Turkish Online Journal of Qualitative Inquiry (TOJQI)
Volume 12, Issue 6, July, 2016: 9444 - 9453

Research Article

Primary Study on the Effect of the 1% and 2% TiO_2 Nanoparticles to the Microhardness, Microstructure and Contact Angle of the SnBi/Cu Solder Alloy

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Abstract

This paper investigates the influence of the 1 % and 2 % titanium dioxide (TiO_2) nanoparticles to the microhardness, microstructure, and contact angle of the Sn58Bi (SB) solder. Results showed increase (2 % increment) on the microhardness for the nanoparticles reinforced solder with the recorded microhardness value of 22 Hv and 23.6 Hv for 1 % and 2 % additions respectively. The TiO_2 presented at the solder side with more Bi island observed in the TiO_2 reinforced solders. Contact angle increased minorly (≈5 °) as the weight percentages of additions increases because of the presence of nanoparticles that will increase the viscosity of the molten solder. The introduction of TiO_2 into the SB solder resulted in satisfactory effect without interrupting the low melting aspect of the solder alloy. Enhancement on the hardness properties via better microstructure affect and presence of TiO_2 as additional strengthening mechanism provides an initial suggestion on the usage of this combination of nanoparticles in to the SnBi solder alloy as the remedy to replace the lead solder in the electronic industry.

Keywords: *SnBi solder, microhardness, contact angle, microstructure*

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Introduction

Though the lead SnPb solder served best in the electronic packaging industry but the hazards coming along leading to restrictions of the usage [1], [2]. This followed by the emerging technologies with more fine-pitched components in complex electronic integrations requiring the development of a whole new low temperature solder alloy that can promise the required results. The silver (Ag), copper (Cu), bismuth (Bi), and zinc (Zn) added with tin (Sn)-based alloys are being developed to fit the role [3], [4].

To further increase the performance of the solder alloy, elements are added, which adds up the weight of the solder. Additions of elements will increase the mass and density of an electronic device which will fail to satisfy current requirement of miniaturized electronic devices [5]. Therefore, to increase the properties and maintain the low mass consumption, reinforcement of nanoparticles are opted to be the feasible solution. Lately, many studies had investigated the effect of the nanoparticle's additions to solder alloys. Ceramics elements such as the titanium dioxide (TiO_2), aluminium oxide (Al_2O_3), zirconia (ZrO_2) and ceramic oxide (CeO_2) are among the most utilized nanoparticles [6] – [8]. Hardness value increased almost 63 % with additions of 1 % Al_2O_3 in the SnBi solder alloy [2]. In a separate research, the microstructure of SnAgCu was refined by adding 0.5 % CeO_2 [9] and [10] similar refinement to the Sn9Zn with 1% Al_2O_3 nanoparticles additions. Their research achieved 27.41 ° reduction in the contact angle with minimal 0.25 % ZnO nanoparticles additions to the Sn3.0Ag0.7Cu solder [11].

Usually, the nanoparticles are added to the high melting temperature solders like SnAgCu, SnAg, SnCu and SnZn as stated earlier. Current problem concerning high temperature soldering seem to damage other components during solder pasting [12]. Higher soldering temperature will cause negative impact on components performance such as thermal damage on the chip, that may need additional cost to be sorted.

Various studies were performed to find the suitable low melting solder, yet the electronic industry still has concern on the transformation. Among the candidate, the SnBi solder alloy is one of the highly demanded [13], [14]. As now, solders should have better or similar properties corresponding to the eutectic SnPb solder to be implemented in the electronic industry. This research will provide initial results based on hardness, microstructure, and contact angle of the

1% and 2% TiO_2 nanoparticles added Sn58Bi (SB)/Cu solder joint. The TiO_2 has a low density that will accommodate less mass usage and a high melting point that will produce discrete effects which is crucial for not interrupting the initial properties of the parent SB solder alloy. The data attained serves as platform to judge and close the research gap involving the study of low melting temperature solder alloys.

