DEVELOPMENT AND CHARACTERIZATION OF THERMOPLASTIC SUGAR PALM STARCH/AGAR POLYMER BLEND, REINFORCED SEAWEED WASTE AND SUGAR PALM FIBER HYBRID COMPOSITE

RIDHWAN BIN JUMAIDIN

FK 2017 62
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By

RIDHWAN BIN JUMAIDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2017
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DEDICATION

To Al-Quran, the greatest source of knowledge

*Bring me sheets of iron*" - until, when he had leveled [them] between the two mountain walls, he said, "Blow [with bellows]," until when he had made it [like] fire, he said, "Bring me, that I may pour over it molten copper." (Al-Kahf:Verse 96)

To my beloved father and mother

&

To my beloved wife

&

To my beloved daughter and son
Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

DEVELOPMENT AND CHARACTERIZATION OF THERMOPLASTIC SUGAR PALM STARCH/AGAR POLYMER BLEND, REINFORCED SEAWEED WASTE AND SUGAR PALM FIBER HYBRID COMPOSITE

By

RIDHWAN BIN JUMAIDIN

May 2017

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Faculty: Engineering

In recent, the needs to develop more environmental friendly product is increasing due to the accumulating of non-biodegradable waste, particularly the disposable product. Hence, various kinds of more environmental friendly materials were developed in order to tackle this issue. Biopolymer derived from renewable resources is a promising alternative material for petroleum based polymer since it is readily biodegradable and thus, more environmental friendly. Among the biopolymer, starch is one of the most promising due to the easy availability, low cost, abundant in nature, renewable, and biodegradable. Sugar palm is a versatile plant that is regarded as renewable source for fibre and starch. However, the inborn deterrent associated with the biopolymer derived from sugar palm starch (SPS) such as the poor mechanical properties has limits its potential applications. Meanwhile, *Eucheuma cottonii* seaweed is a resourceful macro alga which is massively cultivated for the production of its hydrocolloids, namely carrageenan. However, due to the relatively low carrageenan content in the raw seaweed, huge amount of solid wastes were produced during processing which is yet to be utilized. Hence, characterizations of the seaweed wastes were carried out to analyse its potential as reinforcement material. Then, several modification methods were employed to enhance the properties of thermoplastic SPS i.e; (1) blending thermoplastic SPS with agar polymer (2) reinforcement of thermoplastic SPS/agar (TPSA) blend with seaweed wastes, and (3) hybridization of seaweed wastes with sugar palm fibre in the TPSA composites. Consequently, thermoplastic SPS/agar blends were successfully developed by using melt-mixing and compression moulding method. The findings show that the tensile, flexural, and impact properties of the material were improved following the incorporation of agar. The thermal properties of the material were slightly improved as the agar content increased from 0 to 40 wt%. In terms of physical properties, the addition of agar has increased the water affinity characteristics of the polymer blend. Furthermore, the influence of seaweed wastes at varying content (0 to 40 wt%) on the mechanical, thermal, physical, and biodegradation characteristics of TPSA were investigated. Improvement in the tensile, flexural, and impact properties of the composites were evidence after incorporation of seaweed waste. It also evident from the thermogravimetric analysis (TGA) results that the thermal stability of the composites were enhanced with addition of seaweed waste. In terms of the physical properties, addition of seaweed has led to higher water affinity of the composites. After soil burial
for 2 and 4 weeks, the biodegradation of the composites were enhanced with the incorporation of seaweed waste. Lastly, the effects of sugar palm fibre hybridization with seaweed/TPSA composites were evaluated. Hybridized seaweed waste/SPF reinforcement at weight ratio of 0:100, 25:75, 50:50, 75:25, and 100:0 were prepared by using TPSA polymer blend as the matrix. Obtained results indicated that hybrid composites display improved tensile and flexural properties accompanied with lower impact resistance. Thermal stability of the hybrid composites were enhanced than the individual seaweed waste composite. Water absorption, thickness swelling, water solubility, and soil burial tests showed higher water and biodegradation resistance of the hybrid composites. Overall, the findings from the current study demonstrated that thermoplastic SPS modified by agar, seaweed wastes, and hybridization with SPF has shown improved functional characteristics than the origin material. In conclusion, the TPSA polymer blend reinforced seaweed waste/SPF hybrid composites are potential alternative material for biodegradable product i.e disposable tray with enhanced properties.
PENYEDIAAN DAN PENCIRIAN KOMPOSIT HIBRID TERMOPLASTIK CAMPURAN KANJI ENAU/AGAR MEMPERKUKUH RUMPAI LAUT/GENTIAN ENAU

