Comparative studies of Titanium Dioxide and Zinc Oxide as a potential filler in Polypropylene reinforced rice husk composite

M Awang and W R Wan Mohd
School of Ocean Engineering, Universiti Malaysia Terengganu, 21300 Kuala Terengganu, Terengganu, Malaysia
E-mail: wroslinamohd@gmail.com

Abstract. Arising global environmental issues have triggered the search of new products and processes that are compatible with the environment while maintaining novel properties of materials. In this work, green composites containing rice husk (RH), polypropylene (PP), and incorporated with two different fillers namely titanium dioxide (TiO2) and zinc oxide (ZnO) were prepared using an internal mixer and were injected into desired specimen by using an injection molding method. Mechanical properties of the composite were studied using Instron universal testing machine with load cell of 30kN capacity. Morphological of tensile fractured surface of composites was observed using scanning electron microscopy (SEM). The results show that the composites with the addition of TiO2 gave an excellent mechanical properties than the composites filled with ZnO. Furthermore, morphological image of PP/RH/TiO2 also shows a good interaction occurred between polymer matrix and RH particles as compared to that of PP/RH/ZnO.

1. Introduction
The novelty of materials is evaluated based on their mechanical characteristics such as tensile properties, compression properties, impact properties and flexural properties. These characteristics are essential to figure out material ability to withstand extreme and critical conditions resulted to their engineering performance [1]. Polymer composites reinforced natural fiber have attracted a broad attention of researchers in conjunction with arising concern towards environmental issues. This is due to a novel attribute of natural fiber which is renewable, biodegradable and sustainability. They also provide some excellent features such as light weight, low cost, eco-friendly and naturally degradable composites without eliminating its rigidity properties [2]. Rice husk is one of the natural fibers which comes from major agro-waste by-product with an abundance of sources and become a staple food in Malaysia. It is decomposed of cellulose 35%, lignin 20%, hemicellulose 25% and ash 17% (silica 94%) by weight [3]. However, there are some shortcomings of this natural fiber where hydrophilic properties which belongs to lignocellulosic materials made their mechanical properties become lower than their synthetic counterpart. Another reason that led to low mechanical properties of the composites is poor interfacial bonding between the lignocellulosic material and the hydrophobic polymer matrix. Comprehensive studies has been made on polyolefin such as polypropylene and polyethylene and various natural reinforcing fillers, in conjunction with various chemicals that could affect the interface [4,5]. This drawback can be alleviated by the use of inorganic filler such as metal oxide which is TiO2, ZnO, CaCO3 and others. The main purpose of utilization of inorganic
filler in polymer composite not only limited to cost reduction but it also to enhance the performance of mechanical properties such as rigidity, dimensional stability and toughness [6].

TiO₂ is an inexpensive and non-toxic semiconductor and extensively used to enhance the properties of polymers [7]. TiO₂ and ZnO have drawn broad attention in recent years due to their wide application especially in functional devices, pigments, cosmetics and ultraviolet (UV) absorber and antibacterial agent [7–14]. An incorporation of TiO₂ and ZnO into polymers does not only produce functional capabilities such as photostabilization and antibacterial agent but it also can enhance mechanical properties by providing a strong interfacial interaction between polymers matrix and filler [15]. The use of TiO₂ and ZnO with PP composite have been researched by a number of researchers in order to investigate the physical and mechanical properties [7,16-21]. To date, there is no research has been conducted relating to substitution of TiO₂ or ZnO filler into PP reinforced RH composites.

In this study reported herein, the influences of TiO₂ and ZnO on mechanical properties of PP reinforced RH composite is investigated. The morphological studies on fractured tensile surfaces were also carried out by using scanning electron microscopes.

2. Experimental details

2.1 Materials
Polypropylene was purchased from Lotte Chemical Titan in the form of pellets with a density of 0.900g/cm³ and melt flow index of 14g/min. RH was supplied by Bernas rice factory (Besut, Terengganu, Malaysia). TiO₂ and ZnO powder was obtained from Azfa Maju Trading, Terengganu.