Methodology

The Sn-58Bi (SB) Tin (Sn) (99.9 % pure, Sigma Aldrich) and Bismuth (Bi) (99.9 % pure, Sigma Aldrich) was mixed according to the eutectic weight percentage of 42 % Bi and 58 % Bi. These elements were melted at 600 °C for 1 hour in a vacuum furnace. The TiO_2 (Sigma Aldrich) nanoparticles was also weighed respectively at 1 % and 2 % of the total weight of SB and inserted separately after melting at the mentioned temperature. The 1 % and 2 % additions equal to the masses of 0.2 g and 0.4 g each. Table 1 shows all the compositions for the nanoparticles. Both 1 % and 2% TiO_2 reinforced SB nanoparticles solder alloy was further mechanically stirred at 350 °C insider an alumina crucible as shown Fig. 1 (a). The solder alloy was then casted into billets of 50 × 10 mm as shown in Fig 1 (b) to replica the low amount of solder paste used in the electronic industry. Microhardness test was done using the Zwick/Roell hardness machine. Five indentations with 1 kgf load were made on the solder billets to measure the hardness value. The diameter as indicated in Fig. 1 (d) were used to calculate the hardness values. The soldering process for the contact angle test was done using the hot plate with the temperature set as 250 °C and the specimen was let to solidify under room temperature. The contact angle measurement is illustrated in Fig. 1 (c). Prior to the soldering, the zinc chloride (ZnCl) flux was applied on the copper substrate to avoid oxidation and enable better bonding. The Cu substrate was cut into 30mm × 30mm dimension. After completing the soldering process, the specimens were cleaned to remove excessive flux. The samples were mounted using an epoxy resin and hardener and cross sectioned to measure the contact angle. The samples were polished to provide better imaging to measure the contact angle with the VIS Pro software incorporated in the optical microscope. FESEM imaging and EDS analysis was conducted to study the microstructure of the solder alloys. The microstructure property focused on the solder properties with the SB and SB reinforced with TiO_2 nanoparticles.

Table 1. Compositions of elements and nanoparticles for the solder alloys

Solder/Elements	Sn (g)	Bi (g)	TiO_2 (g)
SB	8.4	11.6	
SB + 1% TiO_2	8.4	11.6	0.2
SB + 2% TiO_2	8.4	11.6	0.4

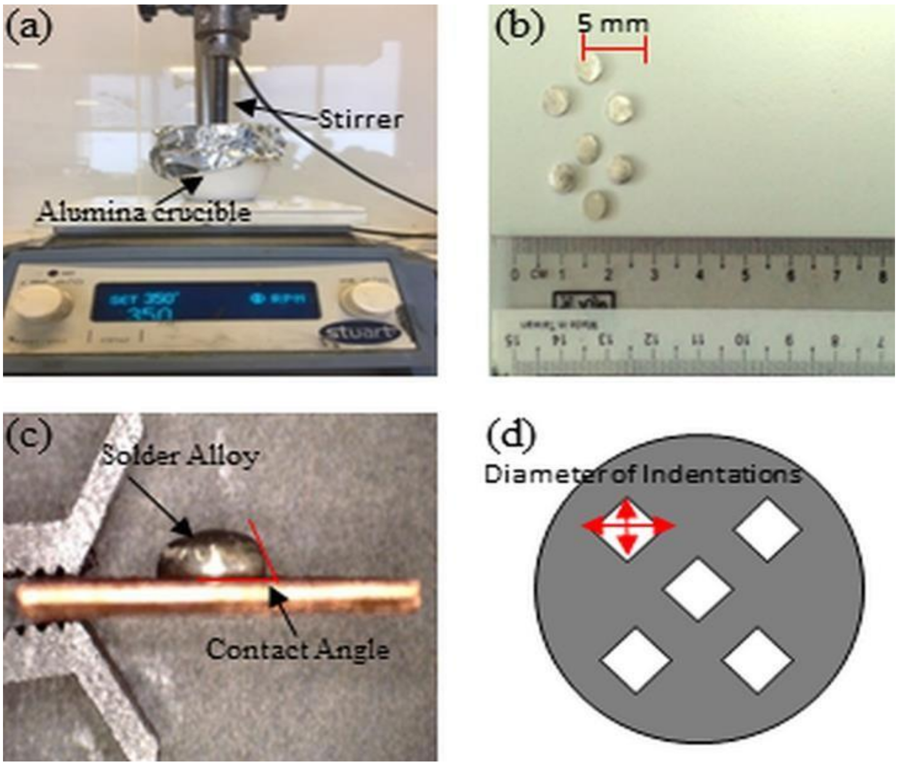


Figure 1. (a) Stirring process, (b) solder billets, (c) contact angle and (d) indentations on solder.