Oleh

RIDHWAN BIN JUMAIDIN

Mei 2017

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Sejak kebelakangan ini, keperluan untuk membangunkan lebih banyak produk mesra alam semakin meningkat disebabkan oleh sisa terkumpul yang tidak terbiodegradasi di tapak pelupusan sampah. Oleh itu, pelbagai jenis bahan-bahan yang lebih mesra alam telah dibangunkan untuk menangani isu ini. Biopolimer yang diperolehi daripada sumber yang boleh diperbaharui adalah bahan alternatif yang menarik untuk menggantikan polimer berasaskan petroleum kerana ianya mudah terbiodegradaskan dan dengan itu, lebih mesra alam berbanding polimer konvensional. Antara biopolimer, kanji adalah antara yang paling menarik kerana ianya mudah diperolehi, kos rendah, banyak dalam alam semula jadi, boleh diperbaharui dan mesra alam. Pokok enau adalah tumbuhan serba boleh yang dianggap sebagai sumber yang boleh diperbaharui untuk gentian dan kanji. Walau bagaimanapun, penghalang semula jadi yang berkaitan dengan biopolimer yang diperolehi daripada kanji enau (SPS) seperti sifat-sifat mekanikal yang lemah telah menghadkan potensi aplikasinya. Sementara itu, rumpai laut *Eucheuma cottonii* merupakan alga makro yang ditanam secara besar-besaran untuk pengeluaran hidrosolloid, iaitu karagenan. Walau bagaimanapun, disebabkan kandungan karagenan yang rendah dalam rumpai laut, sejumlah besar sisa pepejal telah dihasilkan semasa pemprosesan yang masih belum dimanfaatkan. Oleh itu, pencirian sisa rumpai laut telah dijalankan untuk menganalisis potensiannya sebagai bahan penguat. Seterusnya, beberapa kaedah pengubahsuaian telah diambil untuk menambahbaik sifat-sifat termoplastik SPS iaitu; (1) pencampuran termoplastik SPS dengan polimer agar (2) pengukuhan termoplastik SPS/agar (TPSA) dengan sisa rumpai laut, dan (3) penghibridan sisa rumpai laut dengan gentian enau dalam komposit TPSA. Polimer campuran termoplastik SPS/agar telah berjaya dibangunkan dengan menggunakan kaedah pencampuran-lebur dan kaedah pengacuan mampatan. Dapatkan kajian menunjukkan bahawa sifat tegangan, lenturan, dan impak bahan telah meningkat susulan daripada penggabungan agar ke dalam termoplastik SPS. Sifat termal termoplastik SPS menunjukkan sedikit peningkatan apabila kandungan agar meningkat (0 – 40%). Dari segi sifat fizikal, penambahan agar telah meningkatkan sifat pertalian air polimer campuran. Seterusnya, pengaruh sisa rumpai laut pada kandungan yang berbeza-beza (0-40% berat) kepada ciri-ciri mekanikal, termal, fizikal, dan biodegradasi TPSA telah disiasat. Peningkatan dalam
ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, the Most Merciful

Highest gratitude to Allah swt for granting me the strength, resilient, and knowledge to complete this thesis. The accomplishment of this thesis would not have materialized without His blessing and guidance. My deepest appreciation goes to my kind supervisor Professor Ir. Dr Mohd. Sapuan Bin Salit for his enormous support and encouraging supervision throughout my study. I was greatly inspired to explore the world of research and writing under his supervision. Thereafter, I would like to express my sincere appreciation for the guidance and coaching of my co-supervisors, Dr Mohammad Jawaid (Laboratory of Biocomposite Technology, INTROP, UPM), Dr Mohamad Ridzwan Ishak (Department of Aerospace Engineering, UPM) and Allahyarham Dr Sahari Japar (Universiti Malaysia Sabah) (May Allah grant him a peaceful place among the solihin).