2.2 Preparation of the composites and sample
RH was ground and sieved to produce mesh sizes less than 50μm. PP pellets, RH particles and TiO₂ filler were melt-mixed in a Brabender internal mixer. The content of TiO₂ filler was fixed to 3wt% and two levels of RH particle loading (10 and 40wt%) were used. For comparative purposes, ZnO content was also fixed to 3wt% and went through a similar processes. Composite samples were then fed into a Haake injection molding machine to produce specimens in the form of dumbbell shape.

2.3 Characterizations

2.3.1 Mechanical property. The mechanical property of the composites was investigated using an Instron Universal Testing Machine (Model 3366) with maximum load cell of 30kN capacities and cross head speed of 10mm/min.

2.3.2 Thermogravimetric analysis. The measurement of thermal stability was performed using a Thermo Balance SDTA 815E, in the temperature range 30°C to 900°C at heating rate of 10°C /min and under 30ml/min of argon flow.

2.3.3 Scanning electron microscopy. The morphology of the tensile fractured surface of the composite samples was performed using scanning electron microscope (JOEL model JSM 6360LA).
3 Results and Discussion

Figure 1. Tensile strength of neat PP, PP/RH/TiO₂ and PP/RH/ZnO

Figure 2. Young’s modulus of neat PP, PP/RH/TiO₂ and PP/RH/ZnO

Figure 3. Elongation at break of neat PP, PP/RH/TiO₂ and PP/RH/ZnO
3.1 Mechanical properties

3.1.1 Tensile test. Figure 1 depicts the effect of RH particle loading on the tensile strength of PP/RH/TiO$_2$ and PP/RH/ZnO. It shows that the value of tensile strength of PP/RH/TiO$_2$-10wt% and PP/RH/TiO$_2$-40wt% minimally vary. The value of the tensile strength of these both composites are still in acceptable range and are very close to the value of ultimate tensile strength of neat PP which is 40MPa. It was highlighted that an addition of 3wt% TiO$_2$ in PP/RH composite has substantially increased tensile strength thus led to excellent mechanical properties. Esthappan et al. also mentioned that an addition of 3wt% of TiO$_2$, tenacity was significantly increased indicating the uniform distribution of TiO$_2$ in the PP fiber [22]. As compared to PP/RH/ZnO, by increasing RH particle loading to 40wt%, the tensile strength of the PP/RH/ZnO was slightly decreased. By adding 0.5 to 8wt% of ZnO, the values of tensile strength of PP fiber did not much improve because of poor interaction between filler and matrix [23].

3.1.2 Young’s modulus. Overall, all RH particle loading series also indicate that the value of Young’s modulus of PP/RH/TiO$_2$ was higher than PP/RH/ZnO shown in Figure 2. The trends of the plotted graph also increased with increasing of RH particle loading. This phenomenon occurred due to increasing of RH content in composites which directly contributed to an increase in composite stiffness. It was verified that stiffness of the PP/RH/TiO$_2$ composite increased from 2100MPa to more than 3600MPa while for PP/RH/ZnO composite increased from 2047MPa to more than 3300MPa. Luz et al. reported that natural lignocellulosic materials have higher elastic modulus attribute than PP [24]. A number of researchers also have been found that in the presence of high loading of natural fiber being as important factor in increasing composite’s rigidity that causes the reduction of polymer chains mobility thus promote an occurrence of higher stiffness in the composite[25].

3.1.3 Elongation at break. Increasing RH particle loading resulted in an abrupt drop in elongation at break for PP/RH/TiO$_2$ and PP/RH/ZnO as compared to neat PP in (Figure 3). Generally, an incorporation of inorganic fillers into polymer composites enhances their mechanical properties such as tensile strength, elastic modulus but decreases impact strength and elongation at break [18, 26, 27]. Based on Figure 3, it also can be observed that elongation at break for PP/RH/TiO$_2$ was higher than PP/RH/ZnO. Altan et al. also found a similar result in PP composites whereby elongation at break of PP/TiO$_2$ was significantly increased as compared to ZnO reinforced composites especially for the filler loading over 1wt% [28].