Results and Discussion

The following subchapters will be discussing on the results of the main properties that been tested.

3.1 Microhardness Analyses

The hardness properties of materials are known as the ability of the material to resist deformation and often related to the toughness as well. This includes the solder alloys too, with the hardness of the solders will be a preliminary but an important aspect to predict the resistance of the solder interconnections in any electronic device. The microhardness of the SB, SB + 1 % TiO_2 and SB + 2 % TiO_2 are shown in Fig. 2.

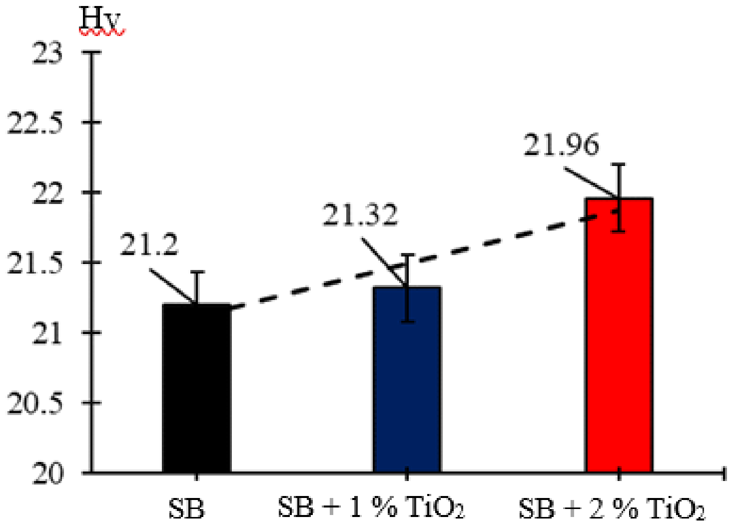


Figure 2. Vickers microhardness of solder alloys.

The microhardness values for the SB were 21.2 Hv, 21.3 Hv for the SB + 1 % TiO_2 and 21.96 Hv for SB + 2 % TiO_2 respectively. The trendline shows that the hardness increases as the weight percentages of TiO_2 increases. This clearly shows that the presence of the TiO_2 influences the increase of the hardness. High melting point of the TiO_2 ensures that the element does not reacts with the Sn and/or Bi and keeping the TiO_2 as discrete particles. This phenomenon is crucial because the TiO_2 as discrete particles will serve as additional strengthening mechanism. Previously, [15] studies proved that the hardness value of the Sn58Bi solder alloy increased due to the presence of Al_2O_3. Similarly, other nanoparticles such as Mo [16] and TiO_2 [17] showed improvement in the hardness of SnBi and SnAgCu solder alloys respectively.

Initially, lamellar structure of the typical SnBi will be the sole mechanism of inhibiting the penetration. In this research, the elemental analyses showed the presence of Ti on the microstructure acts as other source of strengthening mechanism. The ability of the TiO_2 nanoparticles of blocking the penetration of the load is shown in Fig 3 (b). As hard material, the load must bend through the particles, where the dislocation loops built up creating pilling of the loops. The more the pilled-up dislocation loops, the harder the solder alloy [18] reported likewise.

