



Synthesis and Characterization of Mixed Metal Oxide (MMO) nanoparticles by Novel Sol-Gel Method

A.J.K.Prasad^{1,*}, S.M.Shashidhara² and B.K.Muralidhara³¹Department of Mechanical Engineering, Sir M. Visvesvaraya Institute of Technology, Hunasmaranahalli, Yelahanka (via) Bangalore-562 157 India.²Department of Mechanical Engineering, Kalpataru Institute of Technology, Tiptur-572201, Karnataka State, India.³Department of Mechanical Engineering, University Visvesvaraya College of Engineering, K.R.Circle, Bangalore- 560 001, India.

ARTICLE INFO

Article history:

Received: 20 April 2014;

Received in revised form:

15 September 2014;

Accepted: 23 September 2014;

Keywords

MMO nanoparticles,
Nano $\text{Al}_2\text{O}_3\cdot\text{ZrO}_2\cdot\text{SiO}_2$,
MMO micron particles,
Compressive strength of PMMA
nanocomposites.

ABSTRACT

An attempt has been made to prepare mixed metal oxide (MMO) nanoparticles of Zr, Al, Si by sol-gel route from commercially available zircon flour, fly ash and aluminum metal respectively. Isopropoxides of zirconium and silicon from zircon and isopropoxides of aluminosilicates from fly ash were prepared in separate experiments by alkoxylation of corresponding fluorides/fluoro acids that were obtained by digesting separately, zircon and fly ash respectively in hydrofluoric acid. Aluminum isopropoxides was prepared by alkoxylation of sodium aluminate that was prepared by dissolving aluminum metal in sodium hydroxide. MMO nanoparticles was obtained by neutralizing the isopropoxides of zircon and fly ash (1:1, v/v) respectively with aluminum isopropoxide. SEM and TEM analysis of the MMO nanoparticles revealed that the average size of primary particle is in the range of 2nm to 4 nm. EDAX of MMO nanoparticles indicated presence of aluminum (Al), zirconium (Zr) and silicon (Si) and oxygen (O). Compressive strength of poly(methyl methacrylate) [PMMA] reinforced with MMO nanoparticles was found to be superior to that of neat PMMA and PMMA composites reinforced with MMO micron particles.

© 2014 Elixir All rights reserved

Introduction

MMO nanoparticles (also referred to as heterometal oxide nanoparticles) find applications in catalysis, in electronic industry as passive or active component devices etc. The most remarkable MMO nanoparticles are the thermal conducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBaCO) based superconductors. Thermomechanical or optical properties of certain MMOs such as silica-titania ($\text{SiO}_2\text{-TiO}_2$) and silica-zirconia ($\text{SiO}_2\text{-ZrO}_2$) has evoked interest in exploring applications of these MMOs as catalysts [1] or as catalyst supports [2]. For example Corrie et al [3] described significant enhanced catalytic property over micron counterparts. Wunderlich et al [4] reported sol-gel-processed alumina-silica and alumina-titania nano-hybrid oxide as catalysts. Silica-titania ($\text{SiO}_2\text{-TiO}_2$) glasses and zircon (ZrSiO_4) are characterized by very low thermal expansion, which confer them high thermal shock resistance. Steffen et al [5] reported improved thermal shock performance of fine grained alumina refractory ceramics by addition of nano and micrometer of SiO_2 , ZrO_2 and TiO_2 . Owing to their refractoriness, these MMOs are difficult to produce by conventional melting techniques and thus sol-gel technique is used for their preparation [6]. Bapuji and Jain [7] described another application of MMOs prepared by $\text{TiO}_2\text{-ZrO}_2$ multilayer thin films for humidity sensing application. Sol-gel process has been employed by researchers for the preparation of two component and multi-component MMOs. For example Mirinda Salvado and Fernandez [8] and Takashi et al [9] reported sol-gel synthesis of silica-titania ($\text{SiO}_2\text{-TiO}_2$) nano MMOs. Rodrigo and Wander [10] in their work, reported sol-gel preparation of silica-alumina ($\text{SiO}_2\text{-Al}_2\text{O}_3$) nano MMOs, starting with pure precursors of tetraethyl orthosilicate (TEOS) and aluminum isopropoxide to prepare materials within the entire silica-alumina system.