I would like to convey my great appreciation to Universiti Teknikal Malaysia Melaka and Ministry of Higher Education Malaysia for providing the scholarship award for me to pursue this study. Special acknowledgment to Universiti Putra Malaysia for the financial support provided through Universiti Putra Malaysia Grant Scheme (project code GP-IPS/2015/9457200).

I owe a special thanks to my dear wife (Syarmeela Hadzwina Awang Musa) for her continuous support and sacrifice throughout my study. To my beloved father (Haji Jumaidin Haji Abas) and mother (Hajah Bunga Mohd Bakir) for the motivations and continuous prayer for my success in this world and in the hereafter. Special credit to my daughter (Anis Sumayyah Ridhwan) and son (Razin Ridhwan) for providing a cheerful environment during my study period.

I am thankful to all staff in Faculty of Engineering and Institute of Tropical and Forestry Product (INTROP) for their help and guidance. Last but not least, I would like to thank all of my friends in Engineering and INTROP for the knowledge sharing and support to the successful completion of this work.

Thank you all!
I certify that a Thesis Examination Committee has met on 29 May 2017 to conduct the final examination of Ridhwan bin Jumaidin on his thesis entitled "Development and Characterization of Thermoplastic Sugar Palm Starch/Agar Polymer Blend, Reinforced Seaweed Waste and Sugar Palm Fiber Hybrid Composite" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis Of Variance</td>
</tr>
<tr>
<td>CBN</td>
<td>Cellulose Nanofibre</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose Nanocrystal</td>
</tr>
<tr>
<td>CNCs</td>
<td>Kenaf Cellulose Nanocrystals</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EMMT</td>
<td>Ethanolamine activated-montmorillonite</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscope</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
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<tr>
<td>HAS</td>
<td>High amylose starch</td>
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<tr>
<td>HC</td>
<td>Hybrid composite</td>
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<tr>
<td>HDPE</td>
<td>High-density polyethylene</td>
</tr>
<tr>
<td>HIPS</td>
<td>High impact polystyrene</td>
</tr>
<tr>
<td>KA</td>
<td>Alkali treated kenaf</td>
</tr>
<tr>
<td>KB</td>
<td>Bleached kenaf</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-density polyethylene</td>
</tr>
<tr>
<td>MAPE</td>
<td>Maleic anhydride- grafted-polyethylene</td>
</tr>
<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>PBAT</td>
<td>Poly(butylene adipate-co-terephthalate</td>
</tr>
<tr>
<td>PHB</td>
<td>Polyhydroxybutyrate</td>
</tr>
<tr>
<td>PHS</td>
<td>Photo-sensitizer</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly (lactic acid)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PVOH</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SPF</td>
<td>Sugar palm fibre</td>
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<tr>
<td>SPS</td>
<td>Sugar palm starch</td>
</tr>
<tr>
<td>ST-SA</td>
<td>Stearic acid-grafted starch</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal-gravimetric analysis</td>
</tr>
<tr>
<td>TPS</td>
<td>Thermoplastic Starch</td>
</tr>
<tr>
<td>TPSA</td>
<td>Thermoplastic Sugar Palm Starch/Agar</td>
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<tr>
<td>TPCS</td>
<td>Thermoplastic cassava starch</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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<tr>
<td>W</td>
<td>Weight</td>
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<tr>
<td>WS</td>
<td>Water solubility</td>
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<td>WVP</td>
<td>Water vapor permeability</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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CHAPTER 1

INTRODUCTION

1.1 Background

In recent, the needs to develop more environmental friendly product is increasing due to the accumulating of non-biodegradable waste on the land fill. Hence, various kind of “green” materials were developed in order to tackle this issue. Biopolymer derived from renewable resources is a promising alternative material for petroleum based polymer since it is readily biodegradable and thus, more environmental friendly than the conventional polymers. Various kind of natural resources were used to develop biopolymer ranging from lipid, protein, cellulose, and starch. Among these sources, starch is considered as the most promising resource due to several attributes i.e low cost, renewable, and totally biodegradable (Sahari et al., 2013a). Under the presence of heat and plasticizer, starch can be converted into thermoplastic starch (TPS) which possesses similar process ability with the conventional thermoplastic. The thermoplasticity of this biopolymer is the main advantages for the processing of this material. This enables this biopolymer to be processed by using the conventional processing equipment used for synthetic thermoplastic such as extruder, injection moulding, and compression moulding.