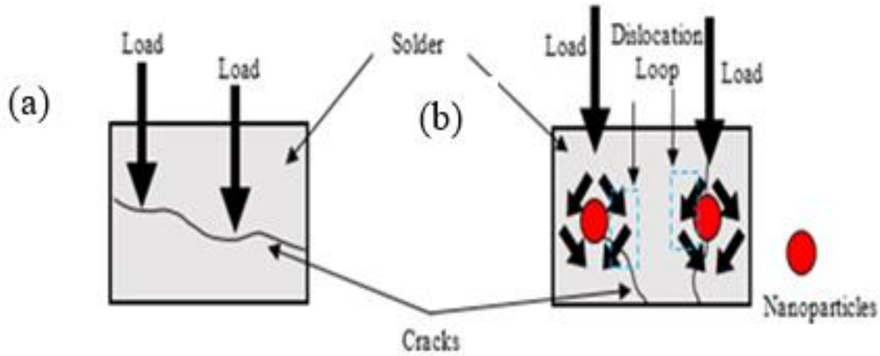


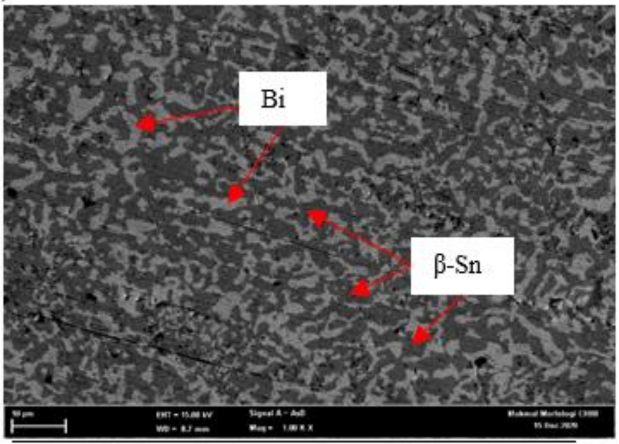
Figure 3. Load penetration of a) SB solder and b) SB added with TiO_2 nanoparticles.

3.2 Microstructure Properties Analyses

A typical morphology of Sn and Bi phases were found in the SB solder alloy. Although the TiO_2 nanoparticles were not visible from the image, the EDS analyses proved the presences of the Ti in the solder. Fig. 4 show the image of the SB, SB added with 1 % TiO_2 and SB added with 2 % TiO_2. Spectrum analyses proved the white phases are Bi and the dark phases are β-Sn as labelled in Fig 4. (a). The Ti and O elements were also found in less nominal weight percentage. The less quantity resembles the less mass upon 1 % and 2 % TiO_2 additions.

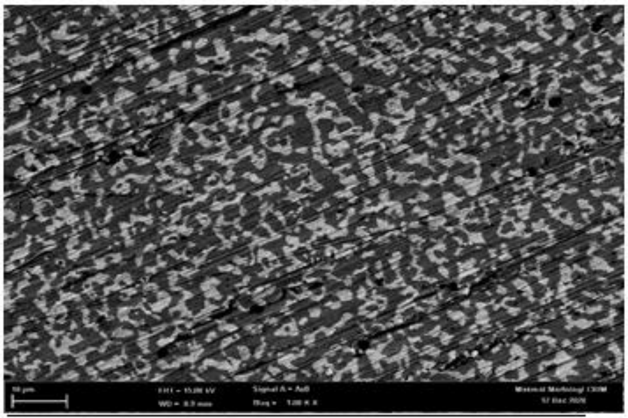
The presence of TiO_2 nanoparticles certainly influences the increase of the hardness. Incorporation of TiO_2 nanoparticles also showed slight changes to the morphology of the SB solder alloys. The island of Bi phases was larger (as highlighted in yellow) and was observed more in the 2 % additions as in Fig 4 (c). Not much changes on the morphology were seen for the 1 % additions compared to the pure SB solder alloy. However, the nominal weight percentages of Bi increased in the 1 % TiO_2 additions. The nominal weight percentage of the Bi upsurges with increase in the TiO_2 percentages of additions as can be seen in Figs 4 (b) and (c). Together with the TiO_2 nanoparticles in this study, the Bi also helps in resisting deformation due to its brittleness. Possible explanation on this is the presence of TiO_2 restricts the growth of β-Sn or limits the Sn to present at the solder side which enables the Sn elements to exist at the interfacial side due to the high reactivity of Sn towards Cu. The detection of less Ti at the solder side may suggest that the TiO_2 would opt to move more towards the interfacial side. As this is a high energy site, the TiO_2 nanoparticles will segregate more there due to the nature of being active nanoparticles. Research by [19] gave similar statement upon additions of TiO_2 nanoparticles in to the SnAgCu solder alloy. The nanoparticles were found to present at the edges of the IMC layer too. [20] similarly described this with the presence of TiC at the IMC layer of the SnAgCu solder joints.

