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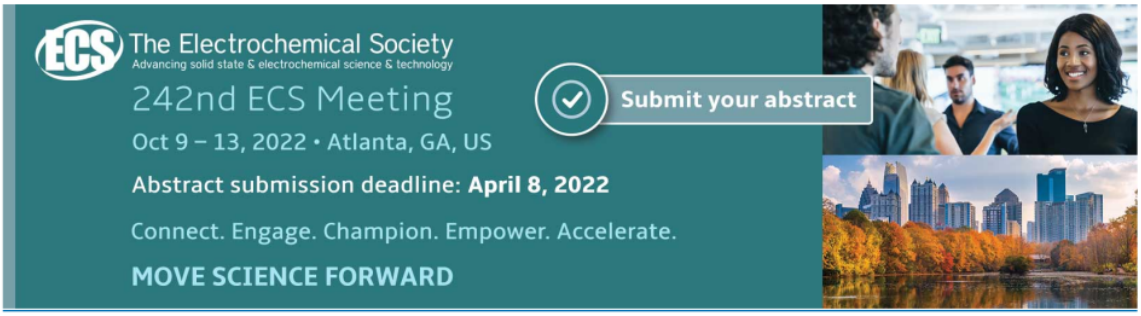

Force-displacement analysis of PMMA/zircon composites using dynamic mechanical analyzer (DMA)

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Abstract. In the study, poly(methyl methacrylate) (PMMA)/zircon ($ZrSiO_4$) composites were successfully prepared using the liquid method at different compositions of 1, 2.5, and 5 wt% of zircon. The zircon filler was processed from a natural, local zircon sand and was processed via a top-down method using wet ball-milling for 5 and 15 h as well as annealing at temperature of 200 °C for 1 h. The force-displacement curves of the composites have been acquired using a DMA (dynamic mechanical analyzer) technique in tensile mode. XRD (x-ray diffraction) data of the composites were collected and analyzed in order to examine the present phases and used as the evidence of the formation of the composites. Furthermore, *MAUD* software was used to estimate the crystallite size of the filler. Results indicated that zircon crystallite size for 15 h wet ball-milling was smaller than that of 5 h. Furthermore, the maximum DMA force (also representing stress) for the composite with smaller filler was generally higher than that of 5 h, *ca*. by 2.5 times. In addition, in general, the composites exhibited an increasing slope of force-displacement curve with increasing amount of filler.

1. Introduction

Polymeric/inorganic composites with enhanced performances have great potential applications in many fields such as sensors, biomedical and optical devices, as well as anti-corrosion issues [1–4]. These composites have replaced many conventional polymers mainly due to the combination of great rigidity, good heat and mechanical properties from the filler with the flexibility and ductility of the organic polymers [5,6].

PMMA [poly(methyl methacrylate)] is a thermoplastic polymer with excellent transparency, which is widely used in applications of optics [7] and biomedics [8]. However, its poor mechanical properties restrict its use in structural and engineering purposes. Adding an inorganic filler into PMMA to form composites improves the mechanical properties of the polymer. Several research have studied the PMMA-based composites with filler of silica [9], carbon nanotube [10], alumina [11], titania [12], zinc oxide [13], and zirconia [14] and showed improved mechanical properties as compared to pure PMMA. On the other hand, zircon ($ZrSiO_4$), which its source is abundant in Indonesia and its elastic modulus is 2.5 times of silica [15,16], has not been reported as a filler in PMMA composites. In other words, zircon becomes a potential filler material that can be incorporated into PMMA to improve its structural and mechanical properties. Moreover, the effect of filler size could be an important factor in such improvement. It is, therefore, imperative to investigate the mechanical characteristics of PMMA/zircon composites with various zircon content and sizes.