3.2 SEM morphology

SEM micrographs of tensile fractured surfaces of neat PP, PP/RH/TiO$_2$-10wt% and PP/RH/ZnO-10wt% were shown in Figure 4 (a), (b) and (c) respectively. It can be observed that the RH particles were distributed uniformly in Figure 4 (b) unlike Figure 4 (c). It was also can be seen clearly, a poor interaction between polymer matrix and RH particles occurred in Figure 4 (c) as compared to Figure 4 (b). As RH particle loading was increased from 10 to 40wt% as shown in Figure 4(d) and Figure 4(e), there were some agglomerations in morphological structure in PP/RH/TiO$_2$-40wt%. Aydemir et al. mentioned that the agglomerations occurred due to increasing of filler loading [29]. An increasing RH particle loading also led to phenomenon of fiber pull out due to less interaction between polymer matrix and RH particle as clearly seen in Figure 4(e). Other works reported that when a free space exist between particles and polymer matrix, it is easy to have fiber pull out phenomenon during brittle fracture [30].
Figure 4. SEM micrographs of tensile fractured surface of (a) Neat PP (b) PP/RH/TiO$_2$-10wt% (c) PP/RH/ZnO-10wt% (d) PP/RH/TiO$_2$-40wt% (e) PP/RH/ZnO-40wt% composites
4 Conclusions

Inorganic fillers such as metal oxides behave differently according to their physical, mechanical, and chemical properties. In this work, two metal oxides namely TiO$_2$ and ZnO were used to improve the properties of polypropylene filled rice husk composites. An addition of 3wt% of TiO$_2$ in PP/RH composites imparted an improvement to the mechanical properties. From tensile test, it shows that higher tensile strength and Young’s modulus in PP/RH/TiO$_2$ than that of PP/RH/ZnO composites due to its hardness and stiff structure. Besides, the elongation at break of the PP/RH/TiO$_2$ was also higher than PP/RH/ZnO composites proven that the compatibility of PP/RH was better with TiO$_2$ compare than ZnO. From SEM morphology, PP/RH composites filled TiO$_2$ have a good interaction between polymer matrix and RH particles while fiber pull out appeared in some regions of PP/RH/ZnO led to the reduction of tensile properties of the PP/RH/ZnO composites.

Acknowledgment

The authors would like to thank the School of Ocean Engineering, Universiti Malaysia Terengganu for providing lab’s facilities and also to the Ministry of Higher Education (MOHE) for the financial support.

References

[1] Rajendra K and Tejeet S 2014 Rice husk-reinforced composites: A review. Proceedings of the International Conference on Research and Innovations in Mechanical Engineering, pp. 395-405

[2] Majeed K, Jawaid M, Hassan A, Abu Bakar A, Abdul Khalil H P S, Salema A A and Inuwa I 2013 Potential materials for food packaging from nanoclay/natural fibers filled hybrid composites Mater. Des. 46 391-410

[3] Premalal H G B, Ismail H and Baharin A 2002 Comparison of the mechanical properties of rice husk powder filled propylene composites with talc filled polypropylene composites Polym. Test. 21 833-839

[4] Lai S M, Yeh F C, Wang Y, Chan H C and Shen H F 2003 Comparative study of maleated polyolefins as compatibilizers for polyethylene/wood flour composites J Appl Polym Sci 87 487-96

[5] Jiasheng Q, Pingsheng H and Kangming N 2004 Nonisothermal crystallization of PP/nano-SiO$_2$ composites J. Appl. Polym. Sci. 91 1013

[6] Nicola C and Mahendra 2012 Nano antimicrobials: progress and prospect Titanium Dioxide–Polymer Nanocomposites with Advanced Properties ed Kubacka A, Fernández-García M, Cerrada M L and Fernández-García M (Berlin Heidelberg: Springer) pp 119–149

[7] Altan M and Yildirim H 2012 Mechanical and antibacterial properties of injection molded PP/TiO$_2$ nano-composites: effects of surface modification Journal of Material Science and Technology 28 686 – 692

[8] Mikesova J, Slouf M, Gohs U, Popelkova D, Vackova T, Hung V N, Kratochvil J and Zhigunov A 2014 Nanocomposites of polypropylene/titinate nanotubes: morphology, nucleation effects of nanoparticles and properties Polym. Bull. 71 795 – 818

[9] Zhao H X and Li R K Y 2006 A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites Polymer 47 3207-3217

[10] Tjong S C, Liang G D and Bao S P 2006 Electrical properties of low-density polyethylene/ZnO nanocomposites: The effect of thermal treatments J Appl Polym Sci 102 1436-1444