Many varieties of natural material have been used as reinforcement in polymer composites. This including both natural fibres (such as kenaf, jute, sisal, and sugar palm) and also natural fillers (such as talc, clay, eggshell, and seaweed) (Bootklad & Kaewtatip, 2013; Coativy et al., 2014; Hassan et al., 2008; López et al., 2015). Incorporation of natural material as the reinforcement in polymer composites has created more environmental friendly characteristics to the composites. Moreover, this green approaches reduce the dependency of the manufacturing industry to the synthetic materials such as glass fibre which often related to high potential of hazard for the manufacturing workers. The development of more environmental friendly materials gives a new perspective to the manufacturing industry which is often related to the environmental pollution for both the production and disposal of the synthetic polymer.

1.2 Problem statement

High consumption of petroleum-based polymer by the society has created serious environmental problems mainly during the disposal stage. These wastes are not readily biodegradable when disposed into the environment i.e land or sea which brought serious problems to the society, wildlife, and environment as well. Moreover, air pollution is another concerning issue following the incineration of this wastes. In recent, many countries have banned the usage of plastic bag as an effort for handling
this issue. Hence, this study attempts to overcome this problem by developing a 100% renewable and biodegradable polymer composite from natural sources.

Sugar palm tree is a versatile plant which was reported to be able of producing 50 to 100 kg of starch from a single tree (Sahari et al., 2013c). Starch extracted from sugar palm tree can be transformed into thermoplastic material in the presence of heat and plasticizer which results to a rigid material. However, the neat thermoplastic starch (TPS) has disadvantage that limit its usage in commercial plastic industry such as the poor mechanical strength. The current thermoplastic sugar palm starch has only 2.42 MPa of tensile strength which is extremely low when compared to the current thermoplastic material (Sahari et al., 2013c). This limitation has restricted the potential application of this material in the real world. Therefore, proper modifications should be employed in order to improve the properties of this material. The potential modifications include blending with other polymers and reinforcing with natural filler and fibre.

_Eucheuma cottonii_ seaweed (also known as _Kappaphycus alvarezii_) is a macroalgae which is largely cultivated in countries like Philippines, Indonesia, and Malaysia. This seaweed is mainly used for producing the hydrocolloids namely kappa-carrageenan (k-carrageenan) which act as thickening agent for food and non-food application as well. However, the content of k-carrageenan varies from only 25 to 35% from the whole seaweed weight, hence, leaving enormous amount of solid wastes which is yet to be utilized (Tan & Lee, 2014). The potential application of this seaweed waste as biosorbent material has been investigated in previous studies (Kang et al., 2011; Lee et al., 2011). The result shows that this material has great potential as biosorbent material for removal of heavy metal element in water namely chromium ion, copper ion, and nickel ion. Apart from these studies, there is no work reported on utilization of seaweed wastes of _Eucheuma cottonii_ species for other applications. Meanwhile, previous works have used various kinds of seaweeds as the potential reinforcement for petroleum derived polymer composites. However, the decrease in the mechanical strength was shown by the composites due to the incompatibility between the hydrophilic seaweed and the hydrophobic polymer matrix (Chitra & Kumari, 2012; Luan et al., 2010). Moreover, the combination of natural materials such as seaweed with the petroleum based polymer matrix will only results to partially biodegradable material. Therefore it is important to utilize seaweed waste as reinforcement in polymer composites which use hydrophilic polymer as the matrix. Hence, the motivation of this study are (1) to improve the properties of thermoplastic sugar palm starch (2) to widen the potential application of seaweed waste (3) to tackle the incompatibility issue of seaweed reinforced composites and finally (4) to produce a fully biodegradable material which can be safely disposed to the environment.

### 1.3 Research objectives

The principal aim of this study is to develop and characterize totally renewable and biodegradable materials based on natural resources. The specific objectives are:
1. To characterize the thermal, chemical, physical, and morphological properties of *Eucheuma cottonii* seaweed wastes.
2. To evaluate the effect of agar on the thermal, mechanical, physical, and morphological properties of thermoplastic sugar palm starch.
3. To investigate the effect of *Eucheuma cottonii* seaweed waste loading on the properties of thermoplastic sugar palm starch/agar composites.
4. To develop and characterize hybrid composites from *Eucheuma cottonii* seaweed wastes and sugar palm fibre by using thermoplastic sugar palm starch/agar as polymer matrix.