Shuqun Ling and co-workers [11] fabricated full density mullite/zirconia composite ceramics with ultra-fine grains from Si-Al-Zr-O amorphous bulk via high temperature sol-gel and *in-situ* controlled crystallization processing techniques. They further mention that the process employed by them *opens* a new way to prepare Si-Al-Zr-O system multi-component ceramics with ultrafine grains or nano-size grains. Chitralkha and co-workers [12] reported a method for synthesis and characterization of fly ash supported sulfated zirconia by sol-gel method and the application as catalyst for benzylation reactions. Norbert Roesch et al [13] in their patent disclosed a method of coating materials containing mixed metal oxide nanoparticles consisting of 50-99% by weight Al_2O_3 and 0.1-50% by weight of oxides of the elements of main groups L or LI of the periodic table, by sol-gel method. Chen and co-workers [14] reported kinetics of fly ash leaching in 1M to 10 M potassium hydroxide at temperatures of 20-75 °C, with a water-to- solid ratio of 40 g/g, maintaining duration of leaching up to 14 days. They reported three stages of leaching process and using modified Jander equation rate constants of each stage was calculated. Further reported that the rate constant for stage one reflected an intrinsic property, chemical durability, which linearly increased with increasing concentrations of network formers in the glass phase of a fly ash.

Although researchers reported preparation of MMO nanoparticles, there is limited published information on the preparation of MMO nanoparticles using commercially available starting materials. Therefore an attempt has been made to prepare MMO nanoparticles using commercially available starting material by sol-gel method.

Polymer nanocomposites possess unique combinations of thermal and mechanical properties that were not exhibited by

micron size particle filled systems. Property improvements in the polymer nanocomposites may be attributable to the large surface to volume ratio possessed by the nanoparticle reinforcements [15-17]. Y Ou et al [18] reported that nylon 6 filled with 50 nm silica particles showed an increase in tensile strength (15%), increase in strain-to-failure (150%), increase in Young's modulus (23%), and increase in impact strength (78%). Pan and co-workers [19] prepared surface modified nanosized SiO₂ (primary particle size 12nm or particles), Al₂O₃ (primary particle size 15nm-90nm) mixed with micron sized PEEK nanoparticles for the fabrication of tensile, compressive and impact strength test specimens. They reported that the tensile and compressive strength increased with the Al₂O₃ particle dimension. It was further reported that comparable trends were detected for the Al₂O₃ and SiO₂ fillers with increase in load and that both fillers showed an optimized concentration of 5% for the rise in tensile, compressive and impact strength, further filler concentration increase resulted in strength reduction. Researchers have prepared polymer nanocomposites with different polymer/nanoparticle reinforcement combinations, for example, polyamide/clay nanocomposites, epoxy layered silicates, biodegradable polymer/layered silicate, polypropylene layered silicate, polystyrene/clay, poly(ethyl acrylate)/bentonite, rubber-clay and clay-acrylate and PMMA-Al₂O₃[20] and have reported their properties, for example flammability, thermal stability, barrier properties and wear resistance [21]. Different types of polymers studied are matrices made of polystyrene (PS), styrene-acrylonitrile copolymer (SAN), polycarbonate (PC) and polypropylene (PP) [22] polyetheretherketone (PEEK), polyamide (PA), polyphenylenesulfide (PPS), polyoxymethulene (POM) and polytetrafluoroethylene (PTFE) [23], poly (methyl methacrylate) PMMA[20] and different inorganic nanoparticles e.g. Si₃N₄, SiO₂, SiC, ZrO₂, Al₂O₃, TiO₂, ZnO, CuO, CaCO₃ as reinforcement materials. Li et al [24] reported in-situ generation of SiO₂ nanoparticles via sol-gel techniques in an organic solvent, containing dissolved PMMA, leading PMMA nanosilica composites after evaporation and drying.

We were interested to evaluate the compressive strength of PMMA composites reinforced with MMO nanoparticles and compare the results with those of neat PMMA and PMMA composites reinforced with MMO micron particles.

Experimental Details

Commercially available electrical grade aluminum (Al > 99.5% pure) wire, zircon flour (ZrSiO₄; ZrO₂= 66.2wt%, SiO₂=32.5 wt%), fly Ash (Al₂O₃=32 wt%, SiO₂=58 wt%) obtained from thermal power plants were used for preparing MMO nanoparticles. Commercially available alumina, zircon flour and fly ash were used for preparation of micron counter parts namely, MMO micron particles. LR grade chemicals, sodium hydroxide, hydrofluoric acid (60 wt%), isopropyl alcohol, liquor ammonia and silver nitrate were used to prepare MMO nanoparticles. PMMA resin used in dentistry (DPI make cold cure variety and Asian Acrylates make Acralyn 'H' heat cure variety) along with respective liquid monomers were used to prepare PMMA composites.