In this work, PMMA/zircon composites were synthesized at different compositions of 1, 2.5, and 5 wt% of zircon. The filler used was milled (5h- and 15h-milling followed by annealing) and unmilled zircon powders. The force-displacement curves, which can also be associated with stress-strain curves, of the composites were determined using a dynamic mechanical analyzer (DMA) in tensile mode to obtain local mechanical material properties of the composites.

2. Method

The polymer was commercially available poly(methyl methacrylate) (PMMA) from Himedia, type GRM1746-250G. HCl (37%), NaOH (98%), and C_3H_6O (99%) were produced from SAP Chemical, Indonesia. Meanwhile, the zircon filler was obtained by processing local zircon sand that was collected from Kereng Pangi, Central Kalimantan, Indonesia.

Purification of local zircon sand and synthesis of zircon powder was done following several stages, i.e., magnetic separation, HCl leaching, and NaOH reaction. The nano-powders were prepared via a top-down method by a planetary ball milling for 5 and 15 h, followed by drying and subsequently annealing at 200 °C for 1 h to remove a residual strain of the milled powder [17].

The PMMA/zircon composites were prepared using the liquid method. The PMMA was solved in aceton (C_3H_6O) at 50 °C for 30 minutes. Next, the dissolved PMMA was added with sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$, abbreviated as SDS, as a dispersant) and stirred for 15 minutes. Subsequently, the filler was added drop wise and stirred for 30 minutes. After that, the mixture was cooled to room temperature to allow solidification. The filler content was 1, 2.5 and 5% $ZrSiO_4$ by weight. The samples were denoted as ZMA5-X% for the 5-hour-milled powder as well as ZMA15-X% for the 15-hour-milled powder, respectively, where X% denotes the weight percentage of the fillers.

XRD (x-ray diffraction) data were collected on a Philips X'Pert MPD diffractometer using a Cu target at 40 kV/30 mA with a 2θ-range of 15–65 °2θ. The XRD data of the fillers were subjected to analysis using *MAUD* software to assess their crystallite size and residual strain. A DMA test in tensile mode was implemented with a dynamic mechanical analyzer Mettler Toledo DMA/SDTA861 instrument at single frequency oscillation mode of 1 Hz and ambient temperature. The applied dynamic forces were varied from 1 to 100 N. The temperature scanning rate was 5 °C/min.

3. Results and Discussion

The XRD patterns of pure PMMA, zircon unmilled (ZM0) and milled (ZMA5 and ZMA15) powders as well as PMMA/zircon composites are shown in Figure 1. The XRD data confirm that the only phase found in the unmilled and milled powders is zircon ($ZrSiO_4$, COD No. 9-000-230). Meanwhile, the XRD patterns of the composites show no new peaks other than those of PMMA and zircon indicating the successful synthesis of the composites.

The crystallite size and residual strain of the unmilled and milled powders were acquired using *MAUD* software and are presented in Table 1. The crystallite size, in general, reduces with increasing milling time. However, extending milling time may not significantly change the crystallite size as shown by data for 15 h sample. In this case, the compressive stress due to collision between particles is presumably below the fracture stress experienced by each of them.

The residual strain data is also shown in Table 1. The presence of residual strain in the milled powder suggests that during milling the crystallite size reduced, a severe plastic deformation (SPD) also occurred [18]. These changes may affect the mechanical characteristics of the composites.

Figure 2 shows the relationship between the force and displacement (hence stress and strain) for PMMA and PMMA/zircon composites at different amounts and types of filler under dynamic loading. At the loading phase, the force increases with displacement and reaches different maximum values. After reaching a peak, each sample would exhibit a sudden failure where the force has not been longer recorded.