### 1.4 Significance of study

1. The findings from the current study are expected to enrich the knowledge in developing biodegradable polymer from thermoplastic sugar palm starch and agar.
2. The development of biodegradable polymer with enhanced properties in this study is expected to aid in addressing the environmental problems regarding the alternative materials for petroleum based polymer.
3. The problems associated with petroleum based polymer such as environmental pollution during the production and disposal can be alleviated by using a fully biodegradable and renewable polymer composites derived from seaweed wastes, sugar palm fibre, and thermoplastic sugar palm starch/agar blend.
4. In terms of waste management, this study has explored a new potential application of *Eucheuma cottonii* seaweed wastes from the carrageenan extraction as novel reinforcement for biopolymer composites.
5. Moreover, this study also utilizes the sugar palm tree for yielding starch and fibre for the development of the composites. Hence, added more value for the sugar palm tree other than producing the sugar.

### 1.5 Scope of study

In this study, *Eucheuma cottonii* seaweed wastes and the raw seaweed were characterized for their thermal, chemical, and physical properties. Later, starch extracted from sugar palm tree was used as the based material for the development of thermoplastic sugar palm starch. Thermoplastic sugar palm starch was developed by using glycerol as the plasticizer and further modified by using agar. Characterizations of their thermal, mechanical, and physical properties were performed. For the composites, *Eucheuma cottonii* seaweed wastes were incorporated into the thermoplastic sugar palm starch/agar blend and their properties were characterized. Hybridization of the composites were carried out by using the combination of sugar palm fibre and seaweed wastes as the reinforcement and the thermoplastic sugar palm starch/agar polymer blend as matrix. The thermal, mechanical, physical, and biodegradation properties of the hybrid composites were carried out. The relevant application for the composites developed in this study is a short-life product. Therefore, the potential application of the hybrid composites as biodegradable product i. e
A disposable tray was evaluated through comparison on the primary characteristics against the conventional material and the current thermoplastic starch.

1.6 Structure of thesis

The structure of this thesis is in accordance with the alternative thesis format of Universiti Putra Malaysia which is based on the publications of this study. Each research chapter represents a separate study that has the introduction, methodology, results and discussion, and conclusions. The details of the structure are as follows:

Chapter 1
The problems that initiate this research and the research objectives were clearly highlighted in this chapter. The significance of this work and the scope of study were also elaborated within the chapter.

Chapter 2
This chapter presents a comprehensive literature review on the areas related to the topic of this thesis. In addition, the research gaps obtained from the review were also clarified within the chapter.

Chapter 3
This chapter presents the methodology used in this study for the preparation of materials, testing procedure, and data collection.

Chapter 4
This chapter presents the first article entitled “Characteristics of Eucheuma cottonii waste from East Malaysia: physical, thermal, and chemical composition”. In this article, the characteristics of the seaweed wastes and the raw seaweed were investigated.

Chapter 5
This chapter presents the second article entitled “Characteristics of thermoplastic Sugar Palm starch/agar blend: Thermal, tensile, and physical properties”. The effect of agar at different concentrations (0 - 40 wt%) on the thermal, tensile, and physical properties (moisture absorption and thickness swelling) of thermoplastic sugar palm starch were investigated In this article,

Chapter 6
This chapter presents the fifth article entitled “Effect of Seaweed on Mechanical, Thermal, and Biodegradation Properties of Thermoplastic Sugar Palm Starch/Agar Composites”. In this article, the effect of seaweed wastes loading (0 – 40 wt%) on the mechanical, thermal, and biodegradation properties of thermoplastic sugar palm starch/agar composites were investigated.
Chapter 7
This chapter presents the seventh article entitled “Thermal, Mechanical, and Physical Properties of Seaweed/Sugar Palm Fibre Reinforced Thermoplastic Sugar Palm Starch/Agar Hybrid Composites”. In this paper, the effect of sugar palm fibre/seaweed hybridization at several ratios (0:100, 25:75, 50:50, 75:25, and 100:0) were investigated.

Chapter 8
This chapter presents the additional results of this research including the analysis and presentation of data, the discussion of results, and the correlation between the findings.

Chapter 9
This chapter presents the overall conclusions from the whole study as well as future recommendations for further improvement of this study.
REFERENCES


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