MMO nanoparticles was prepared as per the steps shown in the flow chart given in figure 1. Dissolution experiments have been carried out in Teflon reactor encased in steel casing, which was kept on electrically heated hot plate (maintained at 180-200°C). Solid liquid ratio maintained in the present study being 0.05, 1.0, 1.5, and 2.0 respectively. Dissolution was carried out for durations of 24, 36, 48, 60 and 72 hours respectively. Fly ash dissolution (percentage) was determined by the weight of the

residue after filtration, in each experiment. It was observed that over 99.5% fly ash has been dissolved in the acid. Details of preparation of alkoxides of zircon and aluminum were described by Prasad [25, 26].

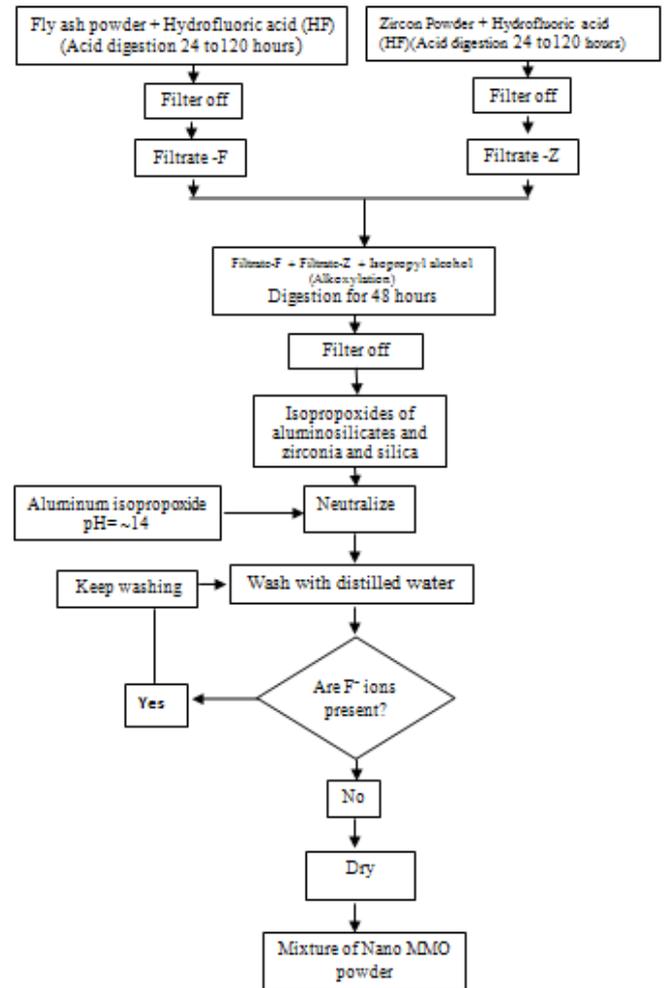
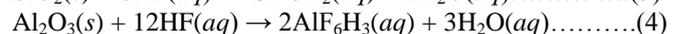
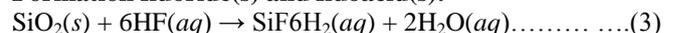


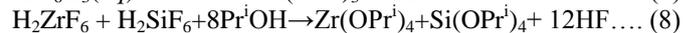
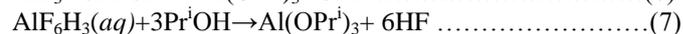
Figure 1. Flow chart for Sol-gel synthesis of MMO nanoparticles

We envisage that the following reactions could be taking place during the various stages of the sol-gel process investigated in the present studies (flow chart, figure 1).

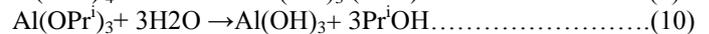
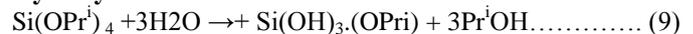
Formation fluoride(s) and fluoacid(s):



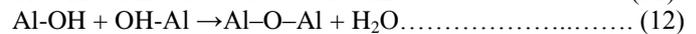
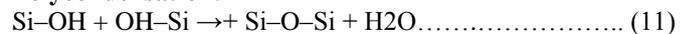
Alkoxylation:



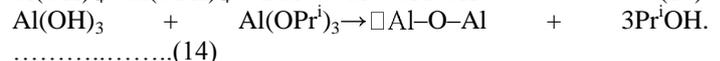
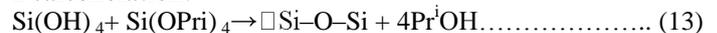
Hydrolysis:



Polycondensation:



Dealcoholation:



Filtrates (having pH~ 1) obtained from alkoxylation of fly ash and zircon (1:1, v/v) were neutralized with filtrate (having pH 14) obtained from alkoxylation of aluminum till pH of the mixture is ~ 7. During neutralization step, sol formation and gel

formation were observed. MMO nanoparticles obtained by washing the gel and were examined under SEM and TEM.

