Mechanical tensile testing at the macroscopic level to assess the interaction between the filler and the polymer matrix There are a range of monomers and polymers that can be used to impregnate MARIMO fillers in order to alter their properties, such as those that are ionic, hydrophilic, and hydrophobic.[18]

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