[11] Sawai J, Igarashi H, Hashimoto A, Kokugan T and Shimizu M 1995 Evaluation of growth inhibitory effect of ceramics powder slurry on bacteria by conductance method J Chem Eng Jpn 28 288-293

[12] Sawai J, Saito I, Kanou F, Igarashi H, Hashimoto, Kokugan A T and Shimizu M 1995 Mutagenicity test of ceramic powder which have growth inhibitory effect on bacteria J Chem Eng Jpn 28 352-354

[13] Li J H, Hong R Y, Li M Y, Li H Z, Zheng Y and Ding J 2009 Effects of ZnO nanoparticles on the mechanical and antibacterial properties of polyurethane coatings Prog Org Coat 64 504-509
[14] Li S C and Li Y N 2010 Mechanical and antibacterial properties of modified nano-ZnO/high density polyethylene composite films with a low doped content of nano-ZnO Journal of Applied Polymer Science 116 2965-2969

[15] Zeng A, Zheng Y, Guo Y, Qiu S and Cheng Lei 2012 Effect of tetra-necked-shaped zinc oxide whisker (T-ZnOw) on mechanical properties and crystallization behavior of isostatic polypropylene composites Mater. Des. 32 1477

[16] Yang C, Wu Y and Liu C 2013 Studies on crystallization and mechanical properties of polypropylene/nano-TiO$_2$ composites Material Design, Processing and Applications 690-693 494-498

[17] Zohrevand A, Ajji A and Mighri F 2013 Morphology and properties of highly filled PP/TiO$_2$ nanocomposites Polymer Engineering and Science 54 874-886.

[18] Kruenate J, Tongpool R, Panyathanmaporn T and Krong P 2004 Optical and mechanical properties of polypropylene modified by metal oxides Surf Interf Anal 36 1044-7

[19] Li X, Schneider K, Kretzschmar B and Stamm M 2008 Deformation behavior of PP and PP/ZnO nanocomposites as studied by SAXS and WAXS Macromolecules 41 4371-9

[20] Zhou J P, Qiu K Q and Fu W L 2005 The surface modification of ZnOw and its effect on the mechanical properties of filled polypropylene composites J Compos Mater 39 1931-41

[21] Zhang Y C, Xie J F, Wu H Y and Qiu Y P 2009 Crystallization and mechanical properties of nano ZnO/PP/PLA composite filaments Mater Sci Forum 620 485-8

[22] Wacharawichanant S and Phutphongsai A 2007 The study of morphology and mechanical properties of compatibilized polypropylene/zinc oxide composites. Journal of Solid Mechanics and Materials Engineering 10 1231-1237

[23] Luz S M, Del T J, Rocha G J M, Gonçalves A R and Del’Arco Jr A P 2008 Cellulose and cellulignin from sugarcane bagasse reinforced propylene composites: effect of acetylation on mechanical and thermal properties Composites Part A – Applied Science and Manufacturing 39 1362-1369

[24] Rana A K, Mandal B C, Mitra R, Jacobson R, Rowell A and Banerjee N 1998 Short jute fiber reinforced polypropylene composites: effect of compatibilizer J Appl Polym Sci 69 329-338

[25] Olmos D, Dominguez C, Castrillo P D and Gonzales-Benito J 2009 Crystallization and final morphology of HDPE: effect of high energy ball milling and the presence of TiO$_2$ nanoparticles Polymer 50 1732 – 1742

[26] Altan M and Yildirim H 2010 Mechanical and morphological properties of polypropylene and high density polyethylene matrix composites reinforced with surface modified nano sized TiO$_2$ particles International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering 4 231–7

[27] Altan M, Yildirim H and Uysal A 2011 Tensile properties of polypropylene/metal oxide nano composites The Online Journal of Science and Technology 1 25-30

[28] Aydemir D, Uzun G, Gumus H, Yildiz S, Gumus S, Bardak T and Gunduz G 2016 Nanocomposites of polypropylene/nano titanium dioxide: effect of loading rates of nano titanium dioxide Materials Science 22 364-367

[29] Rosa S M L, Santos E F, Ferreira C A and Nachtigall S M B 2009 Studies on the properties of rice husk filled PP composites- Effect of maleated PP Materials Research 12 333-338