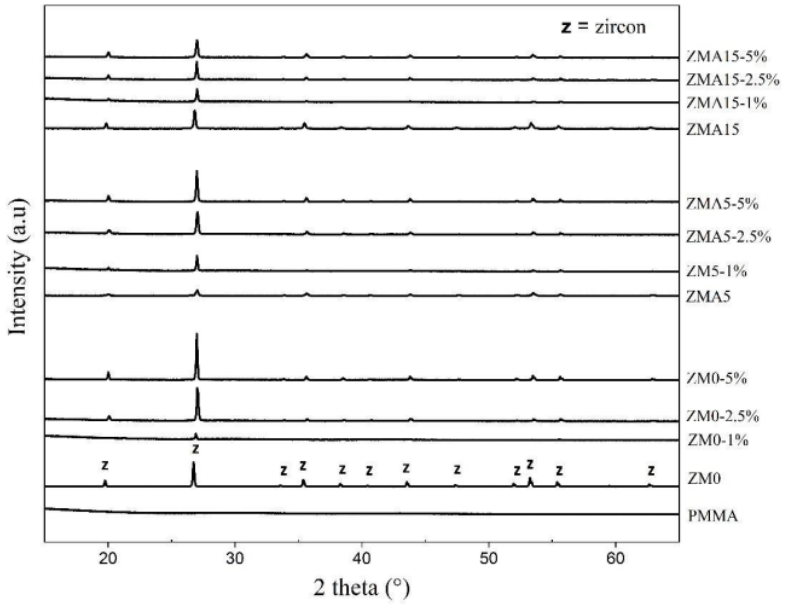

Figure 1. XRD patterns (CuKα) of PMMA, zircon fillers, and PMMA/zircon composites.

Table 1. The crystallite size and residual strain of the unmilled and annealed-milled powder (referred to Figure 1) using *MAUD*. Digits in the parentheses explained the estimated standard deviations to the corresponding average values at the least significant degree.

Samples	Refinement parameters (*GoF*)	Crystallite size (nm)	Residual strain (10^{-4})
ZM0	2.02	184(21)	0.28(5)
ZMA5	1.71	50(2)	2.33(43)
ZMA15	2.32	38(1)	2.84(23)

Furthermore, sample response shows that force (hence stress) increases with filler content as indicated by larger slopes. These slopes can be the indicator of bending stiffness under dynamic loading [19]. Therefore, Figure 2 illustrates that generally the stiffness of the composites increases with composition of the filler. The stiffness values, which is determined by calculating the slope of the curve [20] in the same displacement range, of the composites are presented in Table 2. A higher stiffness of the composites is caused by the fact that the rigidity of the filler is higher than that of the polymer. In general, the stiffness increases with increasing amount of filler especially over a displacement range of 30 μm.

Moreover, the displacement range and the area under the force-displacement curve can respectively indicate the ductility and the toughness behavior of a material. A more ductile material shows a longer displacement range, while a tougher material exhibits a larger area under the force-displacement curve. Table 2 depicts also the calculated area under the curve for all samples. It is apparent that the addition of smaller (15h-milled) powder into PMMA improves the toughness of the polymer, which leads to the increased strength and ductility. Again, the improvement can be addressed to the larger specific area of the smaller filler for better interfacial interactions between the components of the composites.