(a)



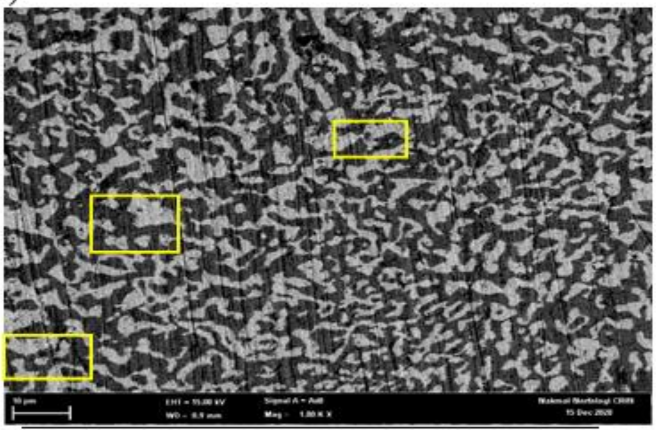
Elements	Wt. %
Bi	53.7
Sn	46.3
Cu	0

(b)



Elements	Wt. %
Bi	60.6
Sn	14.7
Ti	0.2
O	23.4
Cu	1.1

(c)



Elements	Wt. %
Bi	64.6
Sn	25.2
Ti	0.3
O	9.1
Cu	0.8

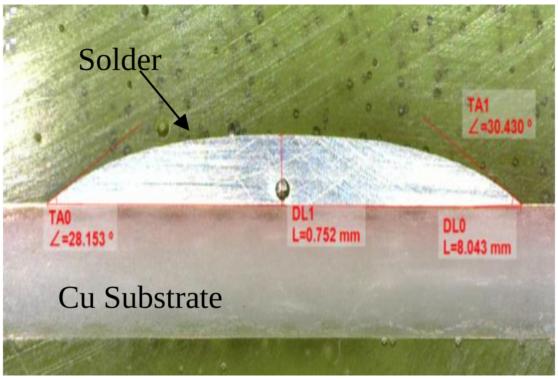
Figure 4. FESEM image and EDS analyses of (a) SB, (b) SB added with 1 % TiO_2 and (c) SB added with 2 % TiO_2

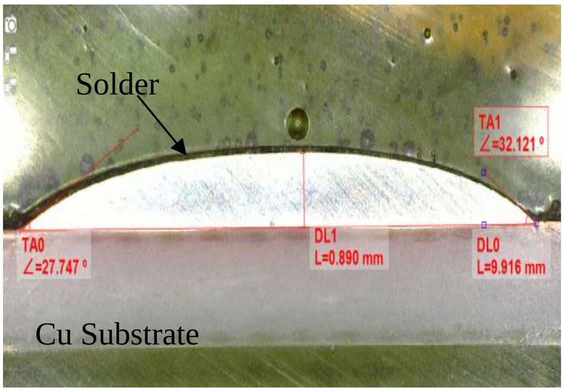
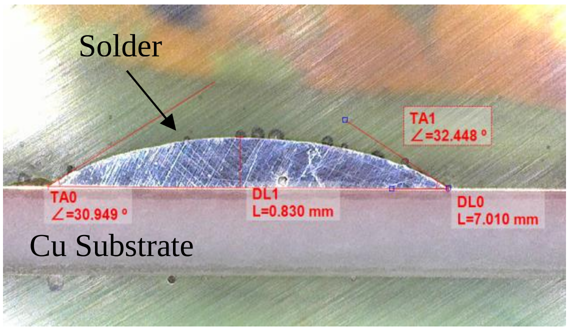
3.3 Contact Angle Analyses

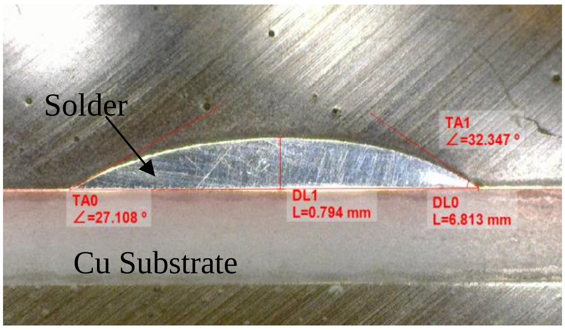
The contact angles were measured between the solder and the Cu substrate to predict the solder joint's characteristic. Although the ideal contact angles are yet to be fixed, gathering data from various researches have categorized a good contact angle fall below 50 ° and angles more than that are undesirable [21].

Table 2 shows the measured average contact angles for the SB, SB added with 1 % TiO_2 and SB added with 2 % TiO_2 nanoparticles. The average contact measured for the SB solder joint is 29.61 °, 30.71 ° for the 1 % TiO_2 additions and 34.75 ° for the 1 % TiO_2 additions.

Table 2. Average contact angles of (a) SB, (b) SB added with 1 % TiO_2 and (c) SB added with 2 % TiO_2 solder joint.