PMMA composites were prepared as per the procedure employed by dentists and details of preparation presented elsewhere [26, 27]. Compressive strength of the PMMA composites was evaluated using a Universal Testing Machine (UTM Dartek make model 9500).

Results and Discussions

Novelty of the sol-gel process employed in the present investigation lies in neutralizing 1:1(v/v) mixture of (a) highly acidic (pH≈1) isopropoxides of aluminosilicates (obtained by HF dissolution of micron fly ash and subsequent isopropxylation step) (b)isopropoxides of mixture of zirconium and silicon (obtained by HF dissolution of micron zircon flour and subsequent isopropxylation step) with highly basic aluminum isopropoxides prepared from commercial electric grade aluminum wire [26].

Results of dissolution studies of fly ash in hydrofluoric acid (HF) are presented in figures 2 and 3. From these figure it can be noted that percentage dissolution is increasing with increase in time for any given solid-liquid (s/l)ratio. A minimum percent dissolution of 83.2 was observed for digestion period of 24 hours with 30 wt % HF (s/l 0.05) and a maximum dissolution of 99.5 % was observed for digestion period of 24 hours with 40 wt % HF (s/l 0.05). Intermediate values of percent dissolution of fly ash in 60 % HF may be attributed to the ion mobility and electrovalent effects of the inter-diffusing ions. In all the experiments, for a particular s/l ratio, dissolution of micron fly ash was found to increase with increase in digestion concentration and that for a particular digestion time dissolution was found to decrease with increase in s/l ratio. Further, for a particular concentration of HF, maximum dissolution was found to take place for an s/l ratio of 0.05, which peaked at 72h of digestion time.

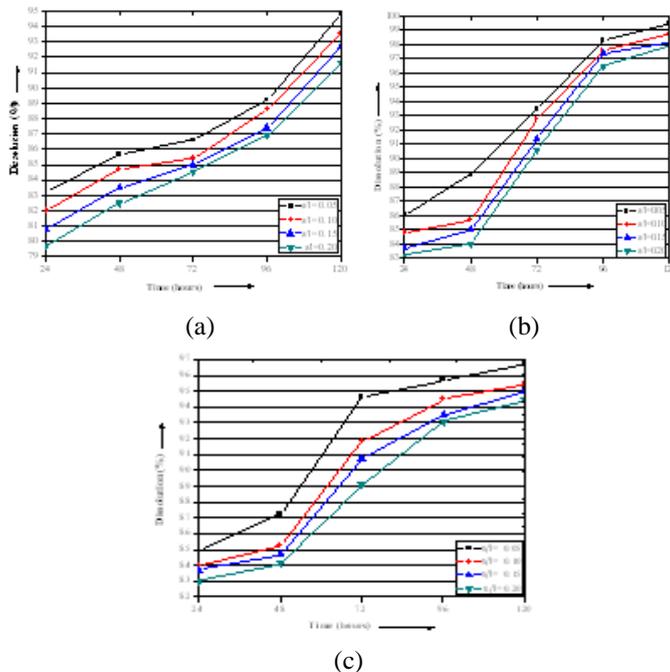


Figure 2. Dissolution of fly ash in (a) 30 wt % HF (b) 40 wt % HF and (c) 60 % wt % HF

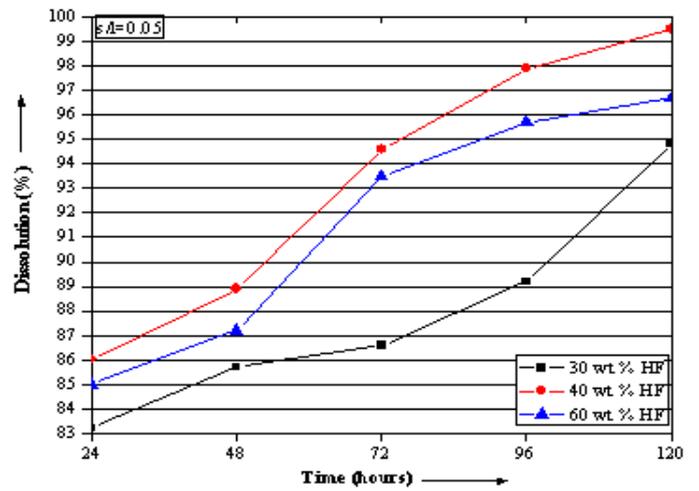


Figure 3. Variation of dissolution of fly ash as a function of time

Dissolution of fly ash nanoparticles may be described by a shrinking core model [28]. In the present investigations, the dissolution was allowed to take place without agitating the mixture similar to the procedure reported by Javier and Dalmacio[29]. As the dissolution of fly ash in HF progresses, constant concentration conditions do not prevail. Once the temperature of ~ 90°C reaches, on-set of boiling takes place with attendant agitation of the solid particles. Consequently the boundaries of various layers which will form around the solid-solution/solute complex dynamically vary with inward diffusion of fluoride and hydronium ions on one hand, and the outward diffusion of the products of digestion process on the other. At higher concentrations of HF and at longer periods of digestion, inter-diffusion of the products and reactants experience ionic interactions and steric hindrances, thereby affecting the dissolution process. This could lead to lower dissolution of solid particles in the acid.

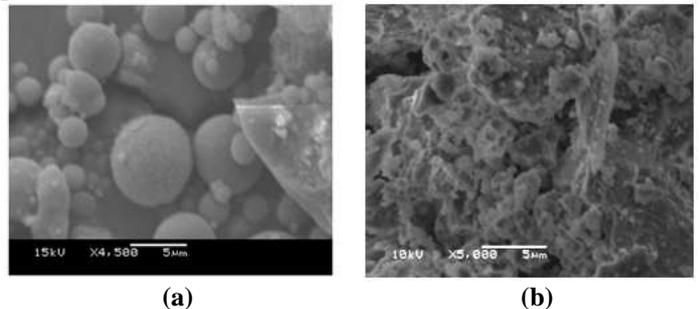


Figure 4. Scanning Electron Micrographs of (a) Fly Ash micron particles and (b) Zircon micron particles

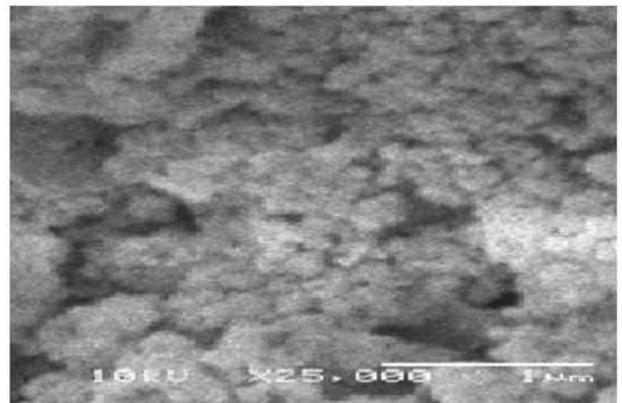


Figure 5. Scanning Electron Micrographs of MMO Nanoparticles

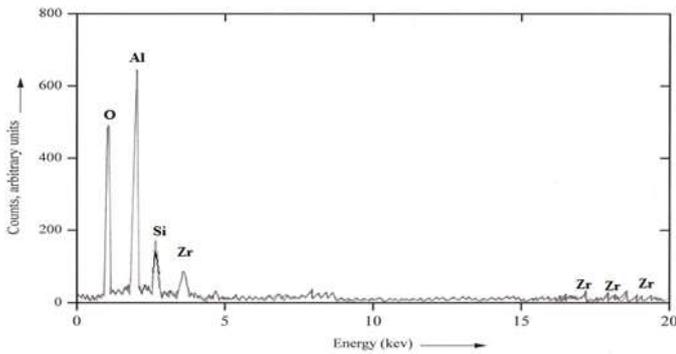


Figure 6. EDAX of MMO Nanoparticles

SEM examination (figure 4) of particles of fly ash nanoparticles are spherical in shape and typical particle size varying from 1µm to 6µm. Particles of zircon are irregular in shape and have sizes ranging from 1µm to 7µm. Scanning electron micrograph of MMO nanoparticles (figure 5) revealed that the average size of primary particle (which agglomerated into secondary particle) is in the range of 1 nm to 4 nm. From the EDAX pattern of MMO nanoparticles (figure 6) discloses the presence of the elements aluminum (Al), zirconium (Zr) and silicon (Si) and oxygen (O)

Transmission electron micrograph and SAED pattern of nano MMO nanoparticles is presented. The average particle size has been observed to be 2nm to 4 nm. SAED is indicative of amorphous nature of the MMO nanoparticles and similar results were reported in the literature [30-32].

Using commercially available, fly ash and zircon flour and aluminum wire as starting materials, the sol-gel process adapted in the present investigation yielded MMO nanoparticles having 1 nm to 4 nm average sized spherical particles comprising oxides of respective elements, namely Al, Zr, and Si and O. Different reactions that could be taking place during the sol-gel process as given in figure 1, are presented in supplementary information

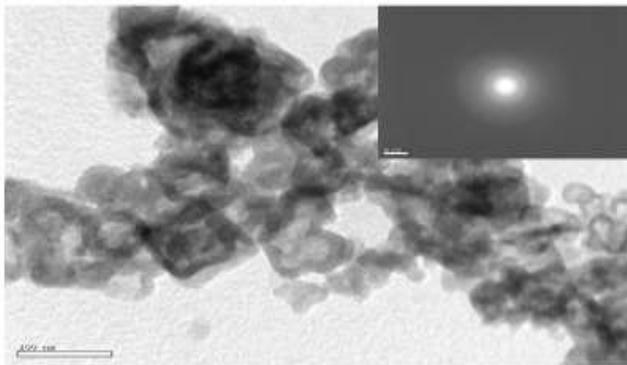


Figure 7. Transmission Electron Micrograph and SAED of MMO Nanoparticles

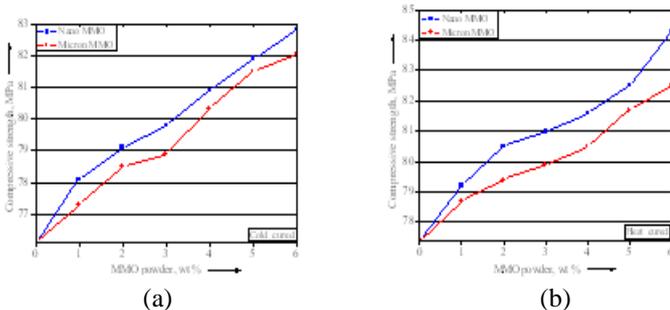


Figure 8. Variation of Compressive Strength of (a) Cold cured and (b) Heat cured PMMA Reinforced with different levels of MMO nanoparticles and MMO microparticles

Compressive Strength of PMMA composites reinforced with nano MMO nanoparticles

The compressive strength of neat cold cured PMMA and heat cured PMMA was determined to be 76.1 and 77.4MPa respectively[33, 34].

Compressive strength of cold cured and heat cured PMMA polymer reinforced with MMO nanoparticles and MMO micron particles (figure 8) is increasing with increase in the content of the MMO particles. Further, compressive strength of cold cured PMMA composites containing MMO nanoparticles is higher than that of cold cured PMMA composites reinforced with MMO micron particles. Within the scope of the present investigation, a maximum compressive strength value of 82.8MPa has been observed for the cold cured PMMA composite reinforced with 6 wt % MMO nanoparticles. Similarly a maximum compressive strength value of 82.0 MPa has been observed for the cold cured PMMA composite reinforced with 6 wt % MMO micron particles.

Compressive strength of cold cured and heat cured PMMA without any reinforcement and that of PMMA composites reinforced with 6 wt % MMO nanoparticles and with 6 wt % MMO micron particles respectively is presented in figure 9. From this figure, it may be noted that the compressive strength of PMMA composites containing MMO nanoparticles has higher value compared with that of PMMA polymer without any reinforcement or PMMA composites reinforced MMO micron particles. MMO nanoparticles is a multi-molecular ceramic oxide.

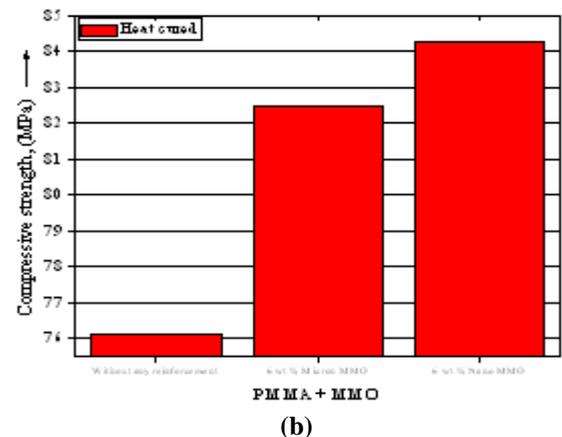
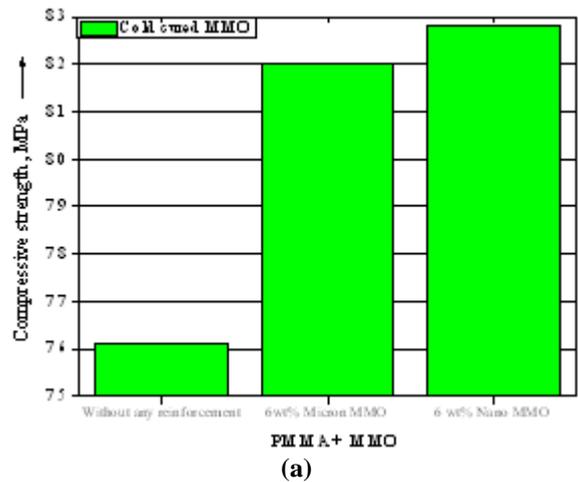


Figure 9. Bar Chart Indicating Compressive Strength of (a) Cold Cured and (b) Heat Cured PMMA Composites Reinforced with 6 wt % MMO Nanoparticles and MMO microparticles

Higher compressive strength values obtained in the present investigations for PMMA containing MMO nanoparticles may be attributed to higher localized resistance offered by locked-in multi-molecular MMO nanoparticles reinforcements in the three dimensional network of PMMA polymer, to the applied compressive stress on the concerned PMMA composite specimen(s).

Conclusions:

- It has been possible to prepare MMO nanoparticles from commercially available zircon flour, fly ash and aluminum metal respectively, by sol-gel route.
- The average size of primary MMO nanoparticle is in the range of 1 nm to 4 nm.
- EDAX of MMO nanoparticles revealed the presence of aluminum (Al), zirconium (Zr), silicon (Si) and oxygen (O) respectively.
- Compressive strength of PMMA reinforced with MMO nanoparticles was found to be superior to that of neat PMMA and PMMA composites reinforced with micron counterparts.

References

1. Liotta, L.F., and Deganello, G., "Thermal stability, structural properties and catalytic activity of Pd catalysts supported on Al_2O_3 - CeO_2 - BaO mixed oxides prepared by sol-gel method". Journal of Molecular Catalysis A: Chemical, 15 September 2003. Volumes 204-205: p. 763-770.
2. Adrianaainarivelo, M., Corin, R., Laclercq D Murin, and Vious P.H.A., *Mixed oxides SiO_2 - ZrO_2 and SiO_2 - TiO_2 by a non-hydrolytical sol-gel route*. J.Mater.Chem, 1996. **6**(10): p. 1665-1671.
3. Corrie, L.C., Pramesh, N., Kapoor, and Klabunde, K.J., "Synthesis, Characterization, and Adsorption Studies of Nano Crystalline Aluminum Oxide and Bimetallic Nano Crystalline Aluminum Oxide/Magnesium Oxide". Chem. Mater., 2002. **14**: p. 2922-2929.
4. Wunderlich, W., Padmaja, P., and Warriar, K.G K., "TEM characterization of sol-gel-processed alumina-silica and alumina-titania nano-hybrid oxide catalysts". Journal of the European Ceramic Society, 2004. **24**(2): p. 313-317.
5. Steffen, D., Dániel Veres, Christos G. Aneziris, Erik Skiera, and Steinbrech Rolf, W., "Nano- and micrometre additions of SiO_2 , ZrO_2 and TiO_2 in fine grained alumina refractory ceramics for improved thermal shock performance". Ceramics International, doi:10.1016/j.ceramint.2011.10.036. **In press**.
6. Pramesh, N., Kapoor., *Mixed Metal Oxide Nanoparticles*. 2004: Dekker Encyclopedia Nanoscience and Nanotechnology. 2007-2017.
7. Kuyyadi, P., Biju., and Jain, M.K., "Sol-gel derived TiO_2 , ZrO_2 multilayer thin films for humidity sensing application". Sensors and Actuators B: Chemical, 15 January 2008. **Volume 128** (2): p. Pages 407-413.
8. Mirinda Salvado I.M and Fernandez Navarro. J.M., " TiO_2 - SiO_2 glasses prepared by alkoxide route". J.Non cryst.solids., 1992. **147 & 148**: p. 256-261.
9. Takashi, H., Yamada, T., and Saito, H., "Preparation of titania-silica glasses by the gel method". J Mater Sci, 1983. **18**: p. 3137-3142.
10. Rodrigo, L.O., and Vasconcelos, W.L., "Sol-Gel Transition and Structural Evolution on Multicomponent Gels Derived from the Alumina-Silica System". J Sol-Gel Sci.Tech, 1997. **9** (3): p. 239-249.
11. Shuquan Liang, S., Qiang, Li., Xiao-ping Tan., Yan Tang, and Yong Zhang, "Preparation of mullite/zirconia composite ceramics with ultrafine grains by in-situ controlled crystallizing from the Si-Al-Zr-O amorphous bulk". Nanoscience, March 2006. **11**(1): p. 32-37.