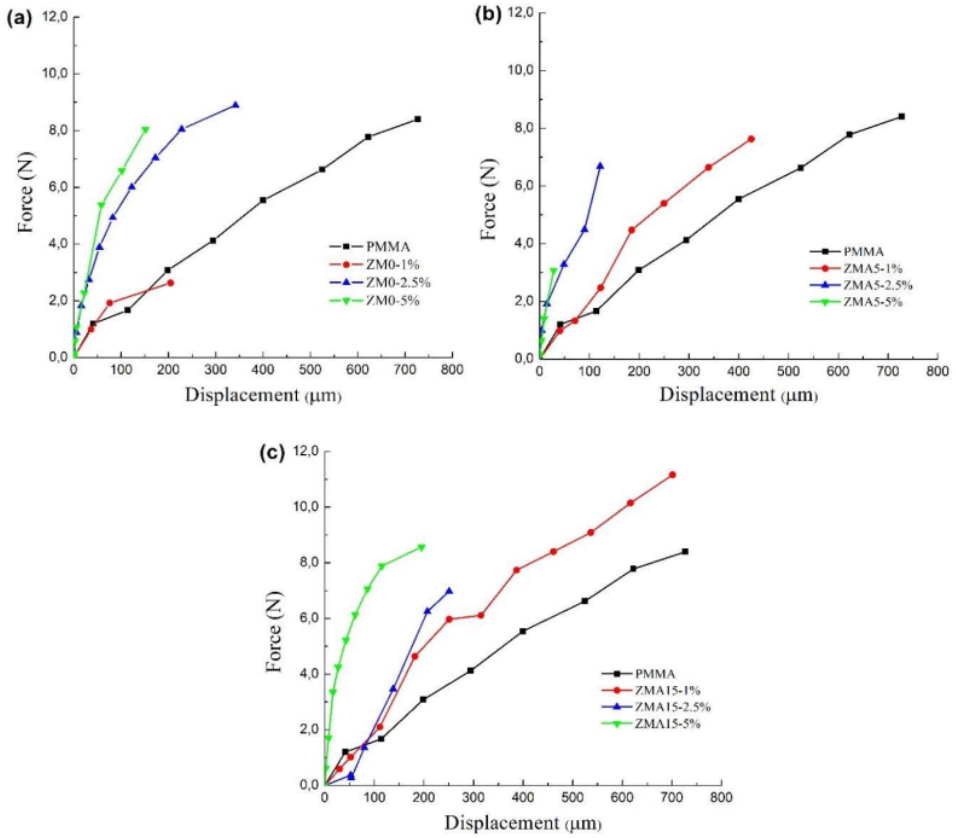

Figure 2. Force vs. displacement curves of the polymer and the PMMA/zircon composites with (a) the unmilled powder, (b) the milled powder for 5 h, and (c) the milled powder for 15 h.

Table 2. Stiffness and area under force-displacement curve of the investigated samples.

	Stiffness [N/μm]		Area (μNm)
Displacement range	0-30 μm	0-100 μm	
PMMA	26.1	15.7	
ZM0-1%	26.1	20,7	388
ZM0-2.5%	88.8	53.9	1887
ZM0-5%	88.8	66.1	884
ZMA5-1%	26.1	19.9	1844
ZMA5-2.5%	83.5	52.5	462
ZMA5-5%	110.0		47
ZMA15-1%	20.2	18.8	4454
ZMA15-2.5%	7.3	21.4	767
ZMA15-5%	147.9	74.5	1069

4. Conclusion

In this study, a local zircon sand had been successfully processed to produce varying-crystallite-size zircon powders which were then used as the filler, at composition of 1, 2.5 and 5 wt.%, of PMMA-based composites. DMA force-displacement curves were developed for the composites from which it was found that the stiffness of the composites are higher than that of PMMA and adding 5wt.% of the 15h-milled powder gave the highest stiffness among the composites. Furthermore, the incorporation of the powder into PMMA resulted in an improved toughness which led to increased strength and ductility.