<table>
<tr><th>Solder Joint Samples</th><th>Average Contact Angle (°)</th></tr>
<tr><td>(a)



</td><td>29.61</td></tr>
<tr><td>(b)



</td><td>30.71</td></tr>
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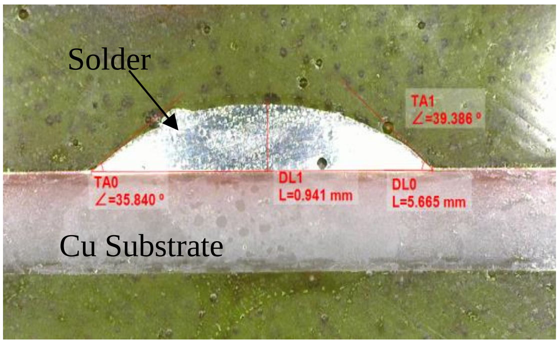

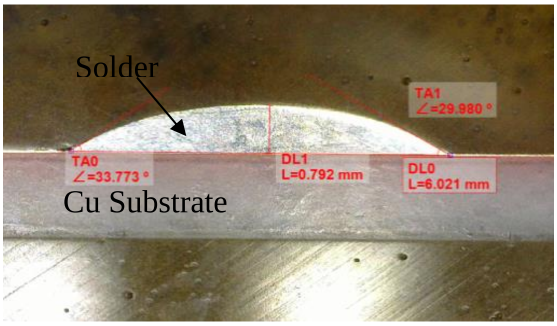

</td>
<td>34.75</td>
</tr>
</table>

Observing the contact of the solder alloy, the additions of TiO_2 certainly slightly increases the angle, almost 5° between the bare solder and the 2 % additions. As mentioned earlier, the TiO_2 with high melting point will not diffuse with the elements in the solder, making the solder more viscous. Rise in viscosity increases the surface tension between the solder and substrate that makes a harder spreading of the molten solder [22]. Moreover, the detection of TiO_2 at the solder side was low, suggesting that the nanoparticles would be pushed to the interface (high energy site) between the solder and substrate or at the leading edge of the solder [23]. This also will reduce the spread ability of the molten SB. This however had minimal effect in this research as the angle increases in a small range. Another reason for this is the usage of lower percentages of additions in this research. Studies have found out that higher weight percentages of additions increased the contact angle that jeopardizes the solder joint [10], [24]. Therefore, the small increase in the contact angle predicted not to cause a defect to the solder joint.

Conclusion

This research provides the initial data and analyses on the effect of adding TiO_2 nanoparticles to the Sn58Bi solder alloy. The microhardness increased with the presence of TiO_2 nanoparticles with 2 % additions having the highest value of 21.96 Hv. Provided that, the solders could resist impact upon drop of an electronic device. The microstructure properties provided more elongated and larger Bi phases with TiO_2 existences. Observation of lesser TiO_2 nanoparticles at the solder side suggests the nanoparticles were pushed to the interfacial site that will help in joint properties such as the intermetallic layer suppression. Contact angle of the TiO_2 added solders did not see a drastic change keeping the solder joint in the good wettability category (< 50 °).

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Ir. Prof. Dr. Rajkumar is currently attached with Universiti Tunku Abdul Rahman (UTAR). He has contributed immensely to the development and enhancement in science & technology in Malaysia, particularly in the field of nanomaterials for electronic packaging materials, medical and composite technology. He has published more than 80 research articles in various ISI/WoS, Scopus listed publications. Prof. Rajkumar has received many accolades as a distinguished scholar. He was the recipient of UTAR Research Excellence Award in 2018. He was also awarded Young Members Award by the Institution of Mechanical Engineers, UK in 2011. Prof. Rajkumar was awarded the prestigious Wighton Titular Fellowship of Engineering in 2010 by the Association of Commonwealth of Universities, United Kingdom. He is serving as an Associate Director for Engineering Accreditation Department, Board of Engineers Malaysia (BEM) since 2020, served as the Chairman of the Young Members Section for the Malaysian Branch of the Institution of Mechanical Engineers (2010 – 2012) and as a Head of Department (2014 to date), Chairman of the University Accreditation and MyRA committee (2017-current). He is serving in numerous capacities as external assessor, professional mentor, resource person, external examiner, advisor, and engineering accreditation panel.

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