12. Chitralekha, K., Mishra, M.K, and Ashu R., "Synthesis and characterization of fly ash supported sulfated zirconia catalyst for benzoylation reactions". Fuel Processing Technology October 2010. **91**(10): p. 1288-1295.
13. Norbert, R., et. al., "Coating materials containing mixed metal oxide nanoparticles consisting of 50-99% by weight Al_2O_3 and 0.1-50% by weight of oxides of the elements of main groups L or LI of the periodic table ", USPTO, Editor. 2009: USA. p. 1-7.
14. Chen, C., et al., *Kinetics of fly ash leaching in strongly alkaline solutions*. Journal of Materials Science, 2011. **46**(3): p. 590-597.
15. Margolina, A., Wu, S., Polymer 1988. **29**: p. 2170
16. Cousin, P., and Smith, P., J. Polym. Sci., 1994. **32**: p. 459
17. Becker, C., Krug, H., and Schmidt, H., in *Mat. Res. Soc. Symp. Proc.* 1996. p. 237, .
18. Ou., Y., Yang, F, and Yu, Z., J. Polym. Sci, Part B, , 1998. **36**: p. 789.
19. Pan, G., Guo, Q., Tian, A, and He, Z., "Mechanical behaviors of Al_2O_3 nanoparticles reinforced polyetheretherketone". Mater. Sci. Eng., A 2008. **492**: p. 383-391.
20. Benjamin, J.A., et al., "Mechanical Properties of Al_2O_3 Polymethylmethacrylate Nanocomposites". Polymer Composites December 2002. **23**(No. 6): p. 1014-1025.
21. Mai, Y., Yu, Z., ed. "Polymer nanocomposites", . February 2006, Woodhead Publishing Limited: Abington Hall, Abington Cambridge, CB1 6AH, England.
22. Vollenberg, P.H.T., and Heikens, D., Polymer, 1989. **30**: p. 1656-1662.
23. Klaus, F., StoÄko, Fakirov, and Zhong, Z., "Polymer composites: From Nano-to-Macro-Scale" 2005: Springer. 170.
24. Li, C., Wu, Z, J, Zhao D, and Fan, Q., "Effect of inorganic phase on polymeric relaxation dynamics in PMMA/silica hybrids studied by dielectric analysis". Eur. Polym. J., 2004. **40**: p. 1807-1814.
25. Prasad, A.J.K., Shashidhara. S M., and Muralidhara B.K., "Synthesis and characterization of mixture of nano zirconia and nano silica obtained from commercially available zircon flour by sol-gel method". Bulletin of Materials Science, December 2011. **Vol. 34, No. 7 pp 1339**.
26. Prasad., A.J.K., "Development and Comparative Studies of Polymer Composites Reinforced with Nano Ceramic Oxide Powders", in *Mechanical Engineering*. 2012, Visvesvaraya Technological University: Siddaganga Institute of Technology. p. 39.
27. Robert Craig., G., ed. "Restorative Dental Materials; Properties and Manipulation" 8th ed. 1989, St Lous Year Book. 277.
28. Wei-Lun Hsu, M.-J.L., and Jyh-Ping Hsu, "Dissolution of Solid Particles in Liquids A Shrinking Core Model". International Journal of Chemical and Biological Engineering 2009. **2:4** p. 205-210.
29. A. Javier ALLER and B. Dalmacio, "A Digestion Procedure for Determination of Major and Minor Elements in Fly Ash by Atomic Absorption Spectrometry". Analytical Sciences, 1990. **6**: p. 309-311.
30. Nagarajan, V.S., and Rao, K.J., "Crystallization studies of ZrO_2 , SO_2 composite gels". J. Mater. Sci., 1989. **24** p. 2140-2146.
31. Nagarajan, V.S., and Rao K J., "In-situ Crystallization studies of gels in the ZrO_2 , SO_2 System " Mat. Res Bull, 1991. **26**: p. 715-721.

32. Do, T.-D.N.a.T.-O., "Size- and Shape-Controlled Synthesis of Monodisperse Metal Oxide and Mixed Oxide Nanocrystals, Nanocrystal", ed. D.Y.M. (Ed.). 2011.

33. Robert Craig, G., "Dental Restorative Materials" 8th ed. 1989. page 514.

34. www.polymerweb.com_datash/pmma.html.