Acknowledgments

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References

[1] Mao Z, Yang Z and Zhang J 2019 $SrTiO_3$ as a new solar reflective pigment on the cooling property of PMMA-ceramic composites *Ceram. Int.* **45** 16078–16087
[2] Arvinte A, Sesay A M and Virtanen V 2020 Designing carbon reinforced PMMA composites for integrated electrodes as electrochemical detectors in PMMA microchips *J. Electroanal. Chem.* **876** 114486
[3] Chrysafi I, Kontonasaki E, Anastasiou A D, Patsiaoura D, Papadopoulou L, Vourlias G, Vouvoudi E and Bikiaris D 2020 Mechanical and thermal properties of PMMA resin composites for interim fixed prostheses reinforced with calcium β-pyrophosphate *J. Mech. Behav. Biomed. Mater.* **112** 104094
[4] Harb S V, Trentin A, Uvida M C, Magnani M, Pulcinelli S H, Santilli C V and Hammer P 2020 A comparative study on PMMA-TiO_2 and PMMA-ZrO_2 protective coatings *Prog. Org. Coat.* **140** 105477
[5] Lee D W and Yoo B R 2016 Advanced silica/polymer composites: Materials and applications *J. Ind. Eng. Chem.* **38** 1–12
[6] Wang H, Xu P, Meng S, Zhong W, Du W and Du Q 2006 Poly (methyl methacrylate)/silica/titania ternary nanocomposites with greatly improved thermal and ultraviolet-shielding properties *Polym. Degrad. Stab.* **91** 1455–1461
[7] Sugumaran S and Bellan C S 2014 Transparent nano composite PVA–TiO_2 and PMMA–TiO_2 thin films: Optical and dielectric properties *Optik* **125** 5128–5133
[8] Ali U, Karim K J B A and Buang N A 2015 A review of the properties and applications of poly (methyl methacrylate)(PMMA) *Polym. Rev.* **55** 678–705
[9] Yang F and Nelson G L 2004 PMMA/silica nanocomposite studies: synthesis and properties *J. Appl. Polym. Sci.* **91** 3844–3850
[10] Banks-Sills L, Shiber D G, Fourman V, Eliasi R and Shlayer A 2016 Experimental determination of mechanical properties of PMMA reinforced with functionalized CNTs *Compos. Part B Eng.* **95** 335–345
[11] Alzarrug F A, Dimitrijević M M, Heinemann R M J, Radojević V, Stojanović D B, Uskoković P S and Aleksić R 2015 The use of different alumina fillers for improvement of the mechanical properties of hybrid PMMA composites *Mater. Des.* **86** 575–581
[12] Patra N, Salerno M, Cozzoli P D, Barone A C, Ceseracciu L, Pignatelli F, Carzino R, Marini L and Athanassiou A 2012 Thermal and mechanical characterization of poly (methyl methacrylate) nanocomposites filled with TiO_2 nanorods *Compos. Part B Eng.* **43** 3114–3119
[13] Sun D, Miyatake N and Sue H-J 2007 Transparent PMMA/ZnO nanocomposite films based on colloidal ZnO quantum dots *Nanotechnology* **18** 215606
[14] Leão R de S, Moraes S L D de, Gomes J M de L, Lemos C A A, Casado B G da S, Vasconcelos B C do E and Pellizzer E P 2020 Influence of addition of zirconia on PMMA: A systematic review *Mater. Sci. Eng. C* **106** 110292

[15] Rendtorff N M, Garrido L B and Aglietti E F 2010 Zirconia toughening of mullite–zirconia–zircon composites obtained by direct sintering *Ceram. Int.* **36** 781–788
[16] Pabst W and Gregorová E V A 2013 Elastic properties of silica polymorphs–a review *Ceram.-Silik.* **57** 167–184
[17] Musyarofah, Lestari N D, Nurlaila R, Muwwaqor N F, Triwikantoro and Pratapa S 2019 Synthesis of high-purity zircon, zirconia, and silica nanopowders from local zircon sand *Ceram. Int.* **45** 6639–47
[18] Galan C A, Ortiz A L, Guiberteau F and Shaw L L 2009 Crystallite size refinement of ZrB_2 by high-energy ball milling *J. Am. Ceram. Soc.* **92** 3114–3117
[19] Ulus H, Üstün T, Şahin Ö S, Karabulut S E, Eskizeybek V and Avcı A 2016 Low-velocity impact behavior of carbon fiber/epoxy multiscale hybrid nanocomposites reinforced with multiwalled carbon nanotubes and boron nitride nanoplates *J. Compos. Mater.* **50** 761–770
[20] Ramakers-van Dorp E, Haenel T, Sturm F, Möginger B and Hausnerova B 2018 On merging DMA and microindentation to determine local mechanical properties of polymers *Polym. Test.* **68** 